LAVAS Y TOBAS VOLCANICAS

Trabajos presentados a la Reunión Internacional
Isla de Pascua, Chile

25 - 31 Octubre, 1990

25 - 31 October, 1990

Easter Island, Chile

Preprints of the Contributions to the International Meeting

LAVAS AND VOLCANIC TUFFS

Editado por / Edited By
A. Elena Charola

Publicado por / Published by
Dirección de Bibliotecas, Archivos y Museos

conaf - WMF - ICCROM

43108

La Reunión Internacional de

"LAVAS Y TOBAS VOLCANICAS"

fue organizada por:

The International Meeting on

"LAVAS AND VOLCANIC TUFFS"

was organized by:

Dirección de Bibliotecas, Archivos y Museos (DIBAM)
Corporación Nacional Forestal (CONAF)
World Monuments Fund (WMF)
ICCROM (International Centre for the Study of the Preservation and the Restoration of Cultural Property)

auspiciada por: / sponsored by:

WMF - Somerville Bequest
ICCROM

Comisión Honoraria/Honorary Committee

Sergio Villalobos R.
Juan Franco
Javier Labra

Comisión Organizadora /Organizing Committee

Carlos Aldunate
Magdalena Krebs
Mauricio Massone
Patricia Vargas
Carlos Weber

Comisión Cientifica /Scientific Committee

Mónica Bahamondez
A. Elena Charola
Eddy De Witte
Wieslav Domaslowski
Lorenzo Lazzarini
Hugo Moreno

Coordinadora/Coordinator: A. Elena Charola

Secretario/Secretary: Angel Cabeza

Registro Propiedad Intelectual No. 76.729

Santiago de Chile, 1990

AGRADECIMIENTOS/ACKNOWLEDGMENTS

Agradecemos la colaboración de todas aquellas personas e Instituciones que hicieron posible esta Reunión y la presente publicación. Entre ellos destacamos a:

We acknowledge herewith all those who have helped to make this Meeting and the present publication possible. Among them we would like to thank:

Julia Arriagada (Museo Chileno de Arte Precolombino)
Erica Doering (Museo Chileno de Arte Precolombino)
María Irene Gonzalez (DIBAM)
Liliana Nahuelfil Matus (DIBAM)
Reginald Budd (Instituto de Estudios de Isla de Pascua)
Marcelo Soriano (FLYER Viajes, Buenos Aires, Argentina)
RPM Turismo Chile (Santiago de Chile)
Hotel Iorana (Isla de Pascua)

Y en especial la ayuda de: and the support received from:

Samuel H. Kress Foundation (U.S.A.)

PREFACE

The conservation of the cultural heritage of Easter Island is a constant concern of the Dirección de Bibliotecas, Archivos y Museos. This concern arose from the consciousness that the archaeological treasures of Rapa Nui, of which the moais, -megalithic statues-, the ahus, -ceremonial structures-, the houses and ritual villages, the petroglyphs and rock paintings, are the main sources from which to learn about this people. During centuries, isolated from the rest of the civilizations, their own culture was developed, which is still, to us, so full of mystery.

The preservation of this unique heritage needs necessarily a comprehensive plan that will take into account all the different cultural aspects, as an indivisible unit and within the context of its natural environment. In March 1988, the Meeting on Conservation of the Heritage of Easter Island was held to propose guidelines along which to develop this conservation plan and to establish priorities for its execution.

It is gratifying to observe that several of the recommendations given during that Meeting have already been carried out in the last two years. One of these is the Competition called for the study of Lavas and Volcanic Tuffs. With satisfaction we note the wide interest raised by this topic and the diversity of specialists that have contributed their studies which are presented in this publication.

The Meeting that will be held this coming October on Easter Island will enable the participating scientists to discuss the completed studies and provide the opportunity to develop new research programs and a co-ordinated plan of action in this field. We believe that only through international co-operation and interdisciplinary collaboration is it possible to succeed in the preservation of the heritage of the Island for the study and the enjoyment of future generations.

Sergio Villalobos R.

Director
Bibliotecas, Archivos y Museos

Santiago, Chile, September 1990

PRESENTACION

La conservación del patrimonio cultural de la Isla de Pascua es preocupación permanente y constante de la Dirección de Bibliotecas, Archivos y Museos, pues existe plena conciencia de que los moais, o estatuas megalíticas, los ahu, o estructuras ceremoniales, las viviendas y aldeas rituales y los petroglifos y pinturas rupestres que conforman las riquezas arqueológicas de Rapa Nui son los principales testigos a los cuales podemos acudir para conocer mejor a este pueblo que durante siglos desarrolló una expresión cultural propia, aislada del resto de las civilizaciones y cuyo significado está rodeado aún de tanto misterio para nosotros.

En el convencimiento de que la preservación de este singular patrimonio requiere necesariamente de un plan de trabajo que considere las diferentes manifestaciones culturales como un todo, inseparable e íntimamente relacionado con su entorno natural, se realizó, en marzo de 1988, la Reunión para el Diagnóstico de la Conservación del Patrimonio de Isla de Pascua, con el objetivo de pensar acciones de conservación coordinadas y establecer la prioridad de cada una de ellas.

Es con gran satisfacción que dos años después podamos constatar que ha sido posible llevar a la práctica muchas de las recomendaciones emanadas de esa reunión, entre las cuales podemos destacar, justamente, este Concurso para el Estudio de Lavas y Tobas Volcánicas. Nos complace detectar el interés que ha despertado el tema y la diversidad de especialistas que han presentado trabajos, los que se reúnen en esta publicación.

La reunión que se realizará en octubre de este año en la Isla de Pascua, permitirá, sin duda, no sólo discutir los actuales trabajos, sino, proyectar hacia el futuro, ante todo, nuevos trabajos de investigación como también un plan concreto de acciones, ahora en esta área específica. Creemos que la cooperación internacional e interdisciplinaria es la única vía para asegurar la preservación del patrimonio de la isla, para estudio y deleite de las generaciones futuras.

Sergio Villalobos R.

Director

Bibliotecas, Archivos y Museos

Santiago de Chile, septiembre de 1990

[illegible]

and ritual villages, the petroglyphs and rock paintings, were the main sources from which to learn about this people. During cen- [illegible]

[illegible] guidelines along which to develop this conservation plan and to [illegible]

[illegible] specialists that have contributed their studies which are pre- [illegible]

[illegible] preservation of the heritage of the island for the study and the enjoyment of future generations.

Sergio Villalobos R.

Director
Bibliotecas, Archivos y Museos

Santiago, Chile, September 1990

INDICE/INDEX

página/page

Introducción/Introduction 10

Concurso/Competition 12

Mapa de Isla de Pascua/Easter Island Map 14

1. Isla de Pascua/Easter Island 15

Rapa Nui: Auge y caída de una cultura megalítica 17
J.M.Ramírez Aliaga

Geologic Outline of Easter Island and Petrographic-Structural Features of its Lithic Monuments 25
H.Moreno Roa

The Petroglyphs of Easter Island: Problems of Natural Erosion and Human Impact 31
G.Lee

Weathering and Conservation of some Tuffs from France and Easter Island 45
J.P.Pauly, J.Loppion, J.Saugnac

Field and Laboratory Study of Deterioration Phenomena of Lavas and Volcanic Tuffs under Subtropical and Temperate Climates by Multisequential Methodology 75
J.Vouvè, J.Aurouze, et al.

Acciones de conservación sobre los moai de Isla de Pascua. Su evaluación en laboratorio 89
M.Bahamondez Prieto

2. Reseña Bibliográfica/Literature Review 101

The Deterioration and Treatment of Volcanic Stone: A Review of the Literature 103
C.A.Grissom

3. Deterioración/Deterioration 123

Volcanic Tuffs. The Description and Quantitative Recording of their Weathered State 125
B.Fitzner

Texture and Mechanical Disgregation of Tuffs from Italy and Ecuador 141
R.Rossi-Manaresi, A.Tucci

página/page

The Volcanic Rocks of the Monuments of the Forum and Palatine (Rome):Characterization, Alterations, Results of Chemical Treatments 151
P.L.Bianchetti, G.Lombardi, S.Marini, C. Meucci

Characterization and State of Decay of the Volcanic Tuff of the Tabularium (Roman Forum, Italy) 167
G.De Casa, G.Giglio, G. Lombardi, M.Mariottini

Deterioration and Conservation Problems of the Rhyodacitic Material used for the Scupltures in the Bomarzo Park (Viterbo) 183
F.Fratini, C.Manganelli del Fà, E. Pecchioni, A.Scala

Deterioration of Some Volcanic Rocks from Egypt 199
F.M.Helmi

Deterioration Induced by Lichens on Volcanite of the Vulsini Complex (Central Italy) 215
O.Salvadori, D.Pinna, G.C.Grillini

4. Tratamientos/Treatments 227

Estudio de consolidación de la fachada de la Iglesia de Santo Domingo de Popayán, Colombia, labrada en toba volcánica 229
L.A.Useche

Interaction between Volcanic Tuff and Products Used for Consolidation and Waterproofing Treatment 245
M.Laurenzi Tabasso, A.M.Mecchi, U.Santamaria

The Application of Silicone Products to Conservation of Volcanic Tuffs 269
J.W.Lukaszewicz

5. Evaluación de Tratamientos/Treatment Evaluation 289

Assessment of the Efficiency of Conservation Treatments Applied to Volcanic Tuffs by Radioactive Labelling 291
J.Sramek, T.Nishiura

A New Concept for Preservation of Porous Natural Stones 303
H.R.Sasse, D.Honsinger

INTRODUCTION

The International Meeting on "Lavas and Volcanic Tuffs", to be held on Easter Island, October 25th to 31st, 1990, is the end point of the Competition for scientific papers on the subject called by the Dirección de Bibliotecas, Archivos y Museos de Chile, through its Centro Nacional de Restauración, in September 1988.

This event was organized following the recommendations given at the Meeting on Conservation of the Heritage of Easter Island that was held in Santiago de Chile in March 1988.

The point of the Competition was to encourage the study of lavas and volcanic tuffs, which were used on the Island for the sculpting of the monumental statues and unusual petroglyphs. The deterioration and conservation problems of these types of stones has not been studied worldwide as thouroughly as those of other types such as marble or sandstone.

The purpose of the prizes given was to facilitate the travel of experts to this remote part of the world. Thus, the scientists selected on the merit of their studies on deterioration and conservation of similar volcanic rocks, will have the opportunity to meet on Easter Island and team-study the problems presented by its monumental heritage in stone.

Six of the seven papers received by the specified deadline were accepted for the Competition. The seventh paper was rejected because it essentially contained published material.

All other papers included in this volume are collaborations received for publication. We thank their authors for the effort that went into the preparation of these manuscripts. The publication gains much from these collaborations, making it an important contribution to the field of stone conservation.

The present volume, to be distributed at the beginning of the International Meeting, will serve as the basis for the discussions to be held on Easter Island.

A. Elena Charola
Co-ordinator

The Volcanic Rocks of the Monuments of the Forum and Palatine (Rome): Characterization, Alterations, Results of Chemical Treatments — 151
P. Bianchetti, G. Lombardi, [illegible] Marini, C. Mucci

Characterization and State of Decay of the Volcanic Tuff of the Tabularium (Roman Forum, Italy) — 171
G. De Casa, G. Giglio, G. Lombardi, M. Mariottini

Characterization and Conservation Problems of the Rhyodacitic Material used for the Sculptures in the Bomarzo Park (Viterbo) — 181
F. Fratini, C. Manganelli del Fa, E. Pecchioni, A. Scala

Deterioration of Volcanic Rocks from Egypt — 197
F.M. Helmi

Deterioration Induced by Lichens on Volcanites of the Vulsini Complex (Central Italy) — 215
O. Salvadori, D. Pinna, G.C. Grillini

[illegible]

Estudio de Conservación de la Portada de la Iglesia de Santo Domingo de Popayán, Colombia, labrada en toba volcánica — [illegible]
[illegible]

Interaction Between Volcanic Tuff and Products Used for Consolidation and Waterproofing Treatment — 245
[illegible]

The Application of Silicone Products for Conservation of Volcanic Tuffs — [illegible]
J.V. Lukaszewicz

3. Evaluation of Treatments [illegible]

Assessment of the Efficiency of Conservation Treatments Applied to Volcanic Tuffs by Radioactive Labelling — 291
J. Brunet, [illegible]

A New Concept for Preservation of Porous Natural Stones — 301
H.R. Sasse, D. Honsinger

INTRODUCCION

La Reunión Internacional de "Lavas y Tobas Volcánicas" a realizarse en la Isla de Pascua del 25 al 31 de octubre de 1990, es la culminación del llamado a concurso de trabajos científicos sobre el tema iniciado en septiembre de 1988, por la Dirección de Bibliotecas, Archivos y Museos de Chile a través del Centro Nacional de Restauración.

Este evento fue organizado de acuerdo a la recomendación formulada durante la Reunión para el Diagnóstico de la Conservación del Patrimonio de Isla de Pascua que se realizó en Santiago de Chile en marzo de 1988.

El objetivo del Concurso fue estimular el estudio de lavas y tobas volcánicas, rocas que fueran utilizadas en la Isla para la ejecución de las conocidas estatuas monumentales y de los singulares petroglifos. Los problemas de deterioro y conservación de este tipo de rocas no está tan estudiado a nivel mundial como el de otros materiales líticos, tales como mármoles o areniscas.

Los premios que se otorgaron tuvieron como objetivo fundamental facilitar la visita de expertos a este lugar lejano. De esta manera, varios científicos, seleccionados en base al mérito de sus estudios de problemas de deterioro y conservación en rocas volcánicas similares, se pueden reunir en la Isla de Pascua y estudiar en equipo los problemas presentados por su patrimonio lítico monumental.

Seis de los siete trabajos recibidos en término para el Concurso, fueron aceptados. El séptimo fue rechazado porque la parte principal del trabajo correspondía a material que ya había sido publicado anteriormente.

Todos los otros trabajos aquí publicados corresponden a colaboraciones recibidas para inclusión en el presente volumen. Agradecemos a esos autores el esfuerzo realizado en la preparación de dichos trabajos. Este material valoriza enormemente la publicación que puede ser considerada como una importante contribución al campo de conservación de la piedra.

El presente volumen, que se distribuirá al inicio de la Reunión Internacional, servirá de base a las discusiones a realizarse en la Isla de Pascua.

A. Elena Charola
Coordinadora

COMPETITION

The six contributions accepted for the Competition were the papers by:

- B.Fitzner
- P.L.Bianchetti, G.Lombardi, S.Marini, C. Meucci
- M.Laurenzi Tabasso, A.M.Mecchi, U.Santamaria
- L.A.Useche
- J.Vouvé, J.Aurouze et al.
- J.Sramek, T.Nishiura

Five papers received awards. The first award was given to:

M.Laurenzi Tabasso, A.M.Mecchi y U.Santamaria
"Interaction between Volcanic Tuff and Products Used for Consolidation and Waterproofing Treatment"

Three second ex-aequo prizes were given to:

J. Vouvé, J.Aurouze, G.Lacazedieu, Ph.Malaurent, P.Vidal y F.Vouvé
"Field and Laboratory Study of Deterioration Phenomena of Lavas and Volcanic Tuffs under Subtropical and Temperate Climates by Multisequential Methodology"

P.L.Bianchetti, G.Lombardi, S.Marini y C. Meucci
"The Volcanic Rocks of the Monuments of the Forum and Palatine (Rome): Characterization, Alterations, Results of Chemical Treatments"

B.Fitzner
"Volcanic Tuffs. The Description and Quantitative Recording of their Weathering State"

It should be mentioned that the versions of these three papers published in the present volume were the result of more or less extensive revisions carried out on the manuscripts received for the Competition.

The third prize was given to:

J.Sramek y T.Nishiura
"Assessment of Conservation Efficiency of Volcanic Tuffs Treatments by Radioactive Labelling"

CONCURSO

Los seis trabajos aceptados para el concurso fueron las contribuciones de:

- B.Fitzner
- P.L.Bianchetti, G.Lombardi, S.Marini, C. Meucci
- M.Laurenzi Tabasso, A.M.Mecchi, U.Santamaria
- L.A.Useche
- J.Vouvé, J.Aurouze et al.
- J.Sramek, T.Nishiura

Cinco trabajos fueron premiados. El primer premio correspondió al trabajo de:

M.Laurenzi Tabasso, A.M.Mecchi y U.Santamaria
"Interaction between Volcanic Tuff and Products Used for Consolidation and Waterproofing Treatment" (Interacción entre la toba volcánica y los productos utilizados para su consolidación y su hidrofobización)

Se otorgaron tres segundos premios ex-aequo a los trabajos de:

J. Vouvé, J.Aurouze, G.Lacazedieu, Ph.Malaurent, P.Vidal y F.Vouvé
"Field and Laboratory Study of Deterioration Phenomena of Lavas and Volcanic Tuffs under Subtropical and Temperate Climates by Multisequential Methodology" (Estudio de fenómenos de deterioro de lavas y tobas volcánicas in situ y en laboratorio bajo climas sub-tropicales y temperados)

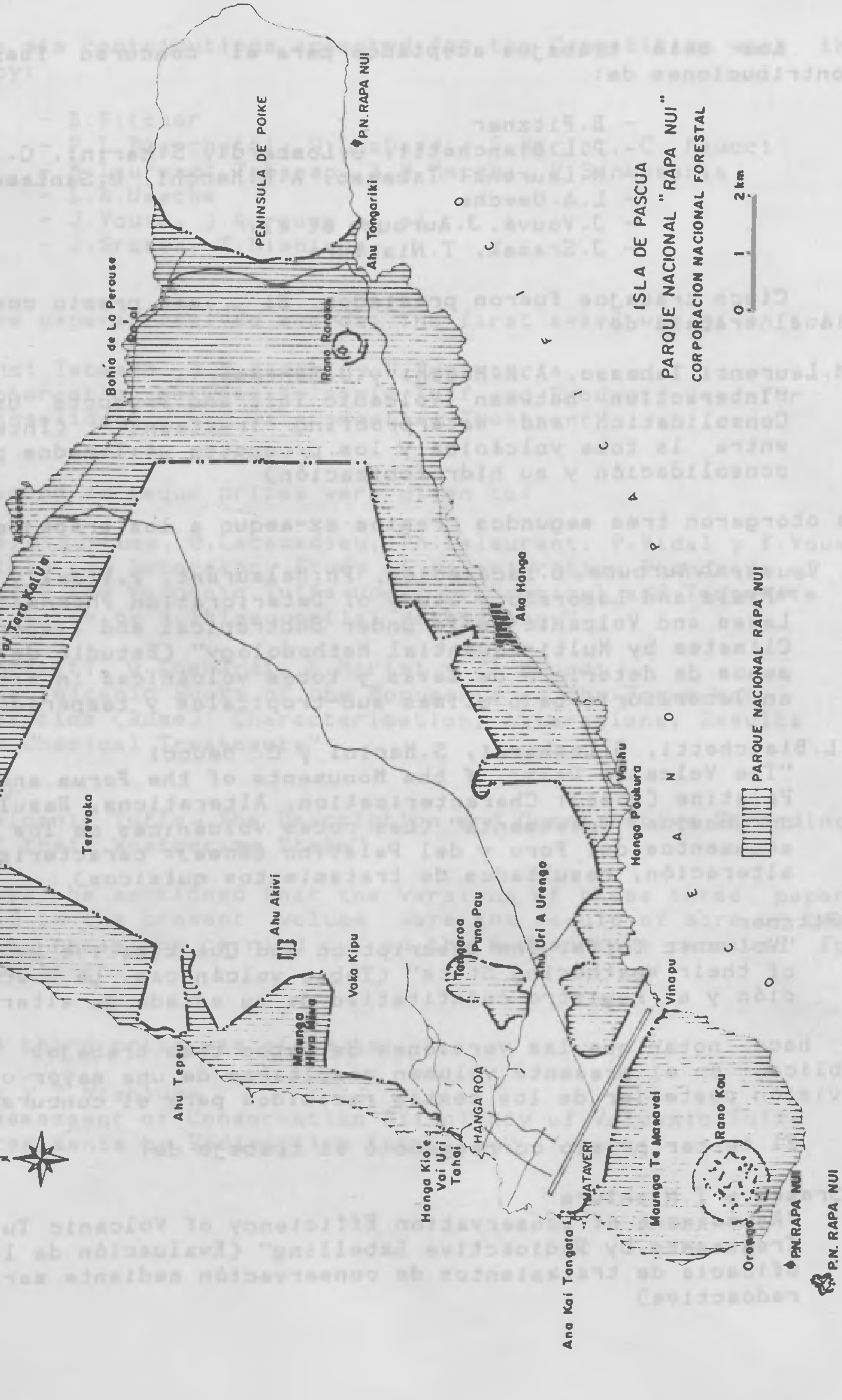
P.L.Bianchetti, G.Lombardi, S.Marini y C. Meucci
"The Volcanic Rocks of the Monuments of the Forum and Palatine (Rome): Characterization, Alterations, Results of Chemical Treatments" (Las rocas volcánicas de los monumentos del Foro y del Palatino (Roma): caracterización, alteración, resultados de tratamientos químicos)

B.Fitzner
"Volcanic Tuffs. The Description and Quantitative Recording of their Weathering State" (Tobas volcánicas. La descripción y el registro cuantitativo de su estado de alteración)

Se hace notar que las versiones de estos tres trabajos que se publican en el presente volumen resultaron de una mayor o menor revisión posterior de los textos recibidos para el concurso.

El tercer premio correspondió al trabajo de:

J.Sramek y T.Nishiura
"Assessment of Conservation Efficiency of Volcanic Tuffs Treatments by Radioactive Labelling" (Evaluación de la eficacia de tratamientos de conservación mediante marcación radoactiva)


ISLA DE PASCUA
PARQUE NACIONAL "RAPA NUI"
CORPORACION NACIONAL FORESTAL
0
1
2km
PARQUE NACIONAL RAPA NUI
P.N. RAPA NUI
O C E A N O P A C I F I C O
PENINSULA DE POIKE
P.N. RAPA NUI
Ahu Tongariki
Rano Raraku
Bahia de La Perouse
Ahu Te Pito Kura
Ovahe
Anakena
Akahanga
Hanga Oteo
Hanga Omohi
Terevaka
Ahu Akivi
Ahu Tepeu
Maunga Hiva Hiva
Vaka Kipu
Tongariki
Puna Pau
Ahu Uri A Urenga
Vaihu
Hanga Poukura
Vinapu
HANGA ROA
Hanga Kioe
Vai Uri
Tahai
Ana Kai Tangata
MATAVERI
Maunga Te Manavai
Rano Kau
Orongo
P.N. RAPA NUI
P.N. RAPA NUI

1. ISLA DE PASCUA
EASTER ISLAND


ISLA DE PASCUA
PARQUE NACIONAL "RAPA NUI"
CORPORACION NACIONAL FORESTAL
0 1 2 km

RAPA NUI: AUGE Y CAIDA DE UNA CULTURA MEGALITICA

J. M. RAMIREZ ALIAGA

Museo Fonck, Viña del Mar, Chile

RESUMEN

El presente trabajo intenta explicar parte del misterio de Rapa Nui, reuniendo los resultados de las investigaciones arqueológicas más recientes y las fuentes documentales.
Se analizan las evidencias a partir de un modelo antropo-ecológico, con el objeto de acercarse al espectacular proceso histórico cultural en condiciones tan especiales, pero que tiene muchos ingredientes reconocibles en el inicio de las civilizaciones neolíticas de diferentes tiempos y lugares.

ABSTRACT

The present paper tries to explain, in part, the mystery of Rapa Nui. It is based on results of the latest archaeological investigations and documented sources.
The evidence is analyzed from an anthropo-ecological point of view to try to understand the grandiose historico-cultural process that occurred under such special conditions. Nevertheless, this process has many recognizable points in common with the beginning of neolithic civilizations in different places and times.

Para muchos, el "misterio" de la Isla de Pascua está centrado más en cómo se hicieron y movieron sus cientos de imágenes monumentales de piedra (MOAI), que en cómo llegaron a ser lo que fueron en la Sociedad Rapanui.

Lo verdaderamente fascinante de Rapa Nui es cómo llegó a desarrollarse una sociedad tan compleja en uno de los lugares más aislados del planeta, y el porqué de su colapso.

Se podría decir que, en Rapa Nui, los moai no dejan ver el bosque. En efecto, esos cientos de moai y cerca de 300 altares megalíticos levantados alrededor de la isla son la manifestación más espectacular y evidente de una de las culturas más avanzadas del mundo a nivel neolítico, pero las condiciones históricas, ambientales y sociales que generaron ese proceso y sus diferentes fases quedaron sepultadas por los cambios internos de la propia cultura, y luego difuminadas por el impacto exterior sobre el pueblo Rapanui, llevado casi al exterminio en la segunda mitad del siglo pasado.

Sin embargo, los estudios arqueológicos sistemáticos-a partir de 1955- y las fuentes documentales y etnográficas han permitido reconstruir un cuadro general bastante coherente del pasado de Rapa Nui.

EL ORIGEN

En la actualidad, las evidencias arqueológicas, etnográficas, lingüísticas y aún biológicas señalan a las islas Marquesas como el más probable lugar desde donde partieron los colonizadores de Rapa Nui o, mas bien, "Te Pito O Te Henúa" (El ombligo del mundo).

Este pequeño trozo de tierra firme habría sido el último eslabón de un proceso que comenzó miles de años antes en el sudeste asiático, para definirse en Tonga - Samoa el centro de irradiación de la Cultura Polinesia, hacia el 1000 a.C.. Luego, las Islas de la Sociedad y las Islas Marquesas serían el núcleo de la Cultura Polinesia Oriental, que colonizaría Hawaii por el norte, Nueva Zelanda por el suroeste y Rapa Nui hacia el este.

Así, el megalitismo como expresión del culto a los ancestros no se desarrolló en forma espontánea en Rapa Nui, pero llegó a niveles únicos en el aislamiento, bajo particulares condiciones ambientales y sociopolíticas.

La tradición y las evidencias hablan de un viaje planificado desde Marae Renga, en Hiva, encabezado por el legendario Rey Hotu Matu'a. Aunque hasta el momento no se han encontrado vestigios arqueológicos directos de ese primer asentamiento en Rapa Nui, se estima que ocurrió hacia el 300 d.C.

EL AMBIENTE

Los colonizadores de la Polinesia Oriental habían llevado consigo el árbol del pan, cocotero, taro, ñame, camote, plátano, caña de azúcar, mahute, calabazas, y también cerdos, perros y gallinas. Sin embargo, la enorme distancia y el clima subtropical de la isla, en los 27° de Latitud Sur, impidieron la aclimatación del árbol del pan y del cocotero, y tampoco llegaron el cerdo y el perro.

En los escasos 163 km2 de esa isla de bajo y ondulado relieve no encontraron la vegetación exhuberante de sus tierras de origen, pero había bosques de palma y toromiro, y en las lagunas del fondo de sus tres cráteres había abundante agua dulce y crecía la totora. El agua de las lluvias se filtraba rápidamente a través del poroso terreno volcánico. Ningún animal poblaba la isla entonces, pero a las gallinas se sumaron lagartijas y ratones. Hasta el contacto con occidente, constituyeron la única fauna terrestre en la isla. Las gallinas llegaron a tener gran importancia, más allá de su valor económico, como objeto de prestigio.

En cambio, las aves marinas llegaban periódicamente a sus costas, y el mar aportaba una variedad de especies. Sin embargo, el extremo aislamiento de Rapa Nui y la falta de una barrera de coral limitaron su abundancia y accesibilidad en relación a las otras islas de la Polinesia oriental.

Más que ninguna otra cosa, la isla ofrecía una amplia variedad de materias primas líticas, desde la cristalina obsidiana hasta el más duro y fino basalto. En consecuencia, serían el medio más importante para la expresión de las creencias, ingeniería, técnica y arte, a un nivel nunca antes visto.

LA SOCIEDAD

La base del desarrollo cultural sería un orden social encabezado por una aristocracia religiosa: el Ariki Henúa (Rey), la familia real (Ariki Paka) y los sacerdotes (Ivi Atúa), luego los guerreros (Matatoa), los especialistas artesanos (Maori), los hombres importantes o líderes de los linajes (Tangata Honui) y, finalmente, la gente común (Huru Manu) y los sirvientes (Kio).

La justificación de esta rígida jerarquía se encuentra en el origen divino del Ariki, como descendiente directo de los dioses creadores Tangaroa y Rongo. Su linaje -Miru- mantendría por siglos ese orden, mediante el derecho de primogenitura. La autoridad y prestigio del Ariki se encarnaba en el MANA, el poder sobrenatural que le permitía influir en los dominios de la vida y de la muerte, en la fertilidad de plantas y animales y en el control de la producción agrícola y del ceremonial, aislado del resto por las estrictas reglas del TAPU (tabú= lo prohibido).

Ese prestigio era determinante para reunir la mano de obra necesaria para la ejecución de las obras monumentales, y sustentar los privilegios de su linaje.

En una sociedad como ésta, el control de la producción agrícola era fundamental para sostener el sistema, incluyendo la redistribución generosa de los excedentes con ocasión de las grandes fiestas y ceremonias.

Dos mecanismos básicos del sistema fueron la regulación del acceso a los recursos marinos de mayor valor económico, mediante un TAPU que impedía la pesca de los grandes peces de alta mar excepto para el consumo de la aristocracia, en los meses de verano, y sólo por especialistas MIRU; y el control científico y ritualizado del calendario de siembras y cosechas, a cargo de sacerdotes astrónomos del linaje real.

Además, el funcionamiento del sistema dependía de una alta densidad de población, organizada en grupos relativamente autónomos y autosuficientes, dominando territorios claramente demarcados.

Se han reconocido hasta 12 MATA o clanes con sus respectivos territorios. La unidad básica era la familia extensa (Ivi o Paenga), asentada en forma dispersa en el territorio común del clan. Los lazos de parentesco entre las familias formaban linajes (ure) que reconocían ancestros comunes, a quienes rendían culto en los centros ceremoniales.

LA ARQUITECTURA

Las grandes construcciones ceremoniales se ubicaron junto a la costa, en donde residía la aristocracia. Las habitaciones más características son las llamadas Hare Paenga, o casas bote, demarcadas por soleras de basalto formando una planta elíptica alargada, sobre la cual se levantaba la estructura de ramas y hojas,dando la impresión de un bote invertido. Tenían una sola entrada baja y angosta en el centro. A veces, frente a la casa bote se encuentra un pavimento de piedras redondas en forma de media luna. El largo promedio era de entre 10 y 15 metros, pero había más grandes.

Hacia el interior de la isla, junto a los campos de cultivo, se encuentran casas bote menos elaboradas, y también otras casas de planta circular o rectangular, asociadas a la explotación de diferentes recursos. Los fogones subterráneos para cocinar (Umu) suelen estar demarcados por losas de basalto.

Otra estructura típica en la costa es la Tupa, un torreón de piedra con una cámara de unos 2 a 4 m de diámetro por unos 2 a 3 m de alto, que según la tradición servía para observar la llegada de las tortugas.

Pero la máxima expresión arquitectónica fueron los Ahu; los altares o plataformas destinados a recibir las imágenes de los ancestros fundadores de los linajes.

En toda Polinesia Oriental es posible encontrar esos altares megalíticos. En Rapa Nui, por el 700 d.C., al antiguo prototipo polinésico (Marae) le habían agregado un plano inclinado frontal (Tahua) con un pavimento de piedras redondas, amplias extensiones laterales, crematorios, y unas imágenes de piedra de estilo único: los Moai.

A lo largo de casi mil años, los grandes maestros constructores levantaron cerca de 300 Ahu, la mayoría siguiendo la línea costera. Con el tiempo, sucesivas ampliaciones y remodelaciones incrementaron su belleza y tamaño, llegando, en el caso del Ahu Tongariki, a un largo de 160 metros, para sostener 15 imponentes moai con sus respectivos tocados de escoria roja (Pukao) en la plataforma central. El momento culminante de este desarrollo arquitectónico está magníficamente expresado hacia el 1200 d.C., con la construcción del Ahu Vinapú, y hacia el 1445, en el Ahu Akivi.

Una docena de esos Ahu presentan orientaciones astronómicas no debidas al azar, en relación a la posición del sol en solsticios y equinoccios. Esto es particularmente notable en un Ahu interior: Huri A Urenga.

LOS MOAI

Al comienzo, las imágenes monumentales de los ancestros fundadores de los linajes fueron realizadas en diferentes materias primas: escoria roja, traquita o basalto vesicular, pero luego prefirieron la toba del Rano Raraku.

Entre los años 1000 a 1500 d.C., unos 164 moai confeccionados en esa cantera llegaron a los Ahu dispersos a lo largo de la costa, y a unos pocos interiores. Los más antiguos eran toscos, de pequeño tamaño, pero con la toba del Rano Raraku se fueron separando del antiguo prototipo polinésico, para lograr la fina estilización que es única de Rapa Nui.

El borde suroeste del cráter fue el lugar escogido para la agotadora y delicada faena. El tamaño promedio de las imágenes es de un poco más de 4 metros de alto, pero el más grande que llegó a destino, en el Ahu Te Pito Kura, medía 10 metros de alto, con unas 85 tons de peso. Según William Mulloy, la construcción de ese moai debió requerir el esfuerzo de 30 hombres durante un año, 90 hombres durante dos meses para moverlo 6 km desde la cantera hasta el Ahu, en la costa norte cerca de la bahía de La Pérouse, y 90 hombres durante 5 meses para instalarlo sobre la plataforma.

La toba volcánica era tallada y pulida con picotas y azuelas de basalto (Toki). Miles de esos artefactos quedaron abandonados en la cantera, así como 394 moai en diferentes etapas de construcción, incluyendo un gigante de 22 metros, que habría llegado a pesar unas 200 tons.

Las figuras se deslizaban por la ladera hasta un hoyo preparado en la base del cráter, en donde se terminaba el diseño de la espalda. Además, quedaba en posición de "caminar", tal como lo señala la tradición, gracias al Mana del Ariki.

Es posible que se hayan usado diferentes técnicas para su traslado, según el tamaño y peso de cada figura, pero el hecho de que la estatua está diseñada para estar en posición vertical, con un centro de gravedad muy bajo, le da sentido a la hipótesis del transporte tirando de cuerdas que van girando alternadamente la figura, como dando pequeños pasos. Evidentemente, mientras menor sea la superficie de roce, menor será el esfuerzo de la tracción.

En cualquier caso, debieron usar abundante madera y cuerdas de fibra vegetal para proteger los delicados detalles de las manos y la nariz, dos puntos críticos del traslado a través de caminos ondulados, cubiertos de rocas. Existían algunos senderos para Moai, especialmente uno que sale desde la cantera hacia el oeste, por la costa sur

Finalmente, el momento culminante del largo proceso, una vez instalada la imagen sobre la plataforma, era la instalación de unos ojos tallados en coral, con pupilas de obsidiana o escoria roja. En ese momento, la estatua de piedra se convertía en el rostro vivo (Aringa Ora) de un antepasado, recibía su nombre propio, y comenzaba a proyectar el Mana sobre sus descendientes y su territorio.

En la fase de esplendor del desarrollo cultural de Rapa Nui, los grupos más importantes instalaron unos enormes cilindros de escoria roja (Pukao) sobre la cabeza de 58 de los 164 moai que alguna vez se levantaron sobre un Ahu, para representar el moño que se hacían los Ariki con su largo pelo teñido con tierra roja (Kiea), el color sagrado.

LA CRISIS

Hacia el 1500 d.C., con una población que debió sobrepasar los diez mil habitantes, la sobre-explotación del frágil ecosistema de Rapa Nui llegó a un umbral crítico, y a un callejón sin salida.

La necesidad de asegurar el acceso a los territorios productivos, en condiciones ambientales críticas, en donde la agricultura de tala y roza fue empobreciendo fatalmente la capacidad sustentadora del medio, tuvo como única respuesta posible la insistencia compulsiva en el culto a los ancestros.

Ese orden social milenario no era capaz de adaptarse por sí mismo a las nuevas condiciones, tampoco disponían de soluciones técnicas y ya no era posible reducir la presión demográfica mediante una migración masiva; la sociedad Rapanui sólo podía recurrir al Mana de los antepasados. Pero se había agotado, como la propia isla.

Entonces, la búsqueda de un nuevo equilibrio sería muy dolorosa. La guerra y el abandono y destrucción de los monumentos megalíticos fueron la consecuencia más dramática. Probablemente, la conocida leyenda de los "Orejas largas" (Hanau eepe) y los "Orejas cortas" se relaciona más bien con el conflicto entre la clase dominante (que se alargaba las orejas como símbolo de su rango) y la clase productora, que culmina con el exterminio de los primeros. La interpretación de que se trataría de dos razas distintas, llegadas sucesivamente a la isla, no tiene asidero en las evidencias arqueológicas.

Cuando un grupo vencía a otro, no sólo saqueaba y mataba, sino que destruía los Moai que habían protegido ese territorio, tratando de quebrar los cuellos de las imágenes al caer y sacándoles los ojos.

Es la época del auge de los guerreros (Matatoa), desde una posición secundaria a una dominante. Aunque la familia real se mantuvo de alguna manera aislada de los conflictos, protegida en los inviolables terrenos de Anakena, la situación al interior de los clanes cambió radicalmente.

El hambre fue el detonante de las crueles guerras, permanentemente reactivada por la necesidad de venganza. En un momento, se formaron dos grandes confederaciones que se repartieron la isla en mitades: Ko Tu'u Aro hacia el oeste, Ko Hotu Iti hacia el este. Un instrumento de muerte caracteriza esta época: el mata'a, una punta de proyectil o de hacha de mano, confeccionada en obsidiana.

La devastada agricultura y la falta de embarcaciones para acceder a las fuentes más importantes de proteínas del mar llevaron la subsistencia a un nivel crítico. La situación es tan desesperada que en buena medida las escaramuzas tienen como principal objetivo la caza de víctimas humanas: es época de antropofagia.

Desde un punto de vista arqueológico, se aprecia una intensificación en la recolecta de pequeños moluscos; el uso intensivo de las cuevas, preparadas como refugios para escapar de la guerra (Ana kionga); la remodelación, ocultamiento o reutilización de los Ahu como osarios, con cámaras especialmente construídas para recibir los huesos de los miembros del linaje; la construcción de terrazas de cultivo en sectores protegidos (ladera interior del Rano Kau); la construcción de muros circulares de piedra, tanto aéreos como subterráneos, para proteger las plantas del viento y la pérdida de humedad (Manavai); y de gallineros de piedra (Hare moa), verdaderas fortificaciones para proteger las gallinas del robo. Pero lo más notable, es el abandono total del megalitismo como expresión de un orden sociopolítico y religioso milenario.

EL NUEVO CULTO

Con el abandono del megalitismo y el alivio de las presiones productivas, la jerarquía hereditaria de los Ariki da lugar a una jefatura temporal, entre los líderes guerreros de los principales clanes, a través de un culto centrado en la magia de la fertilidad y los ritos de los primeros frutos: el dios creador Make Make y la ceremonia del Tangata Manu (Hombre pájaro).

El eje del ritual, que antes se reproducía periódicamente en los Ahu de cada linaje, ahora se traslada a la aldea ceremonial de Orongo, en la cumbre del Rano Kau, en el vértice sur de la isla.

La aldea, de estilo único en la isla, está compuesta por 53 habitaciones elípticas, con muros de lajas de basalto y techo de falsa bóveda, dispuestas en línea a lo largo de la pendiente que mira a los islotes Motu Kao Kao, Motu Iti y Motu Nui.

Cada primavera, a lo largo de unos tres siglos, se reunieron allí para la gran fiesta de la elección del líder político religioso (Tangata Manu), a través de la competencia ritual por el huevo del Manutara, un gaviotín gris (Sterna fuscata) que llegaba a anidar al Motu Nui, a un kilómetro del abrupto acantilado.

Los jóvenes escogidos de cada grupo involucrado debían nadar hasta el islote, ayudados por un flotador de totora (Pora), y esperar la postura de las aves. El primero que conseguía un huevo de manutara le daba a su jefe el honor de ser investido como Tangata Manu.

Entonces, al encarnar la potencia divina, era afeitado y pintado de colores rojo y negro, recibía el Ao, un remo de doble pala que representaba el poder, bajaba en prosesión triunfal a Mataveri, y desde allí se dirigía a su lugar de reclusión por seis meses (era Tapu), en Anakena, si pertenecía a los clanes del oeste, o en Rano Raraku, si pertenecía a los del este. Su clan gozaría de una serie de privilegios, y comenzaba por saquear a sus enemigos tradicionales. El último Tangata Manu fue elegido hacia 1867.

En Orongo quedaron cientos de imágenes de Tangata Manu y de Make Make, así como las pinturas de los Manutara en el techo de la Ana Kai Tangata (la cueva donde comían los hombres que participaban en la competencia, o donde se comían a las víctimas del grupo perdedor).

A pesar de que el antiguo orden cambió radicalmente, y el hecho de que el proceso fue particularmente cruento, la fuerza y continuidad de la Cultura Rapanui se aprecia en que la descendencia directa de Hotu Matu'a mantuvo su prestigio, y se encuentra hermosamente graficada en un moai llamado Hoa Haka Nana Ia (rompedora de olas), que se encontraba en Orongo hasta 1868, cuando fue llevado al Museo Británico.

Esa imagen, de estilo clásico pero confeccionada en basalto, expresa claramente la legitimación de la ideología emergente, que se superpone en la espalda del moai, con grabados en relieve del Ao, Komari (vulvas que simbolizan la fertilidad) y Tangata Manu.

El CONTACTO CON OCCIDENTE

El 5 de Abril de 1722, día de Pascua de Resurrección (de donde viene el nombre Isla de Pascua), los marinos holandeses incorporan una variable imprevista a la crisis. Al principio, esos contactos fueron efímeros, en el espíritu de los grandes exploradores del siglo XVIII (Cook, La Pérouse), pero en el siglo XIX, los más bajos apetitos de la civilización occidental someten a los isleños a la esclavitud y las pestes, diezmando la población, hasta llegar a contarse apenas ciento once sobrevivientes en el año 1877.

En 1864 llega a la isla el hermano Eugenio Eyraud, primer misionero cristiano, quien es el primero en dar cuenta de la existencia de unas tablillas de madera con escrituras jeroglíficas: los rongo rongo. Hasta hoy, su origen y significado sigue siendo uno de los misterios de Rapa Nui. Al menos, hay cierto consenso entre los especialistas en el sentido de que se trataba de uns escritura pictográfica destinada a guiar la recitación de un texto cuya clave estaba en poder de algunos iniciados. Según la tradición, las tabletas llegaron a la isla con el propio Hotu Matu'a; según algunos especialistas, se desarrollaron después del contacto con Europa. En la actualidad, sólo se conservan 28 piezas de madera con escritura rongo rongo, repartidas en diferentes Museos y colecciones privadas del mundo entero, excepto en la propia isla. No existen antecedentes de ese tipo de escritura en ninguna otra isla de Polinesia (y tampoco en América), y parece muy poco probable que se haya podido desarrollar algo tan complejo en el período más crítico de su historia, cuando quienes tenían los recursos para hacerlo ya no contaban con el prestigio y el respaldo de la aristocracia religiosa. Es posible que ya en la época del contacto con occidente se conservara sólo parte de su sentido, repetido mecánicamente. Con la desaparición de los antiguos sabios, se perdieron las claves para siempre.

A partir del 9 de Septiembre de 1888, la isla se incorpora a la soberanía chilena, y durante la mayor parte de esta última etapa se mantuvo casi tan aislada como antes, pero inevitablemente afectada por un mundo ajeno y lejano. La apertura al mundo exterior trajo avances materiales y nuevas perspectivas para el pueblo Rapanui, pero también el deterioro de su cultura, así como ha estado ocurriendo a los monumentos de su glorioso pasado.

Pero hay esperanza, porque la isla y los isleños tienen MANA.

BIBLIOGRAFIA BASICA (Obras de síntesis)

AYRES, W. 1973. The Cultural Context of Easter Island religious structures. PhD Tesis. Tulane University.

ENGLERT, S. 1948. La Tierra de Hotu Matu'a. Imp. San Francisco.

McCOY, P.C. 1979. Easter Island. En: J.Jennings Ed. The Prehistory of Polynesia. Harvard University Press, Cambridge.

METRAUX, A. 1940. Ethnology of Easter Island. B.P.Bishop Museum, Honolulu.

MULLOY, W. 1978. A preliminary Culture-Historical research model for Easter Island. En:Las Islas Oceánicas de Chile, Vol. 1:105-151. Inst. de Estudios Internacionales, Universidad de Chile.

RAMIREZ, J.M.1988. Cultura Rapanui. Col. Culturas Aborígenes. Ministerio de Educación, Chile.

ROUTLEDGE, K.1919. The Mystery of Easter Island. Londres. Reimp. 1978, AMS Press, New York.

VAN TILBURG, J.A. 1986. Power and Symbol: The stylistic analysis of Easter Island monolithic sculpture. PhD Tesis. UCLA.

GEOLOGIC OUTLINE OF EASTER ISLAND AND PETROGRAPHIC-STRUCTURAL FEATURES OF ITS LITHIC MONUMENTS

H. MORENO ROA

Depto. Geología y Geofísica, Fac. Cs. Físicas y Matemáticas
Universidad de Chile, Santiago, Chile

ABSTRACT

A geological outline of Easter Island is given describing briefly the three main volcanic groups: Terevaka, Rano Kao and Poike.
The petrographic nature of the main lithic monuments: moais, pukaos and ahus is described. The deterioration of the statues is discussed in terms of the influence of the bedding orientation during the cutting of the statues from the quarry.

RESUMEN

Se presenta un bosquejo de la geología de Isla de Pascua describiendo brevemente los tres principales grupos volcánicos: el Terevaka, el Rano Kao y el Poike. Se da la naturaleza petrográfica de los principales monumentos líticos: los moais, los pukaos y los ahus. Se analiza la influencia de la orientación del corte en cantera de las estatuas sobre su deterioro.

1. INTRODUCTION

Easter Island is the sunmit of a submarine volcanic complex formed about 500 km east of the East Pacific Rise axis. The island has a triangular shape due to the development of three main volcanoes: Terevaka, the highest (506 masl), covers the northern and central part of the island; Poike stands at the extreme east and Rano-Kao is located at the extreme southwest (Fig. 1).

The island measures about 22x11 km, covers an area of 117 km2 and is located on the Nazca Plate, 4000 km west of the Chile coast.

A geological map of the island at 1:100.000 scale was first published by Baker et al in 1974 (1) and at 1:50.000 scale by González Ferrán and Baker also in 1974 (2). Prior studies, mainly related to the petrography and geochemistry of the volcanic rocks, were done by Verlain (1987) (3), Tilley (1922) (4), Rosenbusch and Ossan (1923) (5), Lacroix (1927) (6), Chubb (1933) (7) added some geology, the same did Bandy (1937) (8). A more recent and complete geologic study of the island was made by Baker (1967) (9). On January 1989), the author of this article spent 2 weeks in the island through the Corporación Nacional Forestal (CONAF) in charge of the Easter Island National Park administration and development, with the purpose of: lithic monuments weathering evaluation, selection of geologic sites of interest for visitors and quarry labours checking.

2. GEOLOGICAL OUTLINE OF THE ISLAND

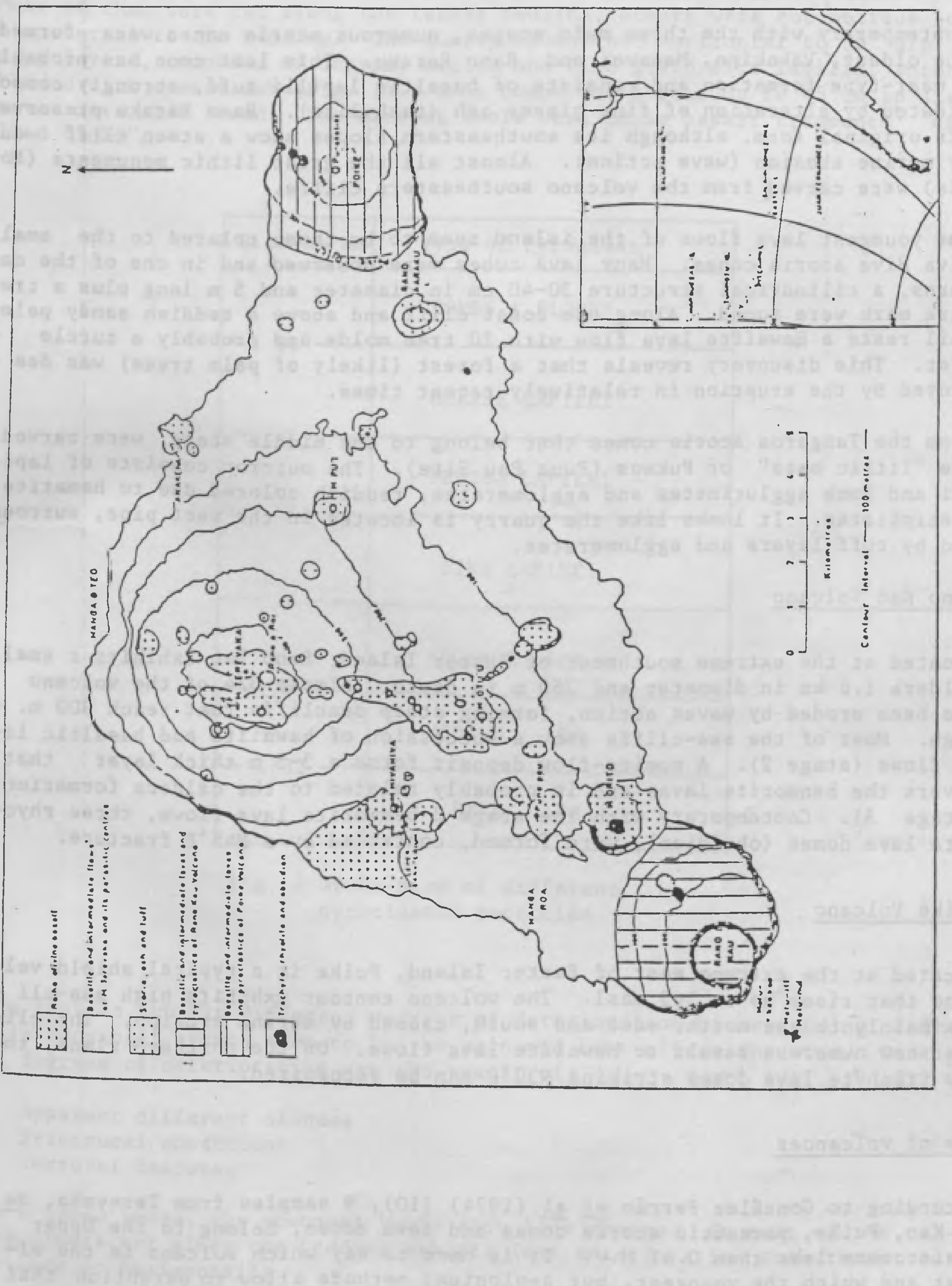
Easter Island volcanic rocks belong to the alkaline suite and have a wide petrographical and geochemical range, from basalt and hawaiite to trachyte - and rhyolite (obsidian). Lava flows prevail over tephra deposits and volcano types can be classified as shield volcanoes, scoria cones and lava domes. The volcanic topography of the island is mostly well preserved, although the waves action has deeply eroded the three main volcanoes slopes, forming steep sea-cliffs.

<u>Terevaka volcanic group</u>

This volcano group covers almost 100 km2 of Easter Island and consists of a main shield volcano built on the mid-northern part of it, scattered by isolated scoria cones or aligned in radial fissures that strike N10°E and N60°W. The slopes of Terevaka consist of basalt and hawaiite lava flows.

According to González et al (2), the main edifice was formed through three stages. Most of the shield volcano consists of an older unit composed of basalt and hawaiite lava flows with little pyroclasts of aphiric basalt.

A middle stage is represented by porphyritic basaltic lava flows erupted from the western N10°E summit fissure that flowed down covering the volcano



TEXT-FIG. 1.—Simplified geological sketch map of Easter Island with inset of South-East Pacific showing location of the island. From BAKER, 1967 (9) western slopes. About 14 scoria cones were built on top of this fissure, 2.5 km long.

The young stage consists of extense lava flows erupted from the eastern N10° E summit fissure that flowed down covering the volcano northeastern slopes.

Contemporary with the three main stages, numerous scoria cones were formed. The oldest, Vakakipo, Manavai and Rano Raraku. This last cone has probably a maar-type formation and consists of basaltic lapilli tuff, strongly consolidated by alteration of fine glassy ash (tachylite). Rano Raraku preserves its original form, although its southeastern slopes show a steep cliff cut by marine erosion (wave action). Almost all the great lithic monuments (Moais) were carved from the volcano southeastern cliffs.

The youngest lava flows of the island seem to be those related to the small Híva Hiva scoria cones. Many lava tubes were observed and in one of the caverns, a cilindrical structure 30-40 cm in diameter and 5 m long plus a tree bark mark were found. Along the coast cliff and above a reddish sandy paleo soil rests a Hawaiite lava flow with 20 tree molds and probably a turtle - cast. This discovery reveals that a forest (likely of palm trees) was destroyed by the eruption in relatively recent times.

From the Tangaroa scoria cones that belong to the middle stage, were carved the "lithic hats" or Pukaos (Puna Pau Site). The outcrop consists of lapilli and bomb agglutinates and agglomerates, reddish colored due to hematite precipitates. It looks like the quarry is located in the vent pipe, surrounded by tuff layers and agglomerates.

Rano Kao Volcano

Located at the extreme southwest of Easter Island, Rano Rao Exhibits s small caldera 1.6 km in diameter and 250 m in depth. Almost 3/4 of the volcano has been eroded by waves action, forming steep seacliffs that reach 300 m. - high. Most of the sea-cliffs show a succession of hawaiite and basaltic lava flows (stage 2). A pumice-flow deposit forms a 3-5 m thick layer that covers the benmorite lavas and is probably related to the caldera formation (stage 3). Contemporary with the stage 2 benmorite lava flows, three rhyolite lava domes (obsidian), were formed, controled by a N45°E fracture.

Poike Volcano

Located at the extreme east of Easter Island, Poike is a typical shield volcano that rises up to 365 masl. The volcano contour exhibits high sea-cliffs mainly to the north, east and south, caused by marine erosion. The cliffs show numerous basalt to hawaiite lava flows. On the northern flank, three trachyte lava domes striking N30°E can be recognized.

Age of volcanoes

According to González Ferrán et al (1974) (10), 9 samples from Terevaka, Rano Kao, Poike, parasitic scoria cones and lava domes, belong to the Upper Pleistocene less than 0.47 M.y. It is hard to say which volcano is the oldest and which the youngest, but geological methods allow to establish that Terevaka and its parasitic centers are the youngest volcano group. Among them, the Hiva Hiva scoria cones and related lava flows seem to be very recent, perhaps Holocene.

3. PETROGRAPHIC - STRUCTURAL FEATURES OF EASTER ISLAND LITHIC MONUMENTS.

The studied monuments at Easter Island were the "Moais", "Pukaos" and their basements or "Ahus". Moreno (1989) (11).

The Moais

Almost all of the Moais were carved from the Rano Raraku lapilli tuffs. Most of them were cut along the tephra bedding, others were cut oblique or transversal to the bedding. The quarry shows thin horizontal to 30° dipping layers, composed of coarse, medium and fine grain size lapilli, interbedded with coarse ash (Fig. 2). Some bombs and blocks up to 45 cm in diameter were also found. The carving tools were dense basalt fragments called "Toki".

Size in mm	Type of Pyroclast
	BOMBS & BLOCKS
64	
	COARSE LAPILLI
32	
	MEDIUM LAPILLI
16	
	FINE LAPILLI
2	
	COARSE ASH
1/4	
	MEDIUM ASH
1/32	
	FINE ASH

Fig. 2 Grain size of different pyroclastic particles.

The statues exhibit different degrees of deterioration by weathering. The main erosional agents seem to be the rain and less effect the wind. Distinct degrees of deterioration are the result of:

- Apparent different oldness
- Structural conditions
- Textural features

In a broad sense, the youngest Moais show less damage. In most of the cases, Moais cut along the bedding exhibit less deterioration than those cut oblique or horizontally.

Moais strongly damaged by the rainfall, are those composed by coarse to medium lapilli grain size. The better preserved consist of ash with minor lapilli fragments.

The Pukaos

The pukaos were carved from Puna Pau quarry, located in a volcanic pipe. The outcrops show medium to coarse scoriaceous lapilli and spatter type bombs which form red colored agglutinates and agglomerates. Lapilli is abundant and vary from 5 to 60 mm in size. On the other hand, bombs reach up to 200 mm in diameter. The pyroclastic rocks density was estimated in 1.5 g/cm3, hence, the Pukaos weight vary from about 9 to 20 Tons.

The Ahus

Most of the Ahus are composed of vesicular basalts, dense basalts and brecciated-lava blocks. Chemical attack by salty sea water is evident in these rock types. The enlargement of vesicles or cavities in the rocks by corrosion has formed alveolar structures. Wind action has removed the loose material.

REFERENCES

(1) BAKER, P.E., BUCKLEY, F. and HOLLAND, J.G. 1974. Petrology and Geochemistry of Easter Island. Contr. Mineral. and Petrol. Vol. 44, 85-100.

(2) GONZALEZ FERRAN, O., and BAKER, P.E., 1974. Easter Island Isla de Pascua, Guide Book, Excursion D-2, IAVCEI. International Symposium on Volcanology, Santiago, Chile.

(3) VERLAIN, V., 1987. Les rockes volcaniques de I'lle de Paques, Soc. Geol. France, Bull. 3, Ser. 7, 410.

(4) TILLEY, C.E. 1922. Density, refractivity and composition relations of some natural glasses. Min. Mag., 19, 176-294.

(5) ROSEMBUSCH, H. and OSSAN, A., 1923. Elements der Gesteinslehre. Viert Ed. Stuttgart.

(6) LACROIX, A., 1927. Le constitution lithologique des iles volcaniques de la Polynésie austral. Acad. Sci. París, Mem, 59, 1-82.

(7) CHUBB, L.J. 1933. Geology of Galápagos, Cocos and Easter Island. B.P. Bishop Mus. Bull., 110, 1-67.

(8) BANDY, M.C. 1937. Geology and Petrology of Easter Island. Bull. Geol. Soc. Am., 48, 1589-1610.

(9) BAKER, P.E. 1967. Preliminary Account of Recent Geological Investigations on Easter Island. Geol. Mag., Vol. 104, N°2, 116-122.

(10) GONZALEZ FERRAN, O., CORDANI, U.G. and HALPERN, M. 1974. Potassium-Argon ages and Sr 87/ Sr 86. ratios of Volcanic rocks from Easter Island. IAVCEI International Symposium on Volcanology, Paper N°37, Santiago, Chile.

(11) MORENO, H., 1989. Observaciones geológicas realizadas en el Parque Nacional Rapa Nui entre el 09 y el 20 de Enero de 1989. Informe preliminar, CORPORACION NACIONAL FORESTAL CONAF.

THE PETROGLYPHS OF EASTER ISLAND: PROBLEMS OF NATURAL EROSION AND HUMAN IMPACT

G. LEE

Institute of Archaeology
University of California at Los Angeles, CA 90024, U.S.A.

ABSTRACT

Rock carvings (petroglyphs) on Easter Island are found on lava flow, basalt outcrops and boulders, volcanic tuff, and red scoria. Although we see evidence of erosion and loss of design elements from weathering, lichen growth, and the spalling of rock surfaces, the greatest impact is caused by man. This paper discusses problems of erosion, effects of visitors to the island, and vandalims. Significantly, a great deal of damage has resulted from various experiments and museum projects in efforts to obtain replicas for display purposes.

RESUMEN

Los petroglifos de Isla de Pascua fueron tallados sobre derrames de lava, afloramientos y rocas de basalto, toba volcánica y escoria roja. A pesar de la evidencia de erosión y de pérdida de elementos gráficos por intemperismo, crecimiento de líquenes y escamación de la superficie de las rocas, el mayor impacto se debe a la acción del hombre. Se describen los problemas de erosión, de los efectos de visitantes a la Isla, y del vandalismo. Significativamente mucho daño ha resultado a causa de diversos experimentos y projectos de museos en sus esfuerzos por obtener réplicas para la exposición al público.

1. INTRODUCTION

Petroglyphs are found in all sectors of Easter Island where adequate surfaces are available. The majority are along the coastal plains where lava flow has created large flat areas called *papa*, and many are associated with important ceremonial centers (*ahu*). Other surfaces with petroglyphs include dense basalt stones or outcroppings, such as are found at Orongo.

However, the ancient Rapanui also placed designs on softer volcanic tuff including the statues carved from Rano Raraku tuff, and red scoria. In the case of red scoria, huge topknots (*pukao*) for the statues as well as facia placed as a decorative element on certain *ahu* were additionally carved with designs, in spite of the fact that this type of relatively soft stone is a very poor surface for petroglyphs.

2. THE PETROGLYPHS

Over 5000 petroglyphs have been documented on Easter Island. They range in size from a few centimeters to 12 meters in length. Rock carvings are surely one of the more important facets of the ancient culture. Petroglyph designs can reveal much about a former society: in the carvings we see such things as clan affiliations, change in the socio-political situation, status concerns of chiefs and priests, legends and myths (and thus the cosmic belief system), and contact with the Western world (1).

In the case of petroglyphs having been added to statues, *pukao*, and the red scoria facia of *ahu* we have evidence for a reuse of the sacred, because these motifs have, for the most part, been carved after the statues and pukao were thrown down in the inter-island wars that decimated the old society (2). The designs on these surfaces are thus time-related, occurring after approximately A.D.1550.

3. THE FIELD PROJECT

The rock art recording project began documenting the petroglyphs (and paintings) on Easter Island in 1981. As the project encompassed more than seven years, it has been possible to monitor petroglyph sites and this has provided a firm data base on changing conditions (3).

As part of the recording project, petroglyph sites were documented in their entirety by means of scale drawings and photography. Scale drawings were made in the following manner: a string grid was placed over the rock surface, using 20 or more centimeter squares. The petroglyph designs were then drawn to scale on cross-section grid paper, using precise measurements. This method forces the recorder to carefully scrutinize that which he is drawing with the result that a detailed record is made of the design and its condition. All possible additional information was recorded such as presence of lichens and areas that were impacted by foot traffic from both man and beast.

Thus, over the years, the constant revisiting of sites revealed changes. The natural processes of weathering is an inexorable and continuing process; it is also slow and not apt to be noticeable on short-term studies, but other factors are more dramatic and can be clearly seen. As part of the study, photographs taken by Routledge (4) in 1914-15 and drawings made by Lavachery (5) in 1935 were checked against present condition; such comparison revealed significant permutations over time.

4. THE PROBLEMS

Lichen. Several fine panels are literally covered with lichens. Eventually these growths will destroy the stone and the designs upon it. The occurrence of lichens varies with the micro-environents of the island; it is rare on the petroglyphs at Orongo, but common on the north coast near Anakena. Some examples occur on flat ground-level *papa* while others are on vertical faces of boulders. Figures 1-2 illustrate lichen growth on various petroglyph panels.

Traffic. The *papa* is often hollow due to air pockets beneath the surface. In those cases where traffic has caused damage it is often due to the breaking down of the stone. As the rock art recording project progressed, it became clear that panels located on or near ground level were being impacted by human traffic (including motorcycles) as well as by cattle and horses. A few petroglyph panels are located directly on pathways and thus receive an inordinate amount of wear. In some cases, whole sections have been broken off. Figure 3 illustrates a finely-carved and complex panel from Omohe, on the north coast. The head of a large petroglyph of a turtle has been broken off, as indicated by the shaded area. This figure was complete when Lavachery (6) sketched it in 1935.

Although other factors may be at work, such as the age of the petroglyphs, the difference between a rock art panel that is far away from roads and seldom visited (Figure 4) contrasts with one that receives heavy visitation from tourists (Figure 5). The latter site is wearing rapidly from foot traffic.

Damage from rubbings. Some petroglyphs have been eroded by attempts to make rubbings of the designs. This sort of wear is very subtle and can only be determined by studying old photographs and comparing them with the present

Figure 1. Petroglyphs on a hillside north of Anakena are covered with lichen; the designs are visible only because islanders scrape them with stones to make them stand out for tourists to photograph.

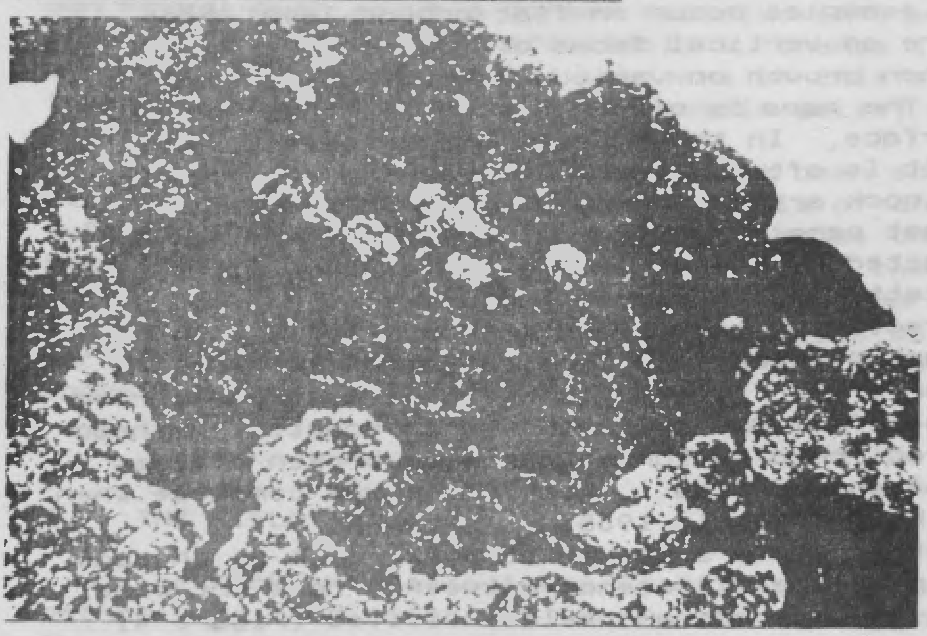


Figure 2. Petroglyphs on Ahu Iho Arero's sea wall, Anakena, are beginning to be impacted by lichen growth.

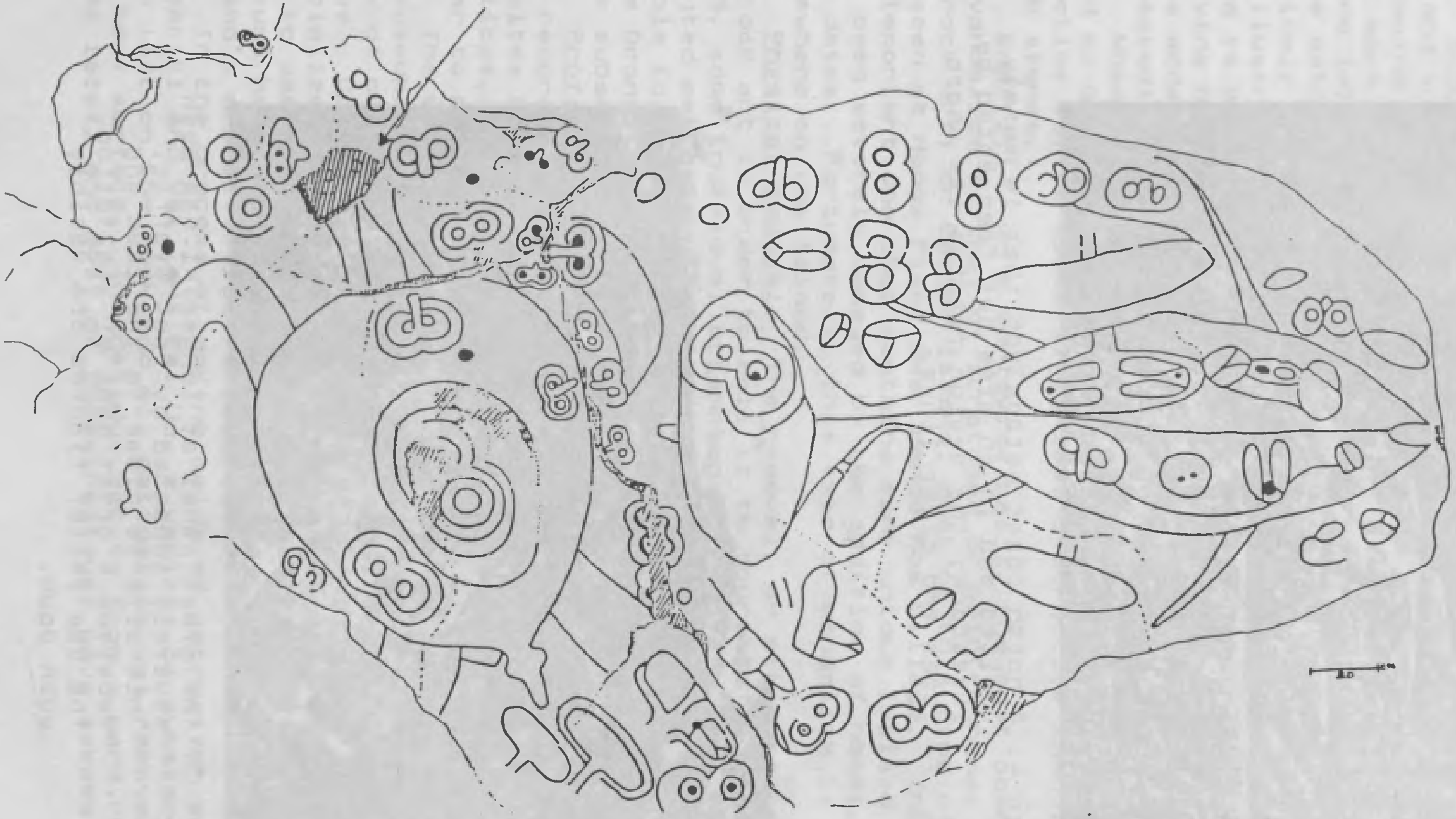


Fig. 3 - Petroglyph panel from Omohe showing erosion and damage from foot traffic. The head of the turtle figure is broken off and other erosion is indicated by diagonal shading.

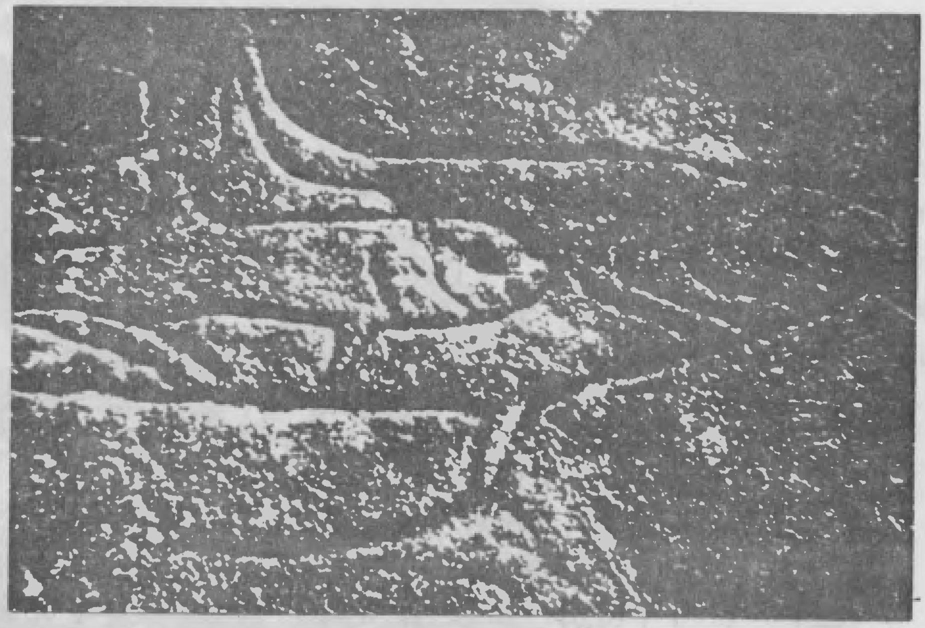


Figure 4. A north coast petroglyph that is rarely visited and in an area not frequented by livestock; the design retains its sharp edges and clear lines.

Figure 5. The great panel at Tongariki has been severely impacted by foot traffic. This site is close to the road and receives a great deal of visitation. The bas relief figures are visibly worn down.

condition of the motifs. Orongo appears to be the main target for making rubbings and from a close scrutiny of earlier photographs, these petroglyphs are definitely "softer," that is, the edges of the bas relief figures are less well defined.

Scoring. One of the most damaging practices to the island's petroglyphs is the local custom of "scoring" or scraping the designs with stones so that the motifs stand out more clearly for tourists. This practice is common among island guides and has done enormous damage to many fine petroglyph panels (Figure 6)(7). In some instances, entirely new motifs have been created by this means. Figure 7 illustrates a bas relief petroglyph from Ahu Ra'ai that is said to be the abode of an *aku-aku* spirit. The original carving had no head (8); it recent years, however, islanders have added the rounded shape in the center by scoring it repeatedly with stones, changing its appearance.

When chalk or crayon are available, these are often used by both tourists and locals; as deplorable as this practice is, at least it is less destructive than scraping with stones.

Graffiti. On a worldwide basis, the most common type of vandalism is that of scratched or painted names and dates on rock art; on Easter Island, most of this type of damage is seen at Hanga Piko, near Hanga Roa village. This site, an important one that contains many unique incised designs, has been severely damaged by the addition of names, initials and dates. Fortunately, this type of vandalism is rare elsewhere on the island.

Physical removal. The removal, or attempted removal, of rock art in order to sell it to tourists occurs also. In 1989, some individual attempted to remove a very fine, painted petroglyph from a cave on Motu Nui. The vandal was unable to pry it loose, but the scars remain. Petroglyphs from Orongo have been removed in the past but most of these were subsequently recovered.

Professional vandalism. The most unexpected result of the recording project was the clear evidence of damage done to sites by professionals who came to the island to make replicas, test various products, or conduct experiments in order to prove various theories.

The use of replicas in displays is an important feature in museums throughout the world, for they give a concrete view of cultural items and have considerable educational value. Conversely, the making of a replica is a delicate, specialized process and must be made with great care so as not to damage the original. Despite impressive credentials, museums have caused irreparable damage to some of Easter Island's archaeological treasures.

In the process of making molds of petroglyph panels at Tongariki and Vai Tara Kai Ua, a variety of substances has been left on the rock and all patination was removed from the rock surface. The residue varies from a hard resin to a gummy latex, and most of these residues have seeped into the

Figure 6. The magnificent petroglyph panel at Ahu Ra'ai has been severely damaged by scoring the designs with stones. Some of the motifs have been altered by this practice.

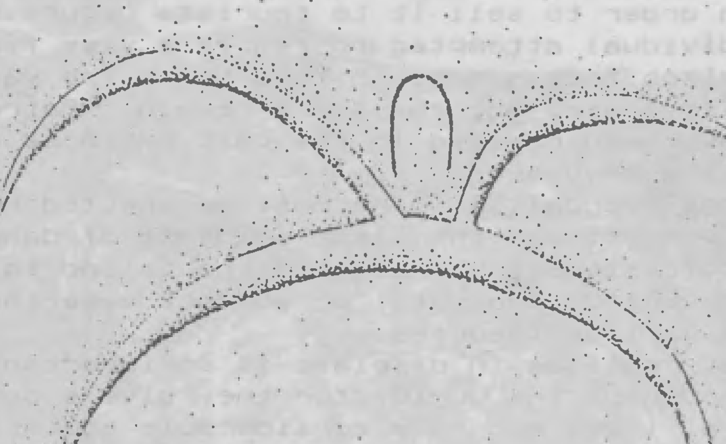


Figure 7. A bas relief petroglyph has been changed in recent years by the addition of a head. This was done by local islanders scraping or scoring the petroglyph with stones.

pores of the stone, leaving unsightly messes that defy attempts at removal.

In the case of two statues in the quarry at Rano Raraku that were being cast for a European exhibit, the removal of molds also removed patination plus some of the stone surface from the weathered west sides of the *moai* (Figures 8, 9)(9). Another *moai* in the quarry with a ship petroglyph on its chest was marred by attempts to take a mold. The fact that this damage occurred as a result of the activities of professional crews is inexcusable. While it is recognized that no damage was intended, (10) museum experts involved in these processes must assume the responsiblity for studying the problem with greater care before attempting replicas. A beautiful replica does not justify irrevocable damage to the original work of art (11).

Experiments conducted on *moai* by Heyerdahl (12), who attempted to prove a theory regarding their transport, were detrimental to the statues; any scientific "experiment" must be fully documented and care taken to minimize risk. The statues chosen by Heyerdahl were poorly suited for testing (their bases had been altered by restoration efforts), they were not in their original location, and the value of the experiments is highly questionable. In addition, they sustained adverse effects from the experimental procedures and the statue at Tongariki was left unstabilized in an upright position (13).

Heyerdahl's excavations of statues at Rano Raraku in 1955 left them exposed to the elements where they have deteriorated from weathering. Other damaging effects from the Heyerdahl expedition can be seen at Ahu Tepeu (14) where a portion of the magnificant sea wall collapsed because an excavation pit was left unfilled.

An experiment with chemical products to preserve the volcanic tuff statues was conducted in recent years by the Centro Nacional de Restauracion and Wacher Company of Germany (15); one can only wonder why a highly visible, restored statue at Hanga Kio'e was selected for experimental testing rather than an obscure one out of the public eye.

Another chemical test occurred in 1987, conducted by a Hawaiian firm, International Chemical Systems. My presence at Anakena during the spraying was totally fortuitous: I personally witnessed experimental spraying of a product containing vinyl and acrylic on a statue fragment at Anakena. There was no documentation whatsoever. The application turned the stone a blue-grey color. I have been monitoring the fragment photographically on subsequent trips to the island. What did the chemical compound include and to what proportions was it diluted? Where is the documentation, and what are plans to follow up on it? Casual non-scientific experiments such as this should not be tolerated.

Figure 8. One of the two moai at Rano Raraku damaged in the process of making molds for museum replicas. Sections of the surface on the west side were removed along with the mold

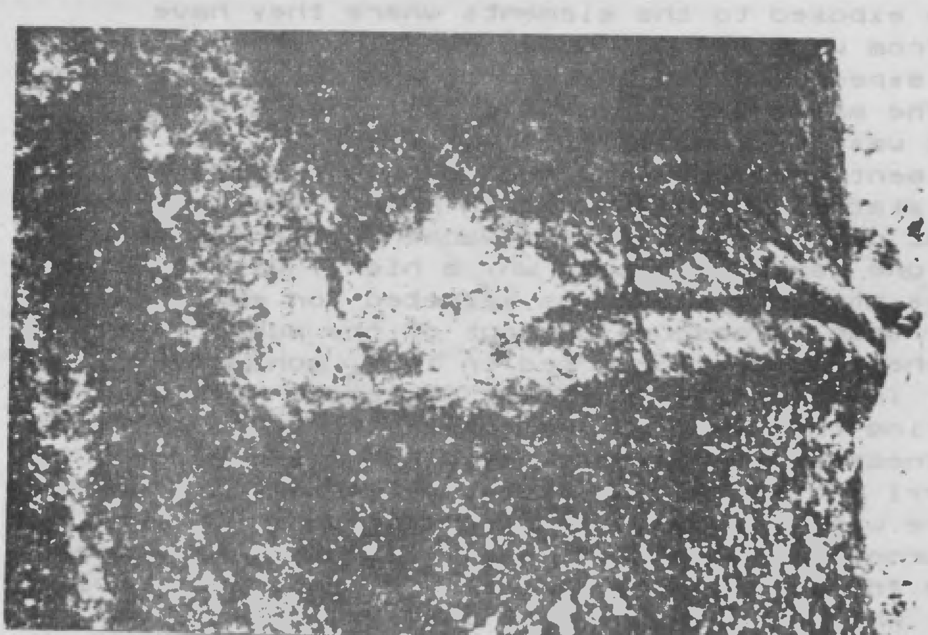


Figure 9. Detail of damage on statue shown in Figure 8.

5. THE SOLUTIONS

Lichen removal. A professional study should be made for ways to treat petroglyph panels that are heavily encrusted with lichens. It may be possible to remove lichen growth, but great care must be taken in the selection and application of a product that will kill these organisms. Without treatment the petroglyphs will eventually be destroyed as the roots of these growths penetrate the rock.

Education. Everyone agrees that education is the solution to many of the problems cited here. It is one of the most important ways that conservation can be approached. A campaign in the island schools, amongst the Park Guards, and in community meetings, would be most beneficial.

Providing guards. An excellent means of preventing damage to sites is to have someone with authority, watching. However, the problems of monitoring sites on an island-wide basis are enormous, not the least of which is funding to hire guards.

Physical restraints. The setting off of petroglyph areas as marked archaeological sites will help in their preservation. Simple walls or fences around the sites will keep animals and motorcycles off, and low-key signs requesting that the petroglyphs be respected and not touched have had good results in other parts of the world. The setting aside of an area by enclosing it has a psychological factor in that it indicates a site is special and protected (16).

Conservation. Undoubtedly, the technology exists to stabilize and/or repair many of the basalt *papa* upon which carvings occur, such as lava flow with air spaces below the surface. A pilot program to study the feasibility of stabilization should be initiated; however, any conservation treatments should first be carried out on *in situ* field tests, not on the actual artifact.

Graffiti removal. It is a proven fact that graffiti attracts more graffiti. Therefore, it is vital to keep sites clean and free of names, initials and dates (17). In the case of Hanga Piko, the site should be cleaned and repaired, and protective measures taken to insure survival of the petroglyphs.

Official policy. Tighter control over requests and permits to make replicas or to do other scientific experiments should be a simple matter and damage from these kinds of projects can be prevented. Even though museums, organizations, or individuals appear to possess adequate qualifications, the potential for damage always must be taken into account. Reviews of all proposals should be made by both conservationists and archaeologists; laypersons may not be aware of potential hazards to the cultural patrimony.

Documentation. In the long run, the scientific documentation of statues, carvings and paintings is the most certain means of preservation.

6. CONCLUSIONS

Easter Island's ancient carvings are an irreplaceable resource: they provide a glimpse into the mind and spirit of those long gone, and are a sacred component of the island's cultural origins, beliefs, and rituals. In size, complexity of design, and excellence of carving, they have no equal elsewhere in Oceania.

Exposure to the elements and natural erosion have caused significant deterioration. Human impact, however, has resulted in irreparable damage to both statues and petroglyphs.

Educational efforts for the island's inhabitants must be accelerated. The archaeological heritage of the island has, for the Rapanui, always been there; they cannot conceive of a time when this may not be so. Although aware that the archaeological sites are an important economic factor of the tourist trade, some Rapanui are unconcerned about protective measures and many are unaware of the damage that can be done by heavy visitation, even without malicious intent. It is ironic that it is outsiders who have a greater awareness of what is happening to the art and archaeology on this tiny island in the center of the world.

7. REFERENCES

1. Lee, G. Ph.D. Dissertation, Ideological Symbols as Evidence of Socio-political Change. University of California, Los Angeles, 1986.

2. Van Tilburg, J.; Lee, G. Symbolic stratigraphy: Rock art and the monolithic statues of Easter Island. *World Archaeology*, 1987; Vol.19(2):133-149.

3. Lee, G. Report, Isla de Pascua, Chile, 1986. Ms. on file, Rock Art Archive, UCLA.

4. Routledge, K. Survey of the village and carved rocks of Orongo, Easter Island, by the Mana Expedition. J. *of the Royal Anthropological Institute of Great Britain and Ireland*, 1920; Vol.L.

5. Lavachery, H. *Les petroglyphes de L'ile du Paques*. De Sikkel, Anvers, 1939.

6. Lavachery, H. op.cit., fig.13.

7. Lee, G.; Millerstrom, S.; Davis-Drake, A. Trouble in Paradise: Problems in Polynesian Rock Art Conservation. *Rapa Nui Journal*, 1988; Vol.2(3):1,9-10.

8. Lavachery, H. op.cit., fig.170.

9. Anon. News from Hangaroa: Preservations. *Rapa Nui Journal*, 1988; Vol.2(2):11.

10. Hänig, U.;Sauer, D. Technique de coffrage et de moulage pour l'obtention de copies fidèles de deux moai et d'une façade ahu de l'île de Pâques, *Ile de Pâques: une Énigme?* Musées Royaux d'Art et d'Histoire, Brussels, 1990:152-159.

11. Van Tilburg, J. Respect for Rapa Nui: exhibition and conservation of Easter Island stone statues. *Antiquity*, 1990; 64:249-58.

12. Heyerdahl, T,; Skjolsvold, A; Pavel, P. The "Walking" Moai of Easter Island, The Kon-Tiki Museum *Occasional Papers*, Vol.1, 1989:36-64.

13. Van Tilburg, J. Easter Island Statues: Observations on Preservation and Protection of a Cultural Resource. Report, Rock Art Archive, UCLA, 1986.

14. Heyerdahl, T.;Ferdon, E. *Archaeology of Easter Island: Reports of the Norwegian Archaeological Expedition to Easter Island and the East Pacific*, Monographs of the School of American Research and the Museum of New Mexico, No.24, Vol.1, 1961:191.

15. Roth, M. La conservation des bustes de pierre colossaux. *Ile de Pâques: une Énigme?* Musées Royaux d'Art et d'Histoire, Brussels, 1990: 145-151.

16. Gale, F.; Jacobs, J. *Tourists and the National Estate.* Australian Heritage Commission, Canberra, 1987:pg.103.

17. Gale, F.; Jacobs, J. op.cit., p.6.

ACKNOWLEDGEMENTS

The author wishes to thank the Consejo de Monumentos, Santiago de Chile; Corporacion Nacional Forestal; Dr. Elena Charola; and former governor, Don Sergio Rapu. The Instituto de Estudios, Isla de Pascua, provided assistance to the rock art project, which was conducted under the aegis of the University Research Expeditions Program, University of California, Berkeley. Many Rapanui worked with the recording project or helped in numerous ways. I am indebted to them for their insight and friendship.

6. CONCLUSIONS

[illegible] resource: they provide a [illegible] spirit of those long gone, and are a sacred component of the island's cultural [illegible] [illegible] However, has resulted in irreparable damage to both statues and [illegible] must [illegible] island [illegible]

[illegible]

WEATHERING AND CONSERVATION OF SOME TUFFS FROM FRANCE AND EASTER ISLAND

J.-P. PAULY, J. LOPPION* and J. SAUGNAC+

3, rue Maréchal Lyautey, 33140 Villenave d'Ornon, France
* O.N.I.P. 127 Av.Fontainebleu, 94272 Le Kremlin Bicetre, France
+ Etudes & Expertises Construction SARL, 78430 Louveciennes, France

ABSTRACT

Investigations using microscopy and x-rays were carried out on sound rocks (trachytic and trachy-andesitic tuffs and pumices) and weathered parts (crusts and honey-combs). The physical characteristics of weathered and unweathered samples (water/ /solvent absorption, drying and capillarity) were measured in view of the two most important parameters for in-situ conservation of the moais (moisture and physical characteristics of the crusts). Measurements of superficial moisture on moais were made to locate the damp areas that define treatment conditions. These have to be developed in laboratory trials. Nine products (consolidants and/or water repellents) were tested by artificial weathering following metereological data. The final selection was based on the results from classical tests. Some treatment conditions are defined.

RESUMEN

Se realizaron investigaciones microscópicas y con rayos-x sobre rocas alteradas (costras y areas alveolizadas) y no alteradas (tobas traquíticas y traquiandesíticas y piedra pómez). Las características físicas de muestras alteradas y no alteradas (absorción de agua o solvente, secado y capilaridad) fueron medidas en función de los dos parámetros más importantes para la conservación in-situ de los moais: contenido de humedad y características físicas de las costras. Medidas de humedad superficial en los moais fueron realizadas para localizar las áreas húmedas y definir las condiciones de tratamiento. Estas deben ser desarrolladas en ensayos de laboratorio. Nueve productos (consolidantes y/o hidrorepelentes) fueron evaluados por ensayos clásicos luego de envejecimiento artificial diseñado sobre datos meteorológicos. Se definen algunas condiciones de tratamiento in-situ.

1/ WEATHERING

The stone decay had been studied previously [1, 2]. It can nevertheless be completed by the observation in thin layer on a depth of 6 cm of a fine-grained tuff and a coarse grained one. Lapillis are .5 ± .2mm long and few in the fine grained tuff. On the contrary, the lenght reaches 20 mm and the lapillis are very numerous and are fairly often edge to edge or almost (cf annexe 6 10/).

1.1./ UNWEATHERED ROCK (AT DEPTH OF 6 cm)

1.1.1./ Lapillis

There are two kinds of lapillis according to the colour of the cement :
- light brownish colour : fewer vacuoles with wooly edges.
- the dark brownish lapillis enclose a great deal of vacuoles with well defined edges : the walls of the vacuoles are more often as not perfectly clear without any product of alteration; lapillis are edged by a dark aureole the origin of which dates back to the eruption or little time after (vapor from the volcano) [3]. It has a high iron oxydes content (magnetite and goethite);
- the fenoblasts are the following : Olivin is sometimes partly deteriorated into iddingsite (under the effect of the vapor from the volcano). Bowlingite described by Mlle HYVERT has not been found; Plagioclases are often twin (CALSBAD'S macles). The optical determination shows that the range of anorthite content is 50-65 % (Labrador); some scarce aegyrinic augites.

So the rock is rather a basalt than a trachyandesite.
The glass cementing the lapillis is light in plain light (PL) and the pores are well edged with a small diameter.

The presence of a fluidal structure shows differences in the temperature of lapilli during setting or in its chemical composition. The vacuoles of lapillis are of two forms :
- round or with a slight flattening ($f > 0,9$) : around 90 %;
- strong flattening ($0,2 < f < 0,3$) : around 10 %.

One can observe different intermediate cases, eg :
- closely jointed to another one a part of a lapilli shows very flat and orientated along a S vacuoles;
- lapilli the vacuoles of which are all flat and orientated;
- lapilli where plagioclases and 3 flat vacuoles have the same direction ± 10°.

1.2./ WEATHERED ROCK (FROM 0 TO 2 cm DEEP)

There are two levels of deterioration : intermediate states also exist.

1.2.1./ Low deterioration

The weathering is limited to cement bounding the lapillis that are in good condition. Light brownish in the unweathered stone the color turns greenish or blueish brown; the cement loses its brightness and becomes almost completely opaque when observed in plain light. The weathering begins at the walls of the pores which lose its sharpness. When the decay is stronger the image of the walls becomes dim. One can notice unweathered plagioclases out of the wall of an enlarged and wooly pore.

1.2.2./ High deterioration

The lapillis too are weathered. One can observe generally an important deterioration of the cement surrounding lapillis. The diameter of pores is two, three... times greater. Sometimes there remains only very thin walls made of magnetite crystals.

In the lapillis the vacuoles sometimes enlarged to anastomosis by vanishing of the walls. In large vacuoles one can sometimes find some free plagioclases or plagioclases looking like bridge from one wall to the opposite One can observe also an either cloudy or opaque cement, an increasing transformation of olivine into iddingsite up to a nearly perfect pseudomorphosis, and unweathered plagioclases. Nevertheless some lapillis may remain completely sound though surrounded by weathered lapillis. More often than not the dark brownish lapillis are stronger and the deterioration begins by a located thinning of the brown aureole.

To conclude the existence of two different kinds of pores (cement and lapillis) and the presence of a thinner or thicker aureole account for the behaviour of the stone to water imbibition :
- three fifth of the porosity is very highly absorbent (pores in cement);
- two fifth absorbs very slowly (pores of lapillis) (see 2.2.1./).

The exact percentage depends on the ratio between lapillis and cement.

The X-ray analysis of the same samples has shown the presence of smectites at the surface and inside : the low organisation of these clays gives evidence of an outstanding decay.

1.3./ HONEY COMB

Honey comb is very frequent in three cases on the south coast where we find it very often.:

1/ Ahus : the pieces of stone the ahus are made of which are eastward (sun rise) or southward (sea) show honey comb the morphology of which is the same as in limestones (respect of edges; 2-5 cm long and 1-3 cm deep cups).

2/ Pebbles : the basalt pebbles are scarced all around ahu at ANA AKENANGA and show honey comb on the upper face : this is true for heavy pebbles down to 20 kg weight. But little and easily turned over pebbles (by tourists or inhabitants) are often alterated on two faces. This decay has been described [4].

3/ Red hats : the particular structure of that lava leads to a curious morphology : there are hemispheric and 5-8 cm in diameter holes. An accidental origin of these holes seems unlikely. One cannot observe any hole on horizontal surfaces of hats set as vertical cylinders. Nevertheless holes can be seen on horizontal surfaces that are ancient vertical surfaces (eg. cleft hat 568 or 555; lying on generant; half-buried hat 554).

There are at least two main orientations :

1- an original orientation when the hats have been set on heads;
2- a secondary orientation after the moais have been overturned.

On the other hand one can notice one or two lines of holes along generants when the hat is set as a vertical cylinder. Therefore at POKURA one can assert that the westward great holes are ancient and that the eastward little holes are growing. At AKAHANGA hat 561 shows a northwestward area with holes. I think it is turned 180°. So is hat 554. Therefore the position of the honeycomb can be used as a sign of the ancient orientation in archeology. Lastly in 1961 at TONKA RIKI the tsunami turned over the statues and modified the early orientation : the tight white varnishes made of silica that cover eyes-holes are now decaying on a statue (east of the site); the eyes are now turned southward (towards the sea) and the varnish is going away in three points and morphologically it looks like the early phasis of honey comb decay on limestone hardened by a previous calcin.

- TABLE 1 -HOLES ON HAT AND ORIENTATION OF THE GENERANT WITH HOLES.

SITE	N°	OBSERVATIONS
AKAHANGA (West)	556	SE
		N : only a small hole
	561	N to W : holes
		S : nothing
	555	S : some holes
	556	Near the ground
POKURA	601	E : some little holes
	lying	W : great holes
PITO KURA	?	W : two holes

The variations of the weight of a pebble (3 kg of basalt from Easter Island) were analysed for 3 months. The more frequent variations are in the range of .1 to .4 $g/m^2.h$; they reach 1 to 2 $g/m^2.h$ in the case of high variations of hygrothermy. The range of value is the same as limestone -tab 2. During the test, the total variation spreads about $40 g/m^2$ It is noteworthy that one can observe that in the same conditions the variations are as high whereas the basalt is so little porous and that the total salt amounts are quite the same in the powder.

- TABLE 2 - HYGROSCOPICITY (g/m^2).

NATURE	NAME	PORO - SITY	HYGROSCO- PICITY	OBSERVATIONS
Limestone	St-Vaast	40%	17	Without salt
Limestone	Tuffeau	40%	120	Without salt
Limestone	Around La Rochelle	10-25%	20	Without salt
Limestone	The sames		40 - 70	With honey comb 1-5% of salts (SO_4^{--}, Cl^-)
Basalt	Easter Island	< 1%	40	Total % of soluble salts at POKURA: eastw. honey comb 1,4 seew. honey comb 2,0

1.4./ CHEMICAL ANALYSIS

It is very interesting to notice that, below the under rock shetter where moai 230 is carved the whole wall is covered with small yellowish or reddish crusts : the area of these crusts is some mm2 and they separate very easily from the rock which is wet and greenish (algae) below. The amount of silica is around 2 % and that of soluble salts is 14,6 % (this last amount is 7 times as high as in honey comb). The morphology and the chemical composition are very similar to "maladie à pustules" which is found on calcin-covered limestones at La Rochelle (France) : this decay seems to be the early stages of honey comb when the formation of calcin is quicker than the one of honey combs. Consequently one can conclude :

- step 1 : formation of siliceous crusts by seepage of rain through the porous structure of the volcano;
- step 2 : destruction of crust place by place.

On the other hand the total amount of soluble salts is less important in crust just above the ground (tab 3). These salts are more important than it seems and it is necessary to undertake more accurate investigations into the salt amounts and their distribution in different sites, etc.

- TABLE 3 - CRUSTS AND SALTS

MOAI NUMBER	SITE	HEIGH ABOVE GROUND	TOTAL AMOUNT OF SALTS
272	RANO RARAKU	40 cm	. 9
586	VAHIKU	10 cm	. 12

2/ PHYSICAL PROPERTIES OF TUFFS FROM EASTER ISLAND

2.1./ EVAPORATION OF WATER

2.1.1./ Drying curves

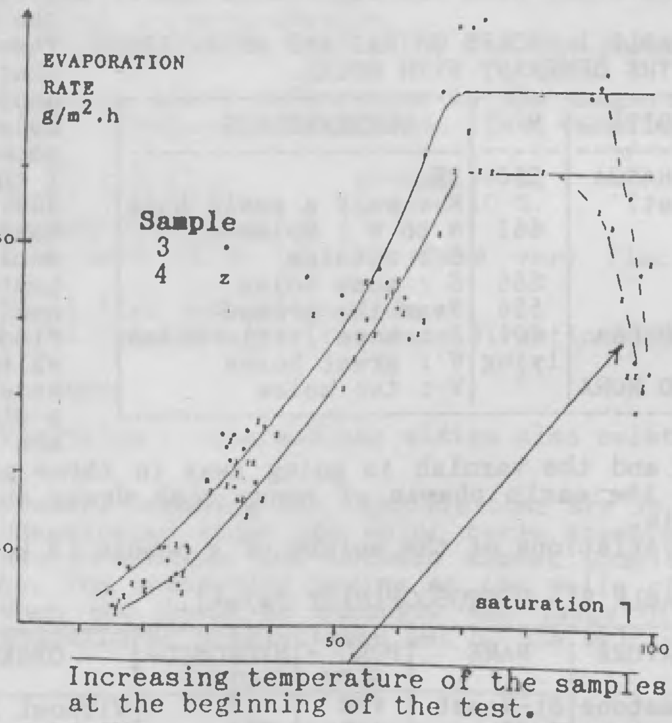
Two series of tests have been undertaken :

1/ Five samples wetted by rain in Easter Island (three fine grained samples and two coarse grained ones) and dried in steady atmosphere (25°C ± 1°C; RM 50 %);

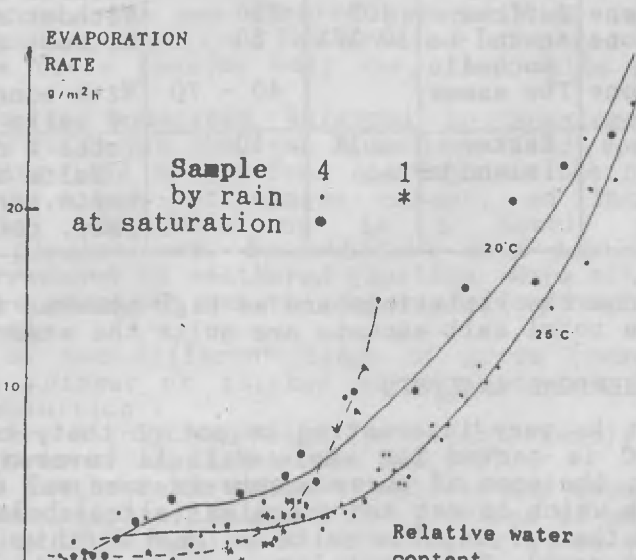
2/ Drying of two samples saturated by distilled water :
- Sample 4 : capillary rise and dipping for six months;
- Sample 3 : saturation by absorption under pressure (pipe insaturated atmosphere. The drying is undertaken in steady atmosphere (20°C; RM 60 %).

We can observe the quasi identity of the drying curves of the saturated samples (diag. 1). However the variations of the evaporation rate of the coarse grained sample (n° 4) are higher than the ones of the fine grained sample(n° 3) and they are higher than the variations expected by calculation according to temperature and moisture variations (see below for explanations).

We can observe (diag. 2) :
a/ an important variability between samples (table 4);
b/ in spite of the higher tempera-ture in the first test it is obvious that the evaporation rate is lower when the water content



Diag. 1- **DRYING CURVES** of the two sample saturated with distilled water for a long time : one can notice some fluctuations in account of the discharge of lapillis in the pores of cement.



Diag. 2- **DRYING CURVES according to the wetting method** i.e. the location of the water for a given water content.

- TABLE 4 - EVAPORATION RATE VERSUS RELATIVE WATER CONTENT

WATER CONTENT	NUMBER OF SAMPLES 1	2	3	4	5
10	1.8	2.5	1.25	2.5	4.5
20	7.5	4.5	-	4.5	5.0
30	-	12.5	-	13.8	7.5
40	-	40.0	-	40.0	16.3
50	-	-	-	-	26.3

fine grained (samples 1-3) coarse grained (samples 4-5)

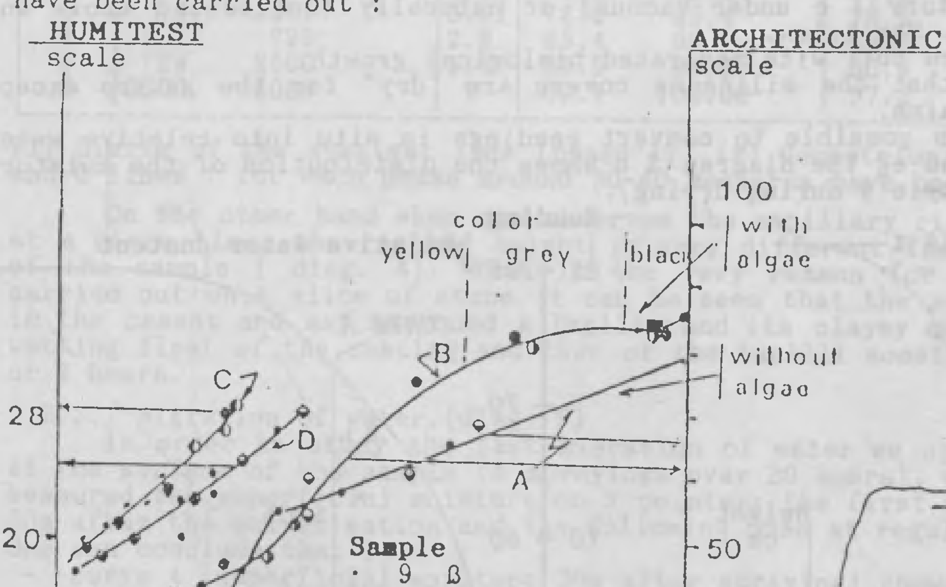
is lower than 16 % (sample 3) and 40 % (sample 4) : this is explained by the location of the water in the sample. For a short time wetting (rains, beginning of capillary rise) water fills only the cement pores (or nearly) : this water goes quickly towards the surface of evaporation when the water content is higher than its critical value.On the other hand after saturation the water located in the pores of cement evaporates first and the water what fills lapillis spread out in an irregular manner in the cement pores (considering the clayey coating of lapillis : this is probably account for the great variations of the evaporation rate of the coarse grained sample).

2.1.2./ Calibration of moisture gauges

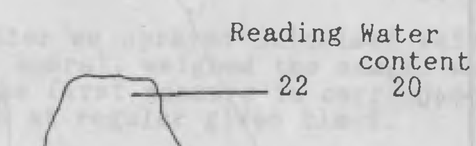
The superficial moisture has been measured using two two-point moisture gauges during the drying : the very twisted surface of the stone does not allow the use of the other types of gauges :

- PROTIMETER HUMITEST SM 13-28 is used especially for woods (16-28 %) and the low water contents for other building materials;
- PROTIMETER ARCHITECTONIC D5785 has both the same scale as the upper gauge and a relative scale graduated from 0 to 100 that needs a calibration.

The calibration is always carried out by applying firmly the points but without penetration in the stone. Moisture was measured in 5 or 6 places which were distributed evenly along the height of the sample. Three series of measures have been carried out :



Diag. 3 A - **CALIBRATION OF THE MOISTURE GAUGES** (HUMITEST on the left, ARCHITECTONIC on the right).One can notice the importance of both biological growths for the higher values of moisture (curves A, B) and grain for the lower moisture (curves C, D).



Diag. 3 B - **An example of the distribution of water during drying.**

- 5 samples naturally wetted by rain in Easter Island;
- 2 samples saturated in distillated water for 6 months;
- 1 slice of rock which is 7 mm thick and has an area of 40 cm².

Very rapidly it appears that the great pores allow the accumulation of water in the lower part of the samples (another drying was undertaken with sample 2 upside down and the result confirms that the heterogeneity of the sample does not account for this observation). Therefore the drying was also undertaken on a thin slice so that the moisture gradient can be neglected.

One can observe (diag. 3) :

a/ sample 9 : this slice had been previously treated by a biocide in order to obtain the calibration of both unweathered and sound tuff (curve A);
b/ the drying curves of the saturated stones are quite the same. During the drying the colour turns (curve B). The presence of important biological growth (algae in particular) probably explains the high reading on the gauge.
c/ the drying curves of the naturally wetted samples can be divided into two groups :
- sample 1 to 4 - curve C
- sample 5 - curve D. It is the curve A after transposition of the scales.

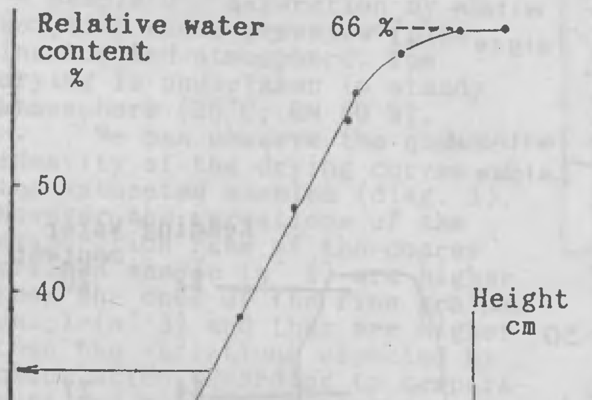
The comparison of the calibration curves of samples 3 and 4 according to the method of humidification corroborates the analysis of the evaporation curve : above a 20 % water content the water of the natural wetted sample is located in the cement and not in lapilli. Therefore the reading is higher than with saturated samples. On the contrary below 20 % the water that is stocked in lapilli diffuses in the cement and wets it.

To conclude one can find three cases :

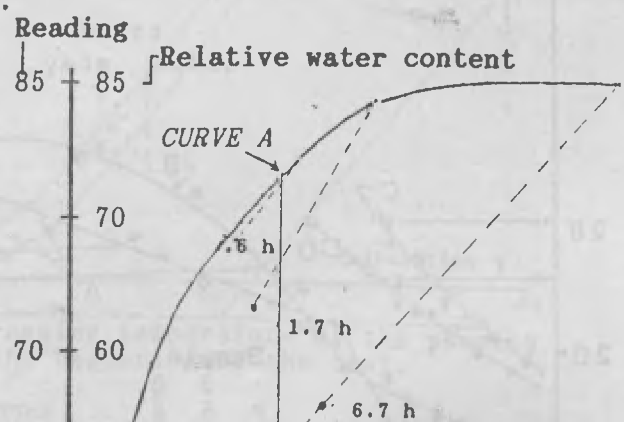
a/ curve A or D (according to the moisture gauge) for tuff without biological growth;
b/ curve B tuff covered by a moderate biological growth and saturated either artificially (laboratory i e under vacuum) or naturally (buried and above any water tight surface). See below.
c/ curve C rain wetted tuff with moderated biological growth.

One can note that the siliceous covers are "dry" for the gauges except soon after pelting rains.

Therefore it is possible to convert readings in situ into relative water content (see 7.1./ and eg the diagram 3 b shows the distribution of the moisture at the surface of sample 4 during drying).



Diag. 4 - **CAPILLARY RISE.** One can observe the high value of the coefficient of capillarity and the heterogeneity of the rock underlined by the difference of the water level in the different parts of sample 4.--------(tuff of **EASTER ISLAND**)



Diag. 5 - **MIGRATION OF WATER :** according to the intensity of the spray ie of the rain.

2.2./ ABSORPTION OF WATER.

2.2.1./ Capillary rise (diag. 4)

We have not carried out capillary rise on samples dried at 105°C (this state does not exist in situ) but on a sample in an hygroscopic equilibrium in conditioned air (25°C, 50 %). After the measure of the coefficient of capillarity we have satured the sample by complete immersion for 6 months.

The results are reported in table 5 where :

- H1 is the relative water content calculated from the hygroscopic equilibrium;
- H2 is the relative water content calculated from the dried state (105°C).

The value of the 48h-capillary coefficient is 285 g/dm² $h^{.5}$.

Therefore, for an accessible water total porosity of about 40 % per volume a quarter is filled by hygroscopic water; 55 % is quickly filled up (<1 h) whereas the saturation is very long to be achieved. Consequently, in situ :

- moais content at least 25 % per volume (7 % per weight);
- under rains or under intermittant but important conditions of wetting, water content between 60 and 80 % are not exceptionnal;
- the only deep zones, the buried statues in the ground and the zones becoming water-tight by impervious crusts can exceed 80 % and reach saturation.

-TABLE 5- WATER CONTENT DURING CAPILLARY RISE B in g/dm² $h^{\frac{1}{2}}$

PHASE N°	TIME IN HOUR AT THE BEGINNING of the phase	TIME IN HOUR AT THE END of the phase	B	MOISTURE H1 AT THE BEGINNING of the phase	MOISTURE H1 AT THE END of the phase	MOISTURE H2 AT THE BEGINNING of the phase	MOISTURE H2 AT THE END of the phase
1	0	.6 (1)	285	0	55.8	25.0	66.7
	.2	.77(2)		0	63.5		72.6
2	.6	44.9	5.63	55.2	72.2	66.7	78.5
3	44.9	361	3.61	72.2	83.4	78.5	86.7
4	361	729	2.8	83.4	88.9	86.7	90.8
5	729	2500	1.4	88.9	89.7	90.8	97.2
6	2500	5069	?	89.7	100.00	97.2	100.00

(1) Limite of the straight line (phase 1). (2) Geometrical cross of the phase 1 and 2 lines : for each phase around 30-40 measures have been taken into account.

On the other hand when one observes the capillary rise it is obvious that, at a given time, the reached height is very different from one to another part of the sample (diag. 4). What is the very reason for it ? When a test is carried out on a slice of stone it can be seen that the water climbs previously in the cement and may surround a lapilli and its clayey coating completely. The wetting first of the coating and then of the lapilli sometimes needs more than 1 or 2 hours.

2.2.2./ Migration of water.(diag. 5)

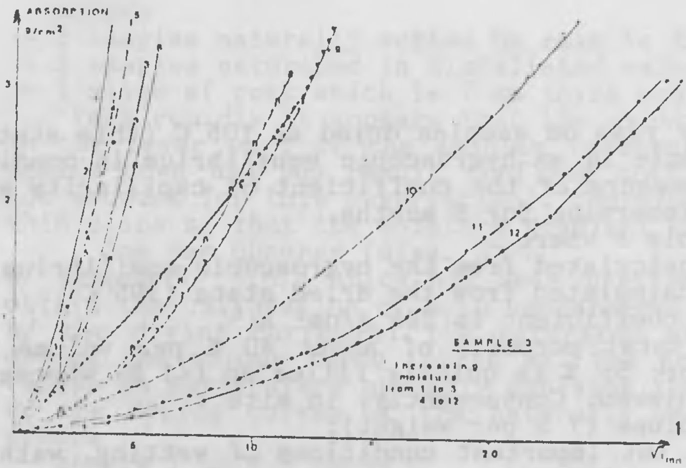
In order to study the fast migration of water we sprayed deionised water at the surface of the sample (5 sprayings over 20 hours), weighed the sample and measured the superficial moisture on 9 points : the first measure is carried out 30s after the pulverisation and the following ones at regular given times. One can conclude that :

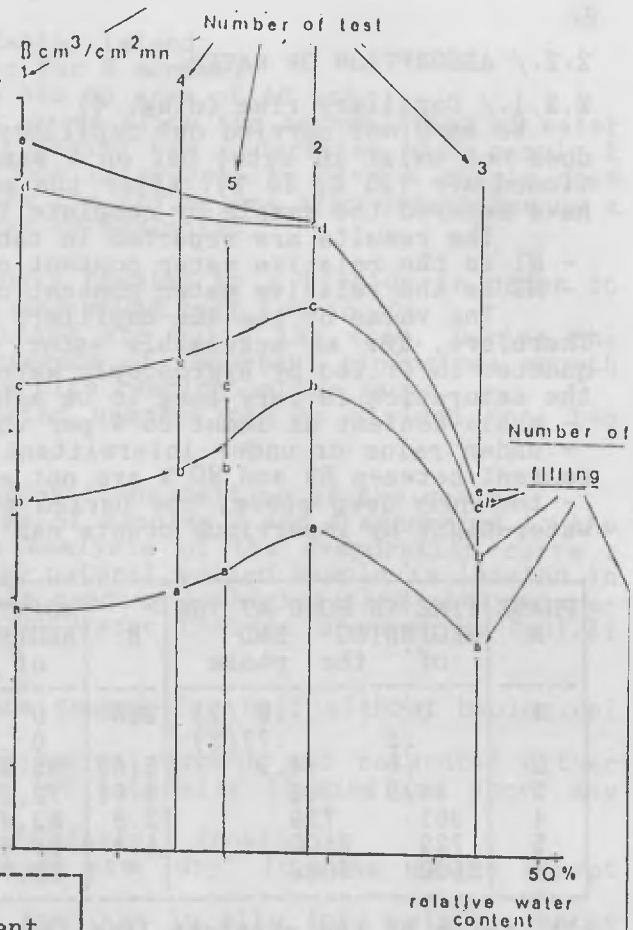
- curve A (superficial moisture 30s after spraying) shows that little water is needed (ie intermittant rains or light or very light rains or drizzles) to saturate the surface;
- evaporation is slow (dotted lines) : 15,5 h after the last spraying the superficial moisture still reaches 47 % whereas WC arounds.15 l/m²;
- for the same WC (.5 l/m² eg) the superficial WC is 73 % just after the rain whereas it only reaches 54 % when this total value is obtained after evaporation and diffusion towards the inside (spraying n° 5).

2.2.3./ Absorption of water under pressure

In order to know the WC and the capacity of absorption of both the crusts and the underlaying stone we have developed the interpretation of the absorption of water under pressure by using an absorption pipe [5]. The maximum pressure corresponds to the dynamic pressure created by a 140 km/h wind : this wind velocity is not scarse and therefore permits an evaluation of the absorption of rain by moais before (weathering) and after the treatments (quality).The cinetic of the absorption depends on the nature of the connexions between pores, the WC and its location and the nature and the importance of alterations or superficial modifications (cf. 8.1./ about SERVIERES'tuff).

The absorption of water when using a pipe or by dripping obeys the capillary law in $\sqrt{t}$ [5, 6] except, in case of natural or artificial modification, the absorption obeys a logarithmic law.[7]





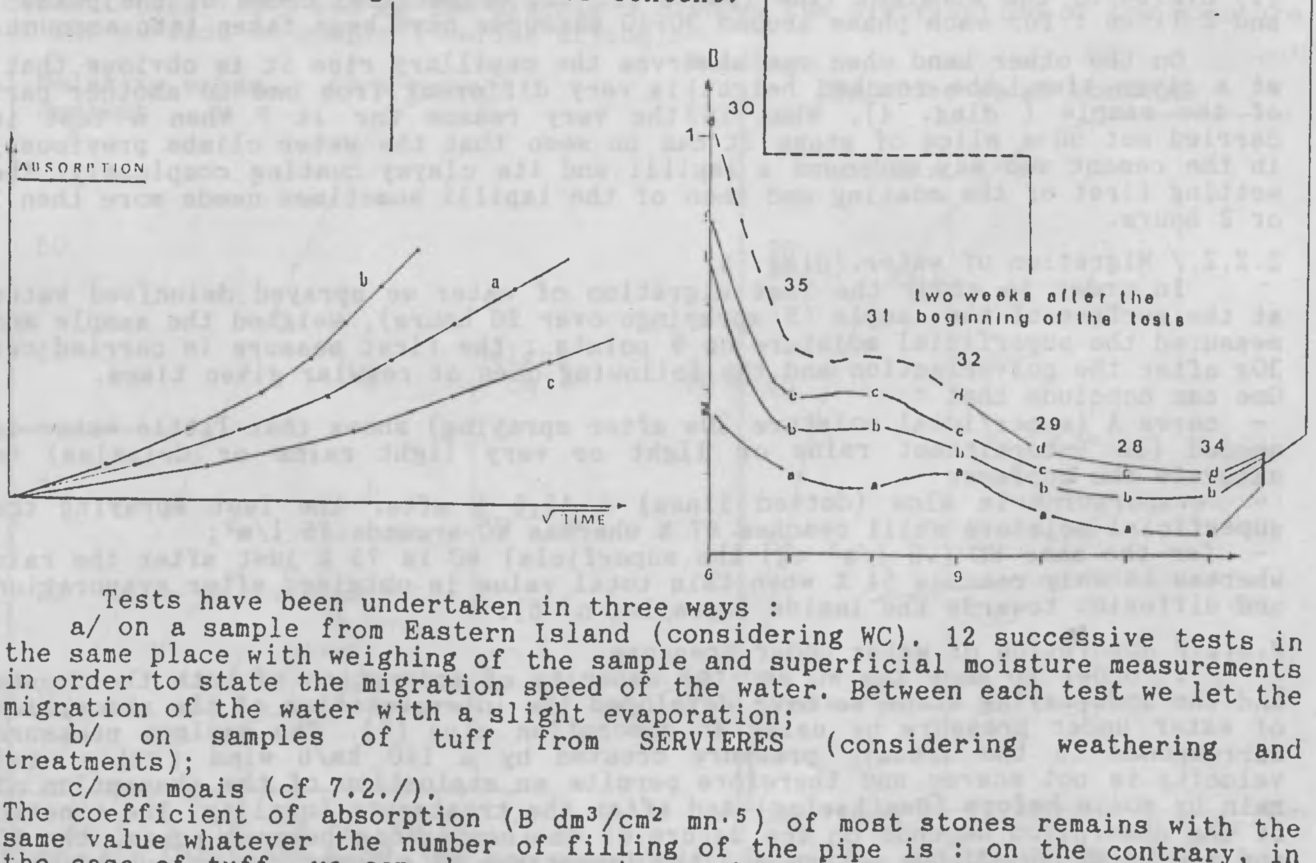
Diag. 6 - **THE 12 SUCCESSIVE ABSORPTIONS** of water under pressure. One can notice that they do not obey the capillarity law.

Diag. 7 - **EVOLUTION** of the capillarity coefficient according to the moisture.

A : the higher value is observed around 28 -30%.

B : downward slip of B for the same WC according to the time.

Diag. 8 - **SCHEME** of the different types of absorption according to the water content.



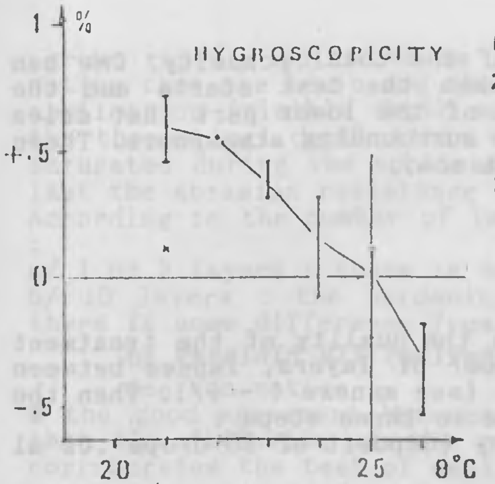
Tests have been undertaken in three ways :

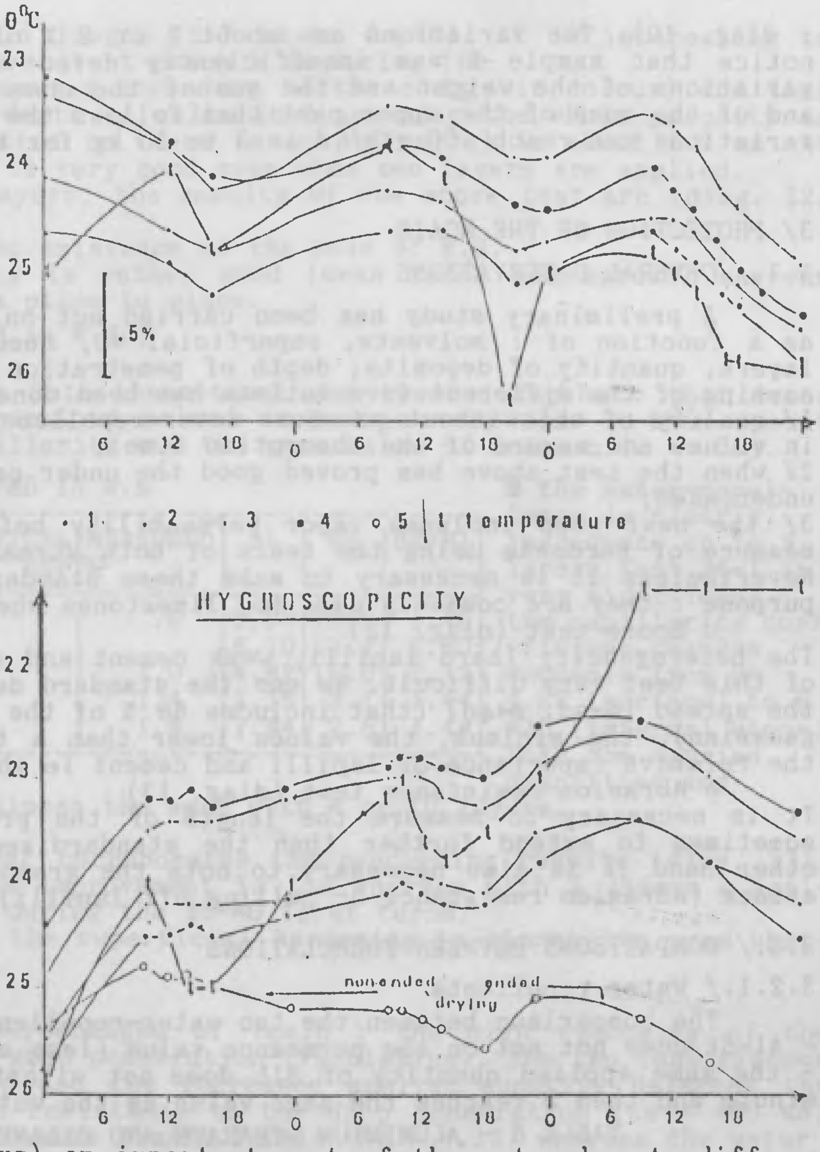
a/ on a sample from Eastern Island (considering WC). 12 successive tests in the same place with weighing of the sample and superficial moisture measurements in order to state the migration speed of the water. Between each test we let the migration of the water with a slight evaporation;

b/ on samples of tuff from SERVIERES (considering weathering and treatments);

c/ on moais (cf 7.2./).

The coefficient of absorption (B $dm^3/cm^2\ mn^{.5}$) of most stones remains with the same value whatever the number of filling of the pipe is : on the contrary, in the case of tuff, we can observe an increasing value up to a constante (diag. 6).In the scale of RWC (0-45 %) one can observe that B grows to a maximum for RWC = 28 % (diag. 7 a) during the 3 or 4 first fillings and that after it becames nearly constant : this value decreases with an increasing RWC. From the 6th test (nearly two weeks after the beginning of tests) one can observe that B





Diag. 10 - VARIATIONS OF BOTH WATER CONTENT AND TEMPERATURE.

Diag. 9.-.VARIATIONS OF THE HYGROSCOPIC CONTENT.

decreases for the same RWC (diag. 7 b). The small fluctuations during the 7th, 8th and 9th test correspond to the slight differences in WC when absorption starts (note that the 5th test is rather confuse).

Interpretation

According to DOMASLOVSKY the swelling of clays is the main reason of the decreasing absorption without pressure he observed. Up to 28 % B increases be cause water diffuses more quickly in moist porous media. During the first tests (15 days) an important part of the water has to diffuse in lapillis through the clayey coating and so contribute to remain an important part of the pore of cement free of water. After 15 days the clays located in the pores of cement swell and impede the propagation of the water or these surronding lapilli swell and so the pores of lapilli keep water (cf. evaporation 2.1./). We must notice that swelling occurs in a significative manner only two weeks after the beginning of the first humidification. This is very important to understand the stone decay and this fact shows the very importance of the nanoclimate of each part of the moais. One must notice too that the bounded RWC (28 %) is nearly the critical WC as termed by VOS [8].

To conclude we may distinguish three states (diag. 8) :
- dry rock (in hygroscopic equilibrium) : type a;
- scarcely wet rock (with WC < 40 %) : type b;
- always wet rock (slow absorption) : type c.

NOTA : when B increases at each filling, it is possible to interprate according to a logarithmic law : $\log D = \log D1 + a \log t$ or $D = D1\, t^a$ where D1 is the value for t = 1 and with D : cm^3/cm^2 ; t : mn.
Without developing this interpretation, it shows that there exists a short early phase which is characterized by a value of a between .65 and .75 and for 1 to 5 minutes and then the absorption continues with a between .85 and .95.

2.2.4./ Hygroscopic behaviour

The variations of the weight of 5 samples (2 coarse and 3 fine grained ones) had been measured for 3 months (6 to 8 weights per day generally). Whatever the fineness of the grains may be, one can observe a good correlation between the variations of the weights among themselves (diag. 9) and when the temperature varies no more than .1°C/h the equilibrium is always reached at each given time and the correlation between temperature and absorption is good (sample 1 eg :

: diag. 10). The variations are about 1 or 2 % of the total porosity. One can notice that sample 5 was insufficiently dried when the test starts and the variations of the weight are the sum of the ones of the lower part that dries and of the ones of the upper part that follows the surrounding atmosphere. These variations can reach 100 g/m².d ie 3 to 10 kg for a moai.

3/ PROTECTION OF THE MOAIS

3.1./ GENERAL OBSERVATIONS

A preliminary study has been carried out on the quality of the treatment as a function of : solvents, superficial WC, number of layers, lapses between layers, quantity of deposits, depth of penetration (see annexe 4 - 9/). Then the sorting of the different formulations has been done in three steps :
1/ quality of the without pressure water-repellency (deposit of 20 drops .05 ml in volume and mesure of the absorption time);
2/ when the test above has proved good the under pressure absorption of water is undertaken;
3/ the next step includes vapor permeability before and after treatment, and measure of hardness using the tests of both streaking and abrasion resistance. Nevertheless it is necessary to make these standardized tests suitable for our purpose : they are commonly used for limestones whereas tuffs are so different.

o Score test (diag. 12)

The heterogeneity (hard lapilli, weak cement and clayey coating) makes the use of this test very difficult. We use the standard deviation sd, the mean value **m**, the spread [m-sd, m+sd] (that includes 68 % of the values if the distribution is gaussian), the minimum, the values lower than a threshold etc. that depend on the relative importance of lapilli and cement ie the diameter of the grains.

o Abrasion resistance test (diag. 13)

It is necessary to measure the length of the print every 5 or 10 turns and sometimes to extend further than the standardized value of 75 turns. On the other hand it is also necessary to note the grain of the tuff and the kind of attack (abrasion resistance or pulling off lapilli).

3.2./ COMPARISONS BETWEEN FORMULATIONS

3.2.1./ Water-repellents

The comparison between the two water-repellents shows that (table 6) :
- Al-St does not act on the permeance value (less a few %);
- the same applied quantity of SIL does not withstand the pressure more than 1 minute and then B reaches the same value as the untreated tuff (B = 4.5).

TABLE 6 - ALUMINIUM STEARATE AND SILANE (TESTS 26.)

TEST NUMBER	APPLIED QUANTITIES IN kg/m² first layer	second layer	amount	DROP Tm	PRESSURE : ABSORPTION B1 1st phase	B2 2nd phase	ratio B1/B2	PERMEANCE g/m².h(**)
18-2	.475	.340	.815	>600	1.5	2.72	1.81	91.8
15-2	.305	.215	.520	>600	2.85	1.92	.67*	88.2
16-2	.245	.215	.460	>600	3.61	6.49	1.8	85.7
17-2	.295	.260	.555	>600	4.88	12.2	2.5	-
26-1	.270	0	.270	±600				-
26-2	.300	.220	.520	>600	.42	4.2	10	-

(*) A third phase exists (B3 = 2.32) : the mean value is B = 2,29.
(**) Check sample 90.7 g/m².h.

To conclude it is obvious that it is almost impossible to obtain a good under pressure water-repellency though it is always good without pressure.

3.2.2./ Strengtheners

a/ Ethyl silicate (Wacker OH)

Let us remember that the penetration is not very important whereas it is not a repellent the time of drop absorption is slightly higher than the untreated tuff (15s < tm = 35s < 55s compared to < 1s). On the other hand hardening is very good (ten layers) (diag. 12) : in spite of the fact that some lapillis have been early pulled away the length of the track does not exceed 5 mm (the corresponding depth is about .1 mm). The gradual pulling away of some grains makes the track up to 10 mm in length for 60 turns of the wheel. Moreover the degradation

grows rapidly up to 48 mm in length (2.7 mm in depth). It is interesting to notice that the resin and the solvent reach 5 mm during the application (visible depth mesured according to the change in colour) and that the theoretical depth (this depth is calculated assuming the whole porosity is saturated during the application ie there is no diffusion) is about 2.7 mm. At last the abrasion resistance is very good even when two layers are applied.
According to the number of layers, the results of the score test are (diag. 12) :

a/ 1 or 2 layers : there is no existence of the role of E.S.
b/ 10 layers : the hardening is rather good (mean value and spread) whereas there is some difference from place to place.

b/ Paraloïd B72 (solved in W.S.)

One can notice :

■ the good agreement between both theoretical and treated depths : that means that the diffusion of the paraloïd solved in W.S. is very slow : this result corroborates the test of capillarity and the poor value of index c (c = .58).

- TABLE 7 -PARALOID B72 SOLVED IN W.S

NUMBER OF TEST	APPLIED QUANTITY	n	THEORETICAL DEPTH	MEASURED	B1	B2	B2/B1
S 23-1	256	1	.5	.6	6.94	10.3	1.48
S 23-2	362	2	.7		6.10	11.1	1.80
S 24-1	508	3	1.0	1.0	4.82	10.0	2.12
S 24-2	674	4	1.5	1.4	2.15	3.1	1.44
S 25	833	10	1.7	1.5	1.94	2.8	1.44

■ the water-repellency is clearly inadequate up to 3 layers. Test 24-1 is very significant : the capillarity coefficient changes suddenly from B= 4.82 (surface) to B =10 (internal stone) Both the applied quantities and the treatment qualities are almost the same with 4 or 10 layers.

■ the abrasion resistance test corroborates the preceeding results (diag. 13). When 3 layers are applied the improvement is low whereas with 4 layers a noticeable hardening is observed during the 30-40 first turns.
■ the score test shows that the superficial hardening is almost the same whatever the number of layers is.

c/ Isobutyl acrylate

We have tested four percentages of resin : the high viscosity of the higher ones does not allow a good penetration (varnishing). The two less viscous ones have a good penetration and the increased applied quantity balances the dilution. In spite of a good resistance to the drop penetration (tm ≈ 400 mn) the results obtained under pressure remain feeble (B1 = 4.12) whereas the water absorption increases slowly up to 6.9 during the fifth filling (that means that the quality of the treatment remains good in depth) The permeance decreases slightly (94 % of the one of untreated stone). The score width is a 1/3 lower than the ones of the untreated stone. It is noticiable that the penetration is good (1.7 mm for one layer) whereas the hardening is not very good (soft resin) and that it is exactly opposite of B72. Therefore it seems interesting to study mixtures between the two resins.

TABLE 8 - **ISOBUTYL ACRYLATE**

N° OF TEST	RESIN %	APPLIED QUANTITY kg/m²	resin g/m²	Tm	B	PERMEANCE %	SCORE WIDTH
S 13-1	28.7	.305	87	± 360			
S 13-2	16.8	.265	45	± 360			
S 14-1	13.5	.210	28	± 420			2.2 mm
S 14-2	10.0	.275	28	± 420	4.12*	.94	2.4 mm

(*) The successive values are 4.12/4.43/4.79/6.4/6.9.

d/ Urethanne oil.

Both the percentages of resin (16 and 25 %) and the mixture with adding water-repellent are studied together when the superficial water content is lower than its critical value. One can notice (table 9) :
■ the improvement coefficient increases with the quantity of resin (diag. 23). Nevertheless one can observe the noteworthy case of the most fine grained sample S1 : the treatment is most efficient even with only one layer;
■ the detailled study of the absorption curves shows that absorption and pressure decrease together (diag. 11). The absorption re-increases after each filling and same phenomenons recur. The absorption of S12 stops completely for half

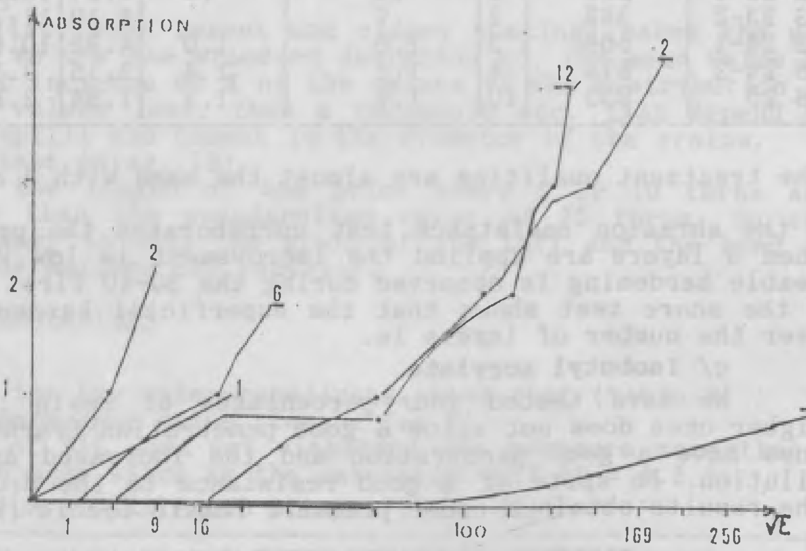
an hour when pressure reaches 4 cm (ie wind velocity ≈ 90 km/h) : we need to fill up the pipe and absorption starts again. The duration of the first phase of absorption depends on both the quantity of resin and the initial absorption of the untreated tuff.

-TABLE 9- URETHANNE OIL

NUMBER OF TEST	PRODUCT kg/m²	RESIN g/m²	n	tm	I
S 7	.196	31.5	1		7.25
S 4	.275	44.0	1		13
S 1	.310	50.0	1		127
S 8	.485	77.0	1		7.24
S 2	.765	122.5	2		15
S 11	.310	77.0	1	280	2.8
S 12	.901	225.0	4	450	140
S 19-1	.252	40.5	1		-
S 19-2	.495	79.5	2		12/18

■ the mixture UO16 + Al-St shows a noteworthy increase of the duration of the drop absorption (diag. 23 a) but under pressure the absorption is not very different : this fact had been described several times in literature: [9, 10, 11, 12]. One can account :
a/ high diameter pores remove water in spite of water-repellency according to DARCY's law rather than POISEUILLE's
b/ the water-repellent first soacked and then covered by the strengthener.
c/ the mixture undergoes a chromatography in the pores : when capillary rise is carried out on a sample of tuff one can observe after diffusion and drying that under repellency is greater on the top whereas the hardening is lower (score and microdrop test) so one can think that the strengthener is rather at the surface and the water-repellent is rather inside.

These three explanations go to prove the previous observations.
Therefore it is necessary to mix similar resins.
■ the score width decreases with the resin deposit. It is noteworthy that the lower limits of the spread of the values are the same whatever the resin deposit is(e = .5-.6 mm) and this value is those of the sound tuff : UO is the only strengthener to show this characteristic.
■ the vapor permeability is correct (90 % of the one of the check sample).
To conclude, UO. is interesting for two reasons :
- good hardening even with a small deposit of resin
- WS is a good solvent.



Diag. 11 - **SOME ABSORPTION CURVES BEFORE AND AFTER TREATMENT** (underlined number). Absorption (cm³/cm²)

To conclude this second step about products one can notice :

1/ the solvent : it is necessary to find the solvent that units the lowest volatility with the best solubility of the resin in order to obtain the greatest penetration. This is the main drawback of resins such as B72, A21 the best solvents of which are, eg, ethyl acetate. Nevertheless for tests on tuffs from Easter Island we have choose an harder resin (A21) in good solvents in order to balance the decrease of dry extract of resin per unit of volume of treated stone (a best penetration means less resin).

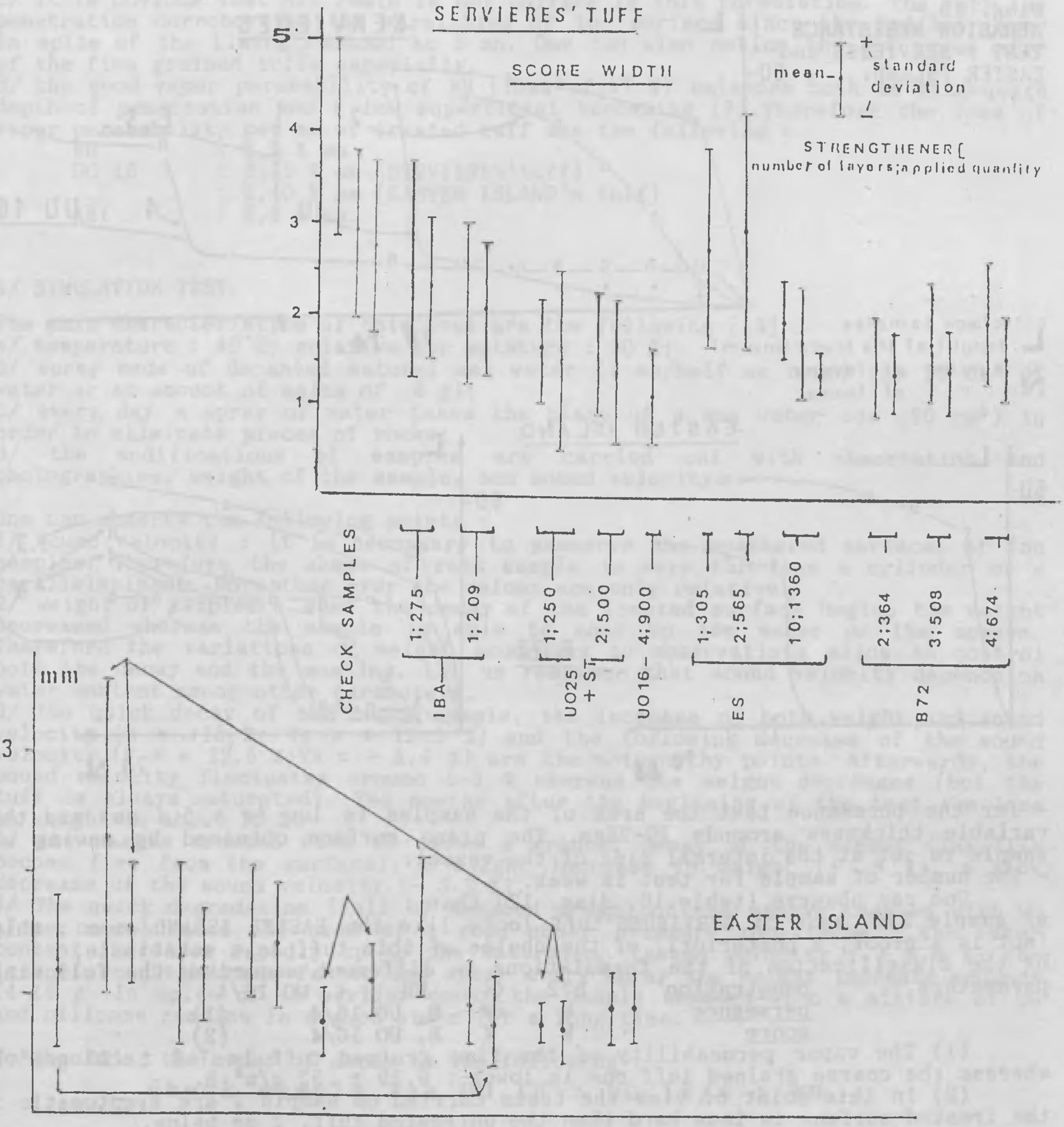
2/ the number of layers : it appears that four layers applied wet on wet are the minimum : the following tests have been carried out with five layers.

3/ the complementary under repellency has to be undertaken with similar resins.

Therefore we have choose to treat tuffs of Easter Island:
urethanne oil mixted with a silicone resin (4518 from Rhône Poulenc);
Wäcker H that mix strengthener and water-repellent;
acryloïd A21 in light solvents.

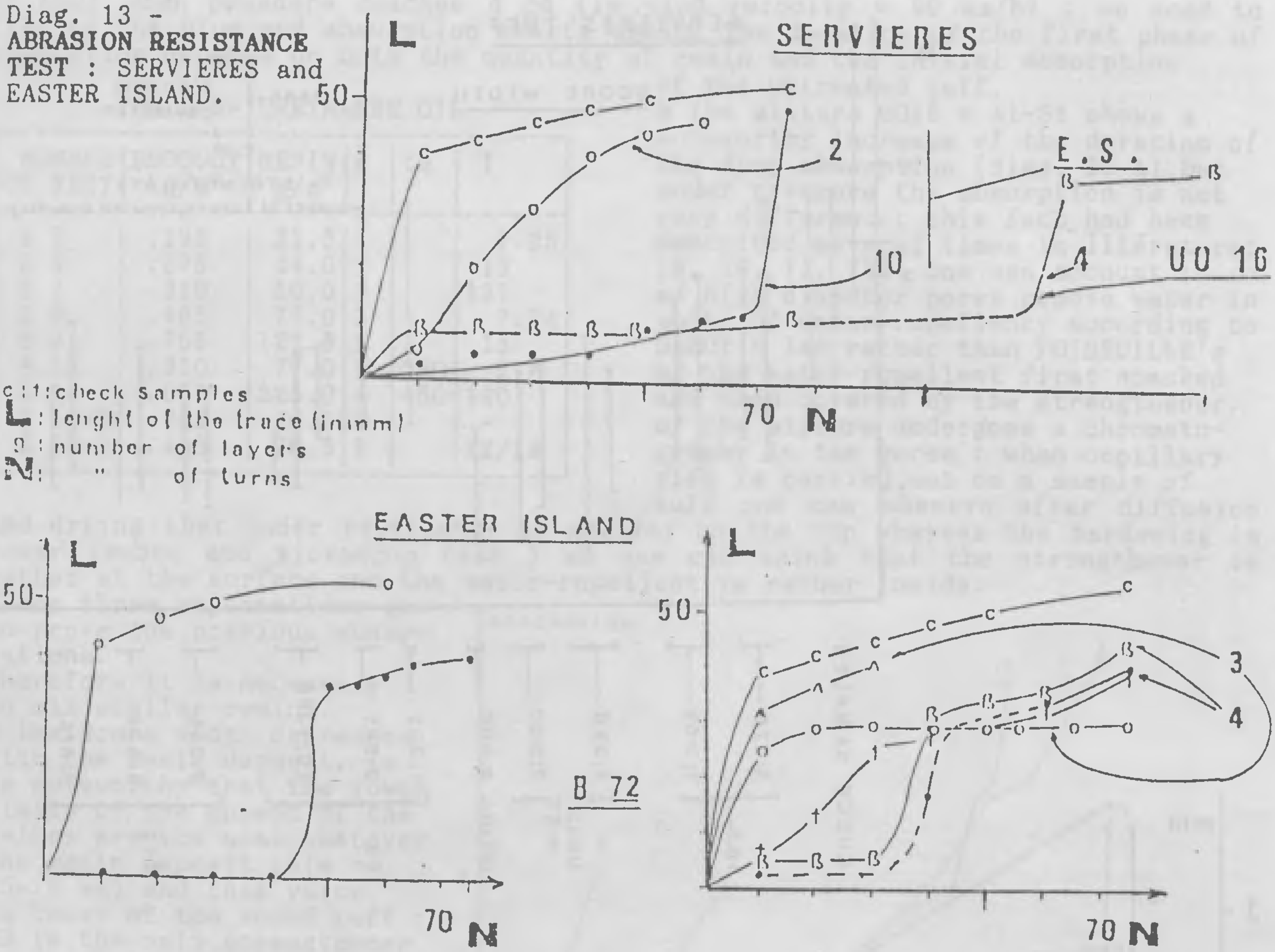
3.2.3./ Tuffs from Easter Island.

The applications have been carried out in atmosphere at 23°C (the medium conditions in Easter Island). All the tests have been undertaken on tuffs with their superficial weathering, but without biological growth (application of .2 l/m² of a solution of succinate phenyl-mercurial). The subjection to treat weathered surfaces and not sound surfaces as usually has two consequences :



Diag. 12 - **SCORE WIDTH** ON SAMPLES OF SERVIERES'TUFFS (upper part) and of EASTER ISLAND's.

Diag. 13 - ABRASION RESISTANCE TEST : SERVIERES and EASTER ISLAND.



- for the permeance test the area of the samples is low (ø ≈ 5.4 cm) and the variable thickness arounds 20-25mm. The plane surface obtained by sawing of sample is set at the internal side of the vessel.
- the number of sample for test is weak.

One can observe (table 10, diag. 12) that :
a/ sample S102 made of SERVIERES'tuff looks like the EASTER ISLAND ones : this fact is a proof, a posteriori, of the choice of this tuff as a substitute;
b/ the classification of the formulations is different according the following parameters :

penetration	B72	<<	WH < UO 16/4	
permeance	W	<<	B, UO 16/4	(1)
score	W	<	B, UO 16/4	(2)

(1) The vapor permeability of the fine grained tuff is 7.8 ± .23 g/m².h whereas the coarse grained tuff one is lower : 6.29 ± .52 g/m².h.
(2) In this point of view the tests carried on sample 2 are symptomatic : the treated surface is less hard than the untreated tuff, 2 mm below.

TABLE 10 - EASTER ISLAND'S AND SERVIERES' TUFF.

NUMBER OF SAMPLE	PRODUCT	APPLICATION APPLIED Q1 QUANTITY	kg/m²	DEEP OF PENETRATION C		min	max	m	PERMEANCE g/m² before	after	loss %	loss %/mm
100 f	UO16/4	1.816	.34	1.033		10	13	11	7.49	4.28	42.9	3.9
101 c		2.262	.45	1.020	(22)	22	>	22	5.79	3.73	35.5	1.61
104 f	WH	2.459	.50	1.008	(18)	10	18	12	7.85	5.76	26.4	2.2
105 c		2.065	.56	.82		10	15	12.5	7.01	5.08	27.6	2.2
107 f	A21	1.550	.62	.58		1	9	4	8.05	5.71	29.1	7.3
108 c		1.419	.48	.68		2	7	4	6.08	3.66	39.7	9.9
102-SERVIERES	UO16/4	2.528	.55	.97	(18)	9	18	15	10.64	7.05	33.7	2.4

f : fine-grained c : coarse grained (22) means thickness of the sample.

c/ it is obvious that A21 resin is not correct in this formulation. The very low penetration corroborates the varnishing of the surface since the 2nd/3rd layer in spite of the timing reduced to 5 mn. One can also notice the low value of c of the fine grained tuffs especially.
d/ the good vapor permeability of WH (loss of 27 %) balances both an inadequate depth of penetration and a low superficial hardening (2).Therefore the loss of vapor permeability per mm of treated tuff are the following :

WH	: 2,2 % mm	
UO 16	: 2,25 % mm	(SERVIERES'tuff)
	: 2,40 % mm	(EASTER ISLAND's tuff)
A21	: 8,6 % mm.	

4/ SIMULATION TEST.

The main characteristics of this test are the following [13] :
a/ temperature : 40°C; relative air moisture : 30 %;
b/ spray made of decanted natural sea water (1 mn/half an hour) (ie 20 cm^3 of water or an amount of salts of .6 g);
c/ every day a spray of water takes the place of a sea water one (20 cm^3) in order to eliminate pieces of rocks;
d/ the modifications of samples are carried out with observation and photographies, weight of the sample, and sound velocity.

One can observe the following points :
1/ sound velocity : it is necessary to preserve the weathered surfaces of the samples. Therefore the shape of each sample is very far from a cylinder or a parallelepipede. More than ever the values are only relative.
2/ weight of samples : when the decay of the treated surface begins the weight decreased whereas the sample is able to soak up the water or the sprays. Therefore the variations of weight according to observations allow to control both the decay and the soaking. Let us remember that sound velocity depends on water content among other parameters.
3/ the quick decay of the check sample, the increase of both weight and sound velocity (W = +15 %; Vs = + 15.3 %) and the following decrease of the sound velocity (W = + 22.5 %;Vs = - 5.6 %) are the noteworthy points. Afterwards, the sound velocity fluctuates around 6-8 % whereas the weight decreases (but the tuff is always saturated). Two months after the beginning of the test the loss in weight is about 15 %.
4/ the sample treated with WH shows a gradual decay of the cement (lapillis become free from the surface), a slight increase in weight (+ .8 %), a slow decrease of the sound velocity (- 3.3 %).
5/ The quick degradation (fall of treated crust) of the sample treated with UO alone corroborates the need of a good under pressure repellency : the water content increases rapidly up to the saturation (sound velocity : + 6.6 %) the loss of weight becomes faster and after every spray the weight increase arounds 14-15 g. In spite of an earlier decay the sample treated with a mixture of UO and silicone remains in a good state for a long time.

To conclude, the order of decay is the following :

check sample >>> UO 16 > UO 16/4 > WH.

5/ CONCLUSIONS

We have to emphasize three points :
1/ the four physical particularities of the EASTER ISLAND's tuff :
a/ structural heterogeneity : coarse and fine-grained beds the absorption laws of which are very different;
b/ acquired heterogeneity : more or less tight clayey crusts cover the moais and increase or decrease the absorption of the beds termed upper;
c/ a high hygroscopic content (≈ 25 % in volume of the porosity);
d/ a differential absorption (cement and lapilli).
2/ two formulations show different suitable characteristics :

	Urethanne oil + silicone	Ethyl silicate + silicone
penetration	the best	
application wet/wet	the best	
vapor permeability per mm of treated tuff	the same	

hardening of the surface	the best : near the sound stone	about half the sound stone
decay of the treated stone	fall of the crust bit by bit	decay of the **cement** (look like the weathering)

The choice of the solvent is very important : it has to be less volatile as possible to allow a good penetration.

3/ the conditions in situ : one have to take account of the physical properties of the tuffs and the chemical characteristics of the choosed formulation in order to modify the technic of application the main parameters remain the same :
- to protect of moai before and during treatment
- to avoid any water soaking after the treatment : therefore it is possible to treat neither the half-buried moais nor the ones carved in volcano RANO RARAKU
- to carry out previous and non-destructive measures in order to forecast and modulate the details of the application.

At last, we have to notice :
- one need to carry out a previous biocide treatment. Therefore we propose the use of a succinate-phenyl mercuriale solution (this molecule gives two advantages : spread spectrum of activity, insolubility in water) according to the followings : spray of .2 l/m² (.4 l/m² on either an important biological growth or a very absorbent tuff), soft brushing two days after; it is also possible to clean with water under pressure (< 20 kg/cm²).
- it is obvious that cement mortar are too water-tight. Therefore it is fitting to limit its use where it is absolutely necessary. In addition, it is better to substitute 2/3 of the cement with lime and to decrease the total amount of the binding material content in order to obtain a both more porous and more resilient mortar. The less number of microcracks in an other suitable point. It is possible in some cases to chock the moai up with pebbles as it was usually done.

BIBLIOGRAPHY

1. HYVERT, G.; Unesco, 1972, 2868/RMO/RD/CLP, p. 53

2. DOMALOVSKY, W.; Unesco, 1982, p. 75

3 A. PONS, J.C.;Thèse D.E. Bordeaux I 1988, 901, p. 151

3 B. PONS, J.C. et al.; in Applied Clay Science, 1989 4, pp. 307-25

4. GUILCHER A. et al., Cahiers Océanographiques, 1962, XIV, 4, pp. 201-07

5. C.S.T.B.; NIT, 1980, 140, p. 24

6. PAULY, J.P.; in Lithoclastia, CREO ed.1975, 1, pp. 17-34

7. PAULY, J.P.; Vème Congrès International sur l'altération et la conservation de la pierre. Lausanne, 1985, pp. 817-29

8. VOS B.H.; TNO, 1968, BI-11, p..22

9. ROSSI MANARESI R.; 2ème Colloque International sur la détérioration de la pierre en oeuvre. Université technique Athènes, 1979, pp. 233-48

10. ROSSI MANARESI R.; Vème Congrès International sur l'altération et la conservation de la pierre. Lausanne, 1985, pp. 871-80

11. TUCCI A. et al.; Ibidem, pp. 891-98

12. ROSSI MANARESI R.; I.I.C. Congress, Washington DC, 1972, pp. 39-45

13. AUGER F.; Géologie de l'Ing. App. aux Trav. Anciens Monuments. 1988, IAEG-Athènes, pp. 797-803

14. U.S. NAVY.; Marine Climatic Atlas of the World, 5, SP Océan. Navaer, 50-1-C-532, 1967, p. 233

15. LANDSBERG.; World survey of climatology vol. 15. Climates of oceans. Elsevier, New York, 1958, p. 564

16. PAULY, J.P.; in The conservation of stone, Proc of the int symposium, Bologne.1975, pp 55-80

17. PAULY, J.P.; in 2ème Colloque International sur la détérioration de la pierre en oeuvre. Université technique Athènes, 1979, p. 79-91

18. LACY, R.E., CHELLARD H.C.; in Meteor.Mag., 1962, 91, 1080, p. 177-184

19. HEILBIG, A.;.Thesis Univer. Karl Max. Leipzig RDA, 1972, p. 112

20. GARENC P.; Mémorial de la Mét Nat, 44, SGACC, Paris,1957, p. 222

21. BOURCART, J.; in Rev Géo. Phys. et Géol. Dyn., 1930, III, 1, pp. 1-17

22. PETERLONGO J.M.; de GOER de HERVE A.: Masson éd., Paris, 1978, p. 224

6/ CLIMATOLOGY ANNEX 1

As we cannot undertake climatological measurements in order to solve the specificity of the stone decay in Easter Island we have interpretated data from literature with our experience on french monuments [14, 15]. The most important data are reported in table 11.

	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Temperature												
mean	23.6	24.1	23.5	21.8	20.4	18.7	18.2	18.0	18.7	19.7	21.0	22.3
maximum	28.9	28.9	28.9	27.8	27.8	25.0	23.9	25.0	25.0	26.1	26.1	28.9
minimum	20.0	21.1	21.1	17.8	16.1	15.0	12.9	12.9	15.0	15.0	17.2	17.2
Rains (mm)	122	94	116	106	117	109	90	77	68	94	117	125
Prevailing wind direction	E	E	E	E	NW	E	NW	NW	N	E	E	E

Mean annual values	Temperature °C			Rains
	mean	maximum	minimum	
	20.8	26.9	17.2	1234.1 mm

- TABLE 11 - CLIMATOLOGICAL DATA

6.1./ INSOLATION AND TEMPERATURE

As Easter Island is in latitude 27° 19 S, so :
a/ during the southern summer the quasi E.W. trajectory of the sun (on december 21st, at noon, the altitude of the sun is 86°) involves that :
- on the northward vertical surface the angle of incidence and the flux of the direct solar radiation are very low;
- short projections (such as chins) cast shadows on important areas of the northward vertical surface;
- the flux density is high on eastward or westward surfaces during half a day;
- the flux density is very low on the southward surface;
- the flux density is high on horizontal surface.

b/ during the southern winter (on june 21st; at noon : H = 40°) all the northward surfaces are directly and highly insulated and during insulated lapses of time very high differences of temperature between air and stone are possible.

6.2./ WAVES (DEPOSITS OF SPRAY)

We have shown, at St-Sauveur's Church, La Rochelle, that there is a relation between the sea state and the deposit of chloride and sulphate on walls [6, 13]. The sea state is a function of the square of the significant height of the waves :

- TABLE 12 - DIRECTION AND SPRAY.

	N	NE	E	SE	S	SW	W	NW
Maximum and corresponding month	240	192	245	521	1002	1080 (1010)	560	500
	7	4	2	1	3	4 (7)	7	7
Minimum and corresponding month	9	9	0	2	104	61	0	0
	2	10	10	7	7	12	11	11
Annual amount	993	843	1234	1609	5555	6236	1709	1277

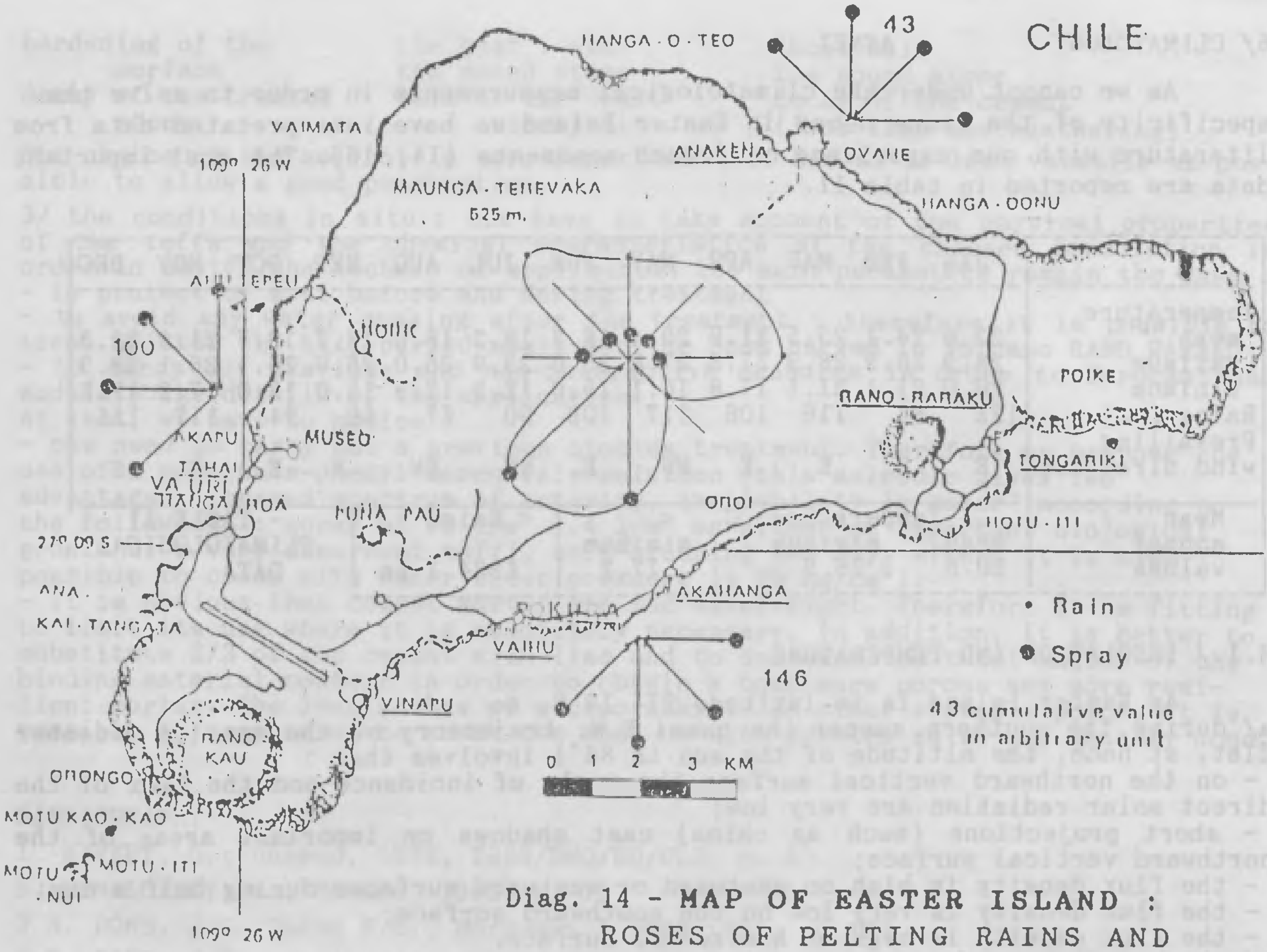
$Qcl^- = k \Sigma h^2$ with
- Q = quantity of chloride;
- h = height of the waves;
- Σh^2 = sum over a lapse of time;

k = factor of site. (unknown here);

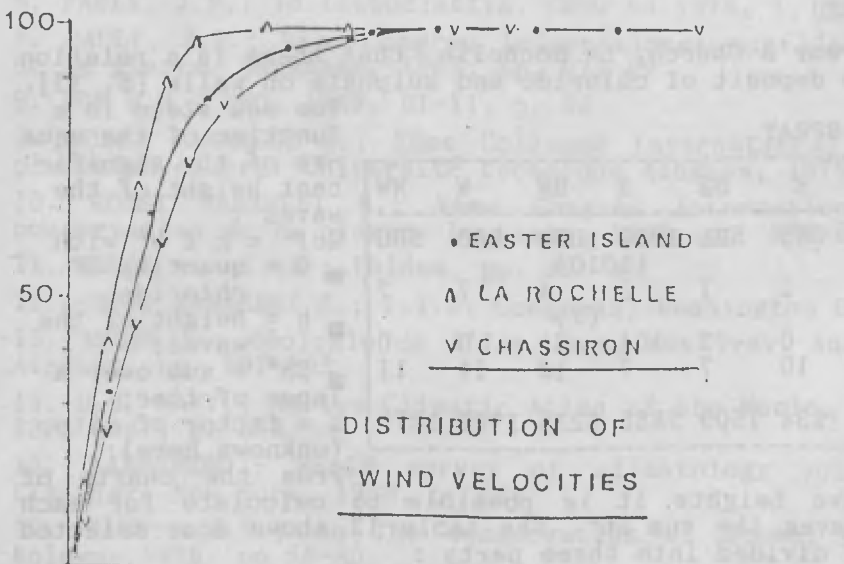
From the charts of the monthly frequency of wave heights it is possible to calculate for each direction of origin of the waves the sum Σh^2. The table 12 shows some selected values.The origin of waves is divided into three parts :
- south and southwest : important deposits of salts are possible;
- north and northeast : low deposits;
- other origins : mean deposits.

By gathering the direction of origin for each coast of the island we find the relative values (diag. 14) :
- north and northeast : 43;
- south and southeast : 146;
- north and northwest : 100.

So we can expect that the deposits of chloride are on the northwest coast twice as high as on north coast and triple on the southeast coast.



Diag. 14 - **MAP OF EASTER ISLAND : ROSES OF PELTING RAINS AND SALTS DEPOSITS** (The visited sites are underlined)



Diag. 15 - **DISTRIBUTION OF THE WIND VELOCITIES** AT LA ROCHELLE, CHASSIRON (20km westward from LA ROCHELLE) AND EASTER ISLAND.

6.3./ RAINS

Rainfalls are rather well distributed monthly (Pmax/Pmin = 1.84). If so it be that the values indicate the rain received on horizontal surface (lying moais), it is not possible to obtain direct information on the rain received by a vertical surface (pelting rain). For St-Sauveur's church we have developed a formula that allows the calculation of the rain received by each vertical surface as a function of the origin and the velocity of the wind and of the rainfall on horizontal surface [17]. But without actual measurements on the site to calibrate the formula (site factor) we obtain an index similar to the rain-

index termed by LACY [18] or the "reigen index" used in Germany [19]. Nevertheless the likeness of the repartition of the wind velocity at La Rochelle and its neighbourhood [20] on the one hand and at Easter Island on the other hand partly justifies the use of this formula (diag. 15). So we used as site factor the value found for the southward wall of the bell-tower ie .05. We have neglected the slip stream in this calculation because the amount of water received by leeward vertical walls generally varies from 4 to 6 % of the corresponding windward quantity (tab 13).
It will be noted that the maximal amount on the vertical surface is near the rainfall on the horizontal surface (we had the same observation at La Rochelle).
We can distinguish three groups :
- east, northeast, north, northwest : well washed;
- southeast-west : slightly washed;
- southwest-south : not washed.

MONTH	E	NE	N	NW	W	SW	S	SE	RAIN mm/ month	MAX x .05
J	2280	522	369	22	22	22	22	22	121. 4	114
F	1907	2052	425	1663	19	19	19	19	94	103
M	2252	1831	3117	35	35	35	35	35	115.6	113
A	770	2481	19	3113	19	19	19	1396	105.9	155
M	193	275	138	1515	633	26	26	26	117.2	76
J	24	24	24	1467	24	24	24	24	109.3	73
J	259	173	19	825	825	168	19	548	90	42
A	291	14	333	498	1477	15	15	15	114	74
S	409	12	172	895	812	12	12	280	68.0	45
O	270	1951	957	11	11	11	11	1103	93.6	9
N	1561	5	1482	5	5	980	5	5	116.9	78
D	1047	14	372	149	14	14	14	14	124.8	52
TOTAL	11263	9354	7424	10198	3896	1345	221	3487		
x.05	563	468	371	510	195	67	11	174		

- TABLE 13 -

COMPARISON OF THE MONTHLY AMOUNT OF PELTING RAINS ON VERTICAL SURFACES (ARBITRARY UNIT)

6.4./ NANOCLIMATE.

Combinating with the salt deposit (diag. 14) we can observe three groups :
- east, northeast, north, northwest : slight deposit and high washing;
- west and southeast : mean deposit and mean washing;
- south and southwest : high deposit and no washing.

This repartition explains the location of honey combs only on the southeast coast where the wall of the ahus made of basalt are decayed :

- southward walls (turned towards the sea) : high deposits of salt; no washing; small solar flux;
- eastward walls : lower deposits; efficient washing; intense drying and thermal shocks.

In the same way great cavities termed "taffonis" in Corsica [21] are frequent on the lying moais and one can see great pits on the red hats (cf 1.3.3./). We can improve these annual results by a monthly analysis of both the salt deposit and the pelting rain (diag. 16 and table 14). In order to get an easier comparison we use arbitrary unit : 10 for the greatest monthly value (all directions) together) for the rain and the deposit of salt.

- TABLE 14 - WASHING OUT AND SPRAYS DEPOSITS

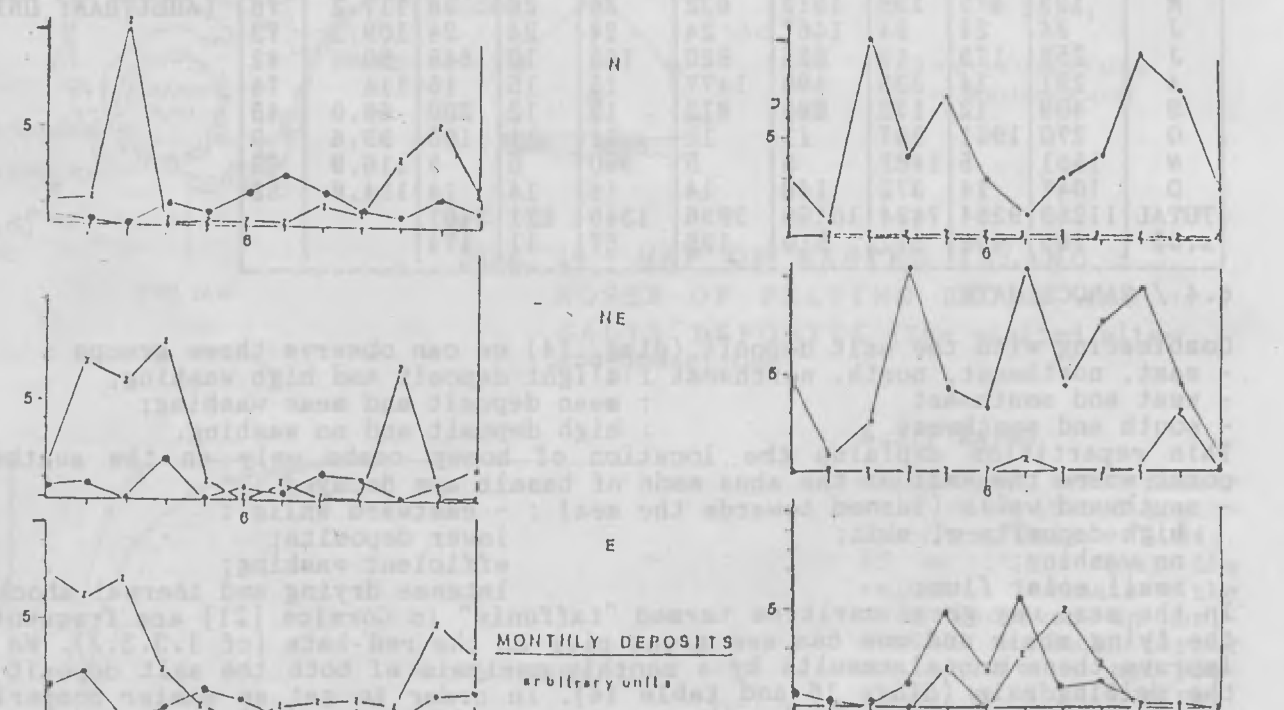
DIRECTION	WASHING OUT BY THE RAIN	SPRAYS DEPOSITS
North	Maximal : in march and november	Maximal : in july
Northeast	Maximal : from february to april and in november	Slight all year
East	Maximal : from january to march	Low maximum in august
Southeast	Maximal : in april	Idem
South	Never	Maximal : in january and february
Southwest	Possible in november	All year but slower in both february and july
West	Maximal : in august	All year but slower in both february and december
Northwest	Maximal : in may '	Maximal : from may to july
		Maximal : in july

Nota : do not forget that the eastward surface of a moai located on the west coast does not receive as much salt as the face of a moai located on the SE coast. So it is necessary to know the location of the moai (for exemple : inside or outside of the RANO RARAKU). Because of the slip stream the surface opposite to the sea receives some salts and if the distance to the sea on the other side of the island is not too high the moai receives also some spray; generally though 2 km far from the sea shore the salt deposits are very very low except when there are very high breakers associated with high wind velocities. So we can define different climates for the moais (table 15).

- TABLE 15 - NANOCLIMATE AND MOAI

COAST	SUN	SALTS	WASHING	BALANCE
NORTH				
.Back of the moais seeward	Drying in winter	Slight	High	++
.Abdomen southward	Slight drying during summer morning and evening	V. low	Null	+
SOUTHEAST				
.Back	Idem	V.high	Very low	+++++
.Abdomen	Drying during winter	Low	High	++
WEST				
.Back	Drying all season in the afternoon	Mean	Mean	++
.Abdomen	thermal shocks	Low	Mean/high	+++

To conclude we can observe a large spread of climate considering :
- the coast where the moai is located;
- orientation and inclination of the surface.



Diag. 16 - DISTRIBUTION OF THE MONTHLY VALUE OF THE PELTING RAINS AND SALTS DEPOSITS (Arbitrary unit : 10 for the highest value of each parameter).

7/ NON DESTRUCTIVE METHODS USED IN SITU   ANNEX 2

7.1./ MOISTURE

The data gathered in Easter Island have been turned into moisture according to the calibration curves (diag. 17 to 19.). One can observe systematically :

1/ a high WC (85 to 100 %) in the neibourghood of cement mortar that acts like a water-tight surface and prevents the whole seepage lower in the statue wherever the mortar is :

- mortar located on the lower part (ahus NAUNAU or VA HURI eg),
- mortar located on the upper part in order to repair the statue. In this case, the rock located under the mortar is drier (35 % instead of 80-90 % eg). This wet area follows both the surface made of mortar closely and the heterogeneity of the rock 21 (the 2nd moai from the left at ahu VA URI : diag. 18) where two black strips 20 or 30 cm in height are above two mortars, one set horizontally at the level of its breast and the other morever inclined at the foot of the statue. At this level efflorescences characteristic of the cement mortar were found on the S.E. side of the moai (see below).

2/ After important pelting rains superficial moisture reaches 80-90 % or even 100 % exactly as after an artificial rain. At VINAPU the measures were carried out just after the storms in the morning and early in the afternoon; let us notice that lichens are located at the boundary of the dripping water (same values at the surface of the lying, half buried moais at POKURA). The restorated moai (HANGA KIOE) shows a residual moisture slightly greater than the hygroscopic content and always an area of accumulation 30-40 cm high at the foot of the statue : there is a slight penetration of water.

3/ The ground probably acts as cement mortar; the lower parts of the moais in contact with the ground are moist : the height of the moist stip is generally greater. Nevertheless unless the cinetic of the movements of the water is studied, it is difficult to distinguish between the three sources (per descensum movement of the water; spurt back of water; per ascensum movement of the water ie capillary rise from the ground). The relative importance of these three modes of humidification implicates for each moai the opportunities of the treatment, its quality and its durability.

The location of the superficial modification of moai 272 half buried in vertical position (outside of RANO RARAKU - SW sector) is very interesting for the main play of a constant and important WC in the formation of a clayey crust 10 mm thick that swells and falls off. In the same manner there is a moist zone 40 cm height on the cleft moai 583 (VAIHU).

TABLE 16 - LOCATION OF THE SUPERFICIAL MODIFICATION (MOAI 272)

LOCATION	NORTH NORTHWEST	WEST-	SOUTHWEST	SOUTH
TOP MIDDLE	Well visible beds of lapillis + some cracks Beds of lapillis and clayey reddish and solid with underlying rock crust	Lichens	Lichens except in eye-holes, nostrils and under the chins	siliceous crust under the chins + lichens down to 1m
FOOT	clayey visible rock crust ± weathered (not solid) up to 40 cm	Solid with underlying rock crust		

4/ At last one can notice the quick drying of the upper surfaces directly exposed to rain and sun : within 48 hours the back and shoulders of moai 103 at NAU NAU have been dried; on the contrary, the southward side remains very wet : this velocity of drying is very similar to the one measured in laboratory.

7.2./ IN SITU MEASURES OF WATER ABSORPTION

We have carried out several measures on the moais 103-104 at ANAKENA (ahu NAU NAU) and on the moais and the rocks at RANO RARAKU volcano; and we have re-interpreted data from DOMASLOVSKY [2]. According to the nature of the crust and the specificity of the tuff one can distinguish several behaviours :

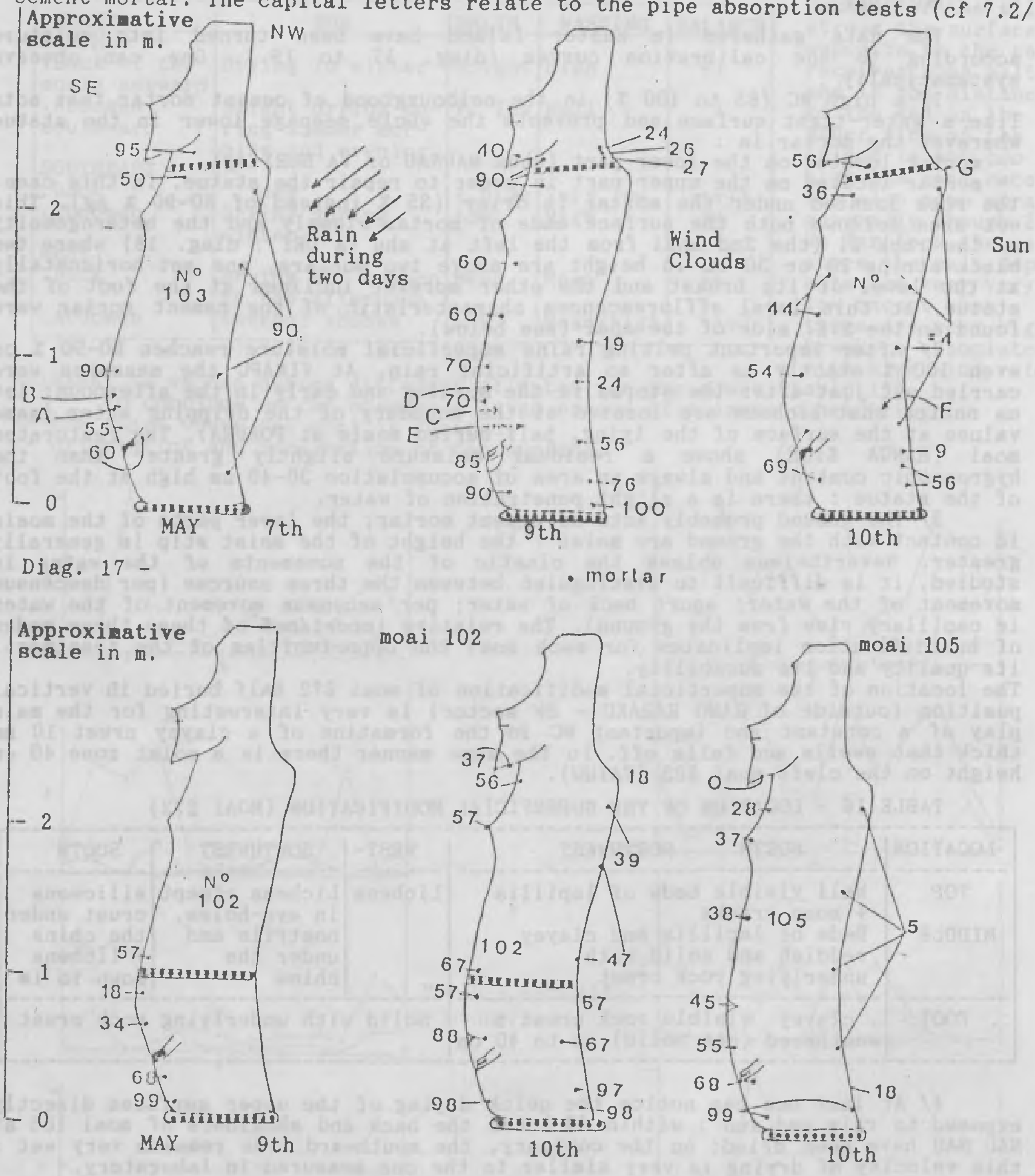
a/ fine grained tuffs : the absorption obeys the capillarity law

- MOAI 230 (lying moai at RANO RARAKU)
  $D = .13 + .415\ t^{.5}$ or $D = .35\ t^{.54}$

b/ coarse-grained tuffs (lapillis 1 cm in length) :

- rock (RANO RARAKU) $D = 30\ t.$
- moai 103 (point B) $D = 2.65\ t^{1.02}$ or $D = 2.76\ t - .42.$

SUPERFICIAL WATER CONTENT (%)according to the calibration, curve (diag. 3A) MOAI 103 AT AHU **NAUNAU (ANAKENA)**. One can notice the main role acted by the cement mortar. The capital letters relate to the pipe absorption tests (cf 7.2/)



So under pressure the seepage of the water obeys less POISEUILLE's law than DARCY's : water flows in great diameter pores (Γ >> 1 mm).

■ One can link up the absorption of point G (moai 103) with this group (swelling of the crust) :

$D = .22\ t + .28$ or $D = .25\ t^{.99}$ (notice the low value of D1 : .25).

c/ weathered stones : (for the location : diag. 17)

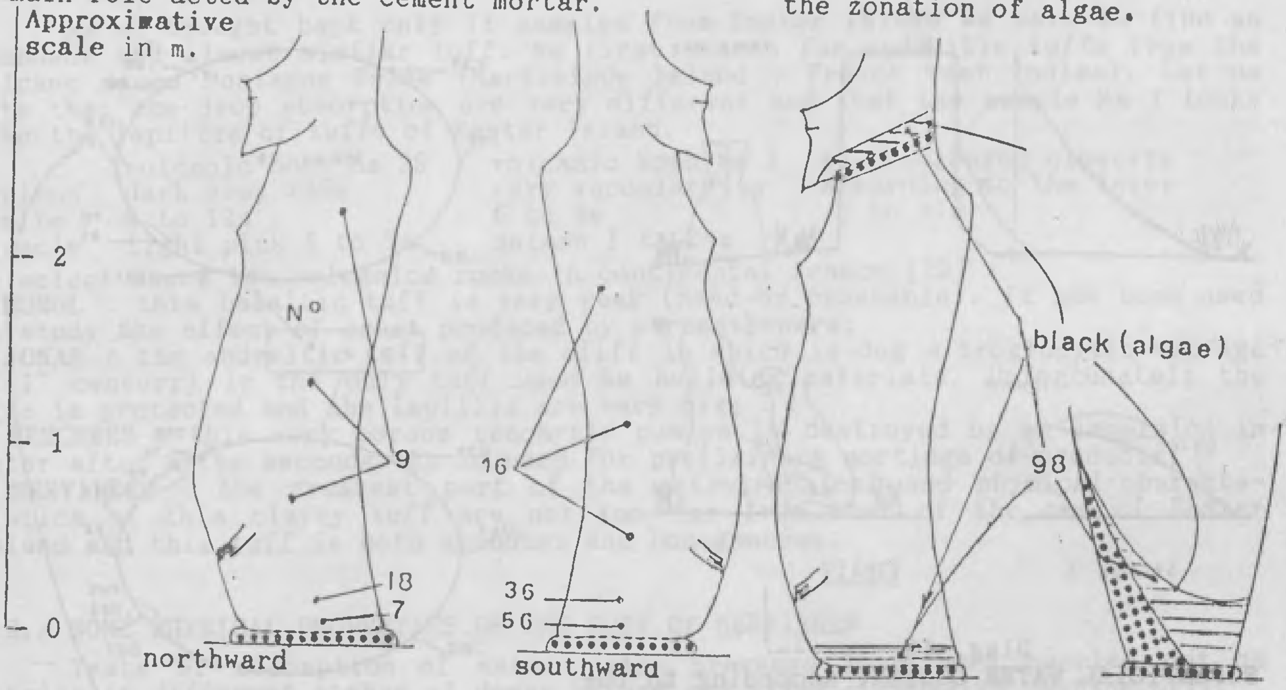
▣ Moai 103 (point A in yellow area) : the water-tightness is shown by the low value of both D1 (.8) and a̲ (about .5).

■ Moai 103 (point C in yellow zone) : one cannot observe any $\sqrt{t}$-phase except perhaps at the beginning but the logarithmic drawn shows two phases :

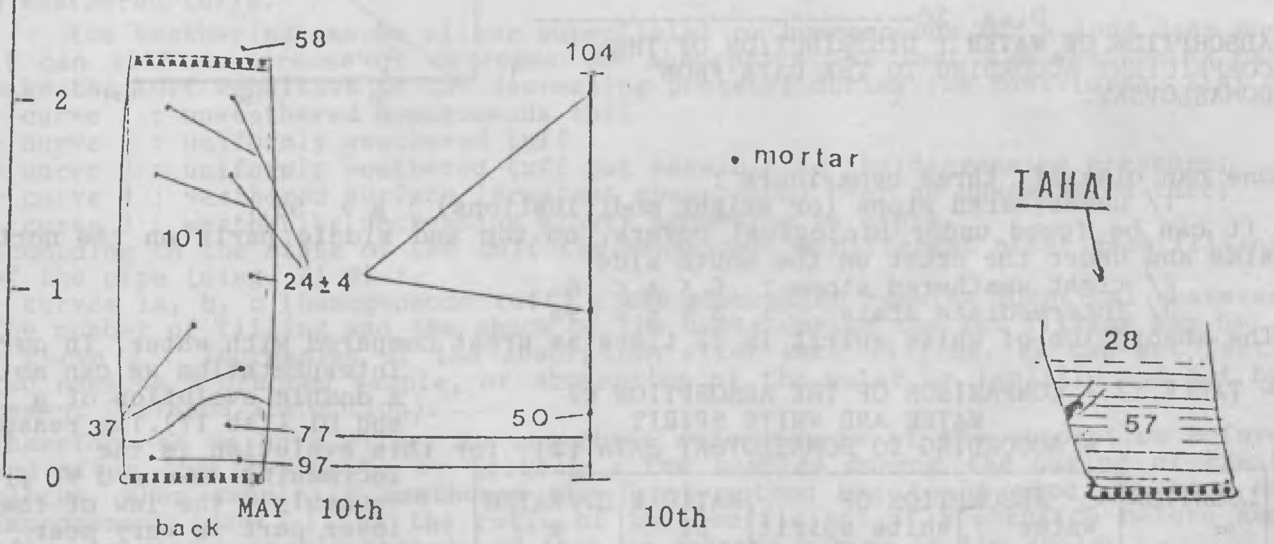
$D = .16\ t^{1.16}$ ($0 < t < 21$ mn) and $D = .016\ t^{.70}$ ($21 < t < 30$ mn)

Consequently an almost impervious surface overlies a very absorbant stone (i. e. dry or coarse grained).

SUPERFICIAL WATER CONTENT according to the calibration, curve (diag. 3A)
AT AHU HANGA KIOE), one can notice the main role acted by the cement mortar.
AT VAI URI on can notice the zonation of algae.

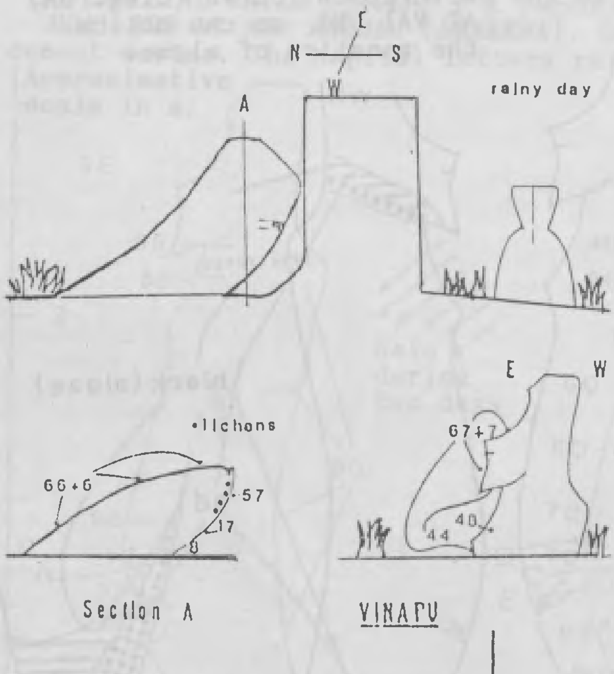


Approximative ----------- AT AHU NAUNAU------------------AT AHU TAHAI
scale in m.------moai 101 moai104

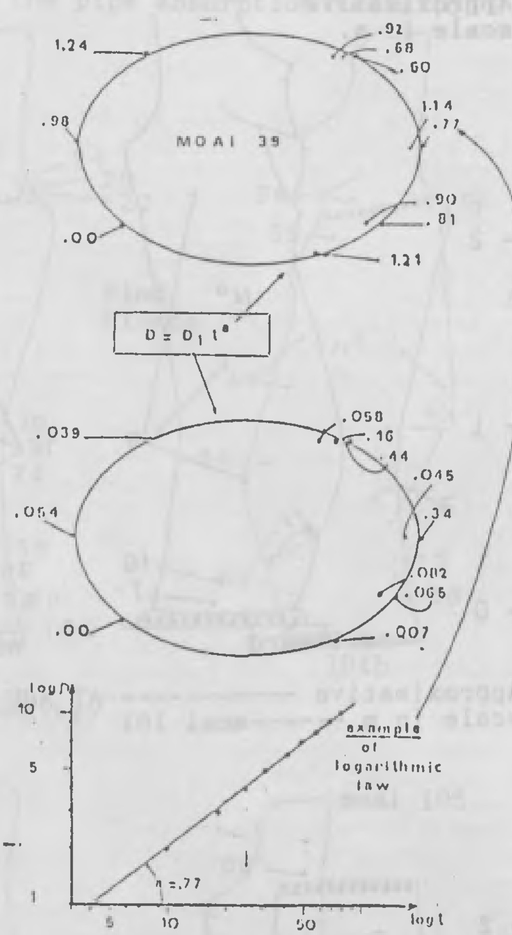


Diag. 18 -

■ Moai 103 (point D with more or less clayey coated lapillis) : this is corroborated by the absorption law (low D1 and a about 1) : $D = .56\ t^{1.044}$.
■ Moai 103 (point F with a very gullied stone turned towards North)
$D = 1.15\ t^{.50}$ ($0 < t < 24$ mn) . $D = .75\ t^{.90}$ ($24 < t < 70$ mn).
We can notice that the first phase looks like that of point A, that the second looks like C (increasing absorption inside), and too that it looks like the absorption of sample 3 for a WC about 30 %.
■ Moai 103 (point E with a water-tight white varnish) D = 0 after 36 mn).
Data from DOMASLOVSKY [2].
We can observe that 21 absorptions (among 24) obey the logarithmic law very closely. The 3 others have a diphasic behaviour; <u>Absorption of the surface</u> (diag. 20 a) :
The mean absorption ranges from .039 to .082 except on south side where it is 8 times more (.34 and .44 and a mean coefficient .16). The lower surface is covered with a grey crust which is nearly tight (D1 = .007).
<u>Variation in deep</u> (diag. 20 b)



Diag. 19---------
SUPERFICIAL WATER CONTENT according to the calibration, curve (diag. 3A)
AT **VINAPU** : ONE CAN NOTE THE LOCATION OF THE LICHENS.



Diag. 20---------------------------
ABSORPTION OF WATER : DISTRIBUTION OF THE COEFFICIENT ACCORDING TO THE DATA FROM DOMASLOVSKY.

One can classify three behaviours :

1/ unweathered stóne (or slight modifications) : $a > .98$.
It can be found under biological covers, on top and middle parts on the north side and under the crust on the south side

2/ tight weathered stone : $.6 < a < .8$.

3/ intermediate state : $.8 < a < .98$.

The absorption of white spirit is 12 times as great compared with water. In our interpretation we can note a double evolution of a and D1 (tab 17).The reason for this evolution is the increasing downward WC pre-sumably : the law of the lower part is very near the one of sample 3 after a 2-weeks imbibition.

- TABLE 17 - COMPARISON OF THE ABSORPTION OF WATER AND WHITE SPIRIT - ACCORDING TO DOMASLOVSKY DATA [2]

LOCATION	ABSORPTION OF water	ABSORPTION OF white spirit	RATIO W.S./WATER D1	RATIO W.S./WATER a
TOP	$.44\ t^{.60}$	$.94\ t^{1.30}$*	2	2
MIDDLE	$.34\ t^{.78}$	$3.4\ t$	10	1.3
BOTTOM	$.06\ t^{.81}$	$.8\ t^{.81}$	12,3	1

* Seconde phase of the absorption = $2.1\ t^{.75}$

CONCLUSIONS

It is possible to carry out non destructive methods in situ (superficial WC, absorption by the surface and the underlaying stone). It is possible to forecast with accuracy the seepage of water or white spirit or other solvent in the moais.

We have to remember :

1/ for the same moai the important heterogeneity of both the rock and the superficial weathering;

2/ clays need 2 weeks for swelling significantly;

3/ in a rather dry stone (RWC < 28 %) the presence of water quickens its moving.

8/ OTHER TUFFS ANNEX 3

8.1./ TUFFS FOR TESTS

As we brought back only 11 samples from Easter Island we have to find an abundant and almost similar tuff. We first search for andesitic tuffs from the volcano named Montagne Pelée (Martinique Island : French West Indies). Let us note that the drop absorption are very different and that the sample Ma X looks like the lapillis of tuffs of Easter Island.

	volcanic bomb Ma 28	volcanic bomb Ma X	multicoloured cinerite
nucleus	dark grey >90s	very vacuolary<1s	according to the layer
limite	9 to 12s	6 to 9s	.5 to 27s
aureole	light pink 4 to 9s	salmon 1 to 24s	

We select among ten volcanics rocks in continental France [22] :
- **MUROL** : this basaltic tuff is very weak (hand-by crushable). It has been used to study the effect of crust produced by strengtheners;
- **JONAS** : the andesitic tuff of the cliff in which is dug a troglodytic village (XII° century) is the only tuff used as building materials. Unfortunately the site is protected and the lapillis are very big;
- **NESCHERS** : this very porous trachytic pumice is destroyed by an immersion in water after a few seconds. It is used for preliminary sortings of products;
- **SERVIERES** : the greatest part of the petrographical and physical characteristics of this clayey tuff are not too far from that of the one of Easter Island and this tuff is both abundant and homogeneous.

8.2./ SOME PHYSICAL PROPERTIES OF THE TUFF OF SERVIERES

Tests of absorption of water under pressure have been carried out on samples in different states of decay before and after successive rasping off.

■ Unweathered tuffs (porosity ≈ 57%)

We can find three different tuffs :

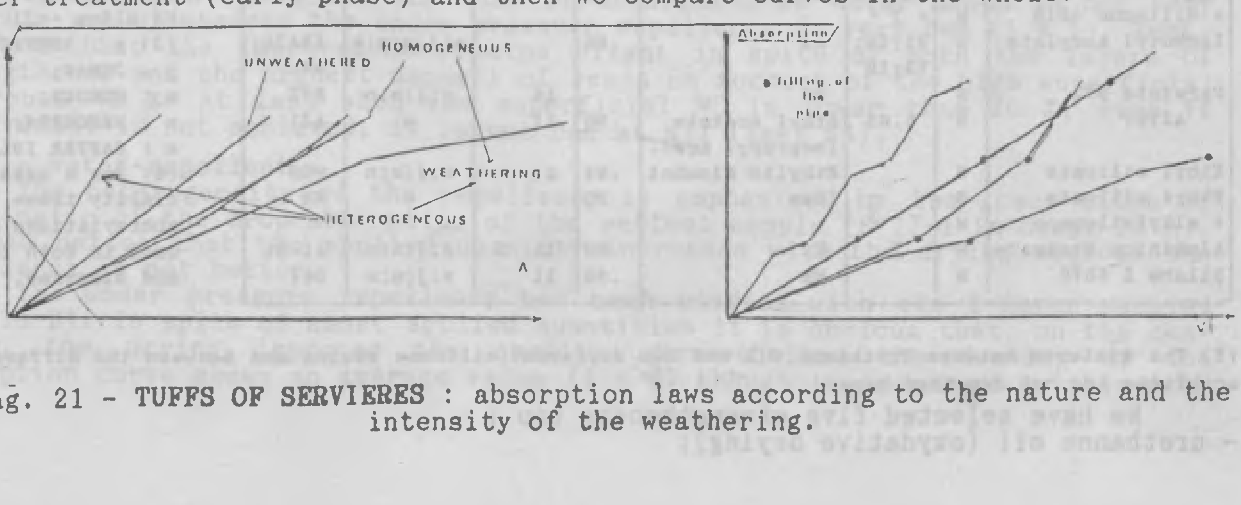
Grain	*fine*	***medium***	***coarse***
B $cm^3/cm^2\ mn^{0.5}$	4.8 to 7.2	.45 to .72	1.9

■ Weathered tuffs.

The weathering can be either superficial or homogeneous for a long deep and it can either increase or decrease the absorption. At last the weathering can make the tuff sensitive to the decreasing pressure during the test.(diag. 21A) :
- curve 1 : unweathered homogeneous tuff
- curve 2 : uniformly weathered tuff
- curve 3 : uniformly weathered tuff but sensible to the decreasing pressure;
- curve 4 : weathered surface (greatest absorption) over an unweathered tuff;
- curve 5 : weathering decreasing slowly according to depth.

According to the state of the tuff the behaviour is different after each filling of the pipe (diag. 21 B) :
- curves 1a, b, c (homogeneous tuff) : the absorption remains identical whatever the number of filling and the shape of the curve during the 1st filling may be;
- curve 2 : increasing of the absorption after each filling. We can set forth two reasons : cracked sample, or absorption of the water by lapillis and not by cement (delayed absorption).

Therefore as we have either to undertake measurements of the absorption before and after the treatments or to keep a few samples during the sawing of great blocks. When sample is weathered the first method has to be used. We term an improvement index, I, as the ratio of the coefficient of absorption before and after treatment (early phase) and then we compare curves in the whole.



Diag. 21 - **TUFFS OF SERVIERES** : absorption laws according to the nature and the intensity of the weathering.

9/FORMULATIONS

9.1./ Rules for the formulation and choice of the resins

The different following established facts set the nature of the resins, the choice of both their concentrations and the solvents :

1/ The chemical decay of the glass of the cement, the shift of silica are the main consequences of the movement of the water in tuffs. The crystallization of salts and the presence of Na+ and Ka+ brought by sprays are secondary though not to be neglected factors (stone decay is higher on the south coast). Therefore exchanges of water must be limited : water-repellency is the necessary complement of the strengthening.

2/ The high permeability to water and the heterogeneity (nests of lapillis and more or less pervious beds) make us fear an incomplete treatment of the moai.

3/ The presence of swelling smectites forbids the use of some solvents.

4/ The high WC (hygroscopicity ≈ 25 %) and the low drying velocity requires the use of solvents able to displace water or at least not impeded by water : it seems that it is not easy to dry the moais completely.

5/ The high mean temperatures and the high wind velocities do not allow to use too volatile solvents.

6/ The low permeability of the crusts sets the choice of solvents.

7/ The weakness of both the decayed and sound stones, and the heterogeneity in the rock (hard lapilli and soft cement) requires the use of pliable resins.

8/ Because of the depth often important of the alteration it is necessary to impregnate layer after layer and to go back in order to reach the good depth.

Some resins had been previously studied [1, 2].

We have not tested methyl siliconate [2] in spite of its interest in wet porous media for any reasons :

1. it is not specifically a strengthener;
2. the high pH (12.5) can promote local dissolutions of the cement before it slopes downward under the action of atmospheric CO2 and the formation of a polymeric compound with a tridimensionnal structure;
3. the polymerisation gives salts as residuum (K+ or Na+ carbonate).

In the same manner we have not tested epoxydes, because one can observe that :
- epoxydes sometimes emphasize the heterogeneity of stones;
- both the low speed and the variability make the choice of the time of polymerization uneasy which also depends on the temperature.
- owing to the high hygroscopic equilibrium, both differential and hasardous impregnations are, a priori, to be feard.

We have selected five hydrorepellent materials :
- aluminium stearate (the presence of goethite in the tuffs can promote the fixation);
- methyl triethoxysilane (Dow Corning);
- methyl silicone, reactive methyl silicone, and silicone oil (Rhône Poulenc).

The first two resins have been used alone and all as additives.

TABLE 18. - MAIN CHARACTERISTICS OF FORMULATIONS

COMPOUND	N (1)	RESIN %	SOLVENT	DENSITY	VISCOSITY(2)	TUFF (3)	ABB
Urethanne oil	S	16	WS	.79	12	s;j;m;n;e	UO16
Urethanne oil	S	25	WS	.80	13.5	s;j;m;n	UO25
Urethanne oil + Al-Stearate	S W	16] + 7	WS	.80	12.5	s;j;m;n	UO25/St
Urethanne oil + Silicone 4518	S W	16] + 7	WS	.80		e	UO16/4
Isobutyl acrylate	S	25;18; 13;10	WS	.80		s;j;m;n;e	IBA25; etc.
Paraloïd B72	S		WS		14	s;j;m;n	B72
A21LV	S	5.65	Ethyl acétate Isopropyl acét.	.90	11	e	A21
Ethyl silicate	S		Ethylic alcohol	.94	11	s;j;m;n	WOH
Ethyl silicate + alkylsiloxane	S W	]	Idem	.90		e	WH
Aluminium Stearate	W	7	WS	.80	11. 5	s;j;m;n	Al-St
Silane Z 6070	W		WS	.80	11	s;j;m;n	Sil

(1) N : nature of the resin :
S : strengthener;
W:water-repellent
(2) Viscosity : measured with CF4 bis second :
WS alone = 11.5.
(3) s : SERVIERES
j : JONAS;
m : MUROLS;
n : NESCHERS;
e : EASTER ISLAND
(4) For a sake of clarity these abbreviations are used in both text and diagrams.

(5) The mixtures between Urethanne Oil and two different silicone resins and between the differents acrylates are not reported here.

We have selected five strengtheners too :
- urethanne oil (oxydative drying);

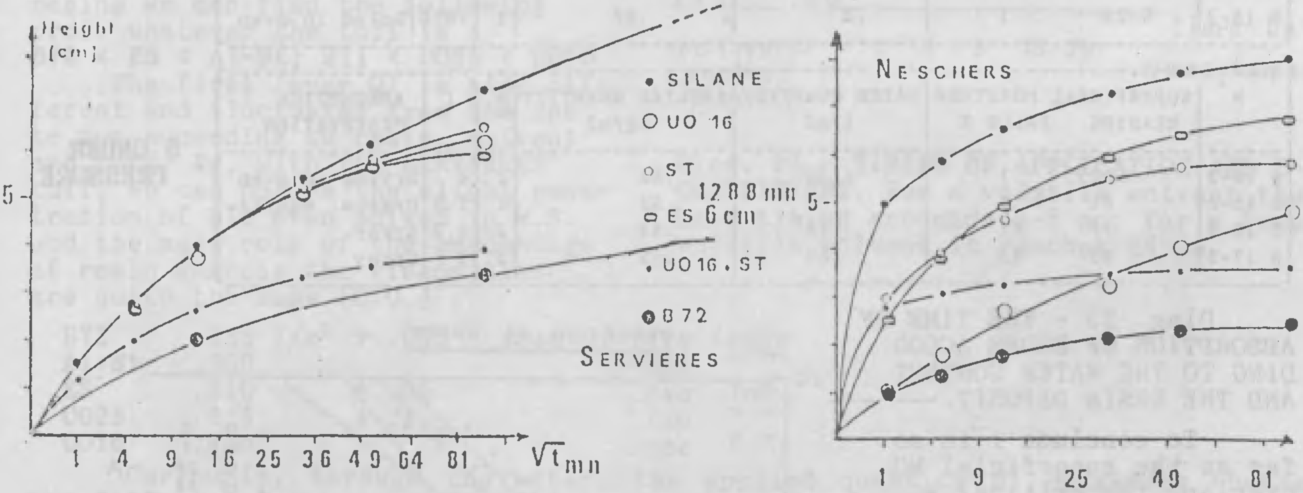
- ethyl silicate (with or without water-repellent WÄCKER OH and H;
- isobutyl metacrylate (soft resin); paraloïd B 72 (mean); acryloïd A 21 (hard).

The main characteristics of the different formulations are shown in table 18.

9.2./ Preliminary tests

a/ Capillary rise (diag. 22)

We have set small samples (2 x 2 x 10 cm) made of SERVIERES'tuff and NESCHERS' pumice, each in a closed cup containing 20 ml of solution. Silane rises more quickly whereas B72 and UO25 rise more slowly. It can be seen that UO16 rises more easily even in the pumice. The top of the samples is reached always after 20 hours except with B72-SERVIERES (6.2 cm) and IBA-NESCHERS (8.5 cm).



Diag. 22 - **CAPILLARY RISE OF PRODUCTS** in small samples of SERVIERES (upper part) and NESCHERS (lower part).

b/ Account of the superficial moisture

This parameter is important in situ. It answers the following question : how long after rain is the treatment possible? Therefore the superficial moisture has been measured systematically and sometimes, after spraying, samples are weighed after the diffusion of water (1 to 20 mn) and before the application.

o Strengthener (table 19 and diag. 23).

N°	SUPERFICIAL MOISTURE READING	VALUE %	WATER QUANTITY l/m2	QUANTITY OF RESIN g/m2	n	tm in mn	I
S1	20	6	0	50	1	240	35
S4	63	26	.12	40	1	130	12
S8	71	45	.11	80	2	390	7
S3	86	98	.54	50	1	100	1
S6	87	99	1.23	20	1	8	1

-TABLE 19 - UO 16 AND SUPERFICIAL MOISTURE SERVIERES'TUFF

Above .6 l/m² (S6) water impedes the penetration (only 20 g/m²) and the repellency is very slight (tm = 8 mn). Above .3-.4 l/m² in spite of a normal quantity of resin (50 g/m²) the time of absorption of water drops is not very long (tm = 100) whereas the under pressure repellency is very bad (I = 1). Test S8 shows that the improvement remains slight in spite of both two layers of strengthener and the highest deposit of resin on account of the high superficial WC around 45 %. At last when the superficial WC is lower than 26 %, even if improvement is not achieved, it is not bad at all (test S4).

o Water-repellent

The heterogeneity of the repellency is emphasized by the lower slope of the kinetic of the drop absorption of the wettest sample (S 17-1 in diag. 23 A). One can notice that the applied quantity increases with the drying whereas the repellency is not better.

The under pressure repellency has been studied with the 2-layer samples (tab 15 B). In spite of short applied quantities it is obvious that, on the contrary, the drying improves the quality. Nevertheless the drawing of the absorption curve shows an average value (I = 4) though it decreased quickly with the depth : 4 minutes after the beginning of the test B reaches the same value as one of S 15-2.

TABLE 20 - Al-St AND SUPERFICIAL MOISTURE (SERVIERES'TUFF)

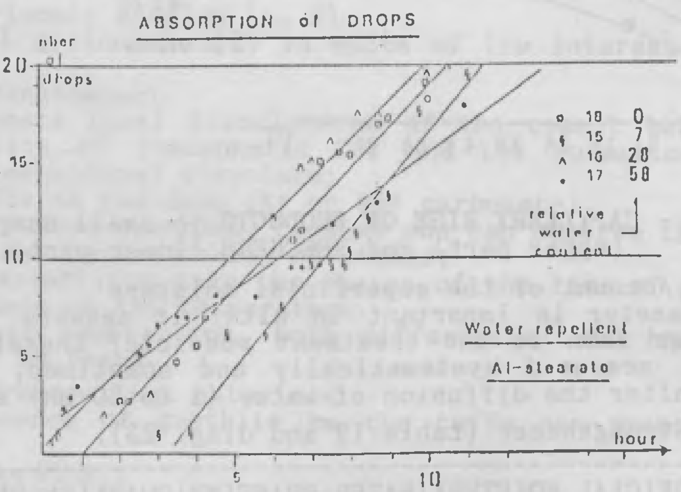
A DROPS

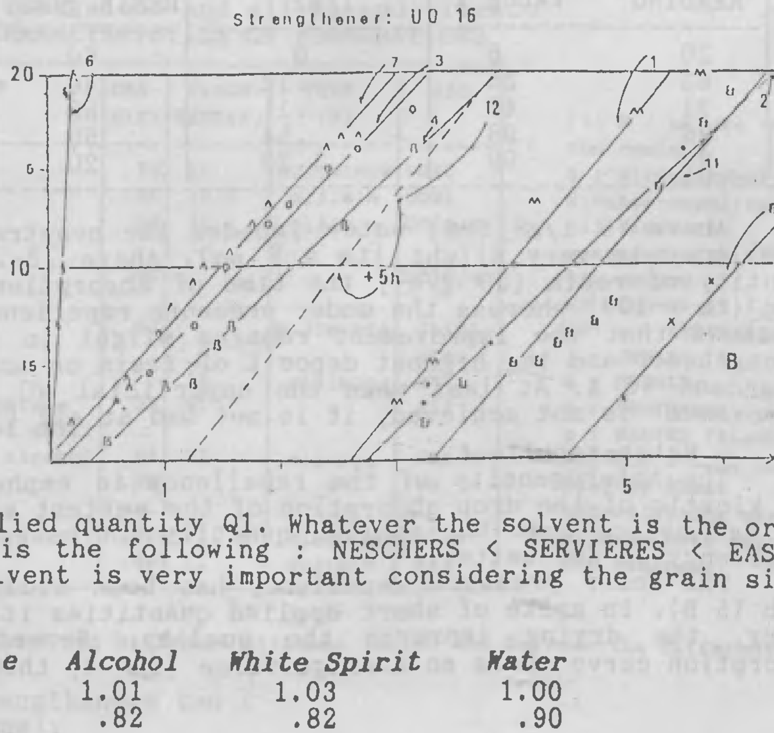
N°	SUPERFICIAL MOISTURE READING	VALUE %	WATER QUANTITY l/m^2	APPLIED QUANTITY kg/m^2	n	tm	OBSERVATION
S 18-1	5-25	1	.3	.49	1	345	Dried in oven
S 15-1	61	6	0	.32	1	450	Hygros.equil.
S 16-1	77	61	.18	.25	1	290	Spray
S 17-1	83	93	.60	.39	1	340	Spray
S 18-2	5-25	1	.3	.82	2	>900	Dried in oven

B UNDER PRESSURE

N°	SUPERFICIAL MOISTURE READING	VALUE %	WATER QUANTITY l/m2	APPLIED QUANTITY kg/m2	n	I	ABSORPTION OBSERVATION
S 18-2	5-25	1	-.30	.82	2	4	Drying in oven
S 15-2	61	6	0	.52	2	1.8	Hygros. equili.
S 16-2	77	61	.18	.49	2	1.2	Spray
S 17-2	83	93	.60	.55	2	1	Spray

Diag. 23 - THE TIME OF ABSORPTION OF DROPS ACCORDING TO THE WATER CONTENT AND THE RESIN DEPOSIT.-------





To conclude : in so far as the superficial WC overlaps the critical WC the quality of the treatment decreases quickly. The critical WC are around 30 % for both SERVIERES' tuffs and EASTER ISLAND's. Therefore in situ it is required to make sure that the RWC is lower than its critical value in any place.

c/ Applied quantity, technique of application and choice of solvents.

One can remember that a depth around 1 or 2 cm has to be reached in any place of every moai : the reached depth is needed to be predicted without any destructive method. One can express the applied quantity Q as a function of the number of layers n, and the applied quantity in the first layer Q1 :

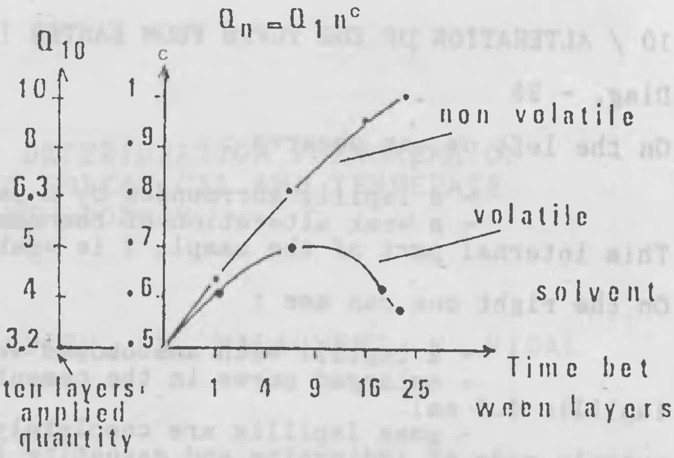
$$Q = Q1 . n^c$$

c : the lower this index is the worse the ability of penetration is. In all the tests c ranges from .5 to 1 : that means that the 10-layer applied quantity, Q10, ranges from 3.2 to 10 times the applied quantity Q1. Whatever the solvent is the order of absorption of the tuffs is the following : NESCHERS < SERVIERES < EASTER ISLAND. The volatility of solvent is very important considering the grain sizes of the EASTER ISLAND'S tuff.

VALUE OF c	Solvent very volatile	Alcohol	White Spirit	Water
Fine grained	.59	1.01	1.03	1.00
Coarse grained	.68	.82	.82	.90

The low penetration of a product made of volatile solvent is the result of pore-blocking by the resin of the previous layers or at least of the increasing viscosity : the fine the grain is, the greater the blocking is. Lapses of time between layers is the main parameter. When the solvent is not too volatile the diffusion is sufficient to allow the next absorption to be equal (diag. 24). Comparing the differents resins we can find the following order whatever the tuff is :
B72 < ES < Al-St; Sil < UO25 < UO16

The first layer Q1 is also different and fluctuates from the one to two according to resin, solvent and tuff. Eg, with the SERVIERES' tuff, we can notice the slight penetration of B72 even solved in W.S. and the main role of the percentage of resin whereas the viscosities are quite the same (U.O.) :



Diag. 24 - **TIMING OF APPLICATION AND C-COEFFICIENT.** For a volatile solvant the best timing arrounds 5-8 mn; for a less volatile solvent it reaches 25 mn.

B72	.233 l/m²	± .015	*mean of*	*five tests*
Al-St	.300			*one " "*
ES	.310	± .05	*" "*	*two " "*
UO25	.315	± .1	*" "*	*two " "*
UO16	.475			*one " "*

Curiously, through the water, the applied quantity Q1 decreases whereas the diffusion increases (c = .91)
- dried oven tuff : $Q = .473\ n^{.78}$
- tuff in hygroscopic equilibrium : $Q = .300\ n^{.77}$
- wetted tuff : $Q = .275\ n^{.91}$

-TABLE 21-METHOD OF APPLICATION QUALITY OF WATER-REPELLENCY (NESCHERS' PUMICE)

NUMBER OF LAYERS	TIMING IN mn	APPLIED QUANTITY g/m²	MEAN TIME OF DROP ABSORPTION in mn
0	-	-	.01
1	-	375	105
2	30 mn	800	250
3	1 mn	700	140

As a matter of fact the diffusion is very slow (cf the capillary rise), thereby we can compare the applied quantities according to the method of application : the application of three layers wet on wet uses less product than with two layers whereas the quality is not too far from the result with only one layer (table 21).
To conclude this first step one can notice that for a good application :
- the superficial WC has to be lower than its critical value;
- solvents characterized by a slow volatility have to be used;
- the best depth of penetration is given by a timing around 15-30 mn.

10 / ALTERATION OF THE TUFFS FROM EASTER ISLAND   ANNEX 5

Diag. - 25

On the left on can observe :

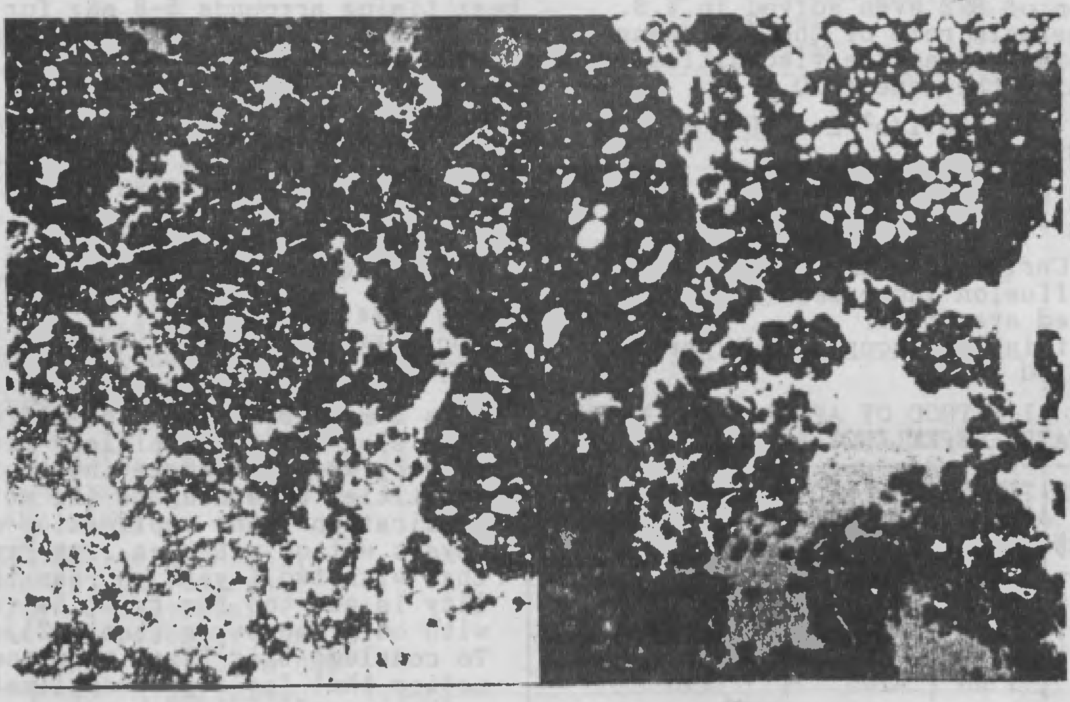
- a lapilli surrounded by a partial aureole.
- a weak alteration of the cement (some pores are fine).

This internal part of the sample 9 is weakly weathered (2 cm below the surface).

On the right one can see :

- a lapilli with anatomosed vacuoles (upper part).
- enlarged pores in the cement that are as large as the smallest lapillis (.5 mm).
- some lapillis are completely weathered : it remains only the black aureole made of iddingsite and magnetite (lower part on the right).

This external part of the sample is very weak.



AKNOWLEDGMENTS

I am gratefull to M. RAPU for his usefull and cordial help in EASTER ISLAND, to M. J.-C. PONS (I.G.B.A. -BORDEAUX : microscopy), to M BEUCLER (Hydrogéologie dynamique -BORDEAUX) and the whole laboratory of O.N.I.P. at HONDOUVILLE.
The different tests have been carried out in the following laboratories :

- simulation : I.U.T. Génie civil - LA ROCHELLE.
- X ray analysis : I.G.B.A. -BORDEAUX.
- chemical analysis : Laboratoire municipal -BORDEAUX.
- mechanical tests on samples : C.E.B.T.P. - SAINT REMY LES CHEVREUSE.

FIELD AND LABORATORY STUDY OF DETERIORATION PHENOMENA OF LAVAS AND VOLCANIC TUFFS UNDER SUBTOPICAL AND TEMPERATE CLIMATES BY MULTISEQUENTIAL METHODOLOGY

J. VOUVE, J. AROUZE, G. LACAZEDIEU, Ph. MALAURENT, P. VIDAL and F. VOUVE

Centre d'Hydrogéologie, Université de Bordeaux,
Avenue des Facultés, 33405 Talence-Cedex, France

ABSTRACT

The petrographic and petrophysic features of lavas and volcanic tuffs are very heterogeneous. They depend on: the original volcanic facies, the evolution during cooling and the geomechanical stresses during movement. The natural outcropping rocks undergo weathering during the course of geological time; the causes and results are very varied. Weathering also operates on "objects" worked by man from these materials when exposed to open air. This process is mainly dependent on climatic and micro-climatic factors, since they control the hydro- and bio-chemical parameters. We emphasize the role played by marine sprays. Technology transfer from previous studies allowed us to develop a specific methodology to study volcanic materials in the broad sense and Easter Island statues in particular.

RESUMEN

Las propiedades petrogáficas y petrofísicas de las lavas y tobas volcánicas son muy heterogéneas. Dependen de: la composición volcánica original, la evolución durante su enfriamiento y los esfuerzos geomecánicos durante su movimiento. Los afloramientos de estas rocas se alteran con el curso del tiempo geológico: causas y resultados son muy variados. Esta alteración también afecta a "objetos" de estos materiales elaborados por el hombre y expuestos a la intemperie. Este proceso depende fundamentalmente de los factores climáticos y micro-climáticos, que controlan los parámetros hidro- y bio-químicos. Se enfatiza la importancia de la niebla salina. Por transferencia de tecnología de previos estudios se elaboró una metodología específica para el estudio de los materiales volcánicos en general y las estatuas de Isla de Pascua en particular.

INTRODUCTION

Two researchers (J.V. and P.V.) carried out a scientific, environmental programme brief (12 days) in February and March 1988.

The results of the field and laboratory studies are interesting but incomplete to understand some of the mechanisms which favour the decay of the statues erected in Easter Island (E.I.) under à subtropical oceanic climate. A team of university researchers was formed in October 1988 to participate in the "lavas and volcanics tuffs competition" and to continue in France (F.) the investigations on the topic "deterioration".

The duration of observations(tests and measures) (November 1988-November 1989) corresponds to a climatic cycle. The stone materials were selected by one of us (J.V.) at 200 km to the East of Bordeaux. They were placed in the climatic conditions of the South-West region in France which are temperate oceanic climate. The principal results of the scientific programme are described below.

The authors have stressed the sequence of indirect, multisequential, repetitive and non-destructive studies owing to the purposes of the investigations which are :

- knowledge of mechanisms and factors which affect the decay of open-air carved and engraved rocks,
- conservation of a megalithic heritage unique in the world.

At the end of this note, the components of a research project programme are suggested to be debated with the other scientific teams.

2. EXPERIMENTAL

2.1 Choice and petrographic study of stone materials.

E.I. = we had chosen two petrographic types of Moais. One is hewn out of a living tuff and two others are hewn out of a living lava.

Their location is on Fig. n°1. They are identified as objects (01,02,03)

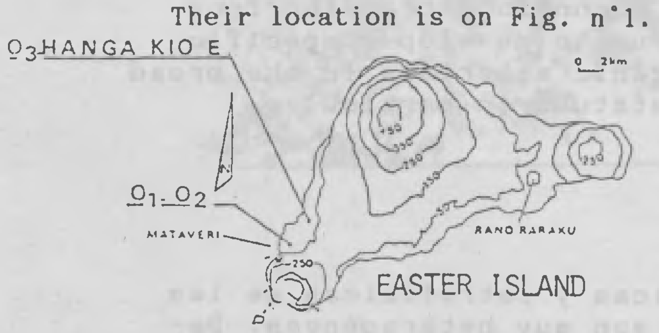


Fig. 1 Location of Moai ("objects")

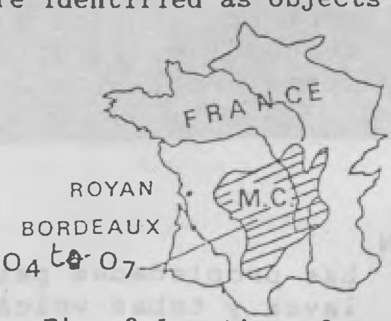


Fig. 2 Location of samples collected in Massif Central(M.C.)

F. = some petrographically similar materials to those described above were selected after studying many out-crops.

The rocks are located in the Massif-Central. It is a large volcanic unit of 85000 km2 (1/6 of France - see Fig.n°2).

There are four collected *objects* (04 - 05 = tuffs, 06 - 07 = lavas).

2.1.1 Laboratory and field tests

The in situ observations and the measures in the laboratory made on all *objects* are placed in table n° I. The detail of the technical programm is in table n° II.

objects / characteristics	Moai Hanga Kio E= 01	Moais 4 and 5 02 - 03	Rock samples 04 - 05	Rock samples 06 - 07
Rock	volc. tuff breccia	lava alc. trachyt	volc. tuff breccia	lava trachyte
Sizes ≃ (x cm)	360x170x85	2 - 215x95x40 3 - 200x100x45	4 - 45x25x20 5 - 30x20x20	6 - 35x20x20 7 - 30x20x20
CEMENT ≃ matrix				
Nature	glass+micro liths	plagioclase feldspars	glass+micro liths	Plagioclase feldspars
State	amorphous dominant	crystallized	amorphous dominant	crystallized
Subordinate minerals	pyroxene	iron and magnesian compounds	?	iron and magnesian compounds
Structure	macro-granular	micro-granular	macro-granular	granular
Aerial area	rough	rough	rough	rough
Hardness color	low/medium chestnut/brown	médium/high crust of bread	low/médium chestnut	médium/high crust of bread
Fissuration (f.)	micro f.	02 = middle 03 = high	micro f.	micro f.
Superficial deposits	amorphous white silicate	lichen encrustings		
ENCLAVES (1)				
Nature	basalt	-	basalt	-
State	microlithic	-	microlithic	-
Appearance	massive	-	slaggy	-
structure	compact	-	bubbly	-
Color	bright black	-	dull black	-
Grain-size	0,2 - 32 cm	-	0,2 - 6 cm	-
fraction	in projection	-	in projection	-
Morphology	max. = 2,6 cm		max. = 1,2 cm	

Table n° I - Petrophysical characteristics of rocks.

(1) ENCLAVES = brecciated heterometric components included in the cement.

Climatic study of the objects : E.I. : 04-02-03 = from 23.02.88 to 8.3.88 (recall) F. : 04 and 06 = Bordeaux-Pessac, from 2.12.88 to 15.09.85 - 05 and 07 = from 2.12.88 to 22.06.89 Samples broken the 23.06.89 for study in the laboratory. Marine sprays study: 04 and 06 = Royan from 17.09.89 to 10.10.89 (date of destruction by vandalism). Laboratory = October-November 1989. Analysis of imagery data : laboratory - Décember 89 - January 90.

Table n° II - Planning of research programme and difficulties.

The comparison between the tuff and lavas facies shows some petrographic, morphologic and petrophysic similarities (see 3.2.1 and tables n° I and IV).
These similarities allow us to consider a scientific comparison of the materials.

2.2 Chemistry of the materials (major components)

In table n° III, we have collected the results of analysis discovered in bibliography 1 . and those reached in the present study.

% N°	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	NaO	MnO	K_2O	TiO_2	P.F. 600 °C	TOTAL
04	58,5	14,8	3,6	3,5	5,8	9,6	1,2	0,1	0,9	0,3	2,1	100,4
06	57,4	16,7	5,5	2,6	5,0	8,6	1,6	0,1	0,8	0,3	1,0	99,6
IP1	53,6	14,2	4,6	3,6	6,8	9,7	2,8	0,2	1,1	0,8	2,8	100,2
417	50,2	12,75	7,3	4,8	3,1	5,9	2,45	0,26	1,0	2,24	x	99,10
418	48,2	12,85	8,3	4,15	3,6	4,9	2,4	0,27	0,91	2,25	xx	99,13
										H_2O^-	H_2O^+	
									x	4,2	4,9	
									xx	6,95	4,4	

Table n° III - Chemical analysis of selected samples (test-rocks and moais). 04 = tuff - 06 = lava(French samples) - IP1 = Rano Raraku sample (J.V.); 417-418 : samples collected near the moais n° 389 and the Tepeu ahu (Hyvert).

2.3 Petrophysical study of rocks

This study included bibliographical investigations, (E.I.) and the numerous measurements executed on the 04 and 06 rock samples (F.).
E.I. = Hyvert data 1 :
The most frequent measurements of porosity are : 31-33%
The extreme values are : minima = 27% - maxima = 42%
F. = The measurements are collected in table n° IV.

Rock samples	04 - tuff						06 - lava					
Spatial locating	Sub cutaneous layer level 2			internal layer level 1			sub cutaneous layer level 2			internal layer level 1		
Instantaneous humidity I.H.%	a 3,7	a 4,3	c 4,4	a' 5,7	b' 6,1	c' 6,3	g 2,2	h 2,2	i 2,3	g' 2,1	h' 2,2	i' 2,3
Porosity Nw	34	36	39	28	32	38	6,5	5,7	6,1	4,2	6,7	6,4
Permeability at 20°C-K	1,01	0,34	0,26	0,22	0,28	0,19	0,12	0,11	0,10	0,08	0,11	0,11

Table n° IV - Physical caracteristics of samples (a, b,...c',...i') taken from the 04-6 samples. The I.H. measure was realized 24 h after fall on the rain 20.06.89. For the definition of level 2, 1, see paragraph 3.3. - Nw = vacuum water porosity (%) - K = water permeability in l/s.m2.

2.4 Field tests

2.4.1 Hydrodynamic tests on 01-02-04-06-07 *objects*

The aim is to discern, to understand and to restitute :
- the hydrodynamic at the surface and inside the open-air *objects*,

- the regime of water transfers between two or more rainfall sequences.

The scientific procedure is as follows :

- acquisition of data by electrical investigation =
  . "trainé" process for the surface measurements,
  . "transparence" process for the internal measurements,
- drawing of isoconductance maps (see Fig. n°3 to 7).

2.4.1.1 Subtropical climate tests E.I. (01-02).

Experimental conditions : the day of 03.03.88
morning : frequent rainfall sequences alternate with sun (end of rainfall = 11 h 30 - "strong" wind W-N.W.-E.S.E.
Afternoon = cloudy weather-without rain-medium and irregular wind W-N.W.-E-S.E - from 22 h : rain.
Hygrometry : 08 h = 90% - 12 h = 100% - 15 h = 88% - 17 h = 70% 20 h = 75% - 21 h = 81%.
Air-temperature : 08 H = 22,2 - 12 h = 26,1 - 15 h = 26,8 -
17 h = 28,0 - 20 h = 27,1 - 21 h = 26,2°C.

2.4.1.2 Temperate climate tests - F.(04-05-06-07)

We have chosen two significant samples of the hydrodynamic behaviour in tuffs dependent on the season[1]; these are selected from numerous measurements made between 12.02.88 and 15.09.89.

. Spring experiment (storm) - Fig. n° 8-a, see previous caption.
-04, 05, 06, 07 in the field = rain on 19.04.89 - monitoring of the rain development during 48 hours - destruction of 05 and 07 testrocks in many small samples to study the levels 3, 2, 1 in laboratory (see table n°4).

. Summer experiment (thundery weather and high heat) - Fig. n° 8-b, see previous caption).
04, 06 in the field = high diurnal heat in June, July and August - measurement of the thermic and mechanical behaviour heary storm on 10.06.89 - measurement of water movements during 48 hours.

2.4.2 Hydrochemical development on and inside the *objects*

2.4.2.1 The role played by water of infiltration.

The idea is to follow the changes in the chemistry of rainwater after percolation in the test rocks. This test was carried out in France only after the rainfall of 19.04.89. In the table n°4 we have collected the results of the analysis of rainwater and of water of infiltration accumulated at the base of tuff rocks (04 and 05).

For 06 and 07, the quantity of infiltration water was too small to allow chemical analysis.

2.4.2.2 The role of marine sprays (sea-mists).

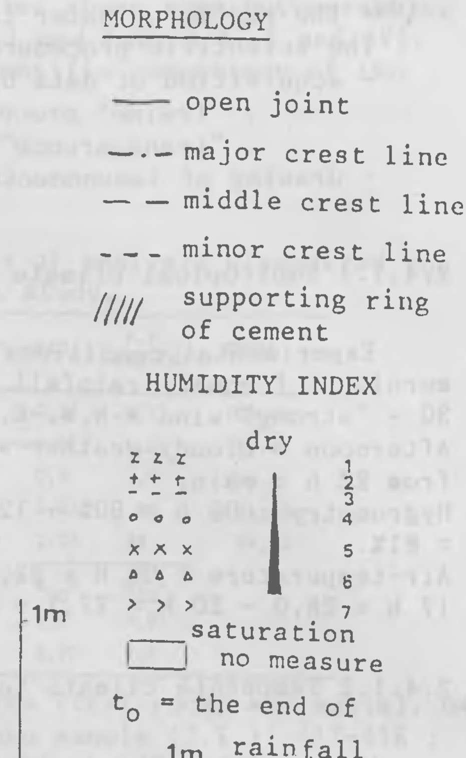
The understanding of the dynamics of marine sprays is a significant problem in the study of the decay of rock materials.

We started the study of these climatic phenomena in E.I. and we continued it in France. It has been completed prematurely !!! (see below).

---

[1] The winter test failed because there was no cold and no snow in the S.W. of France between December 88 and March 89.

CARTOGRAPHY OF HYDRODYNAMIC BEHAVIOR OF OBJECTS



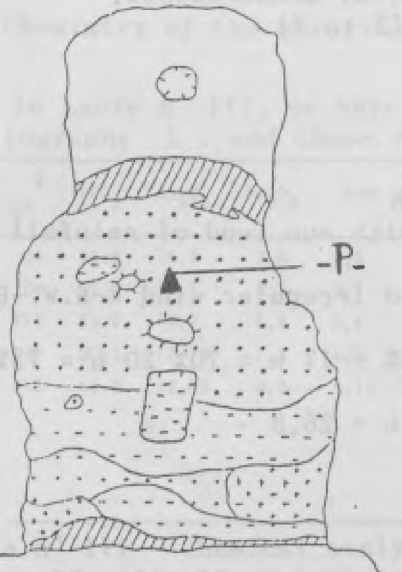


Fig. n° 3 =
O_1 : back - cross wind
map at to + 6 h

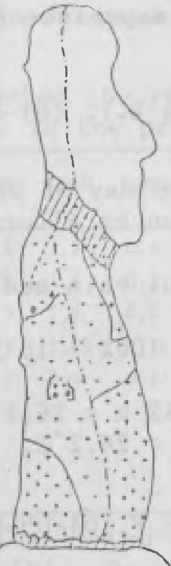


Fig. n° 4 =
O_1 : right side
full face wind
map at to + 6 h 30

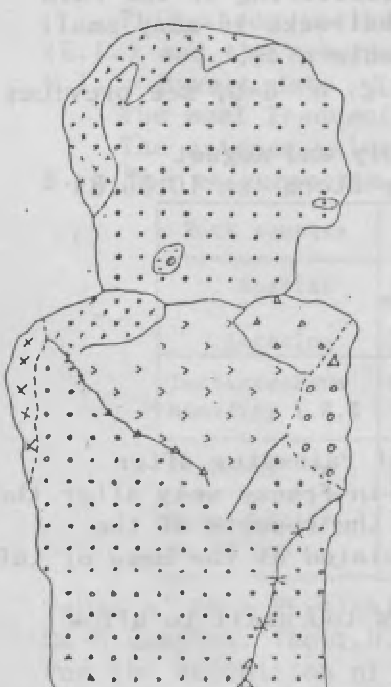


Fig. n° 5 =
O_2 : back - full face wind
map at to + 8 h

Fig. n° 6 =
O_2 : leeward face
map at to + 8 h 30

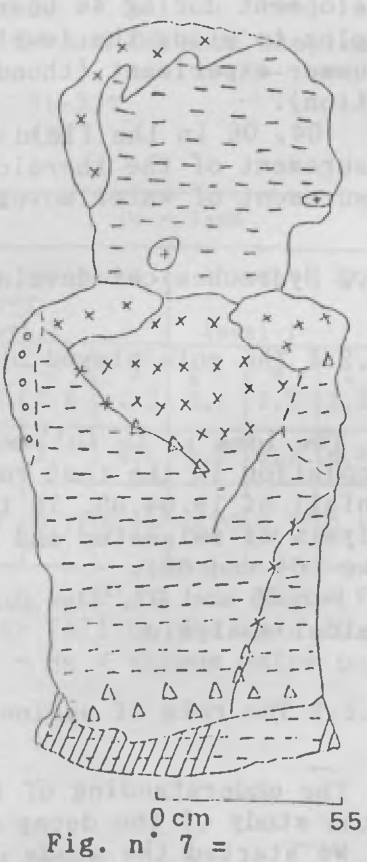
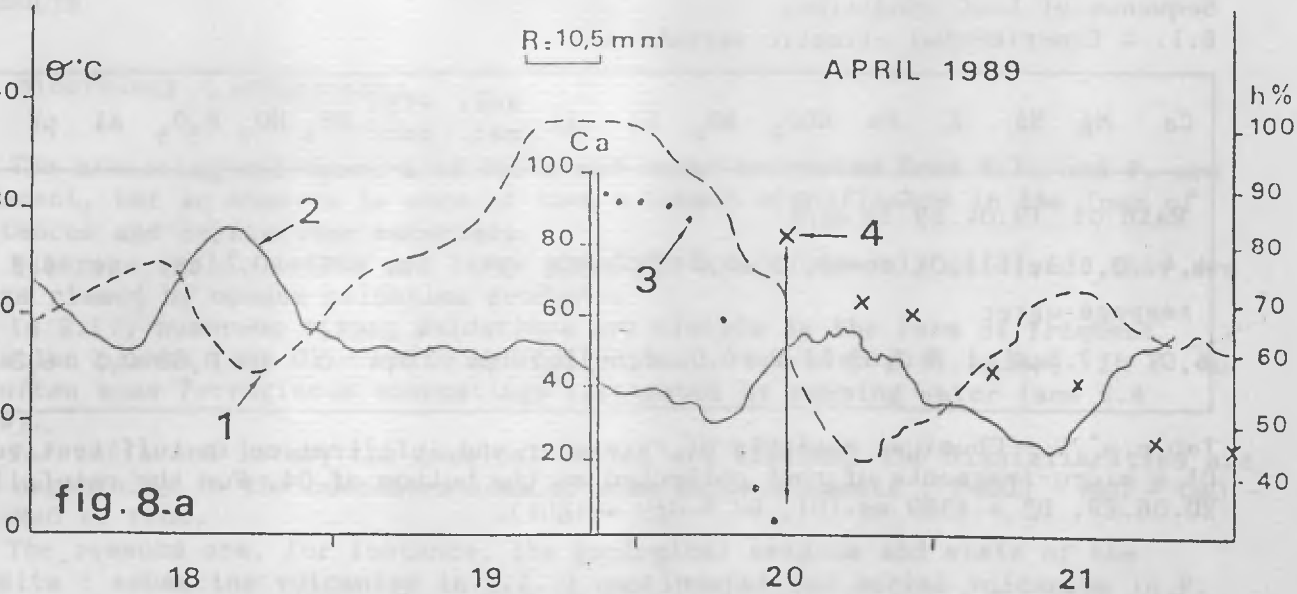
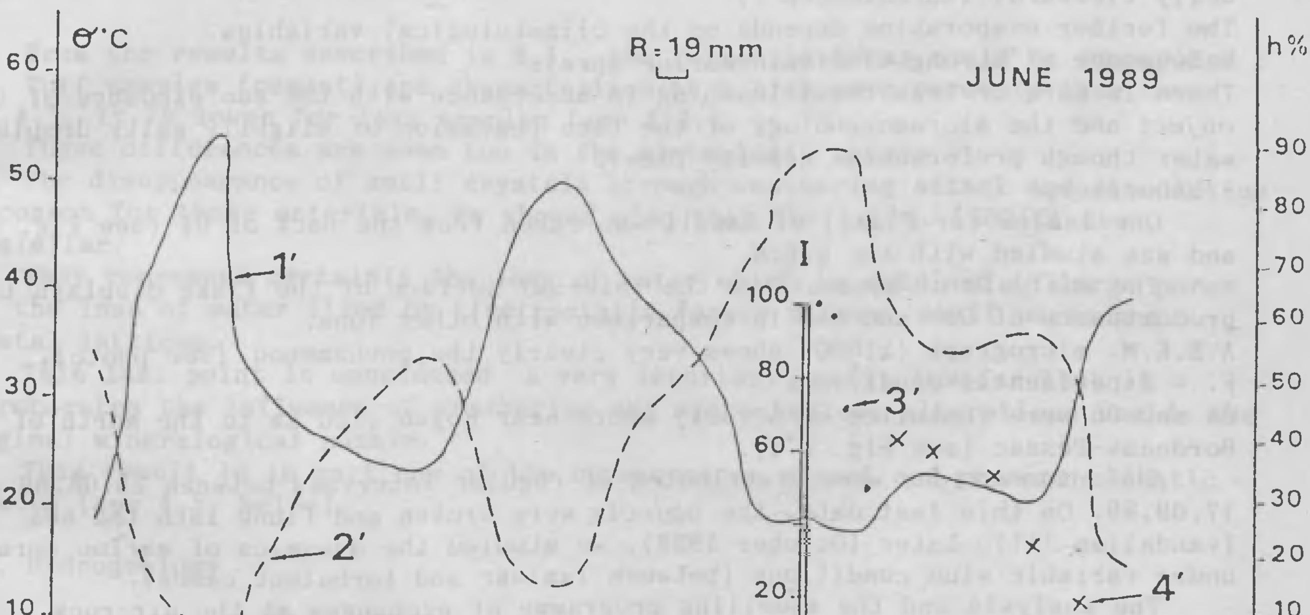


Fig. n° 7 =
O_2 : back - full face winf
map at to + 13 h
($t \approx 5$ h).



DIAGRAMS OF VARIATION OF WATER CONTENTS OF O4 AS A FUNCTION OF CLIMATIC CONDITIONS



Captions for Figs. 8-a/ 8-b

Microclimatic change around a tuff object (04) and hydrodynamic change at the surface and inside 04.
April 1989 - rainy sequence in spring
June 1989 - stormy sequence at the begining of summer
1-1' = suface temperature of the stone;
2-2' = hygrometry of air - R = rainy sequence;
3-3' = humidity change of level 3 dependent of time (apparent isoconductance); 4-4' = idem for the level 2.

Sequence of test conditions
E.I. = Experimental climatic variables

Ca	Mg	Na	K	Fe	HCO_3	SO_4	Cl	Si	sol. mat.	org. mat.	NH_3	NO_2	P_2O_5	Al	pH	D_1
Rain of 19.04.89 in mg/l																
4,4	0,6	3,1	1,0	tr	9,15	3,2	5,7	tr	-	tr	0	0	tr	tr	6,5	820
seepage water																
6,0	1,7	4,0	1,8	0,07	12,2	6,0	6,6	12,2	54	1,4	0	0	0,33	0,5	6,8	-

Table n° V - Chemical analysis of rainwater and infiltration in tuff test rocks. D1 = micro-fragments of rock collected at the bottom of 04. For the rainfall of 20.06.89, D2 = 1380 mg.(D1, D2 = dry weight).

- Sequence = "strong wind/sea breeze+marine sprays"
  .with strong wind and rough sea, the mists settle on part only of the back and sides of the rock (to windward) of 01 and additionally over some parts of the belly (leeward)-(turbulences ?)

The further evaporation depends on the climatological variables.
- Sequence = "strong wind+rain+marine sprays"

There is more or less total leaching in accordance with the sun exposure of the *object* and the micromorphology of the face (emission of slightly salty droplets of water though preferential gravity flow).
- Laboratory

One lamina (or flake) of basalt was taken from the back of 01 (see Fig. n°3) and was studied with the S.E.M.

The analysis of elements on the internal surface of the flake displays the predominance of Cl- and Na+ in comparison with other ions.
A S.E.M. micrograph (x1000) shows very clearly the phenomenon (see photo).
F. = Experimental conditions
04 and 06 were installed on a rocky shore near Royan (120 km to the North of Bordeaux-Pessac (see Fig. n°1).

The observations were distributed at regular intervals between 25.08.89 and 17.09.89. On this last date, the *objects* were broken and flung into the sea (vandalism !!!). Later (October 1989), we studied the dynamics of marine spray under variable wind conditions (between laminar and turbulent cases).

The analysis and the modelling programme of exchanges at the air-rock interface are under storely.

(photo) - Microphotograph of ClNa crystals on the inside surface of the lamina of basalt taken from 01.

3.RESULTS

3.1. Mineralogy - petrography

The mineralogical spectra of tuffs and lavas extracted from E.I. and F. are different, but we observe in each of them a common significance in the loss of substances and crystalline materials.

Numerous small, medium and large phenocrysts are commonly oxidised. They are always rimmed by opaque oxidation products.

In E.I., numerous strong oxidations are visible in the form of frequent exudation planes (see O1 - white hydrosilicates - see also 6.4. below). In F. we see often some Ferruginous encrustings instigated by running water (see 6.4 below).

For tuffs and lavas, the chemical facies are similar. The dissimilarities are seen especially in the concentrations of some major elements : Fe_2O_3 - MgO - CaO - NaO -MnO et TiO_2.

The reasons are, for instance, the geological origins and state of the deposits : submarine volcanism in E.I. ; continental and aerial volcanism in F.

3.2. Petrophysics and geochemistry

From the results described in 3.1., the following ideas could be summarized :

Tuff samples (cement) are characterized by a high open porosity (see too 3.2.4.). It is lower for lava samples (see 2.3.).

These differences are seen too in the mineralogic mosaic.

The disappearance of small crystals through weathering attack and dissolution is common for these materials. We showed also that the I.L's. (600°C) are dissimilar.

They represent certainly the loss of water which is retained in large pores and the loss of water fixed by electrostatic forces between small pores and crystal lattices.

This last point is considered a very important result insofar that it corroborates the influence of weathering and microchemical alterations inside the original mineralogical puzzle.

This result is in part one of the consequences ofpast and present climatic effects (see 4.3. below).

3.3. Hydrogeology

The study of the maps and the circumstantial analysis of local measurements allow us to locate through time, the evolution of the superficial and internal hydrodynamic phenomena specific to the "objects".

This examination allows to separate phenomena on the surface or within the masses which are finite, as a function of different geological elements, (faciology, cracking), geomorphological (head, eye - neck - hand etc...), biological, wind exposure, etc.. etc... We have collected in the table n° VI some of the main results.

Moreover, at the end of the program of measurements in France, we discerned three different levels with variable thickness : (l3 = µm or (x), l2 = mm, cm or (x), l1 = dcm or (x). For each, the hydric exchanges by evaporation, run off and gravity effect are different the one from the other. The temperature and hygrometry of the surrounding air accelerate or slow down the evaporation (bare-rock) and the transpiration (mosses or lichens on rock). It is the knowledge of these dynamics which can help us to understand the nature of the geochemical exchanges (see below).

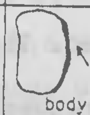
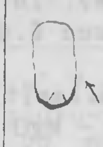
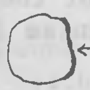
Objects	Study of interface	Drawing figure	Time t_o = end of rain	Evolution of humidity (H)	Identification levels	Hydric phonomenon observed
↑ O_1	 horizontal section wind; body	Fig.3	t_o + 6h	basalte = (H) : "small" desaturation (D) : "fast" cement (C) = (H) : "medium" (D) : "low"	level 3	Soaking (I) then, evaporation (E)
↓	 idem	Fig.4	t_o+6h30	(C) = (D) : "fast" neck, cracks : (H) : "medium"	level 3 level 2	imbibition + infiltration, then, (E)
↑	 idem	Fig.5-6	Δt = 5h	lava = (D) : "fast" lichens = (H) $\simeq$ equal bottom O_2 = (H) : "high"	level 3 level 3+2	(I), then (E). (I), then retention, then run off, + gravity effect
O_2	 idem		t_o+21h	surface + sub-cutaneous bed.(H) = "dry" internal bed = (H) : "medium"	level 3+2 level 1	desaturation infiltration ?? transfer ??
↓	 Socket(s); head nose (N)	Fig.7	t_o+13h	(O) = H : "high" (N) = H : "small"	—	(I), then retention evaporation : "fast"

Table n° VI : Results obtained after checking evolution of humidity.
level 3 = interface air-rock
level 2 = under-layer (x mm or cm)
level 1 = internal layer (x dcm or x 10 cm).

3.4. Hydrogeochemistry

3.4.1. Relations between rainfall and infiltration

The tests were executed in France only. The infiltration water gained a small mineralisation after a time of contact between 12 and 18 h with the rock (tuff).
This water remains subsaturated. The main acquisition is for Si, then Mg, SO4, Ca, HCO3.
The immediate and delayed leaching and the infiltration help to export some dissolved substances in small amounts.
These phenomena facilitate the increase in porosity and permeability with time.
The consequences are : loss of cohesion for the cement, detachment of enclaves associated with micro and macro graining.

3.4.2. Sprays

E.I. : The historical repetition of strong aspersion-abrasion cycle by marine sprays of windward rocky interfaces, facilitates the penetration of salt emulsion in the open pores, microcracks and cracks. A portion is exported by leaching (rains), and a portion is trapped. The high evaporation, which is linked to the climate, facilitates the crystalline growth of ClNa. This crystallisation facilitates the desquamation and mechanical destructuration (superficial peeling off : see O1 for instance).

F. = The results are incomplets. Nevertheless they show that in the case of temperate climate and after the storms, there is no formation of concretion of ClNa crystals on the windward surfaces nor in some microfissured spaces.

The evaporation which is less high in F. than in E.I. can explain these dissimilarities.

In experimental conditions, the leeward faces are not reached by sprays. This result reveals the significance of the geomorphology of the "object" for the dispersion of micro droplets, and of the speed and turbulence of wind.

4. DISCUSSION

The results obtained on E.I. and in F. allow us to differentiate :

- the established facts - (a),
- the still poorly defined facts (b),
- the specific facts (c).

For (a), it is clear that the driven rain, the water flow and the run off help in the mechanical destructuration of "objects".

The hydrogeochemistry shares partly in the decay of materials with export of the solubilised substances. We connect it also with the idea of time.

For (b), we have a partial knowledge of the internal structure of the aquifer "objects" and the same is true for the thermic and hydric flux transfers.

Fresh investigations must be aimed at these subjects.

For (c), the type of climate accentuates one or several of its components :

- the strength of the wind, the hygrometry of the air (E.I.),
- the high thermic differences (hot or cold), the high hygrometric differences of the air.

The decay of the "objects" is dependent in fact on the joint action of two or several of these constituent elements.

For E.I. we insist on the action of marine sprays. It is a major parameter for which the search is continuing in the Atlantic and Mediterranean (micro-dynamics, micro-chemistry of emulsions and droplets).

The whole work would be incomplete if there were no experiments on two other important subjects.

- comparative analysis of climate and paleo-climate,
- creation of a data bank.

First subject :

On E.I. and in F. all the actions described above, are associated with the Present, but of course, they have differed in the course of the many centuries of the Past. In fact, the cycles and climatic environment (daily and seasonal conditions) could have bene smoothed out or reinforced (consider in F. the "Little Ice Age"
- XV th to XVII th S. ; note also on E.I. the paleomovements and marine transfers (el Nino) and other mega meteorological and catastrophic phenomena associated with the Central Pacific.

Second subject :

It must be considered as a priority research program. It is particularly developed in paragraph 5.

5. A SPECIFIC AND PREEMINENT PROJECT : THE M.O.A.I. PROGRAM

The M.O.A.I-1 project is entitled "Megalithic Objects Analysis by Imagery". It includes a broader version M.O.A.I-2, entitled "Monumental Objects Analysis by Imagery". The aim is the creation of a data bank for which the collection and the processing of data are carried out by different, complementary and more or less complex procedures.

The description of them have would be tedious, but we give below some examples to prove the significance of the research undertaken and our hope in this new data processing technology.

First phase : The M.O.A.I-1 program concerns the improvement of our knowledge about the Easter Island statues using computer image processing. The device used for processing is "Pericolor 2001", fitted with the software "Géopéricolor".

At present the program includes four sub-programs and some extensions are possible :

- acquisition by non destructive method of the instantaneous natural features of the statues,
- checking of the weatherind by comparative analysis,
- checking of the spatio-temporal evolution after interventions (s.l.),
- acquisition and processing of environmental data.

Second phase : The authors are trying to determine a non exhaustive list of measurable parameters.

Our experience acquired on Lascaux problems (2), (3), was very useful in the choice of this list. These codified parameters are stocked in an index which is specific to each statue.

Three indexes are in use. They carry the number of the statue in question and we think that debate with other specialists participating in the Congress will be very profitable to improve the system.

Results

The authors are able to present some tests worked out on the *objects* 01-02-03-04-05 objects.

The first codified and numbered results are collected in table n° VII.

The sizing of the pixels and the display are made, on the basis of imagery of restitution, in the form of numeral listings, histograms, statistical analysis, composite imagery, alphanumerical mappings, a.s.o.

A photographic illustration with legend completes the text (see Fig.9 a...f).

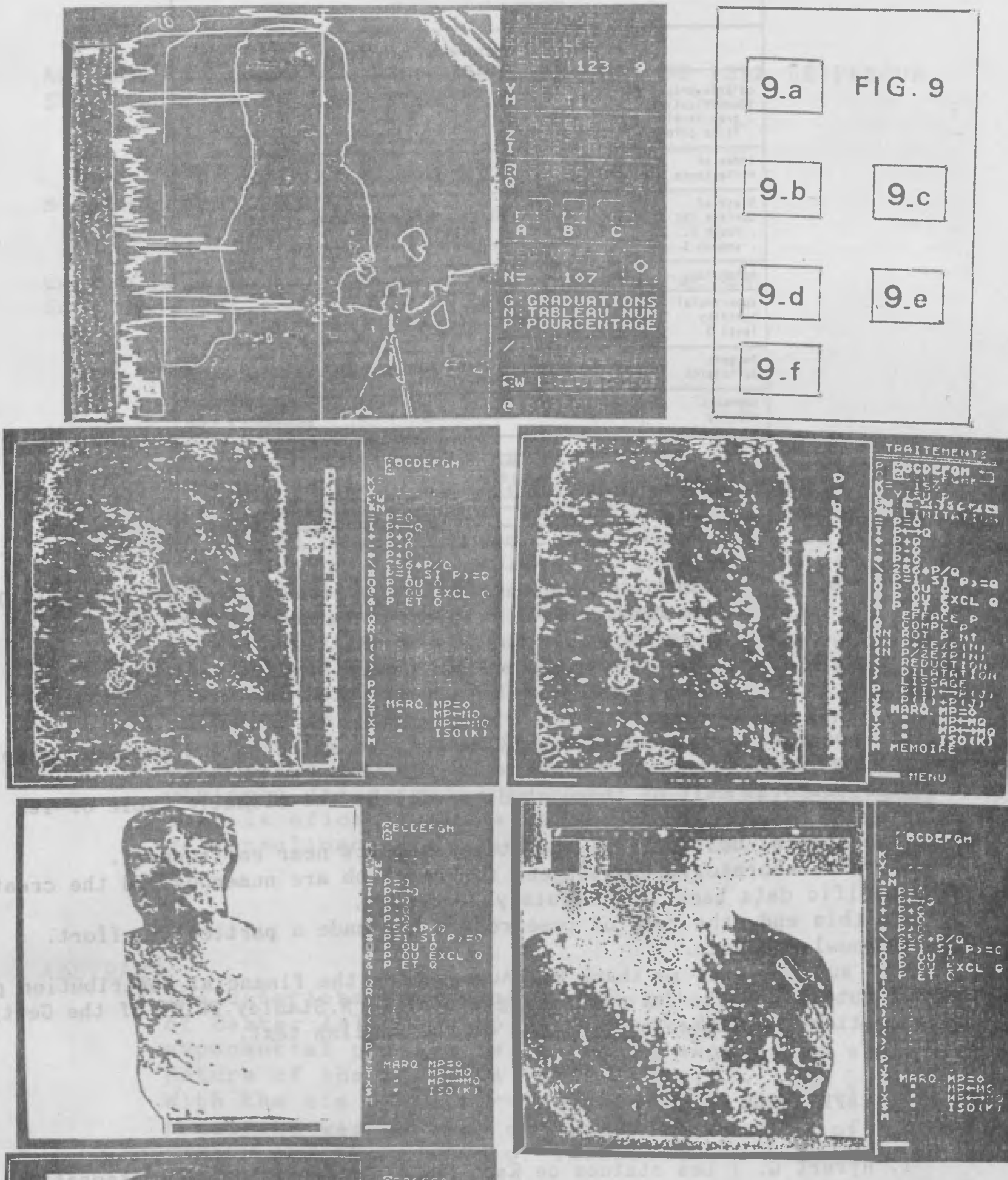
6. CONCLUSIONS

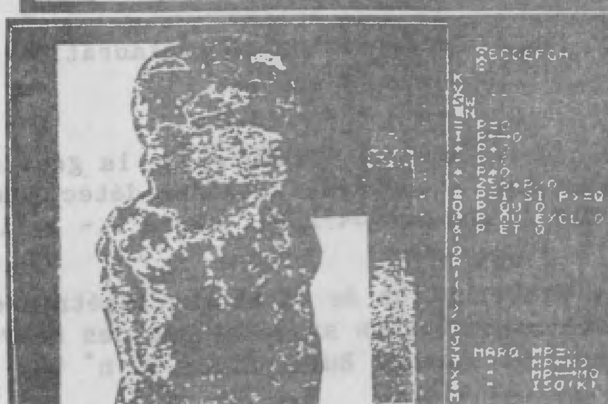
The authors of this publication indicate that tuffs and lavas are porous, permeable and heterogeneous materials (matrix + networking of cracks) which are badly understood.

They indicate also the existence of hydrous, hydrogeologic and hydrochemical introductions and transfers. These are influenced directly and/or indirectly by the climatic and environmental parameters associated with the objects.

For our part, the conditions of decay of volcanic tuffs and lavas in a general sense), and of Easter Island statues (in particular), are still poorly understood.

Concretely, on this subject, it seems to us that the improvement of knowledge will be achiever in the field and in the laboratory.





a - Hanga Kio E (H.K.E.) = False color cartography and linear analysis (Histogram) of hydrochemical and superficial anomalies (h.s.a.)
b - H.K.E. (abdomen)-micro cartography of encrustings
c - H.K.E. inverse micro cartography
d - Moai n° 4 - cartography of algae
e - Moai n° 4 - (breast) micro cartography of wet surface (withe) and lichens (green and yellow)
f - Moai n° 5 - biological stays and rainy trails.

Objects : lavas and tuffs					
	bare rock	concretionments	encrustings	biological deposits	cement matrix
colorimetric identification : . grey levels . false colours	← x x x x →				
Index of reflectance	O_1=62/85 O_3=67/120	163/259 -	- 97/120	- 127/210	85/104
State of surface (S) : . rough S. . smooth S.	Histograms and stereo-diagrams ← x x x x →				
morphology	← x x x x →				
superficial humidity : level 3	- no test for O_1 - O_2 - O_3 - in the laboratory, tests on : O_4 - O_5 : ← x x x x →				
Imagery definition	← 8 mégapixels 16 mégapixels →				
thematic mapping	← x x x x →		x x x	← x x x x →	
inverse	← x x x x →				
imagery superposition	for O_1 and O_4 ← x x x x →				
animation	← x x x x →				

Table n° VII: Referential components for the creation of the M.O.A.I.-1 data bank - 62/85 : spectral values of the index of reflectance. Quality of the tests = X inadequate tests - xx - poor - xxx = medium - xxxx - good.

In the field, some statues will have to be selected and numerous samples (mineralogically comparable) need to be associated with them.

The temporal unit of these studies will be the climatic cycle or its multiple.

The spatial unit will be the statue and its near environment.

In the laboratory, the subject for research are numerous and the creation of a scientific data bank is absolutely necessary.

To this end, the team of researchers has made a particular effort.

Acknowledgements.

The authors want to thank Mr. Aurouze for the financial contribution provided throughout this work. J.V. is very grateful to N.Stanley PRICE of the Getty Conservation Institute for revision of the English text.

7. REFERENCES

1. Hyvert G. ; Les statues de Rapa Nui - Conservation et restauration. Unesco, 1972.

2. Vouvé J. ; Contribution à la conservation des peintures de la grotte de Lascaux à partir de l'étude thermique des surfaces pariétales par détection à distance dans l'infra-rouge. C.R. Ac. Sc. t.272 p.2864-2867, série D - 1971.

3. Vouvé J., Brunet J., Vidal P. ; Contribution de la photogrammétrie et de la thermographie à courte distance à la documentation systématique des oeuvres pariétales préhistoriques en vue de leur sauvegarde. Bull. S.F.P.T. n° 98, p.23 à 34, 1985.

ACCIONES DE CONSERVACION SOBRE LOS MOAI DE ISLA DE PASCUA. SU EVALUACION EN LABORATORIO

M. BAHAMONDEZ PRIETO

Centro Nacional de Conservación y Restauración,
Santiago, Chile

RESUMEN

Las estatuas de Isla de Pascua sufren un acelerado proceso de deterioro, cuyo efecto exponencial es hoy día un hecho evidente. La situación de intemperismo al que se han encontrado sometidas desde su creación, sumado a las características de su instancia material (toba volcánica) se han constituído en los factores preponderantes de su actual estado de conservación. Con vistas a salvaguardar esta muestra patrimonial, se realizó una intervención a modo experimental, la que contó con el apoyo del PNUD-UNESCO y la asesoría de expertos internacionales en el área. El tratamiento realizado fue sometido a una evaluación posterior en laboratorio mediante envejecimiento del material tratado. Los resultados muestran la eficacia del silicato de etilo en procesos de consolidación en la toba volcánica.

ABSTRACT

The deteriotarion process undergone by the statues of Easter Island is to-date an evident fact. This exponential process is caused by weathering and the nature of the stone (a volcanic tuff).
With the aim of conserving this heritage, a test treatment was carried out with the support of UNDP-UNESCO and the advise of international experts in the field.
The treatment carried out was later evaluated on samples by artificial ageing in the laboratory. The results show the effectiveness of ethyl silicate as a consolidant for volcanic tuff.

1.- INTRODUCCION.

Las estatuas de Isla de Pascua se encuentran en grave peligro. Sufren desde hace siglos un deterioro progresivo e irreversible, cuyo efecto exponencial es en la actualidad un hecho evidente.

La condición de intemperismo a la que se han encontrado expuestos desde su creación, los ha sometido a la agresión permanente de los agentes naturales tales como lluvia, viento, aerosol marino, microorganismos etc. Esto, sumado a las características propias de la toba volcánica, material en el que fueron construidos,ha conllevado a un sistemático deterioro, el que se evidencia hoy como pulverulencia superficial, pérdida de superficie original (en algunos casos del orden de varios centímetros de espesor.), así como agrietaduras, microfisuras, desprendimientos, eflorescencia de sales. depósitos de sílice,desarrollo de microorganismos etc...

Con el fin de salvaguardar esta importante muestra patrimonial, se contempló dentro del marco del proyecto CHI/79/013 PNUD/UNESCO/DIBAM, la elaboración de un plan de estudio, diagnóstico e intervención, que permitiera desarrollar, a modo experimental, las acciones de conservación adecuadas a las características del material constitutivo de los moai, así como a las condiciones ambientales de la isla.

2.- ACCIONES DE CONSERVACION REALIZADAS SOBRE LOS MOAI.

En el año 1980, dentro del marco del proyecto mencionado, se invitó al profesor W. Domaslowsky, consultor Unesco, a realizar un estudio de las causas de deterioro de la toba en Isla de Pascua, estudio que, tras un período de investigación concluyó en una propuesta de consolidación e hidrorrepelencia (en base a silicato de etilo y caucho-silicona respectivamente). (1).

Dicha propuesta fué sometida a discusión por un grupo de profesionales determinándose el cambio del caucho-silicona por otro producto en base a silicona que posee una mayor afinidad con la piedra y no actúa como sellante, permitiendo así la libre circulación del vapor de agua.

2.1.- MOAI HANGA KIO'E.

Para implementar la investigación se eligió el moai llamado HANGA KIO'E, al que previamente se le hizo un completo diagnóstico y registro de su estado de conservación. (2). Entre los deterioros mas relevantes observados se puede mencionar:

- Pérdida de su superficie original en la zona de la espalda y ambos costados. (aprox. 5 cm.).
- Faltante importante de material en hombro derecho.
- Gruesos depósitos blancos de sílice en la frente, naríz y zona inferior del cuerpo.
- Grietas y microgrietas en todo el cuerpo.
- Presencia de microorganismos.
- Pulverulencia superficial en toa la espalda. (de frente al mar), y ambos costados.

Otra característica importante de destacar dice relación con la intervención de restauración que el moai sufrió en la década del 70, y que en la actualidad se ha constituido en otro factor de deterioro. Antes de la restauración la estatua se encontraba caida, situación en la que se encuentran la casi totalidad de los moai en la actualidad. La cabeza estaba separada del cuerpo y en la espalda se habían practicado dos orificios circulares de aproximadamente 20 cm. de diametro.

El trabajo realizado entonces consistió, básicamente, en la unión de las dos partes del moai mediante la utilización de barras de fierro y una mezcla de cemento de alta dureza y baja permeabilidad. La estatua fué, además, reerigida sobre su ahu estabilizándola en la base con el mismo tipo de mortero.

Las zonas inmediatamente superiores al cemento presentan un grado de deterioro mayor dado que la baja permeabilidad de éste, en contraste con el de la toba volcánica, las mantenía permanentemente húmedas y por lo tanto con una mayor proliferación de microorganismos.

Por otra parte, no es descartable que las barras de fierro utilizadas en la restauración, al sufrir un natural proceso de oxidación, sean en parte responsables de las microfisuras observables en el moai.

2.2.- TRATAMIENTO REALIZADO

El tratamiento realizado, que ha sido ampliamente detallado en numerosas publicaciones ,(3),(4), constó de tres etapas básicas.

I.- Aislación y limpieza superficial de microorganismos.

Para proceder a la consolidación es necesario previamente proteger el moai del agua, tanto de lluvia como de aerosol marino. Mientras dura este proceso se limpió la superficie de líquenes y sales, en la medida que no se dañara la piedra.

II.- Consolidación.

El moai se envolvió completamente con varias capas de celulosa perfectamente adheridas a su superficie, luego se cubrió con una manga de polietileno a fin de evitar la rápida evaporación del solvente del producto utilizado. El consolidante se aplicó desde la cabeza, impregnándose la estatua por gravedad.

III.- Extracción de sales e hidrofobización.

Aproximadamente dos meses de realizada la segunda etapa, se intentó la extracción de las sales solubles en superficie, situación que no se concretó debido a la dureza y baja solubilidad que éstas presentaban.
Se aplicó el producto hidrorrepelente que actúa a nivel de superficie, pudiéndose comprobar al día siguiente, durante una corta lluvia, el buen resultado de esta etapa.

Como resultado general se puede decir que el tratamiento fué exitoso. La superficie pulverulenta se observa cohesionada. Los microorganismos que crecían sobre la piedra no han vuelto a aparecer y la pátina negra que lo cubría, producto de un ataque generalizado de algas, ha desaparecido retomando el moai su color original.

3.- EVALUACION DE LAS PROPIEDADES CONSOLIDANTES DEL SILICATO DE ETILO SOBRE LA TOBA VOLCANICA DE ISLA DE PASCUA LUEGO DE PROCESOS DE ENVEJECIMIENTO.

A fin de evaluar en el tiempo el comportamiento de los productos utilizados, se realizó en laboratorio una serie de análisis que nos entregan una visión comparativa de las características de la toba natural, con consolidante y con consolidante e hifrorrepelente,al ser sometidos a distintos procesos de envejecimiento y a distintas pruebas de resistencia.

3.1.- PREPARACION DE LAS PROBETAS DE ENSAYO.

De una muestra extraida de los faldeos del volcán Rano Raraku se fabricó un total de 100 probetas en forma de paralelepípedos de 40x40x60 mm.

- Se trabajó sólo con aquellas extraídas del interior de la piedra, de tal manera de obtener un universo homogéneo y no introducir errores en los resultados. Del total de 100, sólo fueron utilizadas 57 probetas.
- Como patrón de comparación, es decir, sin tratamiento: 22 probetas.
- Con tratamiento sólo de consolidación: 22 probetas.
- Con tratamiento de consolidación e hidrorrepelencia: 13 probetas.

El consolidante se aplicó a 35 probetas, por saturación. Se dejaron secar al aire libre, bajo techo, durante tres semanas. Cumplido este período, trece de estas probetas se sumergieron en el hidrorrepelente, dejándose secar por otras tres semanas en idénticas condiciones.

3.2.- ENSAYOS REALIZADOS.

Se buscó, ante distintos procesos de envejecimiento, determinar el impacto del tratamiento en la resistencia a la abrasión, compresión y absorción de agua de la toba volcánica.

GRUPO	TIPO DE PROBETA
Sin envejecimiento	Sin tratamiento (A) Con consolidante (B) Con consolidante e hidrorrepelente. (C).
Envejecidas con Xenotest. (radiación U.V.)	A B C
Envejecidas en oxigeno a presión y temperatura.	A B C
Envejecidas en niebla salina	A B C

3.3.- RESULTADOS DE ANALISIS Y ENSAYOS.

3.3.1.- Análisis de materiales no-metálicos en la toba.
Método: Espectrometría por Fluorescencia de Rayos X. (% en peso con respecto a la muestra seca.).

Tabla I: Composición de la toba volcánica analizada.

Fe_2O_3	TiO_2	CaO	K_2O	SiO_2	Al_2O_3	MnO	MgO	Na_2O	P_2O_5	SO_3	PPC*
12.8	2.5	6.0	1.3	52.0	14.0	0.3	3.4	2.1	0.5	0.1	3.7

Se detectaron además, elementos traza en los siguientes niveles:

Sr: 0,03 Y:0.01 Zr:0.05 Nb:0.01 Zn:0.03

* Pérdida por calcinación a 1.000°C durante 2 horas.

3.3.2.- Ensayos de abrasión por caida de arena.

Tabla N° II: Pérdida de peso por caida de arena de probetas sin envejecimiento.

ARENA Lt	PERDIDA DE PESO EN PORCENTAJE. (A)	(B)	(C)
10	0.42	0.24	0.01
20	0.45	0.26	0.06
30	0.47	0.29	0.08
40	0.51	0.33	0.10
50	0.53	0.34	0.13
60	0.55	0.39	0.15
70	0.59	0.42	0.17
80	0.62	0.43	0.19
90	0.62	0.43	0.23
100	0.71	0.45	0.24

(A): Muestra sin tratamiento.
(B): Muestra con consolidante.
(C): Muestra con consolidante e hidrorrepelente.

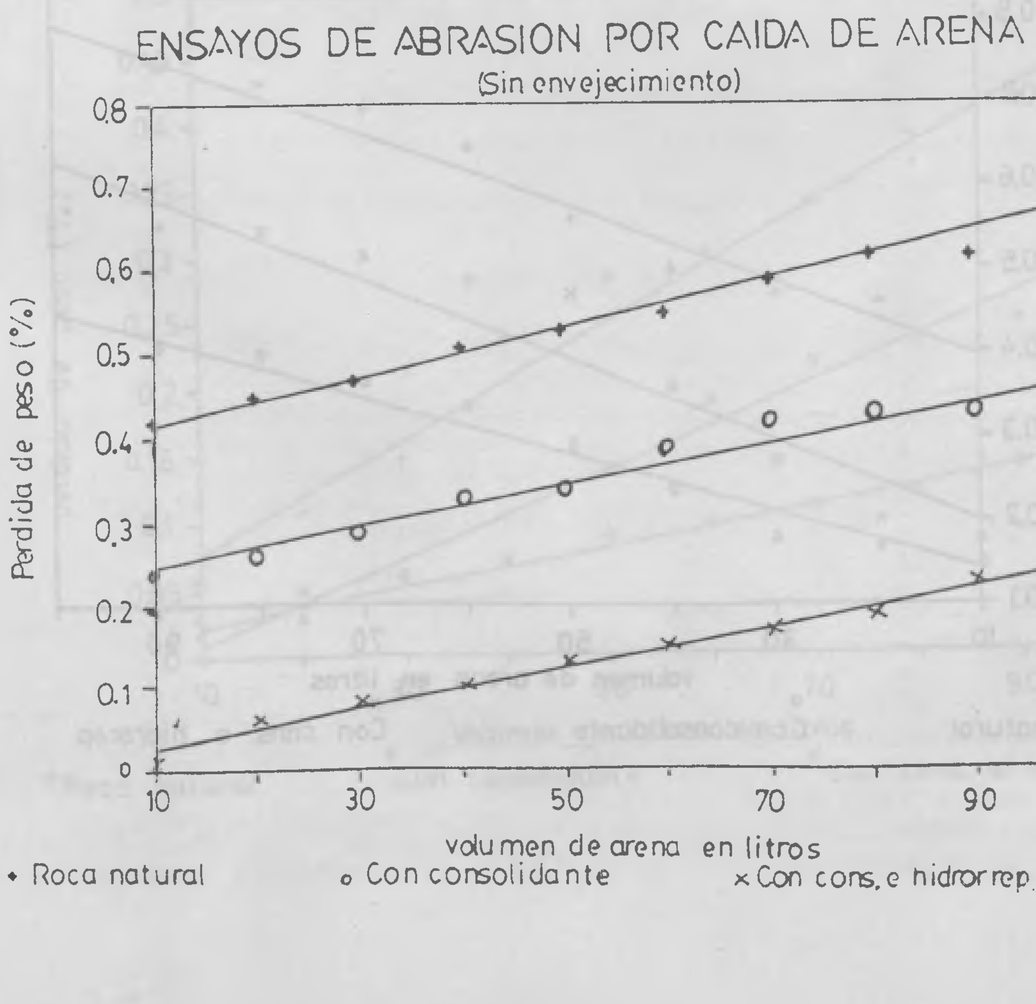


Tabla N° III: Pérdida de peso por caida de arena de probetas con envejecimiento con Xenotest.

ARENA Lt.	PERDIDA DE PESO EN PORCENTAJE (A)	(B)	(C)
10	0.09	0.15	0.18
20	0.46	0.17	0.20
30	0.47	0.18	0.27
40	0.50	0.24	0.36
50	0.56	0.29	0.47
60	0.65	0.34	0.49
70	0.70	0.37	0.52
80	0.73	0.40	0.55
90	0.75	0.41	0.56
100	0.78	0.43	0.58

(A): Muestra sin tratamiento.
(B): Muestra con consolidante.
(C): Muestra con consolidante e hidrorrepelente.

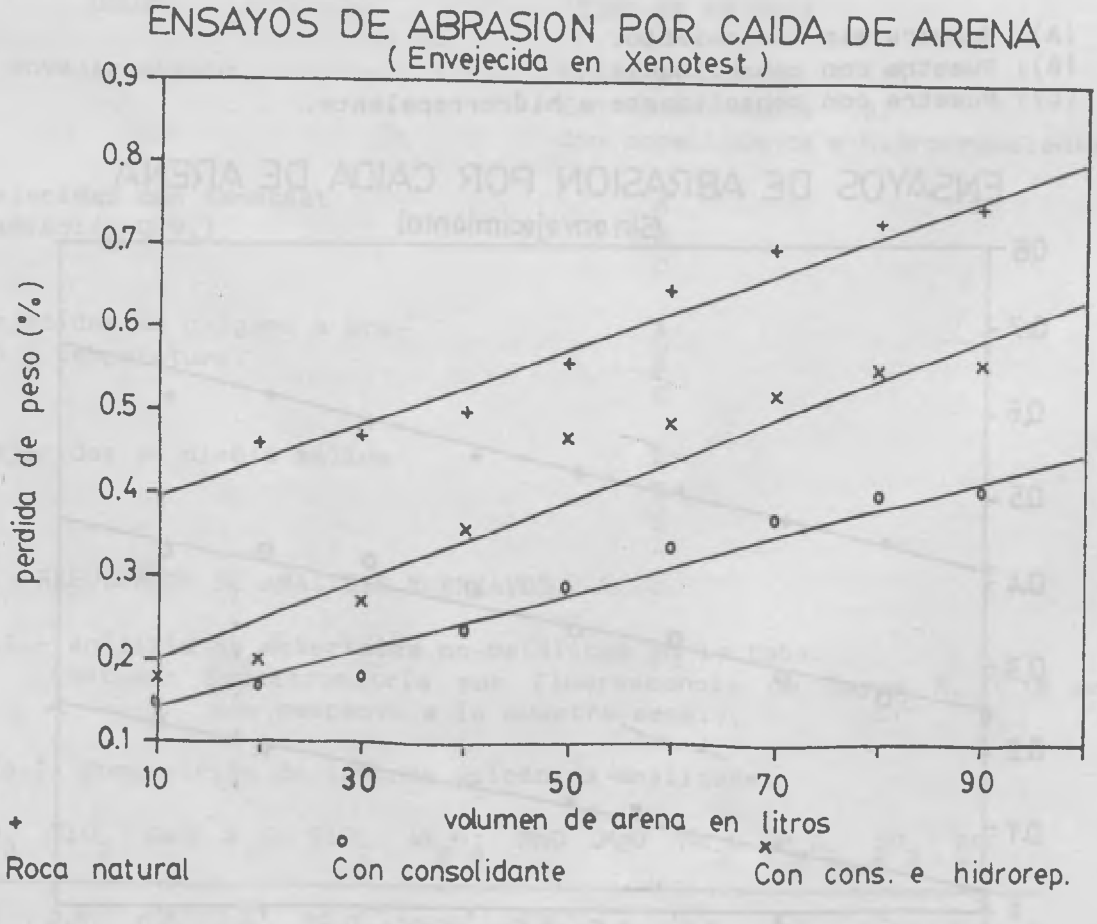
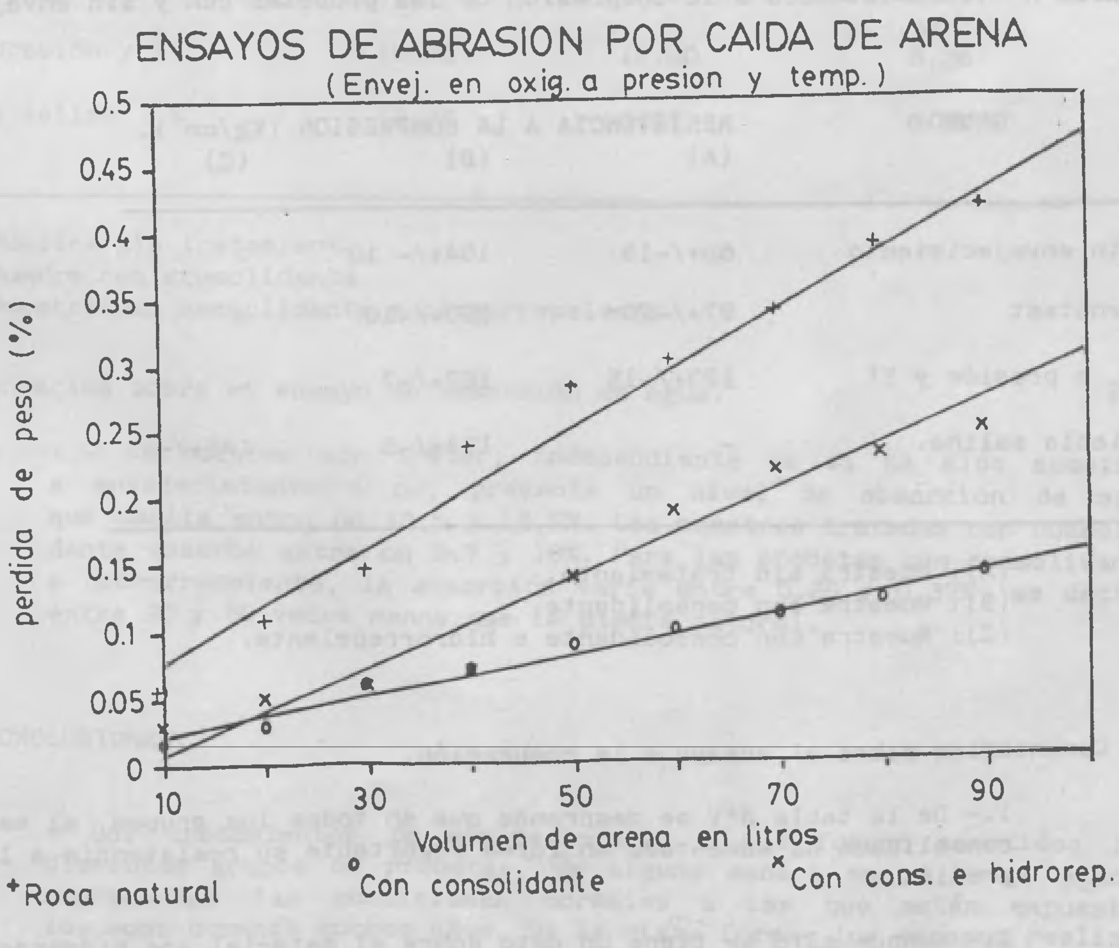


Tabla NºIV: Pérdida de peso por caida de arena de probetas con envejecimiento con oxígeno a presión y temperatura.

ARENA Lt.	PERDIDA DE PESO EN PORCENTAJE. (A)	(B)	(C)
10	0.06	0.02	0.03
20	0.11	0.03	0.05
30	0.15	0.06	0.06
40	0.24	0.07	0.07
50	0.28	0.09	0.14
60	0.30	0.10	0.19
70	0.34	0.11	0.22
80	0.39	0.12	0.23
90	0.42	0.14	0.25
100	0.45	0.16	0.33

(A): Muestra sin tratamiento.
(B): Muestra con consolidante.
(C): Muestra con consolidante e hidrorrepelente.



- Comentarios sobre el ensayo a la abrasión.

1.- En todos los casos analizados, la mayor pérdida de peso o material se obtiene en las muestras sin tratar.

2.- Los menores porcentajes de pérdida de peso por abrasión se obtienen con el material envejecido con oxigeno a presión y temperatura. Para el material sin envejecimiento y envejecido con Xenotest, el porcentaje de pérdida de peso es muy similar, lo que corresponde a lo esperado, ya que una de las características de los productos utilizados es su buena resistenci a la radiación U.V..

3.- En el caso de las muestras sin envejecer, el hidrorrepelente mejora la resistencia a la abrasión con respecto al consolidante. En el caso de las probetas envejecidas, el hidrorrepelente disminuye levementeel efecto consolidante, estando los valores siempre por encima del material sin tratar.

3.3.3.- Ensayos de compresión.

Los resultados obtenidos para los ensayos a la compresión se muestran en la tabla N°V.

Tabla N° V: Resistencia a la compresión de las probetas con y sin envejecito.

GRUPO	RESISTENCIA A LA COMPRESION (Kg/cm^2). (A)	(B)	(C)
Sin envejecimiento	68+/-15	104+/- 10	-
Xenotest	97+/-20	120+/-10	-
O_2 a presión y T°	123+/-15	167+/-7	-
Niebla salina.	-	174+/-5	149+/-1

(A): Muestra sin tratamiento.
(B): Muestra con consolidante.
(C): Muestra con consolidante e hidrorrepelente.

- Comentarios sobre el ensayo a la compresión.

1.- De la tabla N°V se desprende que en todos los grupos, el material consolidado ha aumentado en forma importante su resistencia a la compresión.

2.- Aunque sólo se tiene un dato sobre el material con hidrorrepelente, pareciera ser que, al igual que en el ensayo a la abrasión, este disminuiría ligeramente la resistencia con respecto al material sólo con consolidante.

3.- La disperción de los resultados disminuye aproximadamente en un 50% al pasar de la roca natural a la roca consolidada o con hidrorrepelente, lo que probablemente sea el resultado de una compactación más homogénea.

3.3.4.- Ensayos de absorción de agua.

En la siguiente tabla se muestran los resultados obtenidos para los ensayos a la absorción de agua, medidos como aumento de peso de la muestra y expresados en porcentaje.

Tabla N° VII: % de absorción de agua de las probetas con y sin envejecimiento.

GRUPO	ABSORCION DE AGUA (% aumento de peso)		
	(A)	(B)	(C)
Sin envejecimiento	10.50	7.00	0.31
Xenotest	12.50	5.70	0.29
O_2 a presión y T°	10.70	10.00	0.26
Niebla salina	12.30	8.11	0.37

(A): Muestra sin tratamiento
(B): Muestra con consolidante
(C): Muestra con consolidante e hidrorrepelente.

- Comentarios sobre el ensayo de absorción de agua.

1.- La muestra sin tratar, independiente de si ha sido sometida a envejecimiento o no, presenta un nivel de absorción de agua que oscila entre un 10.5 y 12,5%. Las muestras tratadas con consolidante absorbe entre un 5.7 y 10%. Para las probetas con consolidante e hidrorrepelente, la absorción varía entre 0.26 y 0.37%, es decir, entre 20 y 50 veces menos que la piedra natural.

4.- CONCLUSIONES.

- Los tratamientos de envejecimiento a que fueron sometidos los distintos grupos de probetas, de alguna manera mas o menos exacta representan las condiciones normales a las que están expuestos los moai durante muchos años. De la misma forma, los ensayos realizados permiten formarse una clara idea de la respuesta de cada tipo

de probeta a la solicitud de abrasión, compresión y absorción de agua.
De los resultados obtenidos se desprende que el esquema planteado para la conservación responde a lo esperado, aún en el largo plazo.

- Si bien se observa que el hidrorrepelente disminuye ligeramente las características del consolidante para los ensayos de abrasión y compresión, la disminución de la absorción de agua que provoca en la toba es tan alta, que justifica plenamente su utilización.

- Los resultados del envejecimiento con oxígeno a presión y temperatura, cuyo objetivo era evaluar en el tiempo algún posible cambio de estructura y composición de los elementos propios de la toba y de los materiales agregados, indican que al largo plazo las características del material tratado, en cuanto a resistencia a la abrasión y compresión,habrán mejorado con respecto al corta y mediano plazo.

5.- REFERENCIAS.

1.- DOMASLOWSKI, W.; " Les statues en pierre de l'Ile de Pâques. Etat actuel, causes de détérioration. Propositions pour la conservation." Rapport élaboré pour l'UNESCO. (1981).

2.- BAHAMONDEZ, M.; "Factibilidad técnico económica de la aplicación del método propuesto por el profesor Domaslowski para la consolidación de tres estatuas." Informe elaborado para el PNUD/UNESCO.(1984).

3.- ROTH, M.; "Die riesen haben wiender eine zukunft." Publicación realizada por Wacker. Alemania. (1987).

4.- BAHAMONDEZ, M.; "Acciones de conservación en Isla de Pascua". En vias de publicación. Courier Forschungsintitut, Senckenberg Museum. Alemania.

AGRADECIMIENTOS.

Nuestros agradecimientos al laboratorio CESMEC, en especial al señor Manuel Zuñiga en el desarrollo de los ensayos.

APENDICE

I.- Sobre los productos utilizados:

Es conveniente, a este punto, decir que el producto recomendado por el profesor Domaslowski,Wacker OH, no fué posible aplicarlo el el primer intento de consolidación que se realizó. En efecto, a fines de 1986 y comienzo de 1987 se implementó la estapa I del tratamiento (limpieza y aislación), sin embargo la etapa II, de consolidación, presentó problemas dada la alta volativilidad del solvente utilizado. Al aplicar el producto, éste precipitaba inmediatamente sobre la superficie.

En esa oportunidad fué necesario suspender los trabajos y realizar las modificaciones pertinentes. Es así como la empresa Wacker fabricó en forma especial el consolidante Wacker OH mod.,el que al ser aplicado penetró en la piedra sin problemas.

El hidrorrepelente, W090 S, fué también preparado especialmente para las características climáticas de la isla.

El tratamiento final fué realizado un año después del primer intento.

II.- Sobre los ensayos realizados.

II.1.- Ensayo de abrasión: (NORMA ASTM D 968 - 51)

- La granulometría de la arena utilizada estaba comprendida, sobre un 80%, entre los 600 um y 850 um.
- El flujo de arena fué de 2 lt. en 2.5 s.
- La caída de arena se efectuó en un angulo de 45°.

II.2.- Ensayo de compresión: (Norma Chilena Oficial, NCh 1037).

- El equipo empleado fué una prensa universal de ensayos Instrom, de capacidad 0 a 10.000 kg.
- Se aplica la carga en forma contínua y sin choque a una velocidad uniforne de acuerdo a lo especificado por la norma.
- Los resultados se expresan en (Kgf/cm^2).

II.3.- Ensayo Xenotest. (Realizado durante 500 h.) (West Germany Standard DIN 54004).

- La fuente corresponde a una lámpara de Xenón, XE 1500.
- El espectro emitido varía entre 300 y 700 um.
- Las muestras están sometidas a ciclos alternados de luz y oscuridad (simulando condiciones de día y noche), y a un rociado con agua de 3 minutos cada media hora.

II.4.- Envejecimiento con O_2 a presión y T°.

- Se realizó durante un mes, con las probetas en oxigeno a 25 kg/cm2 de presión y 100°C de temperatura.

[illegible] en agua.

[illegible] planteado [illegible]

- Si bien se observa que el hidrorrepelente [illegible] ligeramente [illegible] de abrasión y compresión, la disminución [illegible] provoca en la toba es tan alta, que justifica plenamente su utilización.

- Los resultados del envejecimiento con oxígeno a presión y temperatura, cuyo objetivo era evaluar en el tiempo algún posible cambio de estructura y composición de [illegible] la toba y de los materiales agregados, indican que al largo plazo las características del material tratado, en cuanto a resistencia a la abrasión y [illegible] corto y mediano plazo.

5.- REFERENCIAS

[illegible] Etat actuel, [illegible] Propositions pour la conservation [illegible]

[illegible] aplicación [illegible] de [illegible] (1984).

[illegible]

AGRADECIMIENTOS

[illegible]

APENDICE

I.- Sobre los productos consolidantes:

Es conveniente, [illegible] decir que el producto recomendado [illegible] Wacker OH, no fué posible [illegible]

2. RESEÑA BIBLIOGRAFICA
LITERATURE REVIEW

THE DETERIORATION AND TREATMENT OF VOLCANIC STONE: A REVIEW OF THE LITERATURE

C. A. GRISSOM

Conservation Analytical Laboratory, Museum Support Center, Smithsonian Institution, Washington, DC 20560, U.S.A.

ABSTRACT

A literature review reveals that conservation study of volcanic stonework has focused on tuffs, which exhibit the most serious deterioration. Other volcanic rocks used for monuments of sculpture are basalt, scoria, andesite, dacite, rhyolite, and trachyte. Important examples include the statues at Easter Island, the Buddhist shrine at Borobodur, the churches at Göreme and Lalibela, the rock-cut Buddhas of Japan, and the caves of the Deccan plateau in India. The application of consolidants has been the treatment most frequently tested, but little is known about long-term efficacy. Monuments carved in-situ present particularly intractable problems.

RESUMEN

El examen de la bibliografía revela que el estudio de la conservación de piedra volcánica se ha concentrado en las tobas, que son las que presentan el mayor grado de deterioración. Otras rocas volcánicas utilizadas en monumentos o esculturas son: el basalto, la escoria, la andesita, la dacita, la riolita y la traquita. Ejemplos importantes incluyen las estatuas de Isla de Pascua, el templo budista de Borobodur, las iglesias en Göreme y Lalibela, los budas tallados en rocas del Japón, y las cuevas del altiplano Deccan de la India. La aplicación de consolidantes ha sido el tratamiento utilizado más frecuentemente, pero poco se sabe de su eficacia a largo plazo. Los monumentos tallados in situ presentan problemas particularmente difíciles.

1. INTRODUCTION

Some of the world's most spectacular monuments, including those at Easter Island, Borobudur, Goreme, and Lalibela, are made of volcanic stone, and they have shown themselves to be vulnerable to deterioration. Nevertheless, volcanic stone has been little reported on in the stone conservation literature compared to other types of stone. In a tally of papers given at congresses on stone weathering and conservation, only 8% were found to refer to igneous rocks;[1] the number of articles referring to volcanic rocks would be fewer still. In part, the small amount of literature on volcanic stonework may be attributed to the fact that most researchers work in Europe and North America where buildings and sculptures are made principally of limestone, sandstone, granite, or marble. Most of the important volcanic monuments are located in other parts of the world. UNESCO and ICCROM (International Centre for the Study of the Preservation and the Restoration of Cultural Property) reports or studies stemming from their projects prove to be an important source of information on these monuments. The purpose of this paper is to review work which has occurred to date as a basis for further study.

The Conservation Information Network (CIN), the libraries at ICCROM and the Conservation Analytical Laboratory, and proceedings of stone deterioration and conservation meetings held during the last twenty years have been used in preparing this review. All papers are on file in the Information Center at the Conservation Analytical Laboratory of the Smithsonian Institution, and hard-to-find copies are available through the Center.

1.1 Geology

Igneous rocks are those which derived from molten material known as magma. The term volcanic rock is used to describe those rocks which have solidified from magma issuing onto the surface, as opposed to those which solidify inside the earth (plutonic rocks), such as granite. While plutonic rocks solidify slowly inside the earth and are thus coarse-grained, volcanic rocks are relatively fine-grained because of rapid cooling. However, large crystals are often visible to the naked eye within their fine-grained matrices. These large crystals are formed during periods of slower cooling before eruption and are known as phenocrysts. Volcanic glass, present in nearly all volcanic rocks, is formed when cooling is so rapid that crystals do not form.

Most volcanic rocks derive from lava flows, including rhyolite, andesite, and basalt. Volcanic rocks are also produced from fragmental material and droplets of lava propelled through air or water and subsequently consolidated. These are known as pyroclastic rocks. Tuff, made from small particles, is the only pyroclastic rock that is used for stonework. Other pyroclastic rocks, made from larger grains, are volcanic breccia and agglomerates. Most of these are far too friable and soft to be used.

Most volcanic rocks contain a variety of silicate minerals, including one or more of the following: feldspars, olivines, pyroxenes, amphiboles, quartz, and micas. Volcanic rocks are divided into acid (sialic), intermediate, and basic (mafic) rocks. However, these designations do not indicate pH but rather the amount of silicon present, in decreasing amounts from acid to basic. To add to the confusion, the amount is always expressed as the amount of silica rather than silicon, because of the method of analysis. Generally, acid rocks are light in color compared to basic rocks, which contain dark-colored ferromagnesian minerals and dark iron-rich glass. Rhyolite, andesite, and basalt are the main types of acid, intermediate, and basic rocks respectively. Tuffs may be referred to on the basis of rock or mineral constituents, such as an andesitic tuff, or the size of fragmental material from which they are formed, such as a lapilli (fragments measuring 4-32mm in diameter) tuff.

1.2 Weathering

Because volcanic rocks were formed at high temperatures, they are not chemically stable at ambient temperatures in the presence of water, which is the principal agent of alteration. Gradually metal ions are solubilized, especially calcium, magnesium, sodium, and potassium. Zeolites, clay minerals, and other hydrous minerals are formed from residual material.[2] Water also transports deleterious soluble salts, damages by freeze/thaw cycling, and encourages harmful biological activity. The rate of weathering increases with temperature and precipitation. Therefore, it tends to be more rapid in tropical climates. Some general rules can also be given as to the weathering characteristics of particular rocks. Porous rocks like tuffs have large surfaces areas and tend to hold water. Thus, they usually deteriorate more rapidly than dense rocks like basalt. As a general rule, the glassy portions of rocks weather more rapidly than crystalline portions, because of the greater instability of the glass. It must be noted, however, that compared to the aqueous dissolution of carbonate rocks, the weathering of volcanic rocks is relatively slow. Moreover, volcanic rocks are not very susceptible to attack by air pollutants like sulfur dioxide, that is so damaging to calcareous rocks.

1.3 Use

Volcanic rocks have been used for both buildings and sculptures. While they do not tend to take a polish or fine detail like marble, they may be easily carved, as demonstrated by the vast quantities of stone removed to create the rock-cut churches of Lalibela. Volcanic stone is often used on a large scale, and this has ramifications for treatment, especially cost. At Borobudur, for example, there are 33,100 relief blocks and nearly 500 sculptures. At Easter Island there are approximately 1000 colossal heads exposed to the open air. Important volcanic monuments such as the churches at Lalibela and Goreme, the rock-cut Buddhas in Japan, and caves in India, are not only large, but they have difficult problems associated with the fact that they are constructed out of in situ rock rather than cut stone. The normal movement of water through the rock frequently causes damage, and it is difficult to control this movement. An in situ monument might also be unstable because of adjacent softer rock, requiring an engineering solution.[3]

1.4 Treatment

In terms of treatment, consolidation is discussed most often in the literature, especially for tuffs. In recent years, the treatment proposed and tested most frequently is the application of an alkoxysilane solution, which results in the deposition of silica in the pores of the stone. Although epoxy resin treatments have lost favor for use on less porous rocks such as marble, they have been successfully tested on tuff. Monomer methyacrylate, polymerized in situ, has also been favorably tested in the laboratory. All of these treatments, however, are relatively costly, and none has been applied on a large scale. Application of water repellents is frequently advocated, especially for tuffs, because of the important role that water plays in deterioration. Removal of biological material and prevention of regrowth has been a major concern for tuff and other volcanic rocks located in tropical areas. Removal of soiling is rarely an issue for volcanic stones, while it is for limestone, marble, and sandstone. Repair of structural problems, like cracks, are discussed particularly in the case of monuments cut in situ.

The paper is organized by the different types of volcanic rocks used for monuments and sculpture, and the section on each type of rock is further divided by geographic location. Characteristics of the rocks, their deterioration, and conservation treatments are then summarized. For the convenience of the reader, a list of commercial products mentioned in the text is given at the end of the article, including the name of the manufacturer and the components, in so far as they are known.

2. TUFF

Tuff has been written about most extensively of all the volcanic building and sculpture stones. This is apparently because there are often large surface deposits present in the vicinity of volcanoes or in volcanic regions, some types of the rock are very easy to work, and it is subject to severe deterioration.

Tuffs are consolidated pyroclastic rocks, made from material expelled through air or water, as opposed to rocks formed from lava flows. Tuffs range considerably in composition depending on the nature of the droplets of lava or of the fragments of the conduit, crater walls, or sub-volcanic basement; and subsequent alterations. As an example, crystals or fragments of feldspar might be present, set in a glassy matrix, but many other materials are also commonly present. Zeolites (hydrous aluminosilicates) are sometimes present, and they have ramifications for both deterioration and treatment because of their capacity for ion exchange. Vesicles left from the gases which propel the pyroclasts produce open porosity as high as 50%, with concomitant high water absorption. This porosity contributes to deterioration, but also allows ready penetration of consolidants.

Care must be taken with the spelling and translation of the word tuff ("tufo" in Italian, "tuf" in French), as the material is not infrequently confused with the sedimentary calcium carbonate stone known as tufa ("tufa" in Italian, "tuffeau" in French). Use of the phrase "volcanic tuff" can be useful in preventing confusion.

2.1 Easter Island

Given the subject of this conference, it is appropriate to begin with the "moai" or colossal heads of Easter Island. Most of these approximately 1000 statues found on the island were carved from a porous tachylitic tuff quarried at the Rano Raraku volcano, while their red topknots were carved from a scoria from a quarry located at Puna Pau.[4] Four statues are known to be made out of other rock. Two statues located at Poike are said to be made from an alkaline trachyte, and two statues located at Tahi are made from a scoria, but not that of Puna Pau.[5]

A recent English-language paper provides an excellent summary of the deterioration and conservation of the statues.[4] Rain is the principal agent of deterioration. It wears the surface mechanically and corrodes the glassy matrix of the tuff chemically, illustrated by scanning electron microphotographs. Deposits of silica formed from dissolved rock are visible on the undersides of sculptures. Wind erosion, differential expansion of the rock components due to temperature changes, and biological attack by algae and lichens are secondary factors. Soluble salts are agents of deterioration in only a few cases close to the sea. Domaslowski's French-language report for UNESCO,[6] later summarized in a Polish article with an English abstract,[7] is based on a 1981 visit. With a view towards treatment, individual statues were examined in detail. Indirect porosity measurements, temperature measurements, and moisture measurements at various depths were made at multiple locations on these statues. Earlier, Hyvert published the results of analysis of 172 stone samples in various stages of deterioration. They were studied by petrographic examination, chemical analysis, x-ray diffraction analysis, differential thermal analysis, and porosity and permeability measurements.[5]

All reports on the statues conclude with the need for stone consolidation. Laboratory testing of the capillary uptake of white spirits, Wacker OH, Wacker H, and a 20% solution of epoxy resin was carried out on samples of the rock.[6] Both alkoxysilanes performed well, but use of the Wacker OH is recommended because the hydrophilic consolidant would permit subsequent removal of biological material. Application of Wacker-Chemie's Elastosil E 41 is recommended as a water repellent surface coating. The condition of three heads selected for treatment[8] and the December 1986 treatment of one of them located at Hanga Kio'o are described.[4] After surface cleaning, consolidation with Wacker H (modified by the inclusion of a fungicide and with a less volatile solvent) was carried out with a thick paper facing/poultice. Three months later, the statue was sprayed with the water repellent Wacker 090 S (modified with a less volatile solvent).

2.2 Italy

Extensive tuff deposits are found in central Italy, and they were used by the ancient Etruscans and Romans for building material, as well as by medieval artisans. Etruscan tombstones[9] and subterranean tombs[10 11] made of tuff have been studied. Tuff from an Etruscan wall at Bolsena[12] and a building at Cerveteri[13 14] have been used in testing. Types of tuff used by the Romans, their quarry sources, use in buildings, and typical sizes and shapes are thoroughly described in a book by Roberto Marta.[15] The Romans' use of tuff commenced with the founding of the city and continued to the time of Augustus, when the embellishment of buildings with marble was encouraged instead. Tuffs from ancient monuments in the forum and throughout Rome,[16 17 18 19 20 21 22 23] at Ostia Antica,[18 24 25] at Capua,[26] and at Caprarola[18] have been included in studies. Samples from the church of S. Maria Maggiore in Viterbo,[17] the twelfth century Castel dell'Ovo in Naples,[27 28 29] and the fifteenth century Capitoline Palace in Rome have also been studied.[30]

The degradation of tuff from two monuments has been studied in detail. Rapid deterioration of the Temple of Cibeles (Palatine Hill, Rome) upon excavation is attributed to the high water absorption value of the tuff.[23] Alarming deterioration of the Castel dell'Ovo in Naples is attributed to the presence of sea salts and wind erosion.[27 28 29] In both cases zeolites are of particular concern.

A number of consolidants have been successfully tested on tuff in Italy, but there are no published reports of large-scale usage. In recent laboratory studies, tuff samples consolidated with monomer methyl methacrylate (polymerized in situ according to Patent 932873 of Nov. 11, 1972) mixed with 10% Sniatron showed the best performance. These were compared with samples consolidated with a polymethyl methacrylate solution[13] and with Tegovakon V followed by application of a water repellent, Tegosivin HL 100.[14] Wacker H and Wacker OH were tested on samples from the Temple of Cibeles.[23] Samples of stone from the Castel dell'Ovo were tested with five products.[28] Rhodorsil 10336 proved the best in accelerated weathering tests, followed by a mixture of 1 part Paraloid B72 at 30% in organic solvents, 1 part Dri-Film 104 silicone resin, and 8 parts trichloroethane. Wacker H, Rhodorsil XR-893, and Product 460 proved unsatisfactory. EP2101, a cycloaliphatic epoxy resin, showed even distribution and good penetration in SEM photographs of test samples.[19] The EP2101-impregnated Viterbo tuff of a Roman acqueduct near Rome showed good results after two years' weathering. This resin is noted for its fluidity, stability, and low cost. Two other epoxy resins, Araldite XG 40 (33% in solvents) and Araldite PZ 820 (80% in solvents) have also been tested.[12] Treated samples showed improved performance under artifical weathering, but samples impregnated with the higher solids Araldite PZ 820 showed poor penetration and much less deposition of the consolidant. Tuff monuments at Ostia Antica which were brush coated with the Araldite XG 40 in 1975 showed no visible alteration 3 years later.

Biological material found on tuffs has been identified in many publications.[11 16 17 18 25 26] Tests with Fluometuron, Clorobromuron, Terbutryn, and Vancide 51 on fifteen pieces of tuff at Ostia Antica showed the first two biocides to be most effective, especially when applied in poultice form. However, none of the biocides worked well on crustose or powdery lichens.[25] Successful removal of biological material from the surface of Etruscan tuff tombstones using a solution of a non-ionic surfactant (Lito 7) followed by application of a biocide (Lito 3) is reported.[9] Lito 7 was also included in the testing of cleaning materials on tuff samples quarried at Viterbo.[31] AB 57 showed slightly stronger action than the Lito 7 and Contrad 2000.

The deterioration and treatment of a recently excavated tuff wall of the Crypt of Balbus is reported.[20] Flaking of the tuff stopped after losses in a plaster coating were filled. Repair of cracks in the Capitoline Palace is reported, using a mixture of hydraulic lime, pozzolana, sodium gluconate (a fluidifier), and Primal AC33.[30]

2.3 Hungary, Germany, Austria

The use of volcanic rock, and tuff in particular, is otherwise little remarked upon in Europe. The most extensive use seems to have been in Hungary, where a rhyodacitic tuff has been used in the northeastern part of the country since the Middle Ages. Results of laboratory analyses of the rock have been reported.[32 33] Deterioration results from the devitrification of matrix glass and the formation of clay; gypsum is found on the surface. Freeze/thaw cycling was used to test thirteen consolidants and water repellents, mostly silicone esters, but none are identified more specifically.

Only two studies have been found which mention tuff from Germany, in both cases used in the early sixteenth century. The deterioration of a local porphyrtic tuff used for the north portal sculpture of the Schlosskirche at Karl-Marx is the subject of discussions about the possible application of epoxy resins.[34] Restoration of a polychromed sacrament house made of Weibern tuff in the Church of St. Martin at Linnich is described, repairing damage occurring during World War II.[35]

A tuff used for a portion of the Linz Cathedral in Austria, constructed in 1938, was examined with ultraviolet fluorescent microscopy to determine the location of gypsum.[36] Gypsum proved to be unevenly distributed at various depths, without correlation between amount and extent of damage.

2.4 Turkey

One of the world's most spectacular tuff sites is the lunar-like landscape on the Anatolian plateau at Goreme in Cappadocia. More erosion-resistant cone-shaped rocks were formed adjacent to conduits for escaping gases. These were carved out during the Middle Ages and decorated with wall paintings for use as Byzantine churches, monasteries, chapels, and hermitages. A number of conservation studies stem from missions sponsored by ICCROM and the Turkish government.[30 37 38 39 40] The stone is identified as dacitic lapilli tuff.[40] Laboratory analyses have been carried out on both weathered samples from the St. Barbara Church[38] and on freshly quarried stone.[40] Decay of the stone is attributed to water erosion and chemical dissolution. Alteration of plagioclase phenocrysts visible with a microscope are thought to provide a good indication of the depth of alteration.[38] Lichen growth produces exfoliation of the stone. Fissuring of the stone, because it permits the entry of water, is perhaps the most serious hazard for the decorated interiors of the churches.[37]

Various solutions have been proposed and tested to slow the erosion of the tuff and prevent infiltration of water into the churches. Application of a polyurethane resin, Pencapsula, tested at the Middle East Technical University in Ankara, was planned in 1972, but it is not clear that any application was ever carried out in situ.[37] Vinavil, applied as a surface coating, sloughed off. Application of a 3cm thick cement/lime/tuff mortar to horizontal surfaces is recommended. Poor results of capping rocks with mortar made of local rock and binders are also reported;[30] after only one year, all were detached. The application of water repellents or a thick plaster layer is recommended rather than the use of a consolidant, because of the depth of alteration and drastic temperature changes at the site.[38] Laboratory testing indicated that multiple applications of the consolidants Tegovakon V and Wacker OH produced the best results without the use of the water repellents Tegosivin HL 100 and Wacker 090.[40] It is possible, however, that poor results when the consolidants were used with the water repellents are due to premature application of the latter. Field application of tetraethyl orthosilicates was carried out in the summer of 1987 as a result of the laboratory work. Securing unstable rock wedges with bolts and sealing cracks with mortars, as has been done at Elmali Kilise, is also recommended.[30 37]

The properties of a green dacitic tuff from the eastern end of the Marmara Sea (Karamursel) used in Istambul during the 6th century for walls of Hagia Sophia and Hagia Eirene are described.[41] Records of sixteenth century orders have been found, but the quarries are no longer functioning.

2.5 Greece

The first century Christian catacombs on the island of Milos near Tripiti, Greece, have been mapped, and the pumice tuff into which they are cut analysed. The principal deterioration phenomenon is loss of cohesion of the matrices, especially in more coarse-grained samples.[42]

2.6 Soviet Union

Tuff has been widely used to the present day in Armenia as a cut stone, with monuments from the fourth to the twelfth centuries cited.[43 44] Five tuffs have been studied in the laboratory: quaternary tuffs from Ani, Artik, Erevan, and Burakan; and tertiary tuff identified as "felsitique." The observed poor durability of monuments made of the tertiary tuff is corroborated by laboratory testing.

The twelfth century site of Vardzia in southern Georgia has 500 rooms and apartments, a chapel, banqueting halls, and stables, cut into a vertical cliff.[45] Deterioration is attributed to precipitation, to southern exposure (the prevailing wind direction), and to the more rapid weathering of the carved layer relative to upper and lower layers. Epoxy, polyvinyl acetate emulsion, and organo silicates were tested as consolidants. The best results were achieved with the latter, depositing 5-8mm in depth when applied in the field. Application of a polyethyl hydrosiloxane water repellent is recommended.

2.7 Japan

In Japan considerable work has been done on the deterioration and treatment of tuffs. A few publications are in English,[46 47 48 49 50] but most are in Japanese with English abstracts. The focus of the work has been the treatment of Buddhas cut into cliffs from the eighth to the nineteenth centuries. These are located at Usuki,[51] at Hakone in Kamto District,[46] in Ohita prefecture,[46 52] and in the caves of Oya Temple[46 53 54 55] in Tochigi Prefecture.[56 57] Tuff used for two historic structures in the city of Otaru has also been studied.[58]

The Oya Temple tuff is identified as a zeolite-bearing acidic stone, with nitronatrite salts ($NaNO_3$) found on the surface.[53] Neutron activation studies found high calcium contents in the surface crust and the enrichment of aluminum in heavily deteriorated portions of Ohita stone.[52] Freeze-thaw cycles are thought to provide a major contribution to the deterioration of Japanese tuffs.[46 58] The effects of freeze/thaw cycles on Oya tuff have been measured with acoustic emission.[54] Salt (mainly gypsum) crystallization from ground water is also considered a major factor.[48 59] The biodeterioration of tuffs has also been studied.[60]

The alkoxysilane SS-101, which is water repellent, produced the best consolidation results in laboratory testing.[61] A variety of tests were conducted on samples, some of which were artificially aged with freeze/thaw cycling.[49 56 57 62 63] These had been consolidated with SS-101, epoxy resin Araldite CY-230, and an acrylic resin (probably Paraloid B-72 at 15% in toluene). Samples impregnated with the SS-101, Tegovakon V, Tegosivin HL-100, and the Tegovakon V followed by Tegosivin HL-100, were also subjected to sodium sulphate crystallization cycling.[59] Color changes were measured after treatment with the SS-101 and artificial aging.[47]

Methyl(triethoxy)silane solutions have been used in the field since 1976.[48] Because of failures observed as a result of shallow impregnation, a method of deep application of the consolidant has been developed. SS-101 is poured into holes bored 100cm into rock; these are subsequently filled with stainless steel bars, epoxy, and stone powder.

As a less expensive alternative, investigations were done with samples impregnated with solutions of potassium silicate and lithium silicate, compared to samples impregnated with Paraloid B-72 and SS-101.[50] Use of a potassium silicate whose molar ratio of SiO_2/K_2O is high (3.8-3.9) is proposed for use in a dry climate.

Construction of a temple, shelter, or roof is proposed as a remedy to protect rock-cut Buddhas from freeze/thaw damage.[48 55]

2.8 India

In India a pyritic volcanic tuff was carved to decorate the Josgeshwari Caves near Bombay.[64 65 66] The deterioration of these caves, with growth of gypsum exudations from the hydrolysis of the pyrite, is described.

2.9 The Americas

Tuff seems to have been little used as a building stone in North America, and references to only two sites have been found. Prehistoric petroglyphs were carved into a tuff at Petroglyph Point in Lava Beds National Monument in northern California.[67] After the draining of an adjacent lake, the site has been damaged by vandalism due to improved access and by the abrasion of wind-borne dust from the dry lake bed. Tuff of the Pajarito Plateau of New Mexico was used by native Americans from the thirteenth century both for masonry construction and for rooms rock-cut against cliff faces.[68] More recently the rock was used by W.P.A. work crews for the construction of the park headquarters at the Bandelier National Monument.

Tuff has been more widely used in Central America as a building and decorative stone, but literature on its conservation is rare. Petroglyphs on the Isla de los Muertos were carved by the ancient inhabitants of Lake Nicaragua into a rock which is volcaniclastic, probably pyroclastic.[69] The rock measures over 50 meters in length, and it is fissuring because of lack of support due to the erosion of a soft underlying layer. Study of the problem has been initiated by the Museo Nacional de Nicaragua. "Tepetate," the local name for a tuff, was used for architecture at the site of Cacaxtla in Mexico, including carved slanted panels.[70] It is generally in a good state of preservation, requiring only mortar repair. The conservation of an andesitic tuff sculpture of Chac-mool is described following its recent excavation at the Aztec Templo Mayor in the heart of Mexico City.[71] Efforts focused on the preservation of painted stucco, which is frequently applied to the surface of pre-Columbian stonework. Tuffs are said to have been used since pre-Columbian times in the construction and decoration of Spanish colonial cities.[68]

In South America a yellowish-brown tuff known as "cancagua" was used for the construction of funeral tumuli at the pre-Inca Caranquis city of Cochasqui, Ecuador.[72 73] Study of the stone and test treatments were carried out in conjunction with excavation of the monuments by the Government of Ecuador for an archaeological park. Because of the poor quality of the stone, its high water absorption, and heavy rains in the region, laboratory tests were carried out with the consolidant Silester ZNS and the water repellent Transkote, applied both individually and consecutively. Transkote alone produced the best resistance to water, and it is recommended for application. When the Transkote was applied after the Silester ZNS, unsatisfactory results were produced. This is attributed to precipitation of the aluminum stearate by alcohol used to dilute the Silester ZNS. Tuff was used for the construction of Arequipa, Peru, known as the white city, but no reports on its deterioration or treatment have been found.[68]

3. BASALT

Many lava flows are composed of basalt. It is a basic rock (45-52% silica), with less silica than other volcanic rocks. It is composed chiefly of calcic plagioclase, clinopyroxene, and glass. Nepheline, olivine, orthopyroxene, and quartz may be present. Because of the ferromagnesian minerals (pyroxenes and olivines), basalt is characteristically black. Phenocrysts of these dark-colored minerals and the light-colored plagioclase are common. Basalt tends to be dense and massive, but it can also be vesicular.

3.1 India

The Deccan plateau which comprises most of central and western India was formed by a series of basaltic lava flows, and from early times, caves and cave temples were carved into the step-like exposures of these basalts. These include temples at Ajanta, Ellura, Elephanta, Karla, Bhaja, Pitalkhara, and Kanheri.[64 65 66 74 75] These rocks are mineralogically similar, mainly labradorite and enstatite-augite, and occur in both vesicular and non-vesicular form.[65]

Damage from water penetrating joints and cracks is the most serious problem for the cave temples. At most sites, heavy rainfall during a few months of the year contributes to chemical dissolution. Stalactites and gypsum exudations occur in several caves, with damage particularly at the Kanheri caves near Bombay.[75] In addition to gypsum, soluble sea salts are damaging the Elephanta Island caves. Caves at Ajanta have damage resulting from bird and bat excreta. Biological growth is a problem at some sites.

Recommendations for treatment include the installation of drains and grouting for the reduction of water damage.[65] Deforestation, removal of soil, and application of coal tar are recommended by one author, but others argue that these methods have caused damage at other sites.[64] Removal of soluble salts with moist paper pulp has been carried out at Elephanta and Kanheri.[75] Consolidation was carried out with a solution of polymethyl methacrylate at Kanheri in 1953. Application of a solution of zinc silicofluoride has been used at Kanheri to prevent biological growth.

3.2 Europe

Miscellaneous references have been found with regard to basalt stonework in Europe. The stark black churches of the Auvergne in Central France are made of basalt.[76] Basalt samples, presumably from Portugal, are included in studies of igneous rocks by Delgado Rodrigues.[77] [78] The thickness of the weathered crust on Bohemian basalts has been correlated with age.[79] Basalt from Mayen/Eifel and Londorf/Hessen are among the stones used in the construction of the Cathedral of Cologne.[80] [81] The porous basalt from Londorf has been used as replacement stone for deteriorated Schlaitdorfer sandstone in the Cathedral, because of the resistance of the basalt to chemical and physical weathering and its suitability for stone cutting.

3.3 Mediterranean Basin

Olivine basalt reliefs at the Hittite site of Karatepe in Turkey are reported to have shown continuous disintegration since their excavation in 1946.[82] In the laboratory, wet/dry and freeze/thaw cycling produced little change in the stone, while salt crystallization testing produced significant deterioration. Since the sculptures are protected from rainwater by roofing, damage is attributed to soluble salts carried by rising damp and to condensation.

Basalt, found in northeastern Israel and generally classed as a calc-alkaline olivine basalt, has been used for both rustic buildings made of field stones and for massive structures with sculptural relief, from the Bronze Age onwards.[83] The foundations of the ancient Greek city of Locri in Calabria, Italy, were constructed of basalt from Mt. Etna, a fact confirmed by recent petrographical and geochemical study.[84] No reports have been found on the deterioration or treatment of these stones.

3.4 Central America

Aztec sculptures were carved in basalt, but nearly all are now found in museums such as the Museo Nacional de Antropologia in Mexico City.[85] They are generally in good condition.

4. SCORIA

Scoria is the name applied to dark, glass-rich, vesicular lapilli and bombs (fragments larger than 32mm) of basic composition. The word is also employed to designate the highly vesicular basalt formed towards the top of a basaltic flow by gases.

4.1 Lalibela

The world-renowned complex of eleven rock-hewn churches in Lalibela, Ethiopia, are carved out of an angular reddish scoria. The mean porosity of samples analysed for an ICCROM study[86] was 25% and water absorption was 12%, while underlying dark grey basalt showed a far lower mean porosity (4%) and water absorption (2%). A key factor in the deterioration of the churches is the low porosity of the basalt, which in effect forms an impermeable membrane. Salts are present throughout, both from natural sources and concrete applied during restoration.

Several campaigns of treatment and testing are reported in the same study. According to oral tradition, treatment was undertaken by Arabs during the 1920's: walls were constructed, cracks filled with lead, and columns restored. In 1954, Bastiano, Rosetta, and Cambusi applied a bituminous layer to the external surfaces of two buildings, then painted it with a wash of red ochre. After failure of that system a few rainy seasons later, corrugated iron roofing was installed. Angelini later removed the bituminous layer and corrugated iron. Finally, in 1967 and 1968 churches were treated with a tetraethyl orthosilicate consolidant by Seymour Lewin.[87]

5. ANDESITE

Andesite is an intermediate rock (52-66% silica), containing more silica than basalt and less than rhyolite. It is composed principally of intermediate plagioclase (half calcic and half sodic) and normally some glass; in some cases small amounts of one or more of the minerals biotite, hornblende, pyroxene, and quartz are present. Andesites are generally dark gray, green, or red. Phenocrysts of light-colored sodic plagioclase and dark-colored biotite, hornblende, and pyroxene are common. The rock is named from the Andes Mountains where it is common.

5.1 Borobudur

This world-famous Buddhist monument was erected in central Java around 800 A.D. While the rock is most often referred to as an andesite and is included in the andesite section here, its composition is actually between that of andesite and basalt. The monument has been the subject of considerable study, particularly in conjunction with major restoration spearheaded by Paul Coremans[88] and begun in 1973, when an entire issue of Studies in Conservation is devoted to the subject.[89 90 91] Work was completed by 1983.

One of the underlying purposes of the work was to correct the irregular subsidence of the monument, which is built on an artifical mound that had been weakened by infiltrating rainwater.[92] In order to carry out structural repairs, the bulk of the monument was disassembled.[89 90] Then a new drainage system and concrete supports were installed. Thorough study of the stone and its deterioration were carried out prior to treatment.[93 94 95] Comparison with photographs taken in 1910 confirms some loss of detail. Biological agents of deterioration, especially crustaceous lichens, are considered a serious hazard, given the heavy rainfall in this tropical environment.[93 96] Salts from old cements have also caused damage through deposition and efflorescence.[94] An excellent account of historical documentation, including many direct quotations about past treatments of the monument, is given in one of the articles.[93] A yellow ochre layer on the surface of the stone, probably applied in 1911, is the subject of much discussion. It was not believed harmful and was not removed during restoration. Proposed treatment included washing all the stones and removal of salts with paper poultices or the Mora mixture known as AB 57 (referred to as 322 at Borobudur).[90 94] Crustaceous lichens were to be removed with a mixture of AB 57 and clay. It is later reported that Hyamine 3550 has been used to prevent the regrowth of algae and protolichens.[96] A 1% solution of Hyvar X-L has been used to eradicate and prevent the growth of mosses.

5.2 Greece and Egypt

In the ancient world, rocks known as green antique porphyry and red antique porphyry were highly prized. The term porphyry comes from Mt. Porphyrtes in Egypt where red porphyry was quarried, but it is now a misnomer. In current usage the word indicates only a particular texture of igneous rocks, i.e., that phenocrysts are found in a fine-grained matrix. In fact both red and green porphyries are porphyritic andesites.

Red antique porphyry was valued for its violet-red color and was designated an imperial stone, used in Rome from the first century B.C.[15] Notable uses include the sculptures of the Tetrarchs on the exterior of the Basilica of San Marco in Venice and the early Christian sarcophagi of Constantine's daughter Constantina and his mother St. Elena now located in the Vatican Museum. The stone is considered particularly durable.[97]

Green antique porphyry is a labradorite (a type of plagioclase) andesite, with light green phenocrysts of labradorite in a dark green matrix. It is quarried near Krokea in the Peloponnesus of Greece and is also known as krokeatis. Other names include laconia or lacedemona marble or "serpentino." The stone was used in Rome from the first century A.D.[15] It is one of the stones used in Venice which is considered most resistant to weathering and air pollution, and in most cases it is shiny and perfectly preserved.[97] In only a very few instances has a partial, superficial fading been found.

5.3 Central America

Andesite was used for the colossal Olmec heads at San Lorenzo, La Venta, Laguna de los Cerros, and Tres Zapotes in Mexico.[98] It is thought to derive from a single source, as yet unidentified. Stones exposed since excavation 40-50 years ago are rounded, with loss of detail.

The important Maya sanctuary at Copan (Honduras), constructed from 400 to 800 A.D. was built of a greenish andesite.[99 100] The stone used for the sculptures is softer and has larger feldspars than that used for the pyramids and walls. Decay of the stone is attributed to heavy rainfall, which dissolves the rock, transports damaging salts, and permits the growth of abundant microflora. Particular concern about the deterioration of the hieroglyphic staircase is reported. The staircase is currently covered with a tent.[101] Tests with commercial ethyl silicates as consolidants were started in 1985. In January 1977 removal of biological material was carried out with Clorox (commercial strength 1:5 in water), followed by sodium perborate (5% aqueous solution) a day later.[102] The treatment was repeated in July 1977 and January 1978. Respraying with Thaltox or Clorox every 4-8 years is recommended. Testing of biocides containing quaternary ammonia compounds with polyhydrodiphenylmethane was begun in 1985.[100]

Andesite is identified as the stone used for the staircases and patio floors at Templo Mayor in Mexico City,[71] as well as for sculptures from Tenochtitlan such as the colossal Jaguar prominently displayed in the Museo Nacional de Antropologia in Mexico City.[85] Most of the Aztec andesite sculptures are covered or have been located indoors since excavation, and they are in good condition.

5.4 Armenia

Andesite from Khendzorout and Kapoutan in the Soviet Armenia has been studied in the laboratory.[42 43] Deterioration near the soil from soluble salts is reported for the Kaptavank Church (dated to 1343) near the village of Kapoutan in the region of Kotaik. Andesite-basalts from Garni and Megrout are included in the same study.

6. DACITE

Dacite (>63% silica) has the same general composition as andesite, but with less calcic plagioclase and more quartz.

6.1 Armenia

Dacite from Karnout in Soviet Armenia has been studied in the laboratory.[42 43] Salt damage is noted on a temple at Karnout.

7. RHYOLITE

Rhyolite is an acid rock (>66% silica) and is characteristically white, gray, or pink. It commonly contains a few phenocrysts, typically of quartz and alkali feldspar, in a glassy to cryptocrystalline groundmass.

7.1 Quirigua, Guatemala

At the humid lowland site of Quirigua, different types of biological growth found on altars and stele made of both sandstone and rhyolite[102] have been identified. A program of removal of this growth, identical to that in Copan, was begun in July 1976, with subsequent spraying in January 1977, June 1977, and January 1978.[103 104] The sculptures are currently protected from rainfall with thatched roofing.

8. TRACHYTE

Trachyte (>58% silica) is a light-colored intermediate to acidic rock which contains potassium feldspar and minor mafic minerals (biotite, hornblende, or pyroxene) as the main components.

8.1 Europe

Trachytes, from Drachenfels/Siebengebirge and from Stenzelberg (Berkum and Wolkenburg), were used during the early stages of construction of the Cathedral of Cologne.[83 84] Because of considerable damage, they have been the subject of testing. Trachyte has also been tested with salt solutions in Czechoslovakia, reported in a Czech-language article.[105]

A local trachyte from the Euganean Hills was used as a building material in Venice from the 10th to 13th centuries.[106] It was used as a damp-proof course in the city, and it is quarried today. Epoxy resin (EP2101) consolidation of a lion sculpture in Padua, made of Euganean trachyte, is reported.[19]

9. CONCLUSION

The deterioration of tuff presents the greatest problems in terms of preservation of volcanic stonework. A number of consolidants have been tested on tuffs in the laboratory, but there has been no long-term testing in the field. While andesite and basalt have been used for stonework, they are much less discussed than tuff, presumably because of greater durability. Biological growth frequently disfigures volcanic stonework and, particularly in the case of crustose lichens, causes damage. Monuments carved in situ present particularly difficult problems, often requiring engineering solutions. Air pollution and stone cleaning, issues which to a large extent drive the research and treatment of calcareous stones and sandstones, are of little importance for volcanic stonework.

10. MATERIALS

The following list of products mentioned in the text shows the company name in parentheses when known, followed by the contents. These are generally as described by the authors. When further information could be obtained from other articles, company literature, or independent analyses, it has been listed.

AB 57: a mixture of ammonium bicarbonate, sodium bicarbonate, di-sodium EDTA, Desogen, and carboxymethylcellulose.
Araldite CY230 & Epomait B-002 (Ciba-Geigy): epoxy resin and hardener, used at 25% in toluene.
Araldite XG40 & XG41 (Ciba-Geigy): epoxy resin and hardener, used at 33% in acetone and isopropyl alcohol.
Araldite PZ 820 & HZ 820 (Ciba-Geigy): epoxy resin and hardener, used at 80% in xylene, butanol, and cellosolve.
Chlorobromuron: 3-(4-bromo-3-chlorophenyl)-1-methoxy-1-methyl-urea.
Clorox: 5.25% sodium hypochlorite in water.
Contrad 2000 (BDH): anionic and non-ionic surfactants, inorganic chemicals, and stabilizers.
Desogen (Ciba-Geigy): quaternary ammonium compound [dodeconoyl N methylamino ethyl (phenyl carbamyl methyl) dimethyl ammonium chloride]
DriFilm 104 Silicone Resin (General Electric): a polyalkal(methyl)siloxane resin, 70% in mineral spirits.
Elastosil E41 (Wacker-Chemie): a silicone rubber water repellent.
EP2101 and K2102: cycloaliphatic epoxy resin, 25% in isopropanol and toluene, and hardener.
Fluometuron: 3-(3-trifluoromethylphenyl)-1,1-dimethyl urea.
Hyamine 3500 (Rohm & Haas): quaternary ammonium compound.
Hyvar X-L (DuPont): lithium salt of 5-bromo-3-secondary butyl-6-methyluracil, arylalkyltrimethyl ammonium chloride and halogen of biphenyl sulphur.
Lito 3 (Ciba-Geigy): 3-(3-trifluoromethylphenyl)-1,1-dimethyl urea.
Lito 7 (Ciba-Geigy): a non-ionic surfactant containing glycol, ethers, complex salts, and sequestrants (pH 7.5-8).
Paraloid B-72 (Rohm & Haas): methylacrylate ethylmethacrylate copolymer.
Pencapsula (Texas Refinery Corporation): polyurethane resin.
Primal AC33 (Rohm & Haas): acrylic resin emulsion.
Product 460: a siliconate-acrylic copolymer in water.
Rhodorsil XR-893 (Rhone Poulenc): a partially condensed polymethyl(phenyl)-siloxane, used with toluene (final solution 15% solid).
Rhodorsil 10336 (Rhone Poulenc): a silicone resin with relatively higher number of methyl groups and lower phenyl groups than the Rhodorsil XR-893, used with toluene (final solution 15% solid).
Silester ZNS (Pietro Carini): tetraethyl orthosilicate, used at 33% in ethanol with hydrochloric acid catalyst.
Sniatron 1629: polyester resin.
SS-101 and Catalyst C (Colcote Ltd.): oligomer of methyl(triethoxy)silane in organic solvent and 3-5% tin or carboxylic acid catalyst
Tegovakon V (Goldschmidt): tetraethyl orthosilicate, 65% in organic solvent.
Tegosivin HL 100 (Goldschmidt): dimethyl(dimethoxy)silane, 6% in organic solvent.
Terbutryn: 2-tertiary-butylamino-4-ethylamino-6-methylthio-5-triazine.
Thaltox: organo-tin and quaternary ammonium compounds.
Transkote (Sandtex): aluminum stearate.
Vancide 51: sodium salts of dimethylthiocarbamic acid and 2-mercaptobenzotriazole
Vinavil (Montedison): polyvinyl acetate emulsion.
Wacker OH, actually Sandsteinverfestiger OH (Wacker-Chemie): tetraethyl orthosilicate monomers and dimers, 75% in methylethylketone, acetone, and dibutyltindilaurate.

Wacker H, actually Sandsteinverfestiger H (Wacker-Chemie): tetraethyl orthosilicate and methyl(triethoxy)silane.
Wacker 090 (Wacker-Chemie): an oligomeric alkyl(alkoxy)silane mixture.

11. REFERENCES

1. Delgado Rodrigues, J.; in Proceedings of the RILEM Congress on Deterioration and Protection of Stone Monuments, Paris, 1978, 2.4

2. Loughnan, F.C.; "Chemical Weathering of the Silicate Minerals"; American Elsevier Publishing Company, New York, 1969

3. Silberbauer, J.; Poisel, R.; Eppensteiner, W.; in "Engineering Geology of Ancient Works, Monuments and Historical Sites"; Marinos and Koukis, Eds.; Balkema, Rotterdam, 1988; pp. 123-128

4. Charola, A.E.; Lazzarini, L; Wiener Berichte ueber Naturwissenschaft in der Kunst 1987/1988, 4/5, 392-401

5. Hyvert, G; UNESCO Report, 2868/RMO.RD/CLP, Paris, 1973

6. Domaslowski, W.; UNESCO Report, Paris, 1981

7. Domaslowski, W; Ochrona Zabytkow 1985, 38, 86-98

8. Bahamondez Prieto, M.; "Factibilidad tecnico economica de la aplicacion del metodo propuesto por el profesor Domaslowski para la consolidacion de tres estatuas de la Isla de Pascua"; Direccion de Bibliotecas, Archivos y Museos, Santiago, Chile, 1985

9. Bettini, C.; Villa, A.; in "The Conservation of Stone II"; Centro per la Conservazione delle Sculture all'aperto, Bologna, 1981; pp. 523-534

10. Accardo, G; Cacace, C.; Rinaldi, R.; Bollettino d'Arte. Supplement 1987, 41, 101-108

11. Barcellona Vero, L; Bettini, C.; Monte Sila, M.; in Proceedings of the 2nd International Symposium on the Deterioration of Building Stones, Athens, 1976, pp. 61-65

12. Alessandrini, G.; Peruzzi, R.; Rossi-Doria, P.; Tabasso, M.; in Proceedings of the RILEM Congress on Deterioration and Protection of Stone Monuments, Paris, 1978, 6.1

13. Laurenzi Tabasso, M.; Mecchi, A.M.; Santamaria, U.; Venturi, G.; in "Engineering Geology of Ancient Works, Monuments and Historical Sites"; Marinos and Koukis, Eds.; Balkema, Rotterdam, 1988; pp. 933-938

14. Laurenzi Tabasso, M.; Mecchi, A.M.; Santamaria, U.; Venturi, G.; in "Engineering Geology of Ancient Works, Monuments and Historical Sites"; Marinos and Koukis, Eds.; Balkema, Rotterdam, 1988; pp. 939-943

15. Marta, R. "Tecnica Costruttiva Romana/Roman Building Techniques"; Kappa, Rome, 1986

16. Barcellona Vero, L.; Bianchi, R.; Monte Sila, M.; Tiano, P.; in "The Conservation of Stone I"; Centro per la Conservazione delle Sculture all'aperto, Bologna, 1976; pp. 257-266

17. Barcellona Vero, L.; Monte Sila, M.; in "The Conservation of Stone I"; Centro per la Conservazione delle Sculture all'aperto, Bologna, 1976; pp. 233-244

18. Barcellona-Vero, L.; Monte Sila, M.; in Proceedings of the RILEM Congress on Deterioration and Protection of Stone Monuments, Paris, 1978, 4.1

19. Cavaletti, R.; Lazzarini, L.; Marchesini, L.; Marinelli, G.; in Proceedings of the Vth International Congress on Deterioration and Conservation of Stone, Lausanne, 1985, pp. 769-788

20. Costanzi Cobau, A.; in Proceedings of the 8th Triennial Meeting of the ICOM Committee for Conservation, Sydney, 1987, pp. 475-478

21. Giacobini, C.; Pietrini, A.M.; Ricci, S.; Roccardi, A.; Bollettino d'Arte, Supplement 1987, 41, 53-64

22. Rota Rossi-Doria, P.; Bollettino d'Arte, Supplement 1987, 41, 11-14

23. Bianchetti, P.L.; Lombardi, G.; in Proceedings of the Fourth International Congress on the Deterioration and Preservation of Stone Objects, Louisville, Kentucky, 1982, pp. 29-38

24. Giacobini, C.; Bettini, C.; in Proceedings of the RILEM Congress on Deterioration and Protection of Stone Monuments, Paris, 1978, 4.3

25. Giacobini, C.; Bettini, C.; Villa, A.; in Proceedings of the 3rd International Congress on the Deterioration and Preservation of Stones, Venice, 1979, pp. 305-312

26. Ciarallo, A.; Festa, L.; Piccioli, C.; Raniello, M.; in Proceedings of the Vth International Congress on the Deterioration and Conservation of Stone, Lausanne, 1985, pp. 607-616

27. Lewin, S.Z.; Charola, A.E.; Scanning Electron Microscopy 1978, 1, 695-704

28. Rossi-Manaresi, R.; in Proceedings of the 2nd International Symposium on the Deterioration of Building Stones, Athens, 1976, pp. 233-248

29. Rossi Manaresi, R.; Bollettino d'Arte, Supplement 1987, 41, 133-144

30. Malliet, J.; in "Engineering Geology of Ancient Works, Monuments and Historical Sites"; Marinos and Koukis, Eds.; Balkema, Rotterdam, 1988; pp. 877-882

31. Laurenzi Tabasso, M.; Mecchi, A.M.; in Proceedings of the Vth International Congress on Deterioration and Conservation of Stone, Lausanne, 1985, pp. 975-982

32. Kertesz, P.; Marek, I.; in "The Conservation of Stone II"; Centro per la Conservazione delle Sculture all'aperto, Bologna, 1981; pp. 711-720

33. Medgyesi, I; Beuer, M.; in Proceedings of the RILEM Congress on Deterioration and Protection of Stone Monuments, Paris, 1978, 7.17

34. Beeger, D.; Geologie 1972, 21, 305-317

35. Frebel, V; Lindenthal, F.; Jahrbuch der Rheinischen Denkmalpflege 1983, 29, 104-122

36. Gruber, P.; Sternad, B.; Studies in Conservation 1981, 26, 161-167

37. Bowen, R.; in "Engineering Geology of Ancient Works, Monuments and Historical Sites"; Marinos and Koukis, Eds.; Balkema, Rotterdam, 1988; pp. 731-737

38. Caner, E.N.; Turkmenoglu, E.G; Gokturk, H.; Demirci, S.; Boke, H.; in Proceedings of the VIth International Congress on Deterioration and Conservation of Stone, Torun, 1988, pp. 287-302

39. Granier, J.; in "The Conservation of Stone I"; Centro per la Conservazione delle Sculture all'aperto, Bologna, 1976; pp. 45-53

40. De Witte, E.; Terfve, A.; Koestler, R.J.; Charola, A.E.; in Proceedings of the VIth International Congress on Deterioration and Conservation of Stone, Torun, 1988, pp. 346-355

41. Erguvanli, K.; Eris, I.; Ahunbay, M.; Ahunbay, Z.; in "Engineering Geology of Ancient Works, Monuments and Historical Sites"; Marinos and Koukis, Eds.; Balkema, Rotterdam, 1988; pp. 631-638

42. Andronopoulos, B.; Tzitziras, A.; in "Engineering Geology of Ancient Works, Monuments and Historical Sites"; Marinos and Koukis, Eds.; Balkema, Rotterdam, 1988; pp. 309-318

43. Hatsagortsian, Z.; in Proceedings of the VIth International Congress on Deterioration and Conservation of Stone, Torun, 1988, pp. 149-158

44. Hatsagortsian, Z.; in Proceedings of the Vth International Congress on Deterioration and Conservation of Stone, Lausanne, 1985, pp. 195-202

45. Iakachvili, T.V.; in Proceedings of the 4th Meeting of the ICOM Committee for Conservation, Venice, 1975, 75/5/6

46. Miura, S.; Nishiura, T.; Fukuda, M.; in "The Museum Conservation of Ethnographic Objects"; Morita, T. and Pearson, C., Eds.; National Museum of Ethnology, Osaka, 1988; pp. 205-216

47. Nishiura, T.; in Preprints of the ICOM Committee for Conservation 8th Triennial Meeting, Sydney, 1987, pp. 509-512

48. Nishiura, T.; in "Case Studies in the Conservation of Stone and Wall Paintings"; Brommelle, N.S. and Smith, P., Eds.; IIC, London, 1986; pp. 155-158

49. Nishiura, T.; Fukuda, M.; Miura, S.; in "Adhesives and Consolidants"; IIC, London, 1984; pp. 156-159

50. Nishiura, T.; Zuixiong, Li; in "The Conservation of Far Eastern Art"; Brommelle, N.S., et al., Eds.; IIC, London, 1988; pp. 108-112

51. De Witte, E.; in "Conservation and Restoration of Stone Monuments"; pp. 152-157

52. Mabuchi, H.; in "Conservation and Restoration of Stone Monuments"; 1985, pp. 55-58

53. Emoto, Y.; Science for Conservation 1966, 2, 39-44

54. Fukuda, M.; in "Conservation and Restoration of Stone Monuments"; 1985, pp. 19-22

55. Miura, S.; Tomisawa, T.; Ishikawa, R.; Japanese Antiques and Art Crafts 1983, 27, 38-42

56. Fukuda, M.; Miura, S.; Nishiura, T.; Matsuoka, T.; Science for Conservation 1983, 22, 1-14

57. Fukuda, M.; Miura, S.; Nishiura, T.; Science for Conservation 1984, 23, 1-12

58. Fukuda, M.; in "Conservation and Restoration of Stone Monuments;" 1985, pp. 41-46

59. Nishiura, T.; In "Conservation and Restoration of Stone Monuments"; 1985, pp. 59-72

60. Arai, H.; in "Conservation and Restoration of Stone Monuments;" 1985, pp. 83-95

61. Nishiura, T.; Science for Conservation 1977, 16, 17-29

62. Miura, S.; Fukuda, M.; Nishiura, T.; Science for Conservation 1983, 22, 21-27

63. Nishiura, T.; in "Conservation and Restoration of Stone Monuments"; 1985, pp. 97-100

64. Lal, S.B.; in "Conservation in the Tropics"; International Centre for Conservation, Rome, 1972, pp. 131-138

65. Lal, B.B.; in Proceedings of the RILEM Congress on Deterioration and Protection of Stone Monuments, Paris, 1978, 7.8

66. Lal, B.B.; in Proceedings of the Vth International Congress on Deterioration and Conservation of Stone, Lausanne, 1985, pp. 213-222

67. Lee, G.; Hyder, W.D.; Benson, A.; Report for the Lava Beds National Monument, U.S. Department of Interior Contract #PX8400-7-0694 and PX8410-8-0185, 1988

68. Heiken, G.; American Scientist 1979, 67, 564-571

69. Ronald L. Bishop, private communication

70. Molina Feal, D.; in "In Situ Archaeological Conservation"; Instituto Nacional de Antropologia e Historia, Mexico, and the J. Paul Getty Trust, Century City, CA, 1987; pp. 194-201

71. Franco, M.L.; in "In Situ Archaeological Conservation"; Instituto Nacional de Antropologia e Historia, Mexico, and the J. Paul Getty Trust, Century City, CA, 1987; pp. 166-175

72. Rossi-Manaresi, R.; Chiari, G.; in Proceedings of the Third International Symposium on Mudbrick (adobe) Preservation, Ankara, 1980, pp. 29-38

73. Rossi Manaresi, R.; Pellizer, R.; in Proceedings of the 3rd Internatinal Congress on the Deterioration and Preservation of Stones, Venice, 1979, pp. 605-611

74. Newman, R.; "The Stone Sculpture of India"; Harvard College, Cambridge, MA, 1984

75. Sharma, B.R.N.; in Proceedings of the RILEM Congress on Deterioration and Protection of Stone Monuments, Paris, 1978, 7.19

76. Herz, N.; in "Conservation of Historic Stone Buildings and Monuments"; National Academy Press, Washington, D.C., 1982; pp. 49-61

77. Delgado Rodrigues, J.; in Proceedings of the 2nd International Symposium on the Deterioration of Building Stones, Athens, 1976, pp. 105-108

78. Delgado Rodrigues, J.; in Proceedings of the Fourth International Congress on the Deterioration and Preservation of Stone Objects, Louisville, 1982, pp. 281-294

79. Cernohouz, J.; Solc, I.; Nature 1966, 212, pp. 606-607

80. Efes, Y; in Proceedings of the 3rd International Congress on the Deterioration and Preservation of Stones, Venice, 1979, pp. 231-243

81. Mirwald, P.W.; Kraus, K.; Wolff, A.; Durability of Building Materials, 1988, 5, 549-570

82. Caner, E.N.; Turkmenoglu, A.G.; in Proceedings of the Vth International Congress on Deterioration and Conservation of Stone, Lausanne, 1985, pp. 411-420

83. Perath, I.; "Stone Building and Building Stone in Israel"; The Geological Survey of Israel, Jerusalem, 1984; Report EG/38/84

84. De Francesco, A.M.; Frisatto, W.; Revue d'Archeometrie, 1986, 10, 25-32

85. Nicholson, H.B.; "Art of Aztec Mexico. Treasures of Tenochtitlan"; National Gallery of Art, Washington, D.C., 1983

86. ICCROM Report, Rome, 1978

87. Lewin, S.Z.; in "The Treatment of Stone"; Centro per la Conservazione delle Sculture all'aperto, Bologna, 1972; pp. 139-144

88. Coremans, P.; Bulletin de l'IRPA, 1958, 1, 70-84

89. Voute, C.; Studies in Conservation 1973, 18, 113-130

90. Hyvert, G.; Studies in Conservation 1973, 18, 131-155

91. Soediman; Studies in Conservation 1973, 18, 102-112

92. Voute, C.; UNESCO Report 1241/BMS.RD/CLT, Paris, 1969

93. Hyvert, G.; UNESCO Report RMO.RD/2646/CLP, Paris, 1972

94. Hyvert, G.; in "Decay and Preservation of Stone;" Winkler, E.M., Ed.; Engineering Geology Case Histories Number 11; The Geological Society of America, Boulder, 1978; pp. 95-100

95. Picot, P.; Ragot, J.-P.; in Proceedings of the 1st International Symposium on the Deterioration of Building Stones, La Rochelle, 1972, pp. 77-88

96. Siswowiyanto, S.; in "The Conservation of Stone II"; Centro per la Conservazione delle Sculture all'aperto, Bologna, 1981; pp. 759-768

97. Lazzarini, L.; Begolli, R.; in Proceedings of the 2nd International Symposium on the Deterioration of Building Stones, Athens, 1976, pp. 249-256

98. David Grove, private communication

99. Riederer, J.; in Preprints of the 7th Triennial Meeting of the ICOM Committee for Conservation, Copenhagen, 1984, 84.10.21-2

100. Riederer, J.; in "Case Studies in the Conservation of Stone and Wall Paintings"; Brommelle, N.S. and Smith, P., Eds.; IIC, London, 1986; pp. 151-154

101. Robert Sharer, private communication

102. Zelaya Rubi, V.; Hale, M.E.; in Atti del Convegno Internazionale: La pietra Interventi, Conservazione, Restauro; Lecce, 1981; Galatina, 1983; pp. 159-170

103. Hale, M.; Yaxkin 1979, 3, 135-149

104. Hale, M.E.; in "National Geographic Society Research Reports. 1975 Projects"; pp. 305-321.

105. Kotlik, P.; Sbornik Vysoke skoly chemicko-technologicke v Praze 1985, 13, 193-197

106. Lazzarini, L.; Proceedings of an International Colloquium: Natursteinkonservierung, Munich, 1984; Bayerisches Landesamt fuer Denkmalpflege Number 31; pp. 167-172

3. DETERIORACION
DETERIORATION

95. Picot, P.; Ragot, J.-P.; in Proceedings of the 1st International Symposium on the Deterioration of Building Stones, La Rochelle, 1972, pp. 77-88

96. Siswowiyanto, S.; in "The Conservation of Stone II"; Centro per la Conservazione delle Sculture all'aperto, Bologna, 1981; pp. 759-768

97. Lazzarini, L.; Bagolli, R.; in Proceedings of the 2nd International Symposium on the Deterioration of Building Stones, Athens, 1976, pp. 249-256

98. David Grove, private communication

99. Riederer, J.; in Preprints of the 7th Triennial Meeting of the ICOM Committee for Conservation, Copenhagen, 1984, 84.10.21-2

100. Riederer, J.; in "Case Studies in the Conservation of Stone and Wall Paintings"; Brommelle, N.S. and Smith, P., Eds.; IIC, London, 1986; pp. 151-154

101. Robert Sharer, private communication

102. Zelaya Rubi, V.; Hale, M.E., in atti del Convegno Internazionale: La pietra. Interventi Conservativi sul Monumento, Lecce, 1981; Galatina, 1983; pp. 159-170

103. Hale, M.; Yaxkin

104. Hale, M.E.; in "National Geographic Society Research Reports. 1975 Projects"; pp. 305-321

105. Kotlik, P.; Sbornik Vysoke skoly chemicko-technologicke v Praze 1985, 13, 193-197

106. Lazzarini, L.; Proceedings of an International Colloquium: Natursteinkonservierung, Munich, 1984; Bayerisches Landesamt fuer Denkmalpflege Number 31; pp. 167-172

VOLCANIC TUFFS - THE DESCRIPTION AND QUANTITATIVE RECORDING OF THEIR WEATHERED STATE

B. FITZNER

Geologisches Institut, RWTH Aachen, D-5100 Aachen, FRG

ABSTRACT

For many centuries volcanic tuffs from western Germany have been used in the construction of important historic buildings. These suffered severe weathering damage which calls for immediate preservation actions. The effectiveness of these actions depends on the accurate knowledge of the causes and state of the damage. By mapping the building according to a classification scheme of tuff weathering forms it was possible to make an objective and reproducible description of the damaged condition. The results of mapping a Middle age minster are presented. Characteristic values relevant to weathering are also presented for Rhenish Tuffs and an Easter Island tuff. The behaviour of tuffs according to laboratory tests is discussed. Pore space analysis constitutes an important method for recording the state of weathering.

RESUMEN

Las tobas volcánicas del oeste de Alemania fueron usadas en muchos edificios de valor histórico. El daño sufrido por su exposición al medio ambiente requiere inmediatas medidas de preservación. La eficacia de estas medidas depende del conocimiento justo de las causas y del estado de deterioro. A través de un mapeado del edificio de acuerdo a un esquema de clasificación de formas de deterioro de las tobas fue posible realizar una descripción objetiva y reproducible de los daños. Se presenta el mapeado de una catedral medieval. Tambien se dan los valores caracteristicos relevantes al deterioro de tobas renanas y de una toba de Isla de Pacua. Se informa sobre el comportamiento de estas tobas en ensayos de laboratorio. El análisis del volumen de poros constituye un método importante para describir el estado de deterioro.

1. INTRODUCTION

Tuffs from the Rhine area have been put to diverse uses as a natural stone for over 2000 years. The stone has been employed in form of bricks for the construction of masonry and also in large blocks for the bases of buildings. More rarely, they have been used for sculptures and decorative architectural elements.

Today, the Rhenish Tuff has lost its great importance as a building stone. The quarries still being worked provide material for restoration work, as well as for some new buildings. The Rhenish Tuffs were utilised extensively above all in western Germany and neighbouring countries because they were easy to quarry and work with, and could be easily transported along the Rhine and its tributaries. Many historically significant buildings were constructed out of tuff. The poor condition of most of these buildings necessitates immediate preservation measures. The effectiveness of such measures depends upon information on important rock properties.

The results of systematic work on tuff buildings - known as building mapping - are presented. In this work the visible weathered condition of this natural stone is recorded quantitatively. Also, the most important characteristic properties which are relevant to weathering are discussed. Finally, the behaviour of various tuff varieties in weathering simulation experiments and after treatment with a stone consolidating agent is investigated.

By correlating the results of investigations at the buildings with those from the laboratory, conclusions on weathering processes and the factors that cause them can be drawn.

2. SAMPLE MATERIAL

The Quaternary Rhenish Tuffs (1) occur in the Laach volcanic area, west of Koblenz on the Rhine. Various phases of vulcanicity can be ascertained for this area. The oldest phases of eruption occurred 500,000 to 300,000 years ago, and the most recent volcanic events took place 11,000 years ago. The tuff varieties, taken from many quarries in the course of many centuries, can be assigned to the following three petrographical types:

- coarse-grained Selbergittuffs
- fine-grained Selbergittuffs
- trachytic tuffs.

Both Selbergittuffs belong to the oldest eruption phase, while the trachytic tuffs are attributed to the most recent phase. The trachytic tuffs have been quarried in the valleys of the rivers Brohl and Nette since Roman times. They constitute the longest-used building stone, going under the name of "Roman Tuff". The fine-grained Selbergittuffs have been used increasingly since the Middle Ages. Due to their relative homogeneity and fine-grained nature, they are also suitable for decorative architectural elements and sculptures. Many of these tuffs come from numerous quarries in the vicinity of the town of Weibern: hence the name "Weiberner Tuff" was adopted for this stone. The coarse-grained Selbergittuffs have only been used in great quantities in the last couple of centuries. Important quarries in the vicinity of the town of Ettringen have given them the name "Ettringer Tuff".

Investigations on-site and sampling of unweathered rock for petrographical investigations and weathering simulation tests were carried out in the three above-mentioned regions. Studies were also carried out at many historical tuff buildings in the Rhine area. The results presented in this paper originate from the St. Quirinus Minster in Neuss.

The author also had access to a small sample of a tuff from Easter Island. Several petrographical characteristic values were determined for this tuff. It purportedly corresponded to the tuff used to make the large figures on the island. The precise origin of this sample could not, however, be determined.

3. METHODOLOGY

In order to be able to reproducibly characterise the state of damage of natural stone historical buildings according to phenomenalogical criteria, investigations are carried out at the building (2). By means of these investigations it is possible to carry out a facade-mapping of the natural stone varieties used in building and the damage suffered by them .

As the first step, all natural stones in the building are noted and documented. They are differentiated according to standard petrographical classification schemes. Next, the distribution of the noted natural stone varieties in the masonry is mapped. Lithological mapping such as this provides an overall view of the inventory of the natural stones used in the building.

In a second stage of building studies, the apparent weathering forms on all accessible building areas are registered photographically and described in detail. Such documentation allows an exact comparison of weathering forms to be made with those which are already registered at other monuments, and which are continuously catalogued using photos and descriptions. In this way a classification scheme (3) is established which ensures the exact and reproducible recording of weathering forms. The mapping of weathering forms follows as the next step. The results of both the lithological mapping and the mapping of the weathering forms are either recorded on large photos or on existing building plans. The nature and accessibility of the buildings, as well as the objectives of the study, determine the degree of precision of the mapping. For instance, only the main weathering forms are recorded during cursory mapping. In contrast, during a detailed mapping, all of the information on each stone is recorded on a "stone by stone" basis. Additionally, the dominant weathering forms are recorded using the criteria type, extent and intensity.

The aim of the petrological investigations is to record the mineral composition and porosity characteristics of the diverse tuff varieties. By comparing the results of investigations on weathered and unweathered zones of a natural stone it is possible to determine the material alterations caused by weathering and to quantify the damaged state of the tuff.

Using macroscopic observations and microscopic analysis methods the mineral composition as well as the structural and textural characteristics are recorded. X-ray diffraction investigations provide additional information on the mineral composition of the tuffs. The pore network of a rock has a considerable influence on the type and intensity of the weathering processes, and is itself at the same time altered by these processes. The change in pore geometry and pore space is, therefore, a quantitative measure of the state of weathering (4). Using mercury porosimetry and the microscope, in combination with image analysis, the pore space of unweathered and weathered tuff samples is investigated. The first method is used to directly record pores with a radius of 3 µm to 1000 µm. Mercury porosimetry facilitates the calculation of pore throat radii between 0.0019 µm and 250 µm and additional porosity values.

The influence of combined weathering factors on the texture of the Rhenish Tuffs is investigated using freeze-thaw cycle experiments and salt crystallization tests (5,6). SO_2-weathering experiments provide information about the ability of the tuff to form gypsum.

In order to prove the efficiency of a silicic ester based consolidating agent, tuff samples were impregnated. The porosity modification due to silica gel deposition in the pore space is measured using mercury porosimetry.

4. RESULTS AND DISCUSSION

4.1 Building Mapping

An important first step towards comprehending the complex process of "weathering" is an exact documentation and evaluation of the material condition of the historical monument. The working procedures to reach this aim can be divided into four steps:

- lithological mapping
- recording, classification and documentation of weathering forms
- mapping of weathering forms
- measuring and sampling at the building.

During lithological mapping, well-known petrographical schemes are used. The mapping serves two purposes: first it provides an inventory of the rocks used, and, secondly, it is a pre-requisite for mapping the weathering forms. This can be illustrated with the results from the lithological mapping of the St. Quirinus Minster, a late Romanesque basilica dating from the 13th century in the Rhineland town of Neuss.

The distribution of the different natural stones in the west facade of the Minster can be seen in Figure 1. According to this lithological mapping, more than 95% of the facade is of volcanic rock, about 65% constructed out of the Roman and Weiberner Tuffs, and some 30% being out of trachytes and basalts. The main surfaces of the facade and some cornices are built out of tuffaceous rocks. Corner pillars, facings, columns, the socle and a part of the cornice are built out of trachyte and basalt. Only the sculptures and individual portal columns of the west facade are of sandstone.

The mapping has documented the great variety and the quantity of the stones used and provides an insight into building phases. The distribution of the stones in a building, irrespective of the damage, has to be taken into account when planning and carrying out restoration and conservation measures.

The mapping of the weathering forms produces qualitative and quantitative evidence on the weathered state of natural stone buildings. A classification scheme of weathering forms is essential when mapping a building. Such a scheme has been developed on the basis of the results of work carried out on a great number of tuff buildings in the Rhine area. The weathering forms were recorded: this constitutes the basis for a classification scheme which facilitates mapping with great accuracy.

The classification scheme (Table I) contains five main weathering forms, which correlate with the development of a weathering profile and material loss. The main weathering forms are assigned to five categories of damage. Each category is further differentiated according to degree of intensity. The weathering forms can, therefore, be evaluated using these categories. It is possible to produce a modified and more exact record of the condition of the building using six additional separate weathering forms. They involve mineral and biogenic layering which weakens the rock surface, causes disaggregation and can result in loss of material. In addition, there are separate weathering forms which are attributed to mechanical stress. The separate weathering forms, some of which are further differentiated according to level of intensity, can be assigned to the five categories of damage.

The mapping of the weathering forms on the west facade of the St. Quirinus Minster in Neuss was carried out using the classification scheme shown in Table I.

TABLE I: Classification Scheme of the Weathering Forms of Rhenish Tuffs

MAIN WEATHERING FORMS	CATEGORY OF DAMAGE
UNWEATHERED	No damage
Stone surface completely intact	1
Some detachment of small components	1-
DETACHMENT OF SMALL GRANULAR ELEMENTS	Slight damage
Detachment to 5mm over < 50% of stone surface	2+
Detachment to 5mm over > 50% of stone surface	2
Detachment to > 5mm, surface begins to recede	2-
FLAKES, SPALLING	Moderate damage
Loosening to 10mm over < 50% of stone surface	3+
Loosening to 10mm over > 50% of stone surface	3
Loosening to > 10mm, surface starts to recede	3-
SCALES	Severe damage
Scales > than 20mm over < 50% of stone surface	4+
Scales > than 20mm over > 50% of stone surface	4
Scales > than 20mm, surface starts to recede	4-
RECEDING OF SURFACE	Very severe damage
Surface receding to 10mm over > 50% of stone surface	5+
Surface receding > than 10mm over > 50% of stone surface	5
SEPARATE WEATHERING FORMS	
SOOT AND DUST BUILD UP	1-
BIOGENIC LAYERING	2
moss, lichens, algae, higher plants	
EFFLORESCENCES	2-3
slight efflorescences	2
severe efflorescences, salt crusts	3
CRUSTS	2-3
attached crusts	2
detached crusts	3
FISSURING	3-5
slight fissuring	3
moderate fissuring	4
severe fissuring	5
OUTBURSTS	4-5
small outbursts	4
large outbursts	5

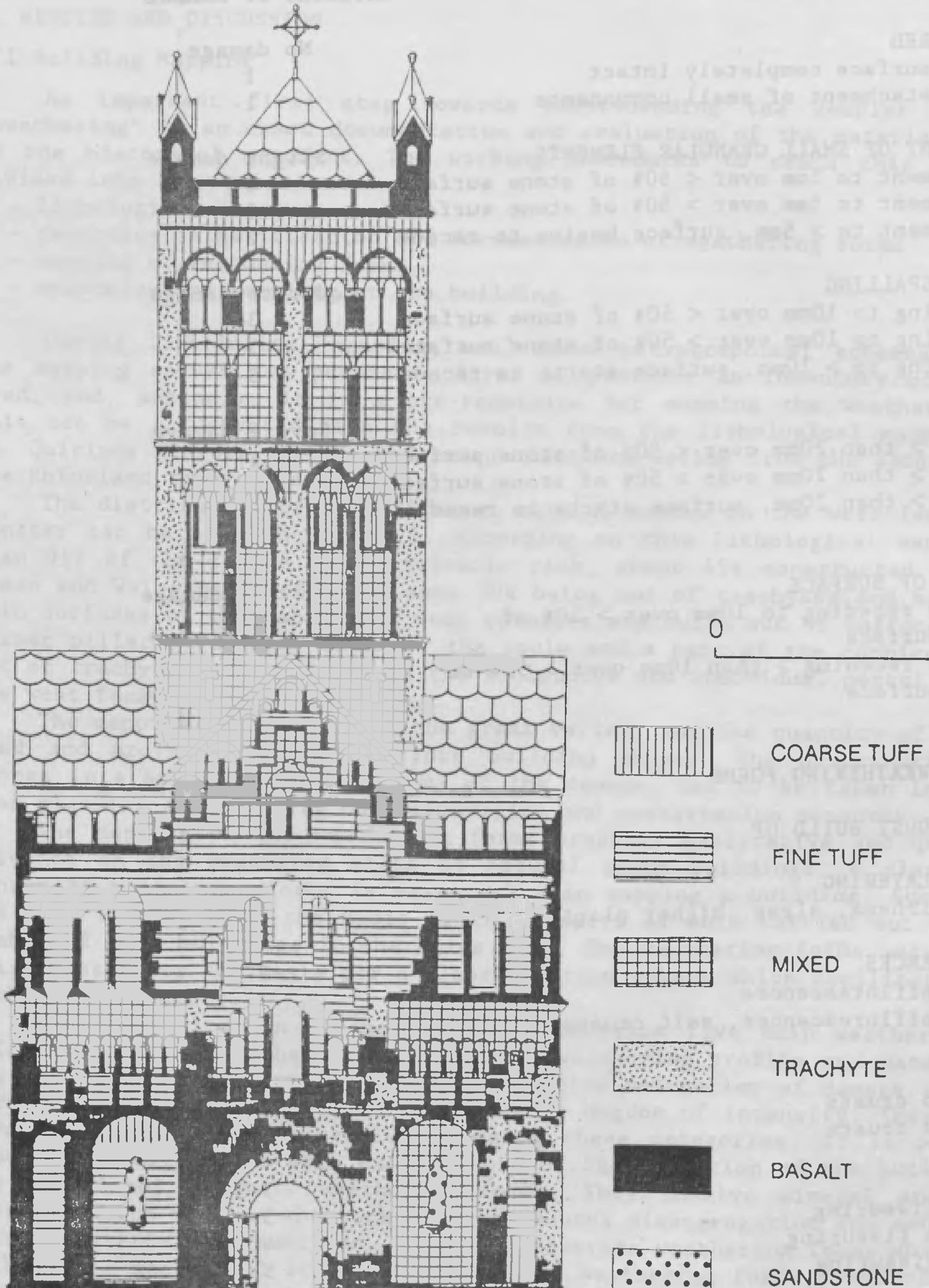


Figure 1: Lithological mapping
West facade of the St. Quirinus Minster in Neuss

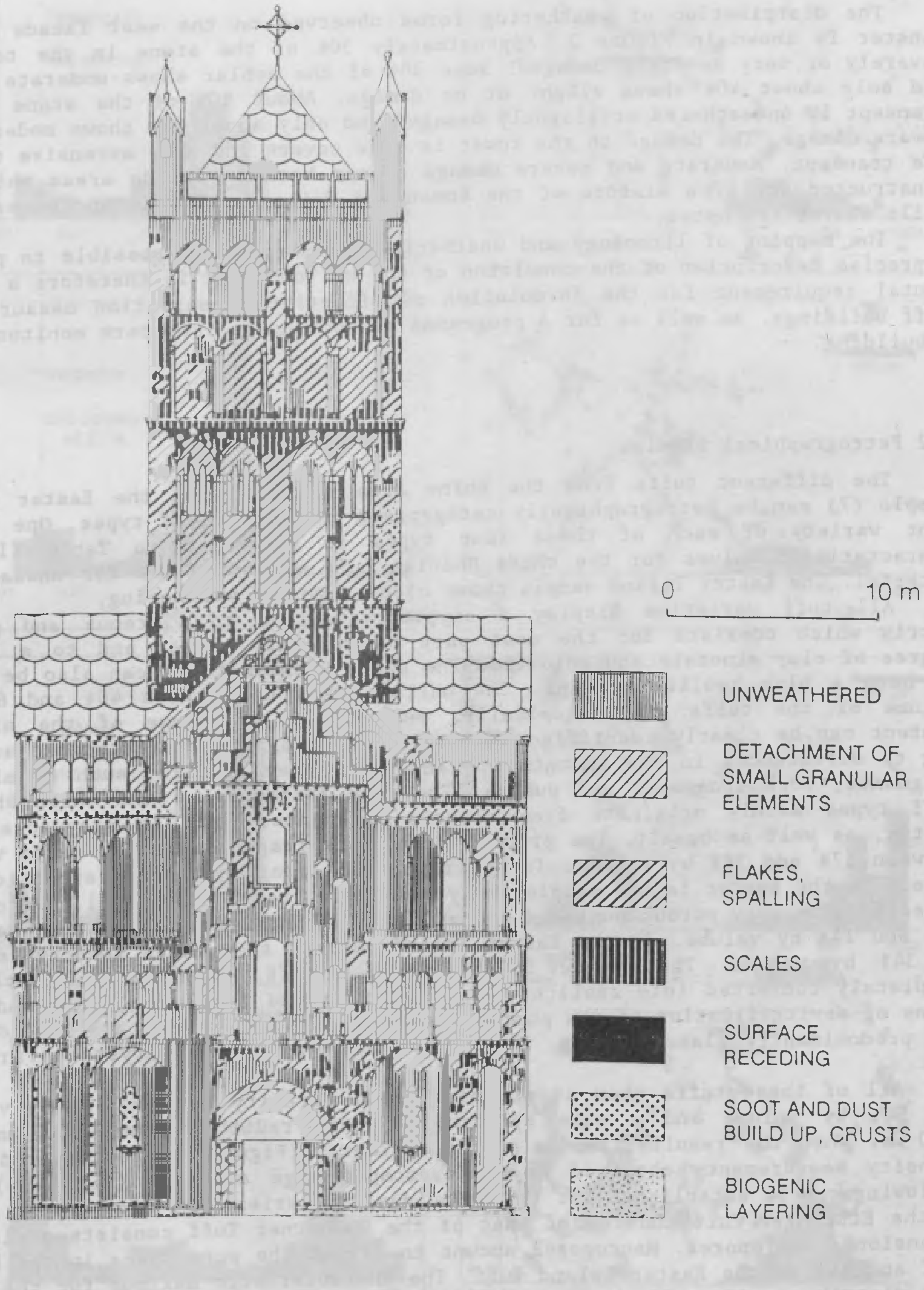


Figure 2: Mapping of weathering forms
West facade of the St. Quirinus Minster in Neuss

The distribution of weathering forms observed on the west facade of the Minster is shown in Figure 2. Approximately 30% of the stone in the tower is severely or very severely damaged, some 30% of the ashlar shows moderate damage and only about 40% shows slight or no damage. About 80% of the stone in the transept is unweathered or slightly damaged and only about 20% shows moderate or severe damage. The damage to the tower is more severe and more extensive than to the transept. Moderate and severe damage appear both on facade areas which are constructed out of a mixture of the Roman and Weiberner Tuffs, and on sections built out of trachytes.

The mapping of lithology and weathering forms makes it possible to produce a precise description of the condition of the building. It is therefore a fundamental requirement for the formulation of effective preservation measures for tuff buildings, as well as for a programme of continuous long-term monitoring of a building.

4.2 Petrographical Studies

The different tuffs from the Rhine area (1) and also the Easter Island sample (7) can be petrographically categorised into four tuff types. One important variety of each of these four types is presented in Table II. The characteristic values for the three Rhenish tuff varieties are for unweathered material. The Easter Island sample shows clear signs of weathering.

All tuff varieties display a cryptocrystalline to vitreous and porous matrix which consists for the most part of volcanic glass, and to a lesser degree of clay minerals and chlorite. The three Rhenish tuffs can also be shown to have a high zeolite content. The matrix makes up between 40% and 60% by volume of the tuffs. Microscopically, only 6-13% by volume of the mineral content can be clearly identified. The tuff varieties are characterised according to differences in the amounts of xenocrysts they contain, such as mineral fragments, rock fragments and pumice. The rock fragments of the three Rhenish tuff types mainly originate from clastic sediments, such as greywackes and slates, as well as basalt. The proportion of rock fragments in the tuffs varies between 17% and 38% by volume. In contrast, rock fragments occur exceptionally rarely in the Easter Island sample. Only basalt in fragments up to 1.5 mm can be detected. The very porous pumice xenocrysts of the Rhenish tuffs make up between 11% and 14% by volume. In the Easter Island variety the pumice xenocrysts make up 34% by volume. The pumice in the Rhenish tuff varieties is partly or completely converted into zeolites. The Easter Island Tuff shows only moderate signs of devitrification of its pumice fragments. The xenocrysts are embedded in the predominantly glassy matrix. The distribution of the xenocrysts is irregular.

All of these tuffs show a very high total porosity between 30% by volume and 50% by volume and a wide spectrum of pore radii between 0.002 µm and 1000 µm. When the results from mercury porosimetry (Figure 3) are compared with porosity measurements obtained from microscope image analysis (Figure 4) the following can be established for the individual varieties: 19% of the pore space of the Ettringer Tuff and 14% of that of the Weiberner Tuff consists of large-dimensioned macropores. Macropores amount to 31% of the pore space in the Roman Tuff and 34% in the Easter Island Tuff. The characteristic maximum for the pore size distribution for all the Rhenish tuffs lies in the pore radius class 0.1 µm to 5 µm. The Easter Island Tuff shows two characteristic maxima. The first is in the radius class > 10 µm; the second is in the radius class < 0.01 µm. This also explains the high specific surface of 34 $m^2 g^{-1}$ of this tuff type.

The weathering forms discussed in chapter 4.1 are controlled by material and structural changes. As a result of these different changes weathering profiles develop.

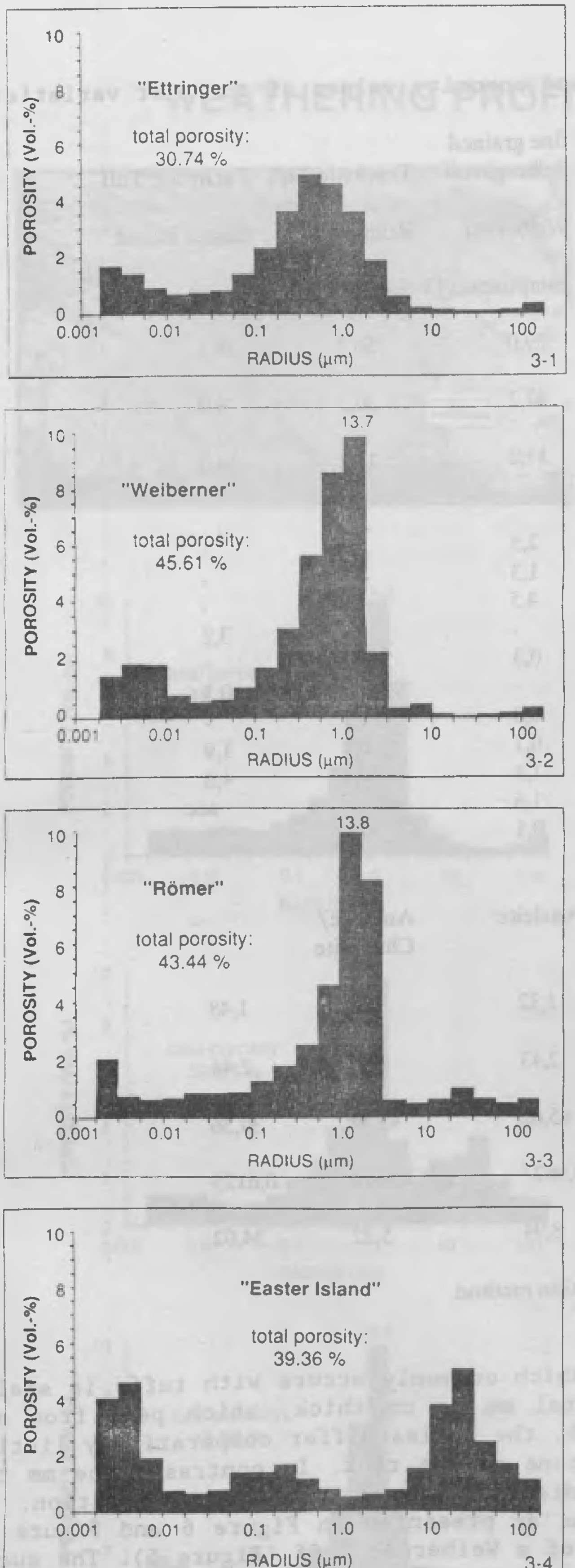


Figure 3: Pore radius distribution - mercury porosimetry

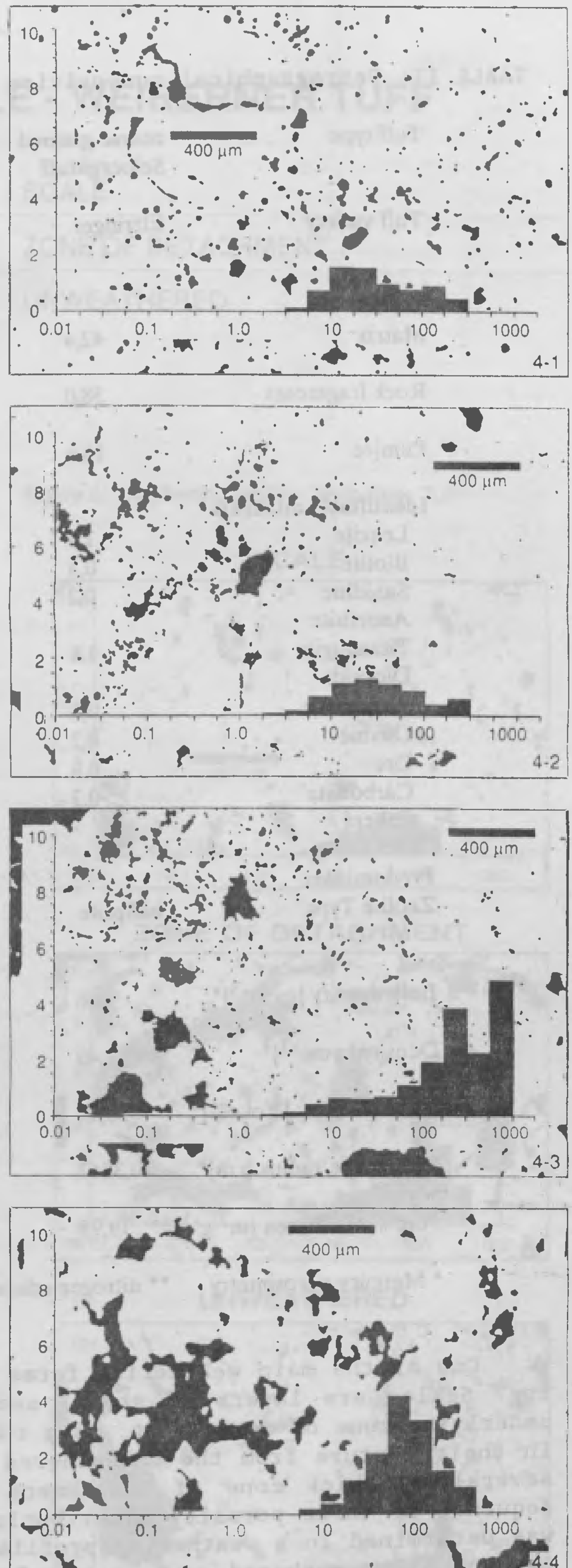


Figure 4: Computer enhanced images of macropores and pore radius distribution - image analysis

TABLE II: Petrographical composition and porosity values of the tuff varieties

Tuff type	coarse grained Selbergittuff	fine grained Selbergittuff	Trachytic Tuff	Tachylitic Tuff
Tuff variety	Ettringer	Weiberner	Roman	Easter Island
		components [Vol.-%]		
Matrix	42,4	59,0	50,2	56,4
Rock fragments	38,0	17,2	30,5	0,9
Pumice	13,6	11,2	13,1	34,0
Identifiable minerals				
Leucite	1,5	2,5	-	-
Biotite	0,3	1,3	-	-
Sanidine	0,2	4,5	4,4	-
Anorthite	-	-	-	3,2
Titanaugite	1,8	0,3	0,1	-
Diopside	-	-	-	0,5
Amphibole	0,9	0,8	1,1	-
Olivine	0,2	0,1	0,4	1,9
Ore	0,8	1,4	0,1	4,0
Carbonate	0,3	1,6	-	acc.
Others	-	0,1	0,1	-
Predominant Zeolite Type	Phillipsite	Analcite	Analcite/ Chabasite	-
Bulk density [$g \cdot cm^{-3}$]*	1,66	1,32	1,35	1,48
Density [$g \cdot cm^{-3}$]*	2,40	2,43	2,39	2,44
Total porosity [Vol.-%]*	30,74	45,62	43,44	39,36
Mean pore radius [μm]*	0,3847	0,9627	1,3512	0,6123
Pore surface area [$m^2 \cdot g^{-1}$]**	19,95	8,94	5,32	34,02

* Mercury porosimetry   ** nitrogen adsorption method

One of the main weathering forms which commonly occurs with tuffs is scaling. Scales are layers of stone, several mm to cm thick, which peel from an underlying zone of detachment. As a rule, the scales differ comparatively little in their texture from the unweathered zone of the rock. In contrast, the mm to several cm thick zone of detachment displays severe textural destruction. A sequence of three porosity distributions as presented in Figure 6 and Figure 7 was determined in a weathering profile of a Weiberner Tuff (Figure 5). The succession of unweathered rock, zone of detachment and scaling corresponds to the spatial succession of unweathered interior to the exposed surface of a building stone from a historical building. In the zone of detachment, a clear increase of large pores emerges. This displacement of the pore radius spectrum in favour of large pores is related to the formation of fractured pores in the zone of detachment, these running parallel and perpendicular to the rock surface. The

WEATHERING PROFILE - WEIBERNER TUFF

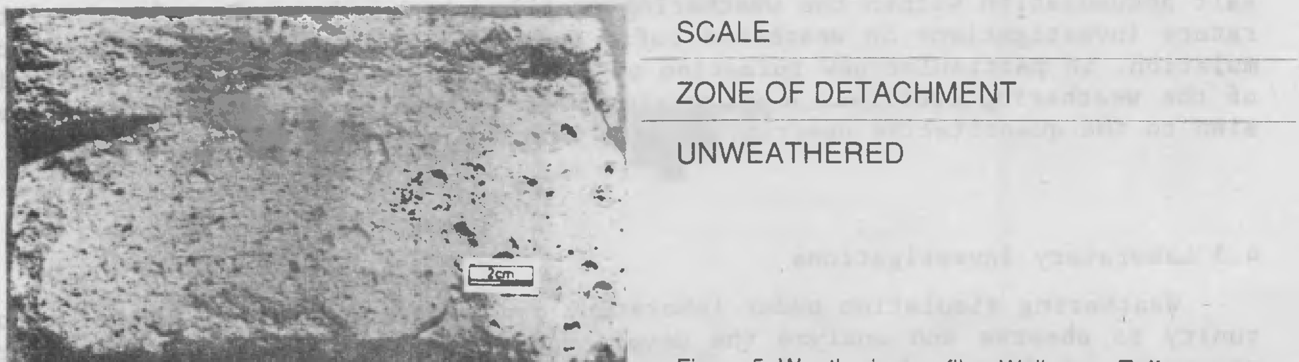


Figure 5: Weathering profile - Weiberner Tuff

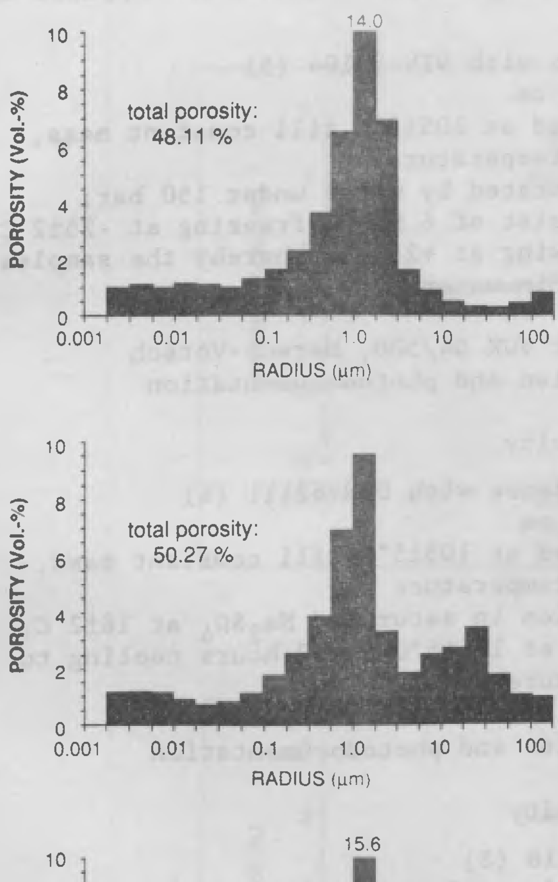


Figure 6: Pore radius distribution
- mercury porosimetry

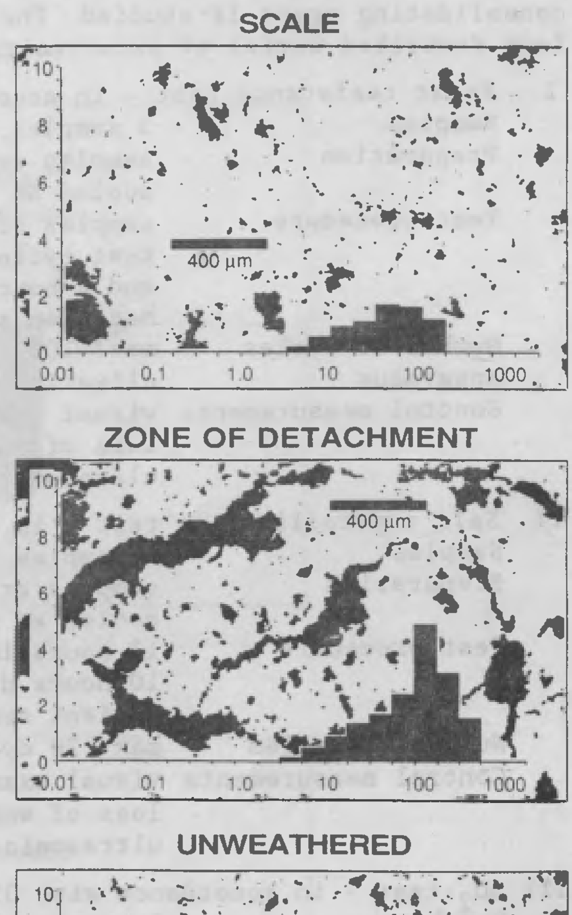


Figure 7: Computer enhanced images of macropores
and pore radius distribution - image analysis

scale shows fewer large pores than the unweathered area. This compaction effect results from the near-surface accumulation of gypsum and mirabilite aggregates.

There is a direct connection between the process of scale development and salt accumulation within the weathering profile. As has been shown by the laboratory investigations on weathered tuffs from the building area, sulphate accumulation, in particular new formation of gypsum, can be detected in the majority of the weathering profiles. A weathering profile such as this adds a new dimension to the quantitative description of a weathering form.

4.3 Laboratory Investigations

Weathering simulation under laboratory conditions provides a further opportunity to observe and analyze the development of damage. The important natural processes of freeze-thaw cycles and salt crystallization and the influence of pollutants are reproduced on laboratory scale. Additionally, the efficiency of a consolidating agent is studied. The following test conditions are applied to the four described series of experiments .

I Frost resistance test - in accordance with DIN 52104 (5)

Samples	5 samples 5x5x5 cm
Preparation	samples are dried at 105±5°C till constant mass, cooled at room temperature
Test procedure	samples are saturated by water under 150 bar; test cycles consist of 6 hours freezing at -25±2°C and 6 hours thawing at +25±2°C whereby the samples had been stored in water
Number of cycles	max. 100 cycles
Apparatus	climatic chamber VUK 04/500, Hereus-Vötsch
Control measurements	visual examination and photodocumentation loss of weight ultrasonic velocity

II Salt crystallization test - in accordance with DIN 52111 (6)

Samples	5 samples 5x5x5 cm
Preparation	samples are dried at 105±5°C till constant mass, cooled at room temperature
Test procedure	12 hours immersion in saturated Na_2SO_4 at 18±2°C; 10 hours drying at 105±5°C and 2 hours cooling to ambient temperature
Number of cycles	max. 20 cycles
Control measurements	visual examination and photodocumentation loss of weight ultrasonic velocity

III SO_2-test - in accordance with DIN 50018 (8)

Samples	5 samples 2x3x0,5 cm; 5 powder samples
Preparation	samples are dried at 105±5°C till constant mass, cooled at room temperature; preparation of powder samples
Test procedure	8 hours in atmosphere of 100% rel. humidity, 35±2°C 2000 ppm SO_2; 16 hours cooling to ambient temperature and atmosphere
Number of cycles	max. 20 cycles
Apparatus	Kesternich chamber
Control measurements	visual examination and photodocumentation X-Ray diffraction SEM

DIFFERENCE PORE RADIUS DISTRIBUTION

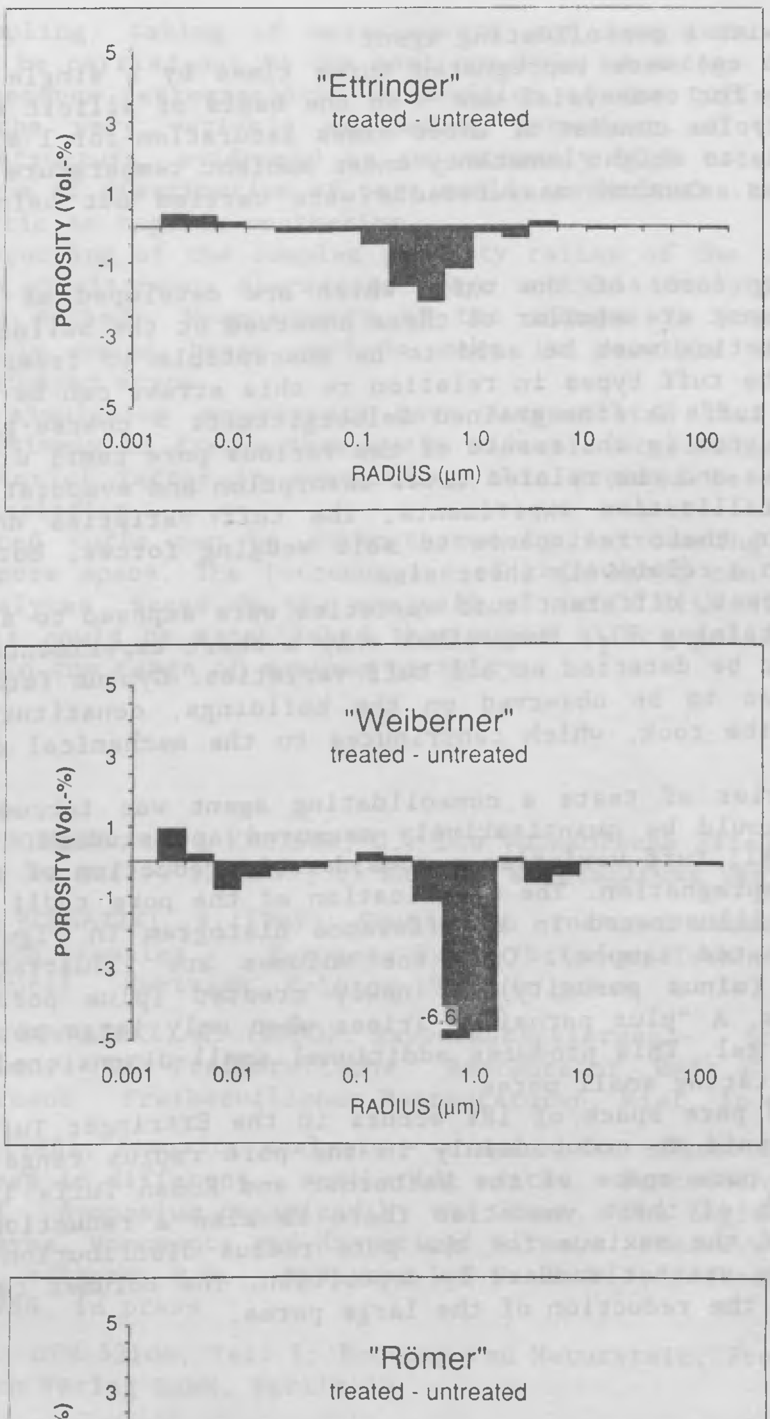


Figure 8: Changes in pore radius distribution after deposition of silica gel

IV Impregnation with a consolidating agent
Samples (5x5x5 cm) were impregnated three times by a single component system - ready for commercial use - on the basis of silicic ester. The impregnation cycles consist of three times saturation for 1 minute with later drying up to weight constancy under ambient temperature and humidity conditions. Control measurements were carried out using mercury porosimetry.

The weathering forms of the tuffs which are developed as a result of a freeze-thaw experiment are similar to those observed at the building. In principle, all tuff varieties must be said to be susceptible to freeze-thaw stress. The stability of the tuff types in relation to this stress can be shown as a sequence: trachytic tuffs > fine-grained Selbergittuffs > coarse-grained Selbergittuffs. This sequence is the result of the various pore radii distributions of the three tuff types and the related water absorption and evaporation behaviour.

In salt crystallization experiments, the tuff varieties do show a very slight variation in their resistance to salt wedging forces, but they are all severely damaged in a relatively short time.

In a further test, different tuff varieties were exposed to a water-saturated atmosphere containing SO_2. Even after only a short experimental time newly-formed gypsum could be detected on all tuff varieties. Gypsum formation such as this, which is also to be observed on the buildings, constitutes a chemical alteration within the rock, which contributes to the mechanical destruction of the rock texture.

In a last series of tests a consolidating agent was introduced into the pore space which could be quantitatively measured and studied. Silica gel is such an agent. In all tuff varieties a considerable reduction of the entire porosity occurs on impregnation. The modification of the pore radii by the silica gel deposition is illustrated in a difference histogram in Figure 8 (treated sample minus untreated sample). Only the volumes are illustrated, as being either eliminated (minus porosity) or newly created (plus porosity) by the silica gel deposits. A "plus porosity" arises when only large pores are partly filled with silica gel. This produces additional small-dimensioned pores, which are added to the existing small pores.

A reduction of pore space of 18% occurs in the Ettringer Tuff. Silica gel deposition can be said to occur mainly in the pore radius range of 0.1 µm to 1.0 µm. 32% of the pore space of the Weiberner and Roman Tuffs is filled with silica gel. In both of these varieties there is also a reduction of porosity within the range of the maximum for the pore radius distribution. Pore spaces with radii < 0.01 µm are not reduced by deposition. The volumes remain constant or increase through the reduction of the large pores.

5. CONCLUSIONS

In order to be able to quantitatively record the weathered state of a natural stone historical monument both accurate investigations at the building and diverse laboratory work are necessary. The work at the building includes registering and mapping the type of building stones and their state of weathering. As a rule, the mapping of the weathering forms comprises the more important and labour-intensive part of the work.

A classification scheme was developed so that the damage to the tuffs could be mapped according to objective criteria. It covers all the weathering forms specific to tuffs. These different weathering forms are assigned to five damage categories to facilitate an evaluation of the state of the damage. Mapping the lithology and weathered state therefore constitutes a necessary pre-requisite for all restoration measures. The results of this mapping can also be used to ensure that sampling, taking of measurements and long-term monitoring of a building can all be carried out to the best possible advantage.

The heterogeneous petrographical composition of the tuffs is an important reason behind the very variable weathering behaviour of these rocks. The "chaotic" pore structure, evidenced by an extremely high total porosity and a very wide spectrum of distribution of pore radii, constitutes the most important rock characteristic as regards weathering.

The real recording of the complex porosity ratios of the tuffs can only be achieved through simultaneous microscope image analysis investigations and mercury porosimetry methods. Measurements of the changes in porosity within the weathering profile using these methods make it possible to quantitatively describe the weathered state.

Weathering simulation experiments have demonstrated that tuffs generally react very sensitively to freeze-thaw cycle and salt crystallization processes. The deciding material factor in controlling this process is the value of the porosity characteristics.

The weathered tuffs can be strengthened by introducing a consolidating agent into the pore space. The introduction of this agent can be planned using the porosity analyses. Based on the analysis of tuffs with different porosity distributions, it could be established that major silica gel deposition always takes place within the range of maximum porosity.

6. REFERENCES

1. FRECHEN, J., HOPMANN, M. & KNETSCH, G.: Die Vulkanische Eifel; Geologische Reihe, Bd. 2, 4. Aufl., 33 Abb., 17 Karten; W. Stollfuss Verlag, Bonn
2. FITZNER, B. & KOWNATZKI, R.(1989): Studies on natural stone monuments - methodology and examples.- European Symp. "Science, Technology and European Cultural Heritage, Bologna 1989, in press
3. FITZNER, B. & KOWNATZKI, R. (1990): Bauwerkskartierung - Schadensaufnahme an Natursteinen. - Der Freiberufliche Restaurator, Heft 4, S.25-40, Hrsg. Deutscher Verband Freiberuflicher Restauratoren, Kiel, in press
4. FITZNER, B. (1988): Porosity analysis - a method for characterization of building stones in different weathering states.- Proceedings of an International Symposium organized by the Greek, "The Engineering Geology of Ancient Works, Monuments and Historical Sites, Preservation and Protection", vol.4, editors: P.G. Marionos & G.C. Koukis, Balkema-Rotterdam-Brookfield 1988, in press
5. ANONYM (1982): DIN 52104, Teil 1; Prüfung von Naturstein, Frost-Tau-Wechsel Versuch; Beuth Verlag GmbH, Berlin 30
6. ANONYM (1989): DIN 52111; Prüfung von Naturstein und Gesteinskörnungen, Kristallisationsversuch mit Natriumsulfat; Beuth Verlag GmbH, Berlin 30
7. CHAROLA, A.E. & LAZZARINI, L. (1988): The statues of Easter Island: Deterioration and conservation problems.- in: Wiener Berichte über Naturwissenschaft in der Kunst, Hrsg.: VENDL, A. et al., 4/5, 392-401, Verlag Orac, Wien
8. ANONYM (1987): DIN 50018; Beanspruchung im Schwitzwasser-Wechselklima mit schwefeldioxidhaltiger Atmosphäre (Gerät nach Kesternich); Beuth Verlag GmbH, Berlin 30

ensure that sampling, taking of measurements and long-term monitoring of a building can all be carried out to the best possible advantage.

The heterogeneous petrographical composition of the tuffs is an important reason behind the very variable weathering behaviour of these stones. The "chaotic" pore structure evidenced by an extremely high total porosity and a very wide spectrum of distribution of pore radii constitutes the most important rock characteristic as regards weathering.

The real recording of the complex porosity ratios of the tuffs can only be achieved through simultaneous microscope image analyses and capillary and mercury porosimetry methods. Measurements of the changes in porosity within the weathering profile using these methods make it possible to quantitatively describe the weathered state.

Weathering simulation experiments have demonstrated that tuffs generally react very sensitively to freeze-thaw and salt crystallization processes. The deciding material factor in controlling this process is the value of the porosity characteristics.

The weathered tuffs can be strengthened by introducing a consolidating agent into the pore space. The introduction [illegible] the porosity analyses. Based on the [illegible] distributions, it could be established [illegible] takes place within the range of maximum [illegible]

6. REFERENCES

1. BRECHEN [illegible] Beiträge.

2. FITZNER, B. & KOWNATZKI, R. [illegible] stone monuments methodology and examples. [illegible] European Cultural [illegible] in press

3. FITZNER, B. & [illegible] Naturwerksteine [illegible] Deutscher Verband [illegible] in press

4. FITZNER, B. (1988): Porosity properties - a method for characterization of building stone in different weathering states. Proceedings of an International Symposium organized by the Greek [illegible] The Engineering Geology of Ancient Works, Monuments and Historical Sites, [illegible] Balkema Rotterdam/Brookfield 1988, in press

5. ANONYM (1982): DIN 52104, Teil 1: Prüfung von Naturstein, Frost-Tau-Wechsel Versuch; Beuth Verlag GmbH, Berlin 30

6. ANONYM (1989): DIN 52111; Prüfung von Naturstein und Gesteinskörnungen, Kristallisationsversuch mit Natriumsulfat; Beuth Verlag GmbH, Berlin 30

7. CHAROLA, A.E. & LAZZARINI, L. [illegible] Naturwissenschaft in der [illegible] Verlag Graz, Wien

8. ANONYM (1987): DIN 52016 [illegible] Beuth Verlag GmbH, Berlin 30

TEXTURE AND MECHANICAL DISGREGATION OF TUFFS FROM ITALY AND ECUADOR

R. ROSSI-MANARESI and A. TUCCI

Fondazione Cesare Gnudi, 40126 Bologna, Italy

ABSTRACT

The pore structure of two tuffs was investigated by measurement with a mercury porosimeter. The high percentage of adsorption pores explains the disruptive effect of wetting-drying previously observed; differences in pore-size distribution shown by the two tuffs are also in agreement with their different resistance to this stress.
Salt crystallization pressures were calculated on the basis of pore-size distribution: the results are in agreement with the results of a previous laboratory study and observations in the field regarding one of the tuffs in particular.
The results show the clear relationship between texture and mechanical failure of these stones.
The possibility and requirements for preservation treatments are also discussed.

RESUMEN

La estructura porosimétrica de dos tipos de tobas fue investigada por porosimetría de mercurio. El alto porcentaje de poros de adsorpción explica el efecto destructivo de ciclos húmedo-seco observado previamente. Las diferencias en distribuciones porosimétricas concuerda con las distintas resistencias presentadas por estas tobas a los ciclos mencionados. Las presiones de cristalización de sales fueron calculadas en base a la distribución de tamaños de poros: los resultados concuerdan con los obtenidos en un trabajo experimental anterior y con observaciones de terreno, sobre todo respecto a una de las tobas. Los resultados muestran una clara relación entre la textura y la falla mecánica de estas piedras. Se discute la posibilidad y los requerimientos para tratamientos de conservación.

1. INTRODUCTION

The volcanic tuffs quarried in the areas of Naples and Cochasqui (Ecuador) show various similarities (1, 2, 3). In particular, both tuffs, have very high open porosity (almost 50%), absorb enormous amounts of water very rapidly and the stress caused by wetting-drying appears to be a main cause of decay of both materials. But the resistance to this stress is different: it leads to much more rapid crumbling of the Ecuador tuff than the Italian one.

It was thought that a more detailed study of the stone textures could allow a better understanding of the deterioration processes and provide evidence of similarities and differences between the two tuffs.

Therefore pore structures were investigated by measuring total porosity, pore-size distribution and specific surface area of stone specimens with a mercury porosimeter.

The experimental results were also used for calculating salt crystallization pressure which is without doubt involved in the decay process of the Naples tuff and, presumably, could also play a part in the deterioration of the Ecuador tuff.

The results obtained are reported and discussed in the present paper.

2. MATERIALS

2.1 The Naples tuff

The previous research was carried out on decayed and well preserved stones from Castel dell'Ovo, on the Naples bay, as well as on the pristine stone from various local quarries (1).

This is a vitreous welded tuff consisting mainly of large quantities of pumice fragments with minor phenoclast and rock fragments. Among the pore filling minerals there are frequently zeolites.

Initially stone decay takes place in the form of crumbling away of exposed surfaces, as clearly shown by walls rebuilt only 15 years before.

In weathered stone speciens, with the surface largely worn away, no variations in composition and structure were observed in the exposed portion with respect to the interior. This indicates a physical-mechanical mechanism of decay rather than chemical, as the latter would cause variations in depth when occuring in a porous stone.

Similar indications regarding the type of decay mechanism came from the slight differences in physical characteristics shown by the different types of specimens examined, which appeared to be correlated to different stone origin rather than to stone weathering: for instance, the higher values of porosity and water absorption coefficient were detected in quarry specimens.

In conclusion, analytical results, weathering tests and indications obtained "in situ" suggested that the tuff decay depends mainly on water imbibition and crystallization of sodium chloride absorbed from the atmosphere and, in the case of Castel dell'Ovo, also directly as sea water spray.

According to Lewin and Charola (4) the strain produced in the crystal lattice of chabazite (the principal zeolite) if calcium is exchanged by sodium ions could result in fracturing of crystal grains and consequent crumbling of the stone. Therefore this ion exchange process and the susceptibility of zeolites to hydrolisis should be, according to the opinion of these authors, responsible for a significant part of the tuff decay. Were this hypothesis correct it would mean that the porosity of a surface portion many centimeters thick (NaCl has been detected at great depth) should be higher than the inside not reached by sea water. But this is not the case, as already mentioned.

Therefore, in our opinion, ion exchange and hydrolisis processes play a minor role with respect to the disruptive effects of water imbibition and sodium chloride crystallization processes.

2.2 <u>The Ecuador tuff (cangagua)</u>

The "cangagua", a slightly hardened volcanic tuff, is the building material of the "tolas", funeral tumuli constructed by the pre-Inca civilization of the Caranquis, in Cochasqui, Ecuador.

Previous investigation were carried out on specimens obtained from Cochasqui (2,3). They have shown that the material is a phenoandesitic tuff made up by a chaotic aggregate of crystalline and lithic fragments (about 50% of the rock) immersed in a matrix consisting of consolidated vitreous powder. The crystalline fragments are mainly plagioclase, green hornblende and small quantities of pyroxenes. The lithic fragments consist of a basic vitreous or microcrystalline mass in which phenocrysts of plagioclase and green hornblende are immersed. The stone shows very poor cohesion (compressive strength about 15 kg/cm^2) and, as already said, is highly porous and water permeable.

The differences between cangagua and Naples tuff as regard to water absorption and its effect should be pointed out. Cangagua absorbs by capillarity about 10 kg/m^2 water in about 4 minutes; Naples tuff absorbs water a little slower, 3-7 kg/m^2 in the same time. Cangagua crumbles on simple immersion in water: after one or two wetting-drying cycles fairly large fragments break off the specimen and after 3-4 cycles the specimens are completely crumbled. Naples tuff is relatively more resistant: after 3-5 wetting-drying cycles only a few, small surface cracks appear and 15-18 cycles are necessary for increasing the number and depth of cracks or for the occurrence of scaling which exactly reproduce a deterioration phenomenon observed "in situ".

3. EXPERIMENTAL RESULTS

The specimens of Naples tuff and cangagua used for the experimental measurements with the mercury porosimeter were cut from the same blocks that the samples used for the previous studies were taken from. Therefore the results obtained can be precisely compared with the preceeding ones.

The results concerning two specimens from two different blocks of Naples tuff and a specimen from the single cangagua block previously investigated, are reported in Table I as representative examples af all measurements carried out.

Table I - Experimental Results

	Naples Tuff				Cangagua	
Sample No	2		3		6	
Bulk Density (g/cm^2)	1.19		1.19		1.34	
Specific surface area, (m^2/g)	16.74		15.02		18.84	
Total Porosity (v%)	47.6		51.4		40.4	
Pore-size distribution (μm)	A	B	A	B	A	B
r<0.01	2	0.95	3	1.54	10	4.04
0.01<r<0.05	25	11.90	19	9.77	21	8.48
0.05<r<0.1	15	7.14	5	2.57	4	1.62
0.1<r<0.5	22	10.47	14	7.2	15	6.06
0.5<r<1	5	2.38	5	2.57	13	5.25
1<r<5	28	13.32	15	7.71	15	6.06
5<r<10	2	0.95	11	5.65	2	0.81
10<r<100	2	0.95	26	13.36	19	7.68

A = Percent of total porosity B = Pore volume %

The specific surface areas are very high for all samples. This is not only due to the high porosity, but also to the great percentage of very fine pores.

The total porosities of Naples tuff are in agreement with those previously determined by saturation with water under vacuum (for the kind of specimens reported in Table I: 48.5% and 52.0% respectively).

On the contrary, the present value of cangagua total porosity is slightly less than those determined by saturation with water under vacuum (47.7%) and by the Kobe method (evaluation of air volume that fills the interconnected pores) which was 48.8%. The present lower value is probably due to the limits of the mercury porosimeter which cannot measure pores with radii less than about 0.005 µm. Therefore it can be deduced that, besides an higher total porosity, cangagua also has a higher percentage of pores with radii less than 0.01 µm than that indicated in Table I. More precise measurements with another method will be carried out to assess this hypothesis.

4. FAILURE BY WATER ADSORPTION

The mechanism of disgregation from water adsorption has been described by Hudec as follows (5). The water molecules structure themselves in an ordely manner on the walls of the pores and adhere to them; a number of molecular layers of water can be so structured, depending on the wall surface forces. Structured water (adsorbed) is rigid, similar to crystals. Therefore, if the pore is small enough, the rigid water fills its entire volume and can exert pressure on the pore walls. By wetting-dryng, the stone is alternatively stressed by the adsorbed water and unstressed when the water evaporates. The fatigue due to sorption-desorption can lead, more or less rapidly, to disgregation.

The pores that can be totally filled with adsorbed water (adsorption pores) are those with radii less than 0.5 µm (6). It can be seen in Table I that in Naples tuff 40-60% of pores are adsorption pores and they represent 20-30% of the stone volume. The high pressure due to water adsorption which can be developed in this structure can exceed the compressive strength and lead to disruption. But actually this disruptive stress appears mainly to occur in a rather thin subsurface zone, although water easily penetrates Naples tuff in great depth. For an explanation, it should be taken into account that the effectivenes with which water penetrates into the stone depends on the amount of capillary pores (radius between 0.5 and 5 µm) and pores with radii greater than 5 µm allowing the passage of free water (6), because the adsorption pores (radius less than 0.5 µm) are filled with oriented water, and consequently are not able to allow the passage of fluid. Therefore, adsorption pores are more likely to be completely filled in the zone close to the exposed surface, also because it is there that all water absorbed in depth is gradually drawn during drying, and the filling of the finest pores may likely occur also at the expense of the inside water migrating through the capillary network.

The total adsorption pore volume of cangagua is more or less similar to that of Naples tuff; but the percentage of smallest adsorption pores (with radius less than 0.01 μm) is more than three times that in Naples tuff and, as already said, possibly even higher. Therefore complete filling of adsorption pores is easier and the pressure developed is higher because it shows an inverse relationship with the pore radius. The higher pressures exerted on the pore walls can easily exceed the very low compressive strength of the tuff and lead to disgregation more rapidly with respect to Naples tuff.

The easier complete filling of pores with adsorbed water, the higher pressure developed and the lower stone cohesion may also explain why the disruptive effect of water adsorption develops not only close to the surface of cangagua, as in Naples tuff, but more in depth. In fact, all the above factors can result in rapid surface fracturing. Then the fractures give water direct access to interior adsorption pores. Therefore, very few wetting-drying cycles are sufficient for complete crumbling of the specimens.

5. FAILURE BY SALT CRYSTALLIZATION

Crystallization of sodium chloride certainly plays a part in Naples tuff decay. Salt crystallization can also play a role in cangagua decay, even if no investigation has been carried out in this regard. Therefore, it can be useful to calculate the crystallization pressures which can develop in these stones, of course, if enough soluble salts are present to produce the necessary supersaturated salt solution (7).

Crystallization pressure has been discussed in thermodynamic terms by Fitzner and Snethlage (8) by analogy with the thermodynamics of frost mechanisms in porous materials developed by Everet (9). According to these theoretical considerations we have already calculated the crystallization pressures which can build up in a number of stones (10, 11); due to the lack of space we refer to that paper for the method details.

The calculation is based on the experimental pore-size distribution and on a model of pore geometry assuming that all small pores of radius r are connected to large pores of radius R where salt crystals grow preferentially.

On the basis of pore-size distribution, it can be assumed that, in the present tuffs, crystals grow preferentially in pores with a radius greater than 1 μm. The pressure can be calculated which develops if crystallyzation takes place also in the smaller pores, when the larger ones are filled with crystals.

Five classes of the smaller pores are considered with pore radii in the following ranges (μm), the ranges already considered in Table I:

$r<0.01$; $0.01<r<0.05$; $0.05<r<0.1$; $0.1<r<0.5$; $0.5<r<1$

with the median radii 0.005, 0.030, 0.075, 0.30 and 0.75, respectively.

The median radii of the pore classes are taken as r values to calculate the respective crystallization pressure (p) according to the equation:

$$p = \frac{2\sigma}{r}$$

where σ is the surface tension between solid and liquid which is taken as equal to 80 dyne/cm.

The calculated pressures for the above classes of pores are 3200, 533, 213, 53, 21 N/cm^2 respectively.

To calculate the effective pressure wich can build up in the stone, it is necessary to take into account the volume percent of small pores of each class, V_r (values B in Table I) which should be related to the volume percent of large pores (with radius greater then 1 μm), V_R. Therefore the effective crystallization pressures related to each class of pores are obtained by multiplying the relative theoretical values of pressure with the factor V_r/V_R. The V_r/V_R values for each class of pores and the crystallization pressures are reported in Table II.

Table II - Crystallization Pressure

Class of pore size (μm)	Naples Tuff 2 C	Naples Tuff 2 D	Naples Tuff 3 C	Naples Tuff 3 D	Cangagua 6 C	Cangagua 6 D
a) $r<0.01$	0.06	192	0.06	192	0.28	896
b) $0.01<r<0.05$	0.78	416	0.37	197	0.58	309
c) $0.05<r<0.1$	0.47	100	0.01	2	0.11	23
d) $0.1<r<0.5$	0.69	37	0.27	14	0.42	22
e) $0.5<r<1$	0.16	3	0.01	0	0.36	8
Total pressure (N/cm^2)		748		405		1258

C = V_r/V_R D = Crystallization pressure (N/cm^2)

Theoretical crystallization pressure:
a = 3200, b = 533, c = 213, d = 53, e = 21 N/cm^2

The total pressures which can build up in Naples tuff are rather high and presumably exceed the strengh of the material which, based on the analysis of thin sections under the petrographic microscope, showed low cohesion (1). The resulting stress can lead to mechanical failure.

The total pressures which can be generated in cangagua are much higher and greatly exceed the compressive strength of the material which is only 15 kg/cm^2, i.e. 150 N/cm^2 (2). If enough soluble salts are present in this tuff, mechanical failure can be very rapid.

CONCLUSION AND DISCUSSION

The results obtained indicate that the particular pore structure of these two tuffs, showing a very high volume of adsorption pores, can actually be responsible for the easy disgregation they undergo by mechanical stress due to adsorbed water. The more rapid failure of cangagua with respect to Naples tuff is also explained on the basis of pore-size distribution. In fact cangagua, besides a lower strengh, also shows an higher percentage of adsorption pores with the smallest radii and therefore it is subjected to higher pressure due to water adsorption.

The high crystallization pressure which can build up (depending on the pore structure) can also explain the disgregating effect of salt crystallization which certainly plays a role in the decay of Naples tuff and could play a higher role in the cangagua deterioration if, due to environmental conditions, soluble salts are absorbed by the stone.

The results concerning cangagua may probably be compared with those of a recent study regarding the volcanic tuff ("Rano Raraku") of the "moais", the famous statues of Easter Island (12), because the petrographic characteristics of these two tuffs show some similarities, at least both have a vitreous matrix. The authors suggest that the frequent strong rain on the island is probably the single most significant deterioration factor and that rain acts upon the sculptures mechanically, by eroding the softer components in the stone, and chemically, by selective dissolution of alkali in the vitreous matrix which can cause it to crack.

It should be interesting also to carry out an investigation of the physical characteristics of the Easter Island tuff, an analysis of pore structure, and wetting-drying weathering tests, to check if the decay due to rain water also involves the stress due to water adsorption, as in the case of cangagua.

The cangagua in the Cochasqui monuments is certainly subjected to a local climate of heavy rains and it seems clear that rain water is here too the most significant deterioration factor. The action of water suggested for the Easter Island tuff may contribute synergistically also to cangagua decay. But the process of selective dissolution of alkali in glass is a rather slow process (13) while, as shown by wetting-drying tests, impregnation with water has an immediate disruptive effect. Therefore, in this case, the most significant deterioration process is the mechanical disgregation caused by the stress due to water adsorption.

To prevent the deleterious action of water (and also sea water) on these kinds of stone, it is first of all necessary to prevent entrance of water by impregnating in depth with an hydrophobic product. In this connection it is significant to note our general experience about conservation treatment of porous stone already summarized (14, 15). The application of a water repellent only to the surface of a porous stone cannot provide effective protection, particularly if the stone is subjected to heavy rain; and even if it has undergone a previous consolidation treatment, because advisable consolidation treatments leave a highly porous stone still very porous.

On the contrary, impregnation in depth with a water repellent (even without a previous consolidation treatment) can produce by itself very good resistance to alteration processes. In particular, this was clearly demonstred by the results of wetting-drying tests carried out on treated cangagua. Cubes of cangagua impregnated with an hydrophobic product (Transkote, aluminium stearate) were very effectively protected against wetting-drying deterioration, much better protected than the cubes impregnated with ethyl silicate, and slightly better protected than the cubes impregnated with ethyl silicate followed by impregnation with Transkote (2, 3).

A final point should be emphasized: these tuffs have a very fine pore structure; therefore it is necessary to assess the possibility of penetration in depth and homogeneous distribution of the conservation products before use in the field. As an example, a commercial product contening an oligomeric alkylalkoxysiloxane and ethylsilicate (Wacker H), which has given good results for the preservation of various types of stone, showed a very poor penetration in Naples tuff and consequently a very low preservative effect (1).

REFERENCES

1. Rossi-Manaresi, R.; in Proceeding of the 2nd International Symposium on Deterioration of Building Stone, Athens, 1976, pp.233-247

2. Rossi-Manaresi, R.; Pellizer, R.; in Proceedings of the 3rd International Congress on Deterioration and Preservation of Stones, Venezia, 1974, pp.605-611

3. Rossi-Manaresi, R.; Chiari, G.; in Proceeding of the Third International Symposium on Mudbrick (Adobe) Preservation, Ankara, 1980, pp.29-38

4. Lewin, S.Z.; Charola, A.E.; Advances in X-Ray Analysis, 1979, 22, 169-180

5. Hudec, T.P.; in "Decay and Preservation of Stone", Winkler, E.M., Ed.; The Geological Society of America, Boulder Co., 1978, pp.3-6

6. Nieminen, P.; Uusinoka, R.; in Proceeding of International Symposium on the Engineering Geology of Ancient Works, Monuments and Historic Sites, Athens, 1988, Marinos, P.G., Koukis, G.C., Eds.; Balkema, Rotterdam, 1988, pp.809-813

7. Lewin, S.Z.; "The Susceptibility of Calcareous Stone to Salt Decay" in Proceeding of the International Symposium on the Conservation of Monuments in the Mediterranean Basin, Bari, 1989 (in press)

8. Fitzner, B.; Snethlage, R.; G.P.News Letters (Group Petrography of the ICOMOS Stone Committee), 1982, 3, 13-24. See also: Snethlage, R.; "Steinkouservierung 1979-1983", Bayer Landesamt f. Denkmalpflege, Munchen, 1982

9. Everet, D.H.; Trans. Faraday Soc., 1961, 57, 1541-1551

10. Rossi-Manaresi, R.; Tucci, A.; "Pore Structure and Salt Crystallization: 'Salt decay' of Agrigento Biocalcarenite and 'Case hardening' in Sandstone" in Proceeding of the International Symposium on the Conservation of Monuments in the Mediterranean Basin, Bari, 1989 (in press)

11. Rossi-Manaresi, R.; Tucci, A.; "Pore Structure and Disruptive or Cementing Effect of Salt Crystallization in Various Types of Stone", Studies in Conservation (accepted for pubblication)

12. Charola, A.E.; Lazzarini, L.; Wiener Berichte uber Naturwissenschaft in der Kunst, 1987/88, 4/5, 392-401

13. Rossi-Manaresi, R.; Tucci, A.; in Proceeding of the 2nd International Conference on Non-Destructive Testing, Microanalytical Methods and Environment Evaluation for Study and Conservation of Work of Art, Perugia, 1988, V/9

14. Rossi-Manaresi, R.; in Proceeding of the IIC Congress on Science and Technology in the Service of Conservation, Washington D.C., 1982, pp.39-45

15. Rossi-Manaresi, R.; Bollettino d'Arte, 1987, 41 (supplemento "Materiali lapidei"), 133-144

THE VOLCANIC ROCKS OF THE MONUMENTS OF THE FORUM AND PALATINE (ROME): CHARACTERIZATION, ALTERATIONS, RESULTS OF CHEMICAL TREATMENTS

P. L. BIANCHETTI, G. LOMBARDI*, S. MARINI+ and C. MEUCCI

Istituto Centrale per il Restauro, 00184 Roma, Italy
*Dip. Scienze della Terra, U. di Roma, 00185 Roma, Italy
+6a Via Innocenzo X, 00152 Roma, Italy

ABSTRACT

A field study was carried out in the Forum and Palatine areas (Rome) and volcanic areas of that province, in order to identify monuments which used volcanic materials as structural or decorative elements. Six main types of volcanic stones were identified. A complete set of data on their petrography, uses, location of ancient quarries, type of alteration was collected. The chemistry of the alteration and its products is described. Results of conservation treatment tests with two consolidands, both in-situ and in the laboratory are given for the six types of stones under study. The treatment efficiency was assessed by means of the water absorption index. Results show that the same consolidating treatment applied once apparently provides better protection than when applied repeatedly.

RESUMEN

Se llevó a cabo un estudio en las áreas del Foro y del Palatino (Roma) y zonas volcánicas de esa provincia, para identificar monumentos en los que se utilizaron materiales volcánicos como elementos estructurales o decorativos. Se identificaron seis tipos principales de roca volcánica y se dan datos sobre su petrografía, usos, ubicación de canteras antiguas y tipo de alteración presente. Se describe la química de la alteración y de sus productos. Se dan los resultados de ensayos de tratamientos con dos productos consolidantes aplicados sobre los seis tipos de rocas, en laboratorio y en situ. La eficacia del tratamiento fue evaluado por medio del índice de absorpción de agua. Los resultados indican que una única aplicación con un producto consolidante es aparentemente más efectiva que aplicaciones múltiples.

1. INTRODUCTION

In several countries volcanic rocks were employed in works of art. Numerous Italian examples of monuments built with volcanics are present in Latium and Campania, mainly, but also in Sicily and Sardinia, whilst abroad they are found f.e. in South America and Far East Asia. Except for some types of lava, the volcanic rocks employed in Monuments generally have a relatively large grain size and are inhomogeneous and porous. As a result, in few instances only they can be employed for finely-decorated elements, more subject to degradation. But with the increasing alteration processes of anthropized environments, volcanic rocks often have problems of conservation.

Latium is the region which has Rome as capital city. Over 6,000 of its 17,000 sq km total area are covered by the products of eight large volcanic complexes, mainly Quaternary. The major settlements of the Etruscan, and subsequently of the Roman civilization, are located in these volcanic areas. The products of the Alban Hills volcanic complex extend over large areas within the Roman Walls, whilst those of the Sabatini are present in the northern periphery and reach their maximum development between the Tiber and the Tyrrhenian sea. In Latium, different types of volcanic rocks may be found: lavas, ignimbrites, phreatomagmatic products, fall tuffs, mudflows, tuffites.

They have very diverse structural and compositional characteristics related to type of originating magma, modes of eruption and of deposition, magma cooling path, influence of hydrothermal and alteration processes which strongly modified most of them. "PYROCLASTIC ROCKS" are all volcanic products which are not lavas, such as tuffs, pyroclastic flows, phreatomagmatic flows, mudflows and tuffites. Out of the volcanological-petrographic literature, "TUFF" is normally used instead of "pyroclastic rocks" to describe any volcanic rock other than lavas and, to help the reader, this term will be used in this paper.

The Author's work was focused on characterization of, study of alteration of and tests of laboratory and in situ application of chemical products to six types of pyroclastic rocks used for structural elements and for decorations in the Monuments of the Roman Forum and of the Palatine. These rocks cover an ample range of structural, compositional and physico-mechanical properties, so that the results of this investigation can be extrapolated to volcanic products of other areas.

First, an example is given of how petrography, physico-mechanical properties, outcrops of each rock type were investigated and described. Then, an inventory is provided of its uses in monuments and of its alterations. The second part of the paper reports the results of analyses on the structural characteristics of samples of the materials employed in the Roman Monuments and discusses the influence of both laboratory and in situ treatments.

2. METHODS AND INSTRUMENTATION

Initially, a detailed field work was carried out in the Roman Forum and Palatine area to identify and describe the pyroclastic rocks used in each monument and their alteration processes according to NORMAL standards. Then samples of the six main pyroclastic formations were collected from the monuments in conjunction with experts from Soprintendenza ai Beni Archeologici di Roma. The field work was extended to the outskirts of Rome where the pyroclastic formations outcrop, to trace back the location of the quarries of the Roman times.

In the laboratory, thin sections, the polarizing microscope, X-Ray Diffractometry (XRD), Scanning Electron Microscopy (SEM), Thermal Analysis, wet chemical analysis, Atomic Absorption spectrophotometry were employed to characterize total samples and various fractions. Then over 180 3 x 3 x 3 cm cubes were analyzed with a Carlo Erba mercury microporosimeter to determine their porosity, pore distribution, surface area and, with standard techniques, the absorption coefficient. In a second stage, these cubes were treated with two consolidating chemical products (Wacker OH and Wacker H) and their properties after the treatments were measured again. In the third stage, these chemical tests of conservation were carried out in situ on areas of approx. 0.25 square meters on the monuments where the original samples had been collected.

3. CHARACTERIZATION OF THE PYROCLASTIC ROCKS USED IN THE MONUMENTS OF THE FORUM AND OF THE PALATINE

The six pyroclastic rocks studied in this work are three ignimbrites ("Tufo rosso a scorie nere", "Tufo lionato" and "Tufo giallo della Via Tiberina") two from phreatomagmatic deposits ("Tufo grigio granulare" and "Pietra Gabina") and one from a mudflow ("Peperino dei Colli Albani"). Due to length limitations, the paper presents only the complete data obtained for the "Peperino", as an example of the work which was carried out. The full results for the other five volcanics are available upon request from the first Author of this paper.

PEPERINO DEI COLLI ALBANI

Volcanic Formation: Peperino del complesso vulcanico dei Colli Albani

Current name: Peperino **Ancient name:** Lapis Albanus

Outcrops: This volcanic formation outcrops in the center of the Alban Hills Complex around the Lake of Albano, near Marino, Castel Gandolfo, Albano Laziale and Ariccia

Old quarries: The Roman quarries were located close to the old gate of the village of Albano and near the Castle of Marino.

Modern quarries: Nowadays, the Peperino from several quarries located near the town of Marino is still extracted and marketed.

Main period of use in Roman Monuments: During the so-called 3rd Period, between 210 and 121 B.C.

Roman monument of the Forum and Palatine where it was used:
TULLIANO PRISON: lower room, middle of the 3rd century B.C.; TEMPLE OF MAGNA MATER: (3 A.C.), external architectural decorations; FLOOR OF THE FORUM: (100-80 B.C.) close to the Lacus Curtius and the Comitium; SAINT OMOBONO (100-80 B.C.): foundations and external slabs; FORUM OLITORIUM (90 B.C.): northern Ionic temple; external architecture with frames of travertine too; median temple; columns, wall of the cella and part of the trabeation; TABULARIUM (78 B.C.): flutes of the half-columns of the balcony; FORUM OLITORIUM (80-50 B.C.): Doric temple and foundations; TEMPLE OF SATURNUM (42 B.C.): podium covered

Figure 1. Temple of Antonino and Faustina: the podium is made of blocks of Peperino.

with travertine; FORUM OF AUGUSTUS (31-2 B.C.): fencing wall where the Peperino is mixed with Pietra Gabina (vide infra); TEMPLE OF MARTE ULTORE (2 B.C.): basis of the columns which are positioned in the basement as "opus quadratum" of lithic tuff; TEMPLE OF GIOVE STATORE (Augustus age): restoration TEMPLE OF ANTONINO AND FAUSTINA (141 A.C.): external walls (Figure 1); TEMPLE OF THE FORTUNA VIRILE (6th - 1st century B.C.): where Peperino was employed together with other pyroclastic rocks and travertine. The Temple was subjected to several re-makings.

Petrographic definition: Mudflow

Macroscopic and microscopic characteristics: Peperino is a compact, fine-grained, grey rock with evident inclusions of of both volcanic and sedimentary rocks. There are frequent white limestone fragments from the basement with dimensions up to decimeters, but usually of a few centimeters. Together with lithic fragments, there are various minerals, such as pyroxenes, biotite, analcimized leucite, magnetite, olivine, biotite, frequently with well-developed habits. The matrix is constituted by very fine ash; only a small fraction of the ash is zeolitized.

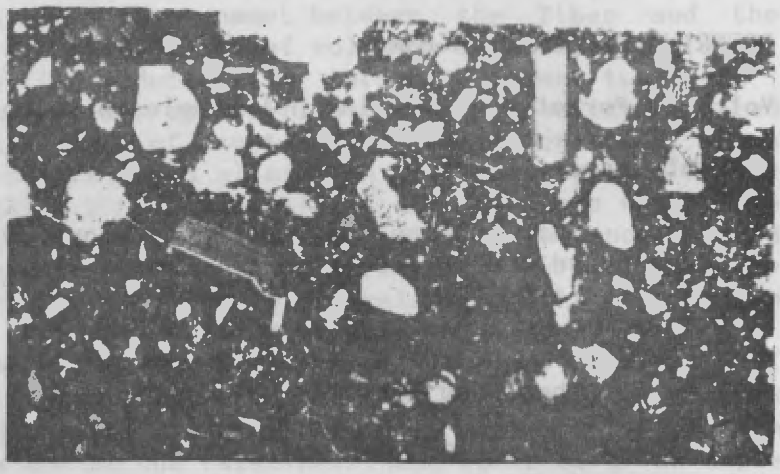


Figure 2. Structure of the Peperino in thin section. Crossed nicols, X 31.

Physico-mechanical properties:
Peperino has good mechanical properties related to its fine grain size and good cementation. It can be cut in slabs of 2 cm thickness and is widely used in the building industry for internal and external coverings. Its commercial value, together with its relatively high bulk density (2-2.13 g/cm3) and scarce diffusion of outcrops, not favours its use as building blocks.

Berry and Sciotti (1974) carried out a series of measurements on samples of the Peperino from Marino which gave the following results.

Unit of vol weight g/cm3:	2.005 - 2.126;	avg 2.075;	σ 0.012
Unit of vol dry weight g/cm3:	1.798 - 1.998;	avg 1.947;	σ 0.026
Absolute specific weight g/cm3:	2.570 - 2.820;	avg 2.672;	σ 0.076
Porosity (n) %:	25 - 32;	avg 27;	σ 0.9
Absorption coefficient:	13 - 18%;	avg 14.3;	σ 0.6
Uniaxial compression resistance kg/cm2:	262 - 276;	avg 267;	σ 1.6
Traction resistance (Brazilian method) kg/cm2:	26.4 - 35.9;	avg 31.6;	σ 1.6
Flexing resistance kg/cm2:	69		
Abrasion coefficient at the tritometer:	mm 15.5		
Abrasion upon sand blasting, loss of weight (g):	0.78		

Alterations in the Roman Forum and Palatine Monuments:
SCALING: all external surfaces show marked phenomena of scaling which may be followed for a depth of a few cm. The process seems related to static problems and is stronger in elements which underwent a structural overload. Scaling may also be related to the flattening work carried out on the surfaces during the preparation of blocks.
FISSURING: is particularly evident on the corners of the frames or of parts of columns and induces the formation of fissures both vertical and normal to the

exposed surface. Again, there does seem to be a connnection with the superficial stresses related to preparation of the architectural elements.
DISAGGREGATION: It is marked under the scales and very often also within the scales themselves.

Like in all other Tuffs, chemical processes of alteration seem to be subordinate.

Analyzed samples:
LOCATION: Temple of Cibele
79/CIB/50 Architectural decoration; capital. Detached scales and 79/CIB/51 powdery deposist under the scales.
79/CIB/52 Architectural decoration; fluted column. Detached scales and 79/CIB/53 powdery deposit under the scales.
79/CIB/54 Architectural decoration; architrave. Detached scales and 79/CIB/55 powdery deposit under the scales.
REFERENCES: (2, 3, 4, 5, 6, 7, 8)

4. ALTERATION PROCESSES OF THE PYROCLASTIC ROCKS IN THE MONUMENTS OF THE ROMAN FORUM AND PALATINE

4.1 Mechanical processes

From the field study of the alterations observed on the Forum and Palatine monuments, some considerations can be made on modes of alteration and factors which influenced them. A large part of what are currently named tuffs were brought to the surface during excavations carried out in the last century. Generally, these materials are saturated with water, as the water table in the Forum is very superficial. As long as environmental conditions allow the rocks to retain their humidity, they appear compact, preserve their original shape and, on the surface, still bear the signs of the chisels used in the quarries.

This may be observed, for example, from the behaviour of the Tufo grigio granulare (locally known as "Cappellaccio") in two monuments. In the archaic basement of the Temple of Saturno the tuff blocks constitute the walls of a 5 x 2 m trench. They are placed in a humid environment and since their excavation (1985) they have showed very little signs of alteration. The Romans must have known that this material was very adequate for humid conditions or for underground structures, as it was used for the walls of wells and water containers long after better-quality tuffs were introduced in the building industry (4). The blocks of the same Tufo grigio granulare of the Archaic Sewage, located between the Temple of the Concordia and the Temple of Vespasiano, were brought to the surface during the excavations carried out in the early 80s and left with no protection. Only two years after, the drying/wetting cycles induced major effects of loss of cohesion and rounding of the upper row blocks. Though no quantitative assessment can be made, it appears that covering of this structure in 1985 slowed down the alteration process considerably.

A similar behaviour was observed in most other tuffs, though with diverse evolution related to their structural variability. Exfoliations, fissures, lifting and detachment of scales, loss of cohesion are common phenomena which are markedly accelerated during the uncontrolled surfacing of water-saturated blocks. The best compactness may be observed in recently-excavated structures (as f.e. the Stipe Votiva) or in structures that since their surfacing have been well protected (as f.e. the floor of the opimian phase of the Temple of the Concordia). These observations are in agreement with what Vitruvius (9) said: "...all these Tuffs when extracted water-saturated in the quarries can be easily adjusted and shaped in the structures they are built in; if they are under a cover and have very good mechanical properties; if in the open and exposed to icing and humidity, they become friable and disaggregate". As regards chemical processes of alteration, their influence on degradation of the tuffs is very limited in comparison to mechanical effects. These tuffs are rich in silicate components and many of them are very rich in zeolites. Zeolites are hydrated aluminosilicates in good equilibrium with the surrounding surface environment and their substitution for glass leads to greater chemical stability and very good mechanical properties of the tuffs.

4.2 Investigations on chemical alteration products

Specific sampling was carried out on patinae, scales, whitish deposits under the scales, efflorescences, whitish surfaces of the diverse tuffs in order to identify secondary components derived from the alteration/modification of the primary constituents. X-ray diffraction analyses enabled to recognize that gypsum in limited quantities is practically the only frequent secondary mineral. Gypsum is much more common in the whitish, powderish material under the scales than within the compact rock and very abundant in the white efflorescences. The maximum content is in some samples of the Pietra Gabina, where the sulphate ion is 8-9% in weight.

The Pietra Gabina of the Tabularium also has minor crystallizations of sodium chloride (NaCl). However, it is well known from the literature that the upper part of the Tabularium was used in the 15th-16th century as a deposit for salt; its leaching reached also the base of this structure. No traces of NaCl were observed in any other analyzed tuff.

A confirmation of the very low amount of secondary components in these tuffs is given by their low soluble salts content. Following the procedure of NORMAL 13/83 (10), colorimetric and spectrophotometric methods were applied to determine the content in Sulphates, Nitrates, Nitrites, Chlorides, Sodium, Potassium, Ammonia, Calcium, Magnesium. Results show that their concentration is very low in most samples. Efflorescences and powderish deposits under the scales are, on average, the richest in soluble salts. The analyzed samples were collected from blocks in situ or which were excavated a few years ago. Therefore, it is not possible to assess the rate of transfer of the soluble salts from the surface towards the deeper layer. A "blank" (zero level of chemical alteration) might be sample 85/SAT/01 from Tufo Grigio Granulare, which was collected only a few months after its excavation. Sulphates, Chlorides, Ammonia, Sodium and Potassium were found, whilst other species were below detection limits. Values are very low and comparable with others from materials exposed for a much longer time.

Among the analyzed species, only the sulphate distribution has a pattern (Figure 3) which may be tentatively correlated with the structural-compositional characteristics of the blocks and with their

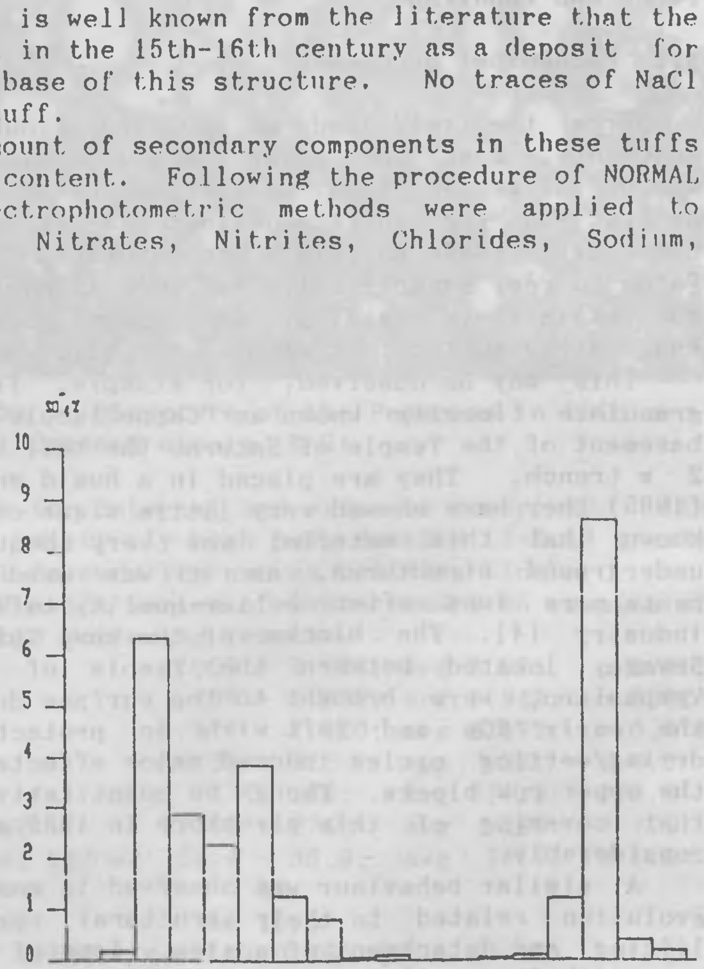


Figure 3. Histogram of the sulphate ion concentration.

exposure to atmospheric agents. Soluble salts appear to derive from interaction of the tuffs with air pollutants where sulphate ions are dominant. Migration of sulphate ion and of other ionic species within the rock pores is conditioned by degree of humidity of the blocks. This movement is obviously dependent also upon the high con centration gradients which develop between the outer surfaces and the internal net of pores of the tuffs. Frequency and intensity of the wetting/drying cycles favours con centration of salts in discontinuities such as fissures, microfractures, in part induced by mechanical stresses, which tend to accelerate phenomena of scaling and exfoliation. Such hypothesis is in agreement with the sulphate richness within the powderish deposits under the scales.

In conclusion, damages related to soluble salts are minor, and due to structure of the tuffs, pattern of the pores and exposure to atmospheric agents.

5. CONSERVATION TREATMENTS

Laboratory tests were carried out on all six types of tuffs in order to measure their physico-mechanical properties and thus evaluate their alteration state and capacity of absorbing consolidating products. The kind help of the local Archeological Authorities allowed the Authors to directly sample the blocks from the studied monuments, though, obviously, the available quantities were limited. Therefore, laboratory tests were carried out on a minimum of ten 3 x 3 cm cubes. As "blank", use was always made of a cube from the sampled material which was obtained from the interior of the block, at not less than 15 cm from the external surface, where macro and microscopic observations inferred that no external process influenced the rock properties. The only exception was the Tufo Lionato, where the lack of a sufficient amount of adequate material allowed in situ tests only.

On each sample (cube), the capillary absorption coefficient (10) and distribution of pore volume as a function of diameter (12) were determined. On this basis relative coefficients of efficiency of the conservation treatments were evaluated. Two consolidating products were used:

- an ethyl ester of orthosilicic acid, commercially known as "Reinforcing OH", (Wacker Chemie) was used on all samples;
- another ethyl ester of orthosilicic acid with polysiloxane added as hydrophobic agent, produced by Wacker Chemie up to a few years ago under the name of "Reinforcing H", was tested on two of the tuffs.

Substances were employed which by hydrolysis precipitate amorphous silica in the pores of the Tuffs. With this process, the silica is chemically similar to the glassy matrix of the tuff and there is no danger of intruding the rock pores with some foreign, possibly active substance. It should be kept in mind these Tuffs contain a high percent of zeolites, highly reactive minerals, with great exchange capacity. This capacity may easily lead to interaction with any chemical substance introduced into the system. In this study however, such interaction never became apparent.

The laboratory consolidation treatments were carried out by utilizing the principle of capillary absorption, by means of total immersion of the sample in the chosen consolidating product, until its total saturation. At the same time, in situ impregnation tests were carried out on the monuments under study, in order to verify results on larger surfaces than the small laboratory cubes. In both cases, undiluted consolidating products were employed to avoid the risks of inhomogeneous distribution of the active fraction in the porous net of the Tuff, owing to potential osmotic effects. In this way interesting data were also obtained on the effect of excess consolidating agent.

Treatments in situ were carried out on dry surfaces, but in environments of average or elevated humidity. Analysis on the treated samples were carried out after at least three months, in order to be sure that the hydrolyzation process was complete.

6. PHYSICAL CHARACTERISTICS OF THE UNTREATED TUFFS

Table I summarizes the values of the porosity, bulk density, specific surface area and of absorption coefficient of the untreated tuffs. Observe the very ample range of values, related to differences existing betweeen their structural characteristics. Porosity varies from 28.9% of the Peperino of Albano to 46.0% of the Tufo Giallo; bulk density from 1.16 of the Tufo Rosso to 2.05 of the Peperino of Albano; specific surface area of two pyroclastic flows from 27.7 of the coarse-grained Tufo Rosso to 6.6 of the fine-grained Tufo Giallo.

VOLCANIC ROCK	POROSITY %	BULK DENSITY g/cm3	SPECIFIC SURFACE m2/g	ABSORBTION COEFFICIENT g/cm2
TUFO GIALLO	37.40	1.42	6.60	0.150
ROSSO SCORIE NERE	31.88	1.16	27.70	0.018
TUFO LIONATO	38.56	1.57	16.20	-
GRIGIO GRANULARE	29.54	1.31	17.23	0.030
PIETRA GABINA	30.42	1.92	11.94	0.007
PEPERINO ALBANO	29.46	2.13	4.86	0.031

Table I. Physical properties of the untreated samples

The first immediate conclusion is that the great variability in the possible conditions which presided over the formation of these tuffs may have led to rocks which are currently named tuffs, but which have very diverse physico-mechanical properties. Therefore, in each case great caution and time are needed to acquire a good knowledge of the material under study before proceeding to any consolidation treatment.

7. ANALYTICAL RESULTS

First, the effect of treatments with the "Reinforcing OH" consolidating agent carried out on all six tuffs will be discussed. Then, results of the tests with the "Reinforcing H" on two tuffs with the most diverse structural properties will be covered.

7.1 Treatments with "Wacker OH"

7.1.1 Tufo Giallo

Data are discussed in paragraph 7.3.

7.1.2 Tufo Rosso a Scorie Nere

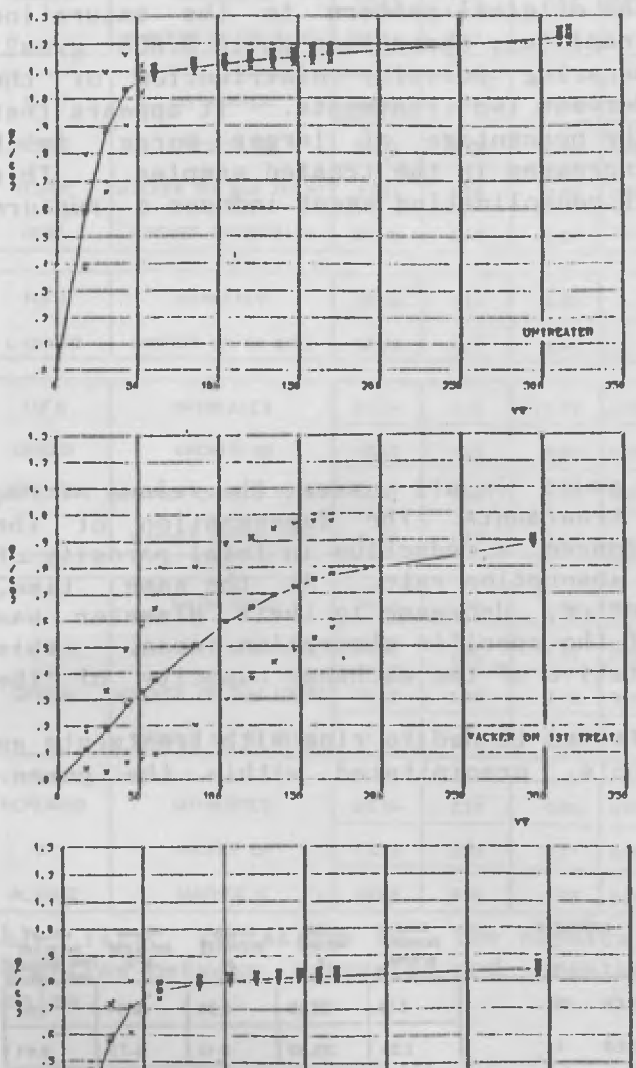
The capillary absorption curves of this rock showed an anomalous pattern. The first impregnation with Wacker OH generated a system which from an initially low absorption rate rapidly passed to fast absorption, with total saturation in approx. six hours. This behaviour is related to the peculiar texture of this material, very rich in glassy scoriae with high porosity. A second treatment with the consolidating agent increased the capillary absorption coefficient to values even higher than those of the untreated material. A decrease in the percentage of the less than 0.4 micron pores and an increase of the large pores (with diameters over 2 microns), related to rupture of internal pore net of the rock was recorded.

7.1.3 Tufo Lionato

Due to lack of an adequate amount of sample from the monuments, only in situ tests were carried out.

7.1.4 Tufo Grigio Granulare

This material too exhibited a clear variation in its capillary absorption coefficient with the treatments. The first impregnation



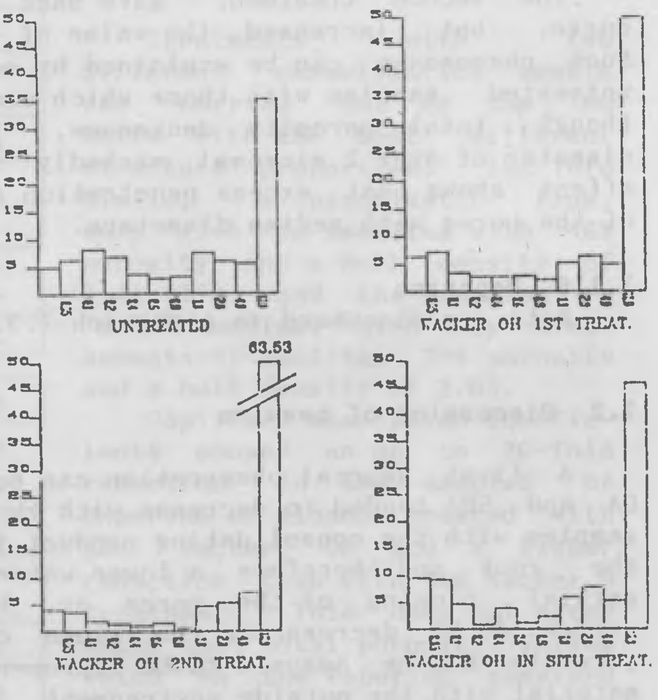


Figure 4. (Left) Curves of water absorption coefficients.

Figure 5. (Above) Pore size distribution histograms of untreated and treated samples of Tufo grigio granulare.

elicited a six-fold reduction in water absorption rate associated with a reasonably good distribution of the consolidating agent within the pore net of the tuff. On the contrary, the second treatment shifted the absorption coefficent (Figure 4) up to values close to those of the untreated sample. This should be related to rupture of the internal pores of the tuff. The more than 10 micron pores of the sample treated twice went up to 63% vs. 35% for the untreated sample (Figure 5). As a consequence, porosimetric distribution flattens down owing to evident decrease in median-small sized pores.

7.1.5 Pietra Gabina

The pattern of capillary absorption clearly showed that water absorption rate in the rock pores is very diverse between the two successive treatments. After the first impregnation, the initial value of 0.007 g/cm2 passed to 0.002 g/cm2 with flattening of the saturation curve down to a near straight line; this means low absorption rate and thus a long saturation time.

The second treatment gave back the original pattern to the saturation curve, but increased the value of capillary absorption up to 0.005 g/cm2. Such phenomenon can be explained by comparing porosity distribution of the untreated samples with those which underwent two treatments. It appears that though total porosity decreases, the percentage of larger pores (with diameter of over 2 microns) markedly increases in the treated samples. This effect shows that excess penetration of consolidating agent induces a rupture of the pores with median diameters.

7.1.6 Peperino

Data are discussed in paragraph 7.3.

7.2 Discussion of results

A first general observation can be made: in all cases the values of P%, CA and SSA tended to decrease with the treatments. The impregnation of the samples with the consolidating product induced a reduction in total porosity of the rock and therefore a lower water absorption rate. At the same time, partial closing of the pores or, better, decrease in their diameter was evidenced by decrease in the values of the specific absorption area. This parameter may be assumed to be representative of the exchange capacity of the material with the outside environment.

As expected, bulk density of the material tended to rise with treatments as the consolidating agent or end-products, precipitated within the pores. Variations in weight (Table II) observed between untreated and treated products gave indications on the amount of agent which penetrated into the sample. In order to check whether an increase in the amount of consolidating agent improved mechanical properties and resistance to alteration, a second treatment was applied to samples of Pietra Gabina, Tufo Grigio and Tufo Rosso. In all three cases (Table III), the second treatment clearly induced a decrease in mechanical properties of the material (increase in P% and of absorption coeficient). This occurring notwithstanding the fact that the relative increase in weight was higher in the

VOLCANIC ROCK	TREATMENT	BULK DENSITY g/cm3	INITIAL WEIGHT g	WEIGHT INCREASE g	WEIGHT INCREASE g %	WEIGHT INCREASE FOR SURFACE UNIT g/cm2
TUFO	WACKER OH	1.71	35.15	2.30	6.54	0.04
GIALLO	WACKER H	1.56	35.80	2.41	6.73	0.04
TUFO ROSSO	WACKER OH	1.48	31.65	3.12	9.85	0.06
SCORIE NERE	WACKER OH 2nd TREAT	1.55	31.65	4.48	14.15	0.08
TUFO GRIGIO	WACKER OH	1.56	31.92	3.01	9.43	0.06
GRANULARE	WACKER OH 2nd TREAT	1.50	31.92	4.73	14.82	0.09
PIETRA	WACKER OH	1.96	46.15	2.43	5.26	0.04
GABINA	WACKER OH 2nd TREAT	1.98	46.15	3.53	7.65	0.06
PEPERINO	WACKER OH	2.01	50.87	1.15	2.21	0.02
DI ALBANO	WACKER H	2.00	50.87	1.55	2.95	0.03

Table II. Weight variations related to treatments.

VOLCANIC ROCK	TREATMENT	POROSITY %	BULK DENSITY g/cm3	SPECIFIC SURFACE m2/g	ABSORPTION COEFFICIENT g/cm2
TUFO GIALLO	UNTREATED	37.40	1.42	6.60	0.150
	WACKER OH	32.81	1.71	8.38	0.081
	WACKER H	26.79	1.56	7.29	0.001
	WACKER OH IN SITU	26.24	1.57	7.29	----
TUFO ROSSO SCORIE NERE	UNTREATED	31.88	1.16	27.70	0.018
	WACKER OH	25.54	1.47	9.94	0.006
	WACKER OH 2nd TREAT	23.21	1.55	7.40	0.021
	WACKER OH IN SITU	28.40	1.73	10.87	----
TUFO LIONATO	UTREATED	30.56	1.57	16.20	----
	WACKER OH IN SITU	22.98	1.79	8.60	----
TUFO GRIGIO GRANULARE	UNTREATED	29.54	1.31	17.23	0.030
	WACKER OH	18.53	1.56	8.52	0.005
	WACKER OH 2nd TREAT	16.92	1.50	4.73	0.021
	WACKER OH IN SITU	21.42	1.73	11.44	----
PIETRA GABINA	UNTREATED	30.42	1.92	11.94	0.007
	WACKER OH	18.52	1.96	4.64	0.002
	WACKER OH 2nd TREAT	12.45	1.98	3.43	0.005
	WACKER OH IN SITU	17.36	1.93	6.76	----
PEPERINO DI ALBANO	UNTREATED	29.46	2.13	4.86	0.034
	WACKER OH	23.90	2.01	4.77	0.005
	WACKER H	20.80	2.00	4.94	0.001

Table III. Variations in the physical properties between untreated and treated samples.

second than in the first treatment.

7.3 Treatments with "Wacker OH" and "Wacker H"

Treatments with two different consolidating agents was carried out on the two tuffs with the most different structural properties: the Tufo Giallo, a pyroclastic flow, very rich in zeolites with 46% porosity and a bulk density of 1.41 (13), and the Peperino, a "cold" mudflow, with only minor amounts of zeolites, 29% porosity and a bulk density of 2.05.

Capillary absorption coefficients showed an up to 30-fold reduction in the samples of Peperino of Albano treated with the Wacker OH and a higher reduction than with the Wacker H treatment. This does not agree with the total porosity values which in the Peperino remained much the same even after treatment, whilst they displayed a more regular pattern in the Tufo Giallo samples. Distribution of the pores in all cases appeared to be pretty regular, with increase in the percentage of the smaller pores and flattening of the distribution curve in the area of the median-sized pores.

7.4. In situ consolidation tests

In order to assess the efficiency of the consolidating treatments with the "Wacker OH" in field situations characterized by an advanced stage of degradation, jointly with the Soprintendenza Archeologica di Roma and the help of their chief restorer Mr. Elio Paparatti, it was decided to apply this product directly to the tuff blocks of the monuments from which the original samples had been collected. The treatment was carried out on an area of 0.25 square meters, large enough to take care of inhomogenities of the material and of alteration effects. When for local reasons it was impossible to work directly on the monument, the treatment was applied to the same material on nearby blocks. The applications of consolidating agents were carried out as follows:

Tufo Giallo: altered blocks at the back of the Temple of Saturno
Tufo Rosso a scorie nere: blocks of the Temple of the Concordia podium
Tufo Lionato: back wall blocks of the cell of the Temple of the Concordia
Tufo grigio granulare: sewage system, in front of the Temple of the Concordia
Pietra Gabina: blocks of the Tabularium, back of Temple of the Concordia.

Laboratory tests on the Tufo Lionato and in situ for the Peperino are missing for the moment.

Applications were carried out by means of a brush, with approx. one liter of undiluted consolidating product per square meter of surface. In all locations, application was continued up to saturation of the rock. The surfaces where the treatment took place were provided with temporary covers, to protect from washing off by rain or direct heating by sun rays. The tests were carried out in October 1989 under favourable climatic conditions, with very low precipitations and mild temperature. The samples for the porosimetric checks, the only type of measurement capable of giving reliable data, were collected in January 1990, after a three-month period, regarded as sufficient to guarantee completeness of the hydrolysis process of the ethyl silicate.

Observations in the field with the help of a magnifying lens showed that the interaction between the "Wacker OH" and the tuff led to increase in cohesion state of the surface with a major decrease in its tendency to formation of powder and to disaggregation. However, the treatment yielded no substantial improvement in tendency to scaling and exfoliation of the tuffs. Moreover, the consolidating agent tended to accumulate in the open fissures which characterize these materials at the surface, preventing homogeneous distribution in a thicker layer of the rock. From the surface of the treated tuff, scales of approx. 5 mm thickness were then detached and on them total porosity, distribution of the pores, bulk density, specific surface of absorption were determined.

The values obtained showed that the consolidating treatment on the superficial layer of these materials gave reasonably good results, as may be seen from decrease in total porosity and specific surface. Moreover, in most cases an increase in specific weight was observed, which may indicate that silica was deposited in these first layers of the Tuffs.

8. DISCUSSION ON TREATMENT TESTS

Assessment of effects of treatments on Tuffs is not easy, as the starting parameters, such as bulk density, porosity, specific surface area are widely variable from one type of tuff to the other. Therefore, it was necessary to process the available experimental data and prepare some "variability indexes" as illustrated in Table IV. The indexes for total porosity, specific absorption surface area and absorption

VOLCANIC ROCK	TREATMENT	POROSITY INCREASE i (P) %	BULK DENSITY INCREASE i (bd) %	SPECIFIC SURFACE INCREASE i (SSA) %	ABSORPTION COEFFICIENT INCREASE i (CA) %
TUFO GIALLO	WACKER OH	12.80	16.96	-26.96	46.00
	WACKER H	28.37	8.97	-10.45	99.33
	WACKER OH in situ	29.84	9.55	-10.45	----
TUFO ROSSO SCORIE NERE	WACKER OH	19.89	21.09	65.34	66.66
	WACKER OH 2nd TREAT	27.19	25.16	73.28	-16.66
	WACKER OH in situ	10.91	32.94	60.76	----
TUFO LIONATO	WACKER OH in situ	40.40	12.30	46.91	----
TUFO GRIGIO GRANULARE	WACKER OH	37.44	16.02	50.55	83.33
	WACKER OH 2nd TREAT	42.72	12.66	72.55	30.00
	WACKER OH in situ	27.49	24.28	33.60	----
PIETRA GABINA	WACKER OH	39.12	2.04	61.14	71.43
	WACKER OH 2nd TREAT	59.07	3.03	71.27	28.57
	WACKER OH in situ	42.93	0.51	43.38	----
PEPERINO DI ALBANO	WACKER OH	17.35	-1.99	1.85	85.29
	WACKER H	28.07	-2.50	-1.65	97.06

Table IV. Variation indexes for checking efficiency of treatments.

coefficient derive from the application of the formula:

$$i = ((Po - Pi)/ Po)*100$$

where: i = index of variation of the parameter, Po = value of untreated sample Pi = value of treated sample.

As treated samples have all bulk densities higher than untreated ones, the index for bulk density was calculated from the formula:

$$i = ((Pi - Po)/Po*100$$

An analysis of the values obtained for the diverse indexes shows an overall agreement with what would be expected from the consolidation treatments. However, there are various inconsistencies when reviewing the single data in detail. The index of porosimetric variability "ip" may indicate that a second treatement leads to better results than a single one. This contrasts with experimental data which indicate rupture of the pores owing to excess impregnation of the consolidating agent.

In the same way, the index "ig" related to variation of bulk density, is not always significant, as in the tuffs there are marked local variations of bulk density due to inhomogeneities of this type of rock. Instead, the values of the index of variation of the specific surface, "issa" and the index of variation of capillary absorption, "ica", seem to offer a good representation of the effects of the consolidation treatment (Figure 6). The histogram derived from the values of "ica" shows that such index can be really considered as representative of the effect of the conservation treatment. In agreement with laboratory test results, a reduction of the effects down to even negative values may be observed for all those materials where a collapse of the internal structure of the pores occurred.

In conclusion, the treatment with Wacker OH is effective provided that not too much consolidating agent is introduced in the tuff. The addition of hydrophobic agent, or better of a product with elastic and binding properties gives much better results and favours sealing of the microfissures. Scaling and exfoliation should be resolved with other than chemical restoration works.

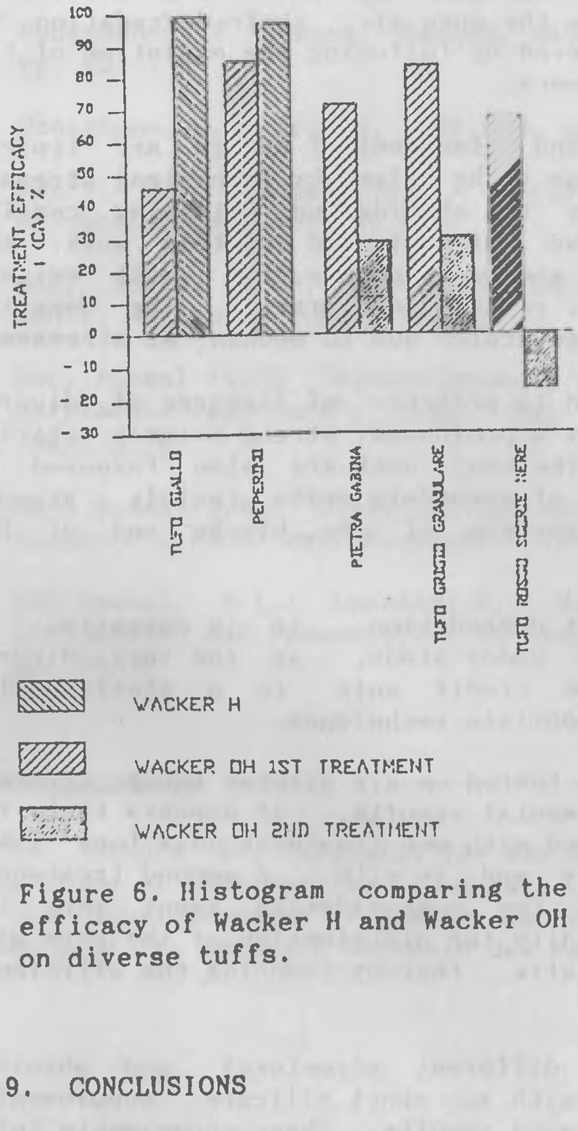


Figure 6. Histogram comparing the efficacy of Wacker H and Wacker OH on diverse tuffs.

9. CONCLUSIONS

9.1 From the examination of over 40 Roman monuments of the Forum and Palatine it appears that at first tuffs outcropping in this area were used, and then other, better, materials were excavated further away. Most of the main quarries were located along the valleys of the Tiber and Aniene rivers, the ancient "motorways" for goods, which led to the center of Rome. The exception are the quarries of "Peperino di Albano", located away from the rivers but which, not by chance, offered a very good building material which might also be used for architectural elements.

9.2 The "tuffs" used in the monuments are in fact Ignimbrites, Mudflow, Phreatomagmatic deposits with different structural and physico-mechanical characteristics. This diversity occurs between elements of the same material but also from diverse quarries or diverse levels of the quarries. The mode of use of these Tuffs varied from foundations to structural elements to architectural decorations.

9.3 Mechanical alteration processes are by far the most important and cause the worst damages. Chemical processes are subordinate. The overall impression from a series of field studies carried out in diverse seasons and years, observing the evolution of the tuff blocks after their excavation, allowed to draw some conclusions on development of their degradation. The blocks are well preserved at depth, though water saturation decreases their mechanical strength. Surfacing is a critical moment. If loss of their humidity is not controlled and regulated by protective structures against icing and heating/cooling cycles in the open air, their degradation is rapid. This degradation may be observed by following the evolution of the excavated material over a period of 1-2 years.

9.4 Fissuring, exfoliation, lifting and detachment of scales are typical forms of mechanical alteration. They appear to be helped by mechanical stresses induced on the surface of the block by the shaping and chiseling carried out in the quarries. Among the diverse tuffs studied in this work, the Tufo grigio granulare and the Tufo giallo presents the most evident phenomena of degradation, loss of cohesion, rounding of corners. The Peperino of Albano suffers from detachment of large scales due to mechanical stresses.

9.5 Most of the alterations are related to presence of fissures of diverse dimensions. Large ones were caused also by a prolonged, strong seismic activity which occurred in the area of Rome. The small ones are also favoured by development of small crystallizations of secondary salts (mainly gypsum) which grow under the scales on the surface of the blocks and of the architectural elements.

9.6 Before deciding any treatment against degradation, it is essential to acquire a detailed knowledge of the Tuffs under study, as the very diverse characteristics of these materials give credit only to a statistically significant number of analyses with appropriate techniques.

9.7 In this work, chemical treatments were tested on six diverse tuffs, with two consolidating agents. From the experimental results, it appears that the best results with the Wacker OH are obtained with one treatment only (one liter per square meter), both in the laboratory and in situ. A second treatment, or a prolonged action of penetration of the consolidating agent into the porous net of these rocks, seems to modify the distribution of the pore size owing to a collapse of the internal pore walls, thereby reducing the efficiency of the treatments.

9.8 On the two tuffs with the most different structural and physico-mechanical characteristics, a treatment with an ethyl silicate supplemented with a hydrophobic polysiloxane gave very good results. These experiments infer that the presence of a binding agent betters the conditions of the blocks at the surface, reducing dishomogneneous distribution of the pores.

10. REFERENCES

1. Berry, T.; Sciotti, M.; Proc. Int. Cong. on Exploitation of Ind. Minerals and Rocks, Turin, 1974, p. 50

2. Coarelli, F.; "Guida archeologica di Roma"; Mondadori, Verona, 1975; pp. 340-342

3. Coarelli, F.; "Il Foro romano. Il periodo arcaico"; Quasar, Roma, 1983; p. 329

4. Lugli, G.; "La tecnica edilizia romana"; Vol. I, Bardi, Roma, 1957; pp. 169-334

5. Pensabene, P.; Quad. Centro Studio Archeol. etrusco-italica 1979, pp. 67-74

6. Pensabene, P.; Quad. Centro Studio Archeol. etrusco-italica 1980, pp. 75-82

7. Pensabene, P.; Quad. Centro Studio l'Archeol. etrusco-italica, 1981, pp. 101-118

8. Pensabene, P.; Archeo, 1989, 48, pp. 74-83

9. Ferri, S.; (Translation) - "Vitruvio, De Architectura 2nd and 7th Books"; Palombi, Roma, 1960; p. 303

10. Doc. Normal 13/83; "Dosaggio sali solubili"; Cons. Naz. Ricerche - Ist. Centr. Restauro, Roma, 1983; p. 3

11. Doc. Normal 11/85 "Assorbimento d'acqua per capillarità. Coefficiente d'assorbimento capillare"; Cons. Naz. Ricerche - Ist. Centr. Restauro, Roma, 1985; p. 6

12. Doc. Normal 4/80 "Distribuzione del volume dei pori in funzione del loro diametro". Cons. Naz. Ricerche - Ist. Centr. Restauro, Roma, 1980; p. 10

13. Bianchetti, P.L.; Lombardi,G.; Meucci C.; Proc. 4th Int. Cong. Deterioration and Preservation of Stone Objects, Louisville (Ky, USA), 1982, pp. 29-38

ACKNOWLEDGEMENTS

The Authors are grateful for the collaboration offered during the long preparation of this work to F. Sagala, E. Monti, E. Paparatti and I. Sciortino of the Soprintendenza ai Beni Archeologici di Roma and to A. Ferroni and G. Buzzanca of the Istituto Centrale del Restauro.

10. REFERENCES

1. Berry T.; Sciotti M.; Proc. Int. Conf. on Exploitation of Ind. Minerals and Rocks, Turin, 1974, p. 50

2. Coarelli, F.; "Guida archeologica di Roma", Mondadori, Verona, 1975, pp. 340-342

3. Coarelli, F.; "Il foro romano. Il periodo arcaico", Quasar, Roma, 1983, p. 329

4. Lugli, G.; "La tecnica edilizia romana", Vol. I, Bardi, Roma, 1957, pp. 169-334

5. Pensabene, P.; Quad. Centro Studio Archeol. etrusco-italica 1979, pp. 67-74

6. Pensabene, P.; Quad. Centro Studio Archeol. etrusco-italica 1980, pp. 75-82

7. Pensabene, P.; Quad. Centro Studio Archeol. etrusco-italica, 1981, pp. 101-118

8. Pensabene, P.; Archeo, 1989, 48, pp. 74-83

9. Ferri, S.; (Translation) - "Vitruvio, De Architectura 2nd and 7th Books", Palombi, Roma, 1960, p. 303

10. Doc. Normal 13/83, "Dosaggio sali solubili"; Cons. Naz. Ricerche - Ist. Centr. Restauro, Roma, 1983, p. 3

11. Doc. Normal 11/85 "Assorbimento d'acqua per capillarità. Coefficiente d'assorbimento capillare"; Cons. Naz. Ricerche - Ist. Centr. Restauro, Roma, 1985, p. 6

12. Doc. Normal 4/80 "Distribuzione del volume dei pori in funzione del loro diametro"; Cons. Naz. Ricerche - Ist. Centr. Restauro, Roma, 1980, p. 10

13. Bianchetti, P.L.; Lombardi G.; Meucci C.; Proc. 4th Int. Cong. Deterioration and Preservation of Stone Objects, Louisville (KY, USA), 1982, pp. 23-38

ACKNOWLEDGEMENTS

The Authors are grateful for the collaboration offered during the long preparation of this work to P. Sagala, E. Monti, L. Paparatti and I. Sciortino of the Soprintendenza ai Beni Archeologici di Roma and to A. Peroni and G. Buzzanca of the Istituto Centrale del Restauro.

CHARACTERIZATION AND STATE OF DECAY OF THE VOLCANIC TUFF OF THE TABULARIUM (ROMAN FORUM, ITALY)

G. DE CASA, G. GIGLIO, G. LOMBARDI* and M. MARIOTTINI+

Dip. Idraulica, Università di Roma, 00184 Roma, Italy
CNR Centro di Studio per la Geologia Tecnica, Roma, Italy
*Dip. Scienze della Terra, U. di Roma, 00185 Roma, Italy
+Istituto Centrale per il Restauro, 00184 Roma, Italy

ABSTRACT

The Tabularium, old Town Council of the Romans burned down in 83 B.C., was reconstructed employing a volcanic tuff named Lapis Gabinus. The results of a detailed study of the minero-petrographic characteristics and the physico-mechanical properties of this tuff are reported. The use of the Tabularium as a salt deposit in medieval times induced a marked decay of the tuff blocks and columns, with extensive phenomena of scaling, crumbling and alveolar weathering. Chemical consolidating products were used 20 years ago and the results of tests with acrylic resins and silicic compounds are discussed together with their possible interaction with the abundant zeolitic component of the tuff.

RESUMEN

El Tabulario, el antiguo Concejo municipal de los Romanos, se incendió en el año 83 A.C., y fue reconstruído utilizando una toba volcánica llamada Lapis Gabinus. Se presentan los resultados de un estudio detallado de las características minero-petrográficas y de las propiedades físico-mecánicas de esta toba. El uso del Tabularium como depósito de sal en el medioevo produjo un marcado deterioro en los bloques de tobas y en las columnas, con fenómenos de escamación, disgregación y alveolización. Productos químicos consolidantes fueron aplicados hace 20 años y los resultados de estos ensayos con resinas acrílicas y compuestos silícicos se analizan en conjunción con su posible interacción con el alto contenido zeolítico de esta toba.

1. INTRODUCTION

The Tabularium dominates the Forum Valley towards southwest and constitutes an important "substructio" built in a Quaternary volcanic tuff locally named "Lapis Gabinus" or "Pietra Gabina", which was used as a building stone up to the period of the Empire. The Tabularium was erected by Q. Lutetius Catulus in 78 B.C., after the fire that burned the Capitolium (83 B.C.), probably close to a complex that as early as the 5th century B.C. was to be the most ancient archive of the Roman State (1). Its function was to preserve government documents and public deeds (tabulae) but during the Middle Ages, as frequently occurred with "monopoly" facilities, it was used as a warehouse for storing salt.

The masonry and the columns of the monument have suffered the action in time of the salt, which in some points caused considerable decay, so much so that the very stability of the monument was undermined. In this paper are presented the results of a study of the structural, mineralogical, petrographic, and mechanical characteristics of the tuff blocks used to build the Tabularium and an evaluation of the restoration measures taken twenty years ago.

Fig. 1 - The structure of the Tabularium is located at the base of the Capitolium and overlooks the Roman Forum. In the lower part, there may be seen the lines of blocks of the Lapis Gabinus tuff, which also constitutes the columns bordering the entrances at half height. In the last few years excavations considerably lowered the field level and exposed the base of the wall.

2. CHARACTERIZATION OF THE LAPIS GABINUS

2.1 Geological setting and petrography

The "Lapis Gabinus" is one of the varieties of granular tuff, a product of the explosive activity of eccentric apparatuses which developed in a late stage of the volcanic activity of the Alban Hills (2, 3). The Lapis Gabinus outcrops mainly in the crater depression of Lake Castiglione, 20 km to the east of Rome, near the remains of the town of Gabii (Fig. 2). This Roman town was crossed by Via Preneste and was only a few kilometres away from the Aniene River which played a major role in the Roman economy, serving as a waterway for the transportation of tuff blocks and other important stones such as travertine.

The largest outcrops of Lapis Gabinus extend (4) out to the west of the Saponara leucitic lava flow and along the eastern border of Lake Castiglione, which had already been reclaimed by the 15th century. In situ, the Lapis Gabinus often presents a typical bedding with layers containing larger inclusions alternating with uncoherent sandy layers . The thickness of the formation is up to 60m. The structural and textural characteristics are typical of the products of a phreatomagmatic activity (7, 10) with depositional characters of a base surge (6, 8).

The material used in the buildings of the Roman Forum may be classified as a volcanic conglomerate, with a variety of sedimentary and volcanic fragments embedded in a matrix of pumices, lapilli and fragments of varying sizes. The carbonatic or marly inclusions range in colour from white to pink to deep orange, and have rounded edges. In some facies, as the one which characterizes

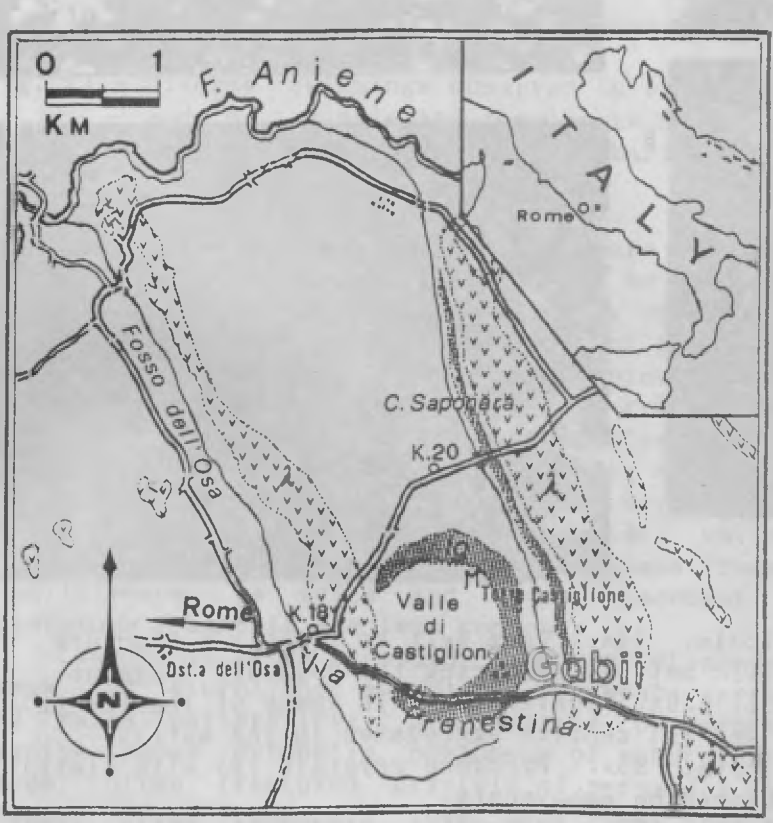
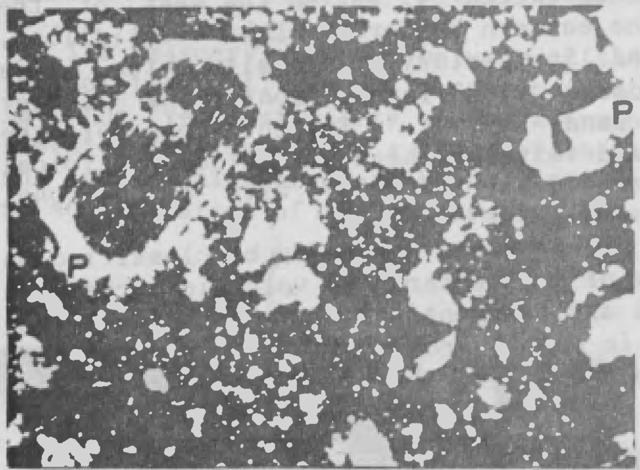


Fig. 2 - The area where the Lapis Gabinus outcrops is located 20 km east of Rome. lg = Lapis gabinus tuff: λ = leucititic lavas.

Fig. 3 - A typical surface of a block from the Tabularium, with evident exfoliation and scaling.

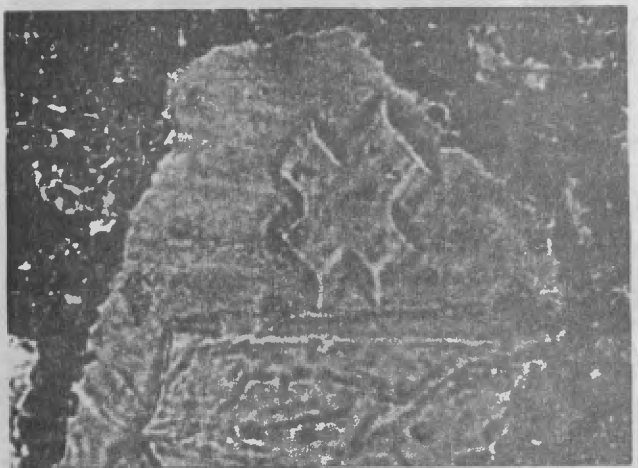
4

5



6

7



8

9

Fig. 4 - Thin section, crossed nicols, 12x. From left to right, a fracture develops across the zeolitic matrix, bordering the volcanic fragment.

Fig. 5 - Thin section, pol. nicol, 50x. Icositetrahedric shape of leucite (L) with cross-shaped ghosts and (Z) zeolite aggregates in the matrix.

Fig. 6 - Thin section, crossed nicols, 95x. Pyroxene crystals (P) with (left) zoning and (right) reabsorption embayments.

Fig. 7 - Thin section, crossed nicols, 50x. Aggregates of fibrous phillipsite associated with pseudocubic crystals of chabazite.

Fig. 8 - Thin section, pol. nicol, 350x. Cross twinning of phillipsite within a cavity of the tuff.

Fig. 9 - Thin section, pol. nicol, 85x. Euhedral cubic crystals of chabazite (CH) associated with calcite (C) filling up the voids.

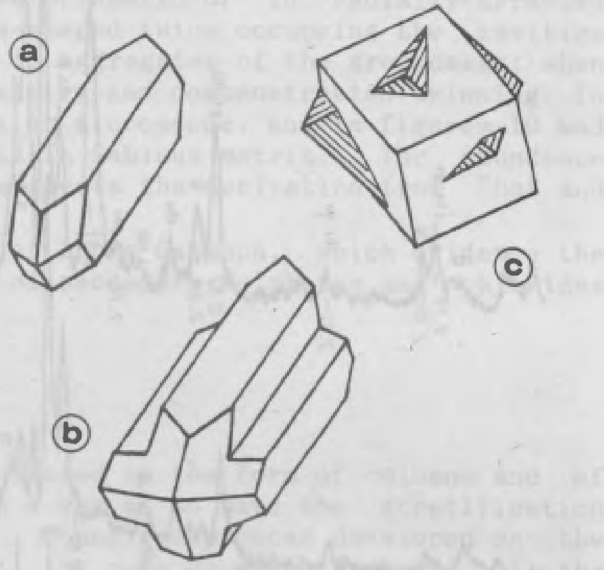


Fig. 10 - SEM micrograph. Twinned chabazite on a fracture surface from a tuff block of the Tabularium.

Fig. 11 - Diverse twinnings observed in the zeolites of the Tabularium tuff. A and B, simple and complex twinning of phillipsite; C pseudo-cubic compenetrated crystals of chabazite.

the blocks used for the Tabularium, there is an abundance of zeolites (Fig. 7, 8, 9, 10). This mineralization may be seen on polished section as whitish veinlets that mark the outline of darker volcanic elements.

Thin sections from both blocks of the Tabularium and from the ancient quarries were studied. The Lapis Gabinus has a clastic structure with an abundance of lapilli immersed in a fine-grained matrix of clustered ashes, with the glassy component in an advanced stage of zeolitization. Among the few minerals dispersed in the matrix, there are leucite, pyroxenes, biotite and little olivine. The lithic fragments are made of tuff, lavas and sedimentary rocks; porphyritic leucitic rocks prevail, whilst the granular structures are occasional. Carbonates are present as common fragments of diverse size, at times fossiliferous, as veins and void replacement, as substitution of leucite. Flintstone fragments are less common.

Leucite is often shrouded, in icositetrahedron having at times crystalline germs and microlithic and glassy fragments arranged according to a concentric and radial pattern (Fig. 5), whereas polysynthetic twinnings are very rare. Leucite shows extensive phenomena of substitution by zeolites and calcite. Large, often fractured crystals of pyroxenes with evident cleavage are very common; often euhedral, they sometimes show a slim reaction boundary and reabsorption recesses (Fig. 6), zoned for chemical inhomogeneities, with apatite and opaque minerals inclusions, they can be referred to members of the augite and aegirinaugite series. Pleocroic, very thin stressed laminae of biotite are also frequent. Much less common among the minerals in the matrix, are olivine with the typical meshwork grid, plagioclase, garnets and perowskite.

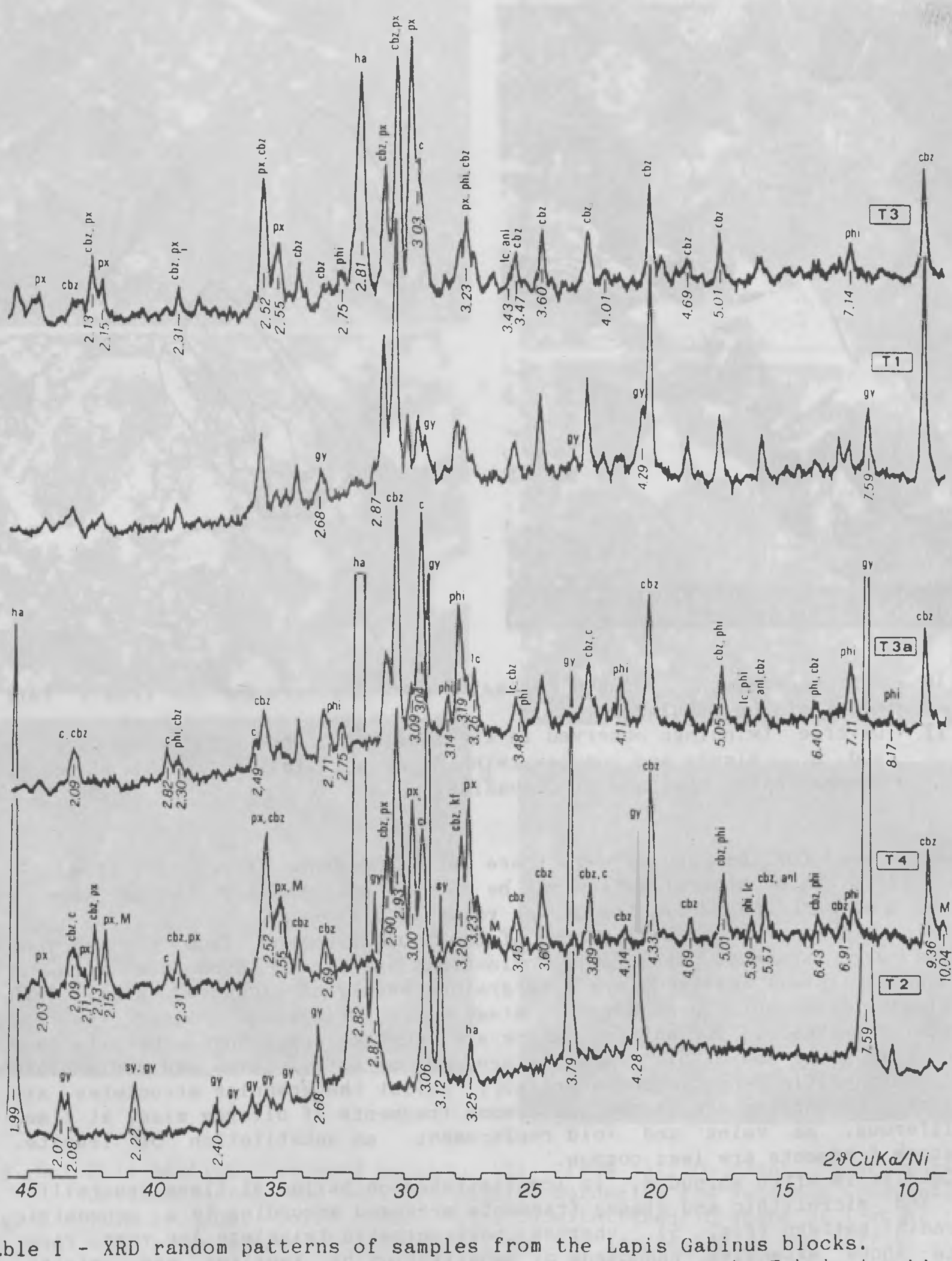


Table I - XRD random patterns of samples from the Lapis Gabinus blocks.
T 1 Gypsum-rich, whitish, soft patinae on the surface of the Tabularium blocks.
T 2 Salts extracted from sample T 3 with abundant NaCl, KCl and sulphates.
T 3 Whole rock sample from the surface of a tuff block of the Tabularium.
T 3a Whole rock sample at a 5 cm depth of a tuff block of the Tabularium.
T 4 Zeolitic matrix of a tuff block from the ancient quarries of Gabii

anl = analcime; c = calcite; cbz = chabazite; gy = gypsum; ha = halite; kf = K-feldspar; lc = leucite; M = mica; phi = phillipsite; px = pyroxene; sy = sylvite.

The matrix of this tuff is characterized by a mosaic of low birefringent crystals of zeolites embedding the lithic fragments and the crystals. Relatively large phillipsite crystals are often intimately associated with chabazite. The phillipsite crystals are prismatic or in radially-arranged fibres but there are also the typical cross-shaped twins occupying the cavities of the lapilli. Chabazite is more commonly in aggregates of the groundmass; when in cavities, it presents a pseudocubic symmetry and compenetration twinning. In figures 7, 8, 9 are images at the polarizing microscope, and in figures 10 and 13 SEM micrographs of the zeolites in the Lapis Gabinus matrix. The abundance of well-developed zeolites in the matrix suggests the derivation from "hot and wet" phreatomagmatic products (9).

In table I are XRD traces of samples of Lapis Gabinus, which evidence the richness in phillipsite and chabazite and of secondary sulphates and chlorides (vide infra).

2.2 State of decay

The Lapis Gabinus of the Tabularium was used in the form of columns and of large parallellepiped blocks placed in such a way as to have the stratification normal to the direction of maximum load. Conspicuous decay developed on the outer surfaces of both blocks and columns; the outside walls and some of the columns present damage resulting from mechanical stress besides exfoliation and

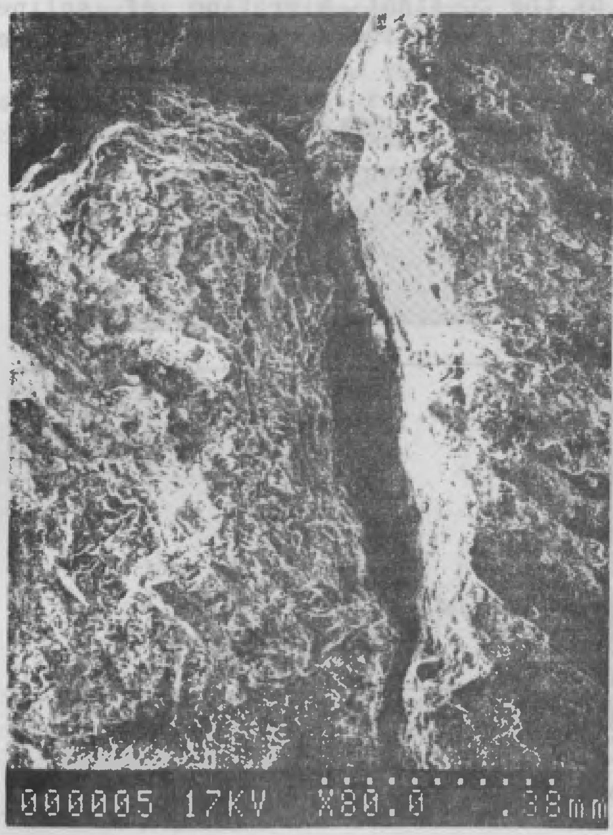


Fig. 12 - (left) Microfractures that tend to spread out towards the external surface of a block of the Tabularium tuff.

Fig. 13 - (right) SEM micrograph. On a fracture surface of a block from the Tabularium, pseudocubic twinned crystals of chabazite with (whitish) secondary gypsum granules on the surface and, center right, a microfracture.

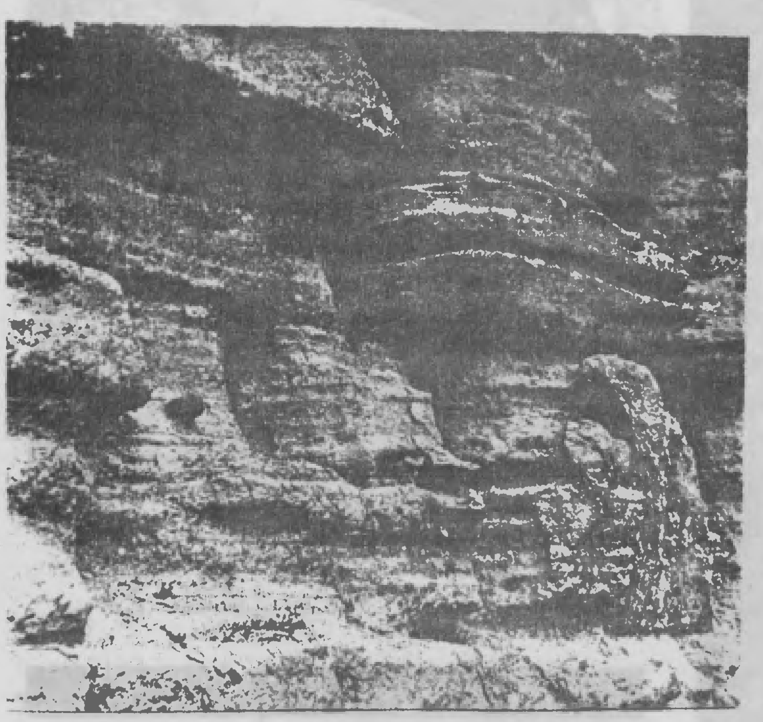
alveolar weathering. The surface of the walls became crumbly, for groundmass decaying, with considerable pulverization and release of the clasts.

SEM studies of surfaces from the tuff blocks showed diffused fracturing with fissures beginning almost always in the zeolitic or glassy matrix (Figures 12 and 13) along the boundaries of the various clasts, and only in some instances propagating across the debris and the phenocrysts (Fig. 4). Fracturing as in the blocks of the Tabularium was also observed in blocks from the closest to the soil level of ancient construction of the town of Gabii.

2.3 Chemical tests

Tests were carried out to measure the salt content of the inner portions of the Tabularium masonry, in order to identify the nature and amount of salts present (11). Two main types of salt were identified: chlorides and sulphates, while nitrates were found to be present in very small amounts (< 0,001%). Chloride content varies widely across a block. As may be seen in figure 15, it decreases from 0.37% on the surface to 0.12%; it then abruptly increases again up to 2% at the centre of the block, and decreases again to 1.6% near the inner surface of the wall. The percentage of sulphates was found to be virtually constant (0.35%) inside the block for a depth of approx. 35 cm. It then increase up to 1.0% at the interface with the mortar and to 2% in the mortar on the backside of the block.

On the external surface of the blocks of the Tabularium, contents of chlorides of 1.6 - 3.3% and of sulphates 7 - 10% were measured. This high concentration of salts can be explained by the constant migration of saline solutions from the inside towards the outside, where they crystallize for the temperature and humidity gradient change.



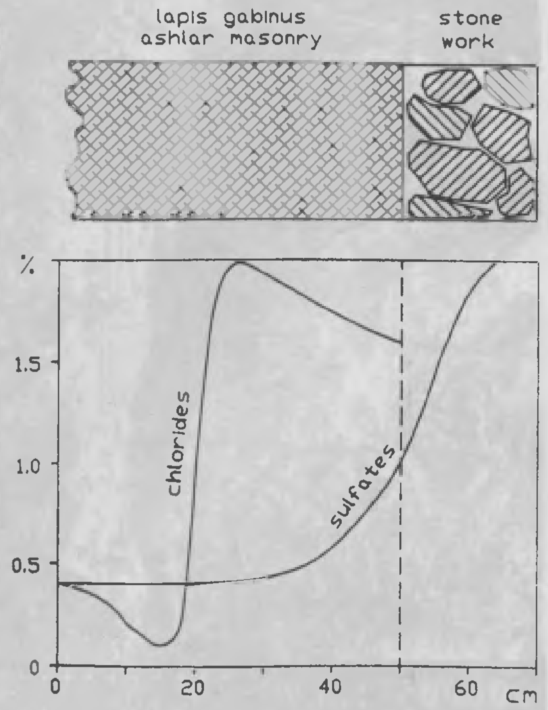


Fig. 14 - (left) On the exposed surface of the Tabularium tuff blocks it is evident the marked decay, with alveolar weathering evidencing the stratification of the tuff. The protruding strata are richer in zeolites.

Fig. 15 - (right) Distribution of soluble salts across a tuff block from the Tabularium. Chlorides maximum content is at the center of the block, whilst sulphates are enriched towards the interior.

2.4 Physical properties

Volume weight and pore distribution, at a pressure of 3.5 MPa by mercury volumeter were determined on cylindrical and shapeless samples of the Lapis Gabinus taken from both the Tabularium and the Gabii area (Fig. 16). The mean values of the apparent specific weight of the Tabularium material was found to be 18.24 kN/m3 with a minimum value of 17.41 kN/m3 and a maximum of 19.50 kN/m3. For the quarry material the mean value was 18.02 kN/m3.

For a mean value of 27.50 kN/m3 of the specific weight, the porosity varies between 29.9% and 33.9% with mean values of 32.7%. The pore distribution at a pressure of 3.5 MPa averages 28.9% with a minimum of 19% and a maximum of 48%. The difference between the two values provides an indication as to the percentage of completely isolated cavities within the individual granules, that cannot be accessed to not even at a pressure of 3.5 MPa.

Water saturation tests were carried out on the Tabularium material in diverse humidity conditions: ambient humidity, water-saturated atmosphere, through capillarity and through immersion (Figures 18 and 19).

A first sample, with initial weight 1300 g, was placed at 105°C for 168 hours to attain constant weight. The dried sample was then kept at 20°C and 60% humidity in normal laboratory conditions for 12 days. In these conditions, the sample absorbed 3.1% wt of water. The sample was then placed in a water-saturated environment at 22°C, where in 26 days absorbed 10.6% water. Finally, the sample was immersed in a tank with the waterline at 20 cm and in 48 hours it absorbed 15.4% of water. Drying in normal environmental conditions for 35 days, the sample at constant weight mantained a 3.5% water content.

Result on a second sample subjected to the same cycle of tests gave no significant differences.

These tests show that the Tabularium Lapis Gabinus, as may be expected, absorbs large amounts of water very easily, capturing it from the air or through capillarity from the soil, and in much the same way it easily loses the humidity

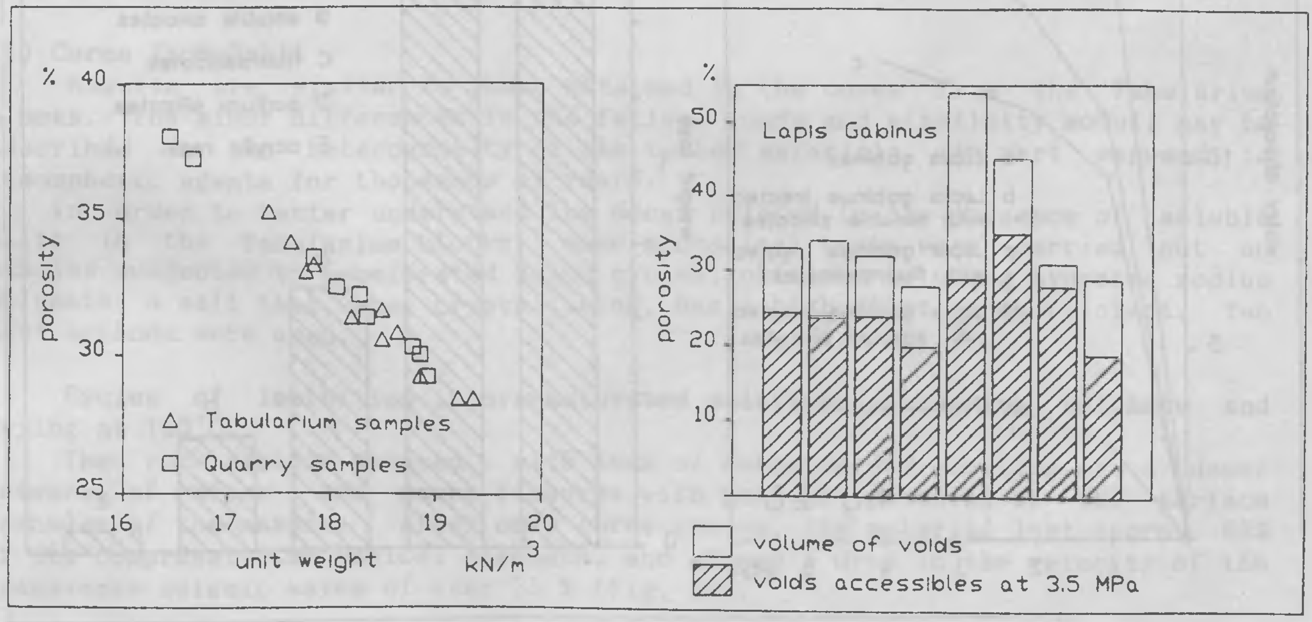


Fig. 16 - (left) The unit weight/porosity in samples from the Tabularium and from the Lapis Gabinus quarries. The Tabularium blocks have a slightly smaller porosity than the samples from the quarries.

Fig. 17 - (right) Relation between volume of voids and voids accessible at a pressure of 3.5 MPa in samples from the Tabularium.

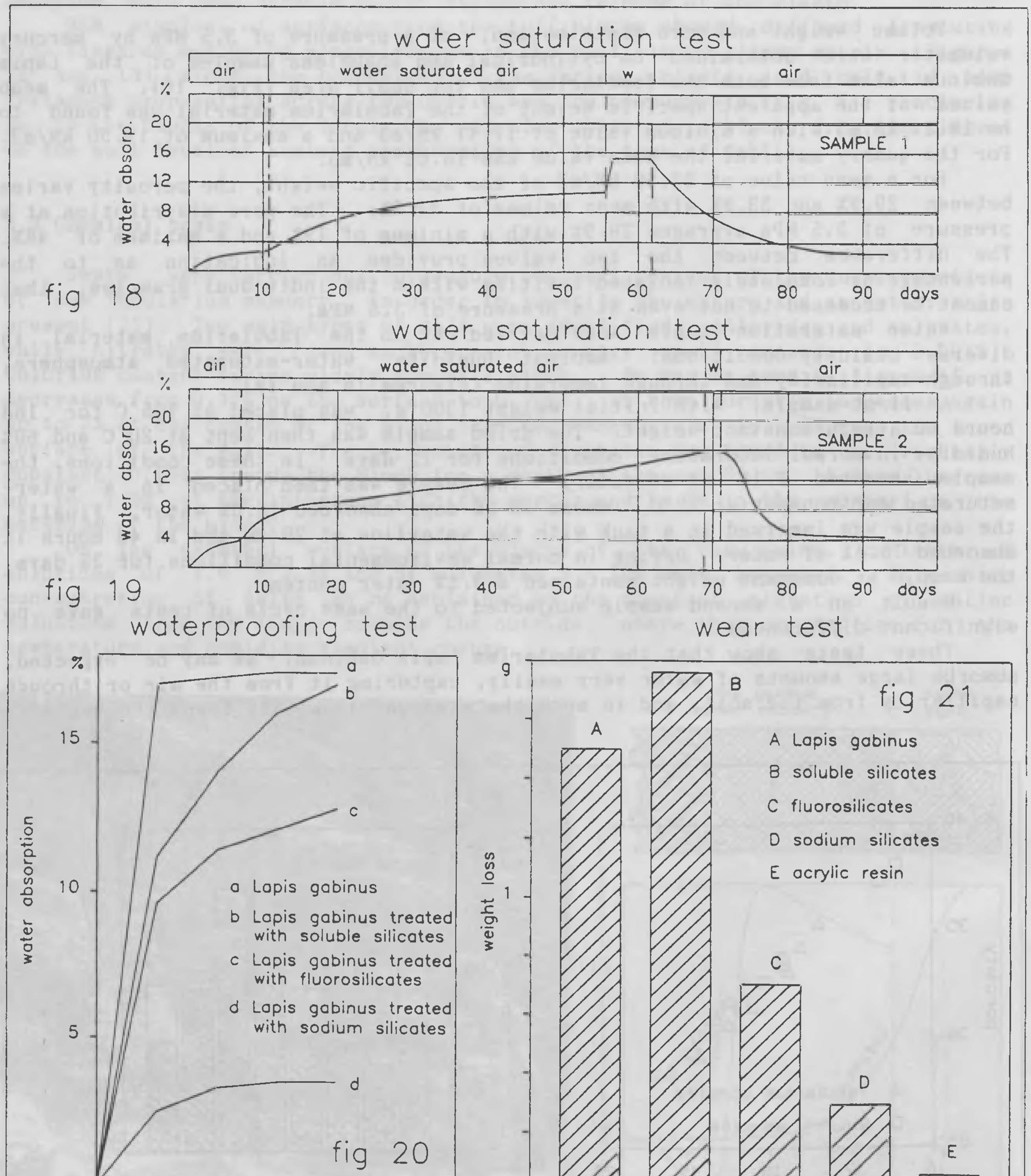


Fig. 18, 19 - Water saturation tests on two samples of the Tabularium tuff. From the left, results of tests in air, water saturated air, immersed in water and re-equilibration in air.

Fig. 20 - Waterproofing tests on tuff samples with diverse consolidating products.

Fig. 21 - Wear test on untreated and treated tuff samples.

as soon as the environment becomes dryer. The absorption values give an order of magnitude of the amount of water that can be absorbed by the Tabularium tuff, possibly very diverse in other blocks, due to the heterogeneity of this material. However, this result demonstrates that the tuff is markedly affected by weather variations in temperature and humidity, but also that the tuff can easily absorb any protective fluid whose capillary tension is similar to that of water.

2.5 Mechanical characteristics

Tests were carried out on:
- 56 mm diameter cores from the Tabularium walls;
- fragments from the Tabularium walls;
- 56 mm diameter cores sampled from the Lapis Gabinus at Gabii.

From the test data, the uniaxial failure loads, the static and dynamic moduli of elasticity, the static and dynamic Poisson coefficients were calculated.

I) Cores from the Tabularium

The cores were taken from blocks with a highly degraded surface. However, the tests showed that the rock overall preserved virtually unaltered its original mechanical properties without any apparent signs of decay. The uniaxial failure load reached values of 25.0-29.0MPa, that are consistent with those found for the cores taken from the outcrops. The stress-strain curves for the materials from the Tabularium and the dynamic moduli of elasticity are shown in Table 2.

The propagation of the longitudinal and transverse seismic waves in these materials confirmed the very good state of preservation of the wall blocks, highlighting the absence of major microfissuring phenomena, up to the external surface of the blocks, where degradation effects are observed for a thickness of a few mm only.

II) Cores from Gabii

Results are similar to those obtained in the cores from the Tabularium blocks. The minor differences in the failure loads and elasticity moduli may be adscribed to the heterogeneity of the tested materials, in part exposed to atmospheric agents for thousands of years.

In order to better understand the decay related to the presence of soluble salts in the Tabularium blocks, some mechanical tests were carried out on samples subjected to accelerated aging cycles, obtained by using hydrated sodium sulphate, a salt that, when crystallizing, has a high dilation coefficient. Two test methods were used.

I) Cycles of imbibition in oversaturated solutions of sodium sulphate and drying at 100°C.

The rock rapidly decayed, with loss of cohesion and creation of a dense network of micro- and macro-fissures with partial loosening of the surface granules of the sample. After only three cycles, the material lost approx. 65% of its compressive mechanical strength, and showed a drop in the velocity of the transverse seismic waves of over 35 % (Fig. 24).

II) Control of the mechanical characteristics and of the transmission of seismic waves in samples saturated with saline solution during crystallization.

The Lapis Gabinus specimen, previously saturated with saline solution of sodium sulphate, was subjected to a static load of approx. 2.0 MPa. This value was chosen on the basis of the mean values of the vertical tensions found in the Ta-bularium blocks. The specimen was then checked during 24 hour cycles, following the variations in the loads and the velocities of the P and S waves during the crystallization process of the salts. Also in this case, at the end of the tests the sample was found to be in a state of decay, but not as severe as in the I) test. This is due to the fact that vertical load caused the salt to crystallize only in the vicinity of external surface of the sample, but already after three test cycles a 10% drop in the yield load of the material was noted (Fig. 24).

Though such tests obviously only in part approximate natural conditions, they show that crystallization processes inside the pores and microfissures of

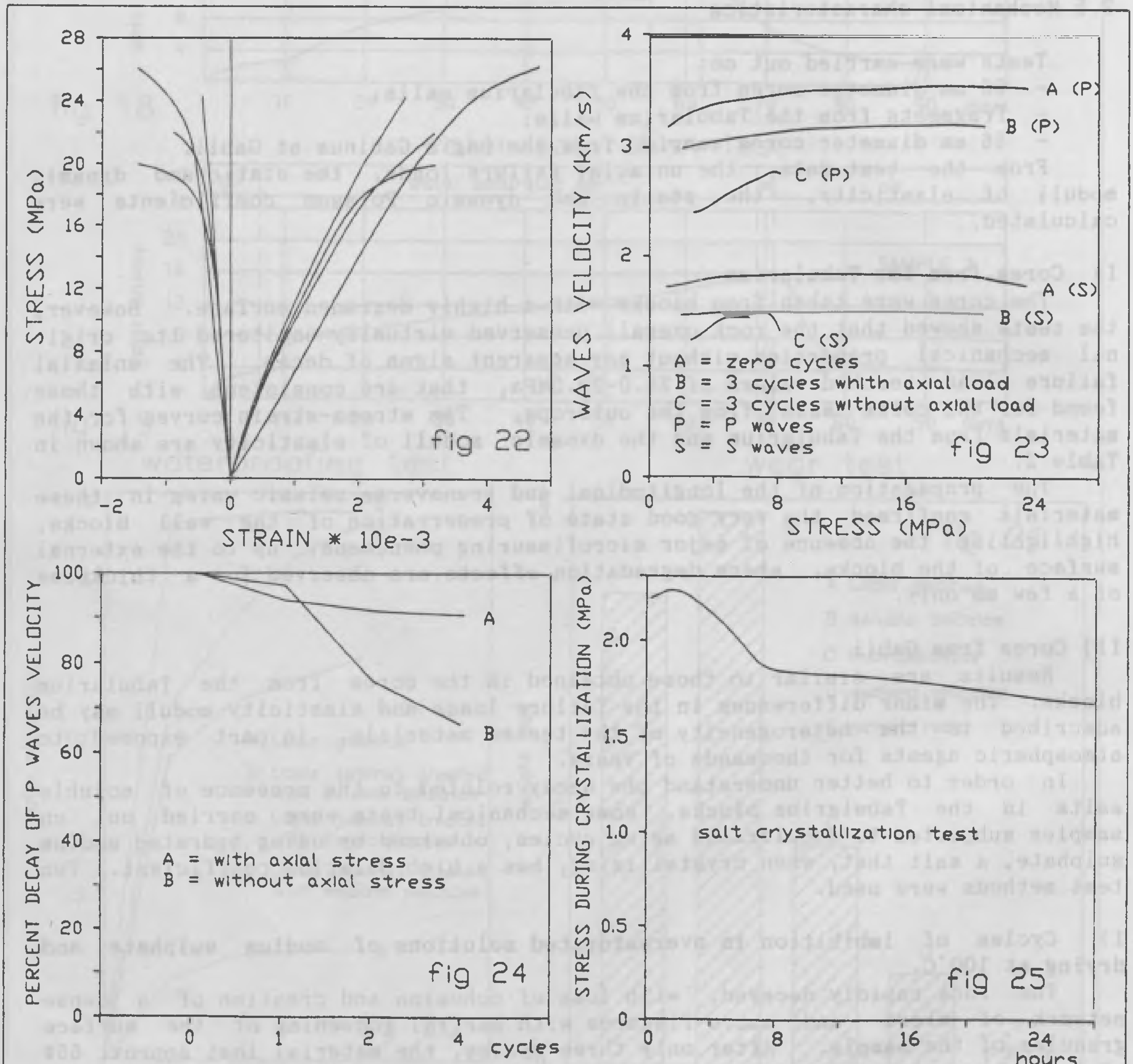


Fig. 22 - Stress/strain diagram for three samples of tuff from the Tabularium and for one from the quarries of Gabii.

Fig. 23 - Crystallization tests of salts in the Tabularium tuff.

Fig. 24 - Percent decay of waves velocity with and without axial stress in the Tabularium tuff samples.

Fig. 25 - Axial stress variation during salt crystallization in the tuff.

the Lapis Gabinus lead to a marked decay of the tuff. This occurs only if the saline solution has the possibility of evaporating as on the external surface of Tabularium blocks, whereas inside, where salts remain in solution, no variation of the mechanical properties occurs.

3. TREATMENT TESTS

In the early 70s, consolidation treatments with five chemical compounds were tested both in the laboratory and in situ on tuff blocks of the Tabularium (11). The exact composition of the chemical compounds was not known but they could be classified as: I) fluorsilicates; II) sodium silicates; III) soluble silicates; IV) paraffined hydrorepellents; V) acrylic resins.

Preliminary measurements of absorption coefficients and abrasion resistance before and after treatments (Figures 20 and 21) led to the decision of using soluble silicates, which favoured a marked reduction of water absorption and an increase in mechanical properties, and acrylic resins which induced a significant increase of the abrasion resistance of the tuff. Soluble silicates were then applied directly on blocks of the internal and external walls of the Tabularium. However, soon after application, the surfaces of the blocks were covered by a very evident white patina, which never did appear in the laboratory tests. Chemical and mineralogical investigations led to the conclusion that the chlorides and sulphates on the surface of the blocks reacted with the sodium silicate consolidating agents giving an insoluble white precipitate of silicates. Such effect was not observed in the laboratory samples, as these were cut under abundant water, the treated surfaces were "new" and not exposed to the atmospheric agents and to salt accumulation, and absorption tests implied a long immersion in water and consequent leaching of soluble salts.

A check made soon after application of acrylic consolidating compounds to the surface of the blocks of the Tabularium showed that they greatly reduced permeability of the surfaces and improved mechanical properties. The protective action acted both on the surface, and inhibiting crystallization of salts through migration of interstitial waters. Due to to difficulties in reaching today the blocks, because of extensive excavations which lowered the field level, and lack of evident macroscopic differences, it has not been possible to check the efficacy of these treatments after twenty years.

4. CONCLUSIVE REMARKS

Petrographic and mineralogical data on the Lapis Gabinus were extremely scarce (4, 5), though this tuff is well known and cited in the archeological literature for its use in important Roman monuments. Therefore, attention was dedicated to the characterization of its structure and composition. The blocks employed in the construction of the Tabularium are made of a pyroclastic material constituted by lapilli, scoriae, lithic fragments, bound by an originally glassy matrix where are dispersed crystals such as micas, pyroxenes and leucite. The matrix is largely substituted by zeolites (phillipsite and chabazite); analcime, another zeolite, is present as a product of the modification of leucite. This tuff is also characterized by the presence of carbonates, as micritic clasts and as common aggregates of secondary sparitic calcite filling the empty space in the zeolitezed matrix.

As regards the state of conservation of the Tabularium tuff, on all the exposed surfaces are evident extensive phenomena of detachment of scales, similar to those present in blocks close to the foundations of structures in the ancient city of Gabii (where the Roman quarries were located). Moreover, in the Tabularium, there are marked processes of alveolar weathering and of micro- and macro-fracturing. Detailed analysis of the fracturing systems revealed that they preferentially develop across the zeolitic aggregates of the rock matrix, though in some instances they continue across lapilli and scoriae.

In the Tabularium tuff there are also evident phenomena of chemical alteration, with diffused chlorides (mainly) and gypsum. The presence of chlorides is related to the fact that the upper part of this structure was once used as a salt deposit. The mode of emplacement of gypsum within the tuff does not offer clues to its origin. It may derive from reaction of the abundant carbonate component of the tuff with atmospheric pollutants or from sulphur compounds present in cements employed many years ago in the restoration of the Tabularium.

In the conservation treatments carried out approx. 20 years ago (11) the best results were obtained using acrylic resins which increased the mechanical properties, whilst soluble silicates proved unadequate giving rise to whitish precipitates on the surface of the blocks. These results could be linked to the peculiar exchange properties of zeolites (12, 13), minerals with large internal communicating cavities where H2O and large cations can be accomodated to balance the positive charges missing for the substitution of silica in the aluminum tetrahedra. In the ideal chabazite structure, only the site at the center of the 8-membered ring is 100% occupied by H2O, whilst the occupancy by H2O of other site varies (13, 14, 15). Therefore, zeolites have a great exchange capacity which must be taken into account when introducing chemical agents in a zeolitized tuff. Recently, Lewin and Charola (16) evidenced in a chabazitic tuff from Naples that the calcium of the zeolite was exchanged with sodium from marine water, inducing an anisotropic distortion of the crystalline lattice, with a 0.2% expansion along the "a" and "b" crystallographic axes. Such effects are known to occur also with other cations and organic molecules.

There is indeed a wide field open for investigations on the interaction between consolidating products and the zeolitic matrix of tuffs. Among these products, acrylic monomers seem to be particularly suitable. Satisfactory improvements of the mechanical and physical properties of the Neapolitan chabazitic tuff named "Yellow Neapolitan Tuff" were obtained by Aurisicchio et al. (17) using metilmetacrilate MMA, though in situ and long-term experience still have to provide conclusive evidence on the validity of these treatments.

5. REFERENCES

1. Coarelli, F.; "Guide Archeologiche Laterza. Roma"; Laterza, Bari, 1980; pp. 32-60

2. Fornaseri, M.; Ventriglia, U.; Scherillo, A.; "La regione vulcanica dei Colli Albani"; C.N.R., Roma, 1963; p. 561

3. Locardi, E.; Lombardi, G.; Funiciello, R.; Parotto, M.; Geologica Romana 1977, 15, 279-300

4. Fornaseri, M.; Periodico Mineral. 1947, 16, 141-199

5. Sabatini, V.; Mem. Descrittive Carta Geol. It. 1900, 10, 177-183

6. Corda L.; De Rita D.; Tecce, F.; Bull. Soc. Geol. It. 1976, 95, 1235-1252

7. Mattson, P.H.; Alvarez W.; Bull. Vulc. 1974, 37, 553-572

8. Civitelli, G.; Funiciello, R.; Parotto, M.: Geologica Romana 1975, 14, 1-39

9. De Rita, D.; Parotto, M.; Stocchi, V.: Mem. Soc. Geol. It. 1986, 35, 769-773

10. Fisher, R.V.; Walters, A.C.: Am. J. Sci. 1970, 268, 157-180

11. Ventriglia, U.; Cavallo, R.; "Degradazione del tufo "Peperino" del Tabularium. Comportamento al trattamento con sostanze protettive": Unpublished report, Roma, 1971, p. 30

12. Breck, D.W.; "Zeolite molecular sieves", John Wiley and Sons, New York, 1971, p. 202

13. Galli, E.; Rend. Soc. It. Miner. Petrol. 1975, 31, 549-564

14. Passaglia, E.; Am. Mineral. 1970, 55, 1278-1301.

15. Alberti A.; Galli, E.; Passaglia, E.; Vezzalini, G. Zanazzi, P.F.; Zeolites 1982, 2, 303-309

16. Lewin, S.Z.; Charola, A.E.; Advances in X-ray analysis, 1988, 22, 169-180

17. Aurisicchio, S.; Evangelista, A.; Nicolais, L.; Riv. It. Geotecnica, 1985, 19, 89-100

ACKNOWLEDGEMENTS

Authors thank Prof. R. Cavallo for providing unpublished data on the physico-mechanical properties of the Lapis Gabinus and R. D'Inverno, L. Corso and M. Petri for the collaboration given in the laboratory tests.

This work was financially supported by the Centro di Studio per la Geologia Tecnica of the CNR and by Ministero della Pubblica Istruzione grant no. 9020903094-60%-1989

macro-fractures. Detailed analysis of the fracturing systems revealed that [illegible] zeolitic aggregates of the rock matrix, though in some instances they continue across lapilli and scoriae.

In the Tabularium tuff there are also evident phenomena of chemical alteration, with [illegible] and gypsum. The presence of chlorides is related to the fact that the upper part of this structure was once used as a [illegible] [illegible] within the tuff does [illegible] to its origin. It may derive from reaction of the abundant carbonate component of the tuff with atmospheric pollutants or from sulphur compounds present in cements employed many years ago in the restoration of the Tabularium.

In the conservation treatments carried out approx. 20 years ago (11) the best results were obtained using acrylic resins which increased the mechanical properties, whilst [illegible] silicates [illegible] giving rise to whitish precipitates on the surface of the blocks. These results seem to be linked to the peculiar exchange properties of zeolites [illegible] with large internal communicating cavities where H_2O and large cations can be accommodated to balance the [illegible] charge arising from the substitution [illegible] the aluminum in tetrahedra. In the ideal chabazite structure, [illegible] the center of the [illegible] of [illegible] have a great exchange capacity, which must be taken into account when introducing chemical agents in [illegible] tuff from Naples that the calcium of the zeolite was exchanged with sodium from marine water, inducing an anisotropic distortion of the crystalline lattice, with a [illegible] expansion along the "a" and "c" crystallographic axes. Such effects are known to occur also with other cations and organic molecules.

There is indeed a wide field open for investigations on the interaction between consolidating products and the zeolitic phases of tuffs, [illegible] those [illegible]

[illegible]

6. REFERENCES

1. Coarelli, F.; "Guide Archeologiche Laterza, Roma"; Laterza, Bari, 1980; pp. [illegible]

2. Fornaseri, M.; [illegible]; [illegible]; "La regione vulcanica dei Colli Albani"; C.N.R., Roma, 1963, p. [illegible]

3. [illegible]; Funiciello, R.; Parotto, M.; Geologica Romana [illegible]

4. [illegible], M.; Periodico Mineral. [illegible]

5. [illegible] Mem. Descrittive Carta Geol. It. [illegible]

6. Corda L., De Rita D., [illegible]; Boll. Soc. Geol. It. [illegible]

7. Mattias, P.P.; Ventriglia U.; Bull. Volc. [illegible]

8. [illegible]; Funiciello, R.; Parotto, M.; Geologica Romana [illegible]

DETERIORATION AND CONSERVATION PROBLEMS OF THE RHYODACITIC MATERIAL USED FOR THE SCULPTURES IN THE BOMARZO PARK (VITERBO)

F. FRATINI, C. MANGANELLI DEL FA', E. PECCHIONI and A. SCALA*

CNR, Centro di Studio sulle Cause di Deperimento e sul Metodo di Conservazione delle Opere d'Arte, 50121 Firenze, Italy
* Ausimont-Montefluos SpA, Centro Ricerche e Sviluppo, Milano, Italy

ABSTRACT

A large part of the historical buildings in central Italy have used volcanic rocks in their construction. These materials, however, have seldom been used in the artistic field. An interesting exception can be found in the Bomarzo Park where a large number of sculptures have been carved in the local trachytic rocks. The environment created by the natural outcrops and the easily carved rock, suggested the realization of the sculptures directly from the dispersed boulders. These sculptures, which date back to the sixteenth century, are suffering from alteration processes mainly related to the high moisture of the site. The causes of these alterations and the present condition of the stone has been studied with the aim to suggest suitable conservation procedures.

RESUMEN

Una gran parte de los edificios históricos de Italia central han utilizado rocas volcánicas en su construcción. Estos materiales, sin embargo, se utilizaron muy poco en el campo artístico. Una excepción interesante es el Parque Bomarzo donde muchas esculturas han sido creadas con la roca traquítica del lugar. El entorno creado por el afloramiento de estas rocas y su fácil tallado inspiró la creación de estas esculturas directamente de las rocas dispersas. Estas esculturas, que datan del siglo dieciséis, están deteriorándose fundamentalmente debido a procesos de alteración relacionados con la alta humedad del sitio. Se han estudiado las causas de estas alteraciones y las condiciones presentes de la piedra con el fin de sugerir tratamientos de conservación adecuados.

1. INTRODUCTION

The "Sacro Bosco" (holy forest) lies in a green valley at the foot of the Bomarzo village, near Viterbo. It is one of the most peculiar monumental complexes of the Italian "Cinquecento" and it is characterized by a large number of big sculptures spread between medows and luxuriant vegetation (Figure 1).

Fig. 1 - The frightful head of the orkus. It represents the entrance to the underground world as stated by Dante's paraphrase written on his lips.

Compared with the usual configuration of Renaissance gardens, the "Sacro Bosco" does not show ordered and simmetrical perspectives; on the contrary it provides an exciting succession of apparitions revealing themselves to the unaware visitor among the trees, along the paths, behind the rocks.

These sculptures have been carved from the dispersed boulders made of a riodacitic ignimbrite called "Peperino".

The visitor meets at first a giant quartering a victim, then he finds a big tortoise with a woman on its back. Going on, there is a fountain with the representation of a winged horse, Pegaso, then a nymphaeum which leads to an open space dominated by a leaning house. The wide terrace that stretches in the higher portion of the park, shelters two big figures flanked by monsters and animals: an ork, an elephant that clutchs a warrior with the proboscis, an infernal face with open jaws . But the surprises are not finished yet. The whole park is strewn with inscriptions engraved into the rocks; one of them mentions the name "Sacro Bosco".

The author of these verses and inventor of the park was Pierfrancesco Orsini, named Vinicio. He began working on this idea in 1558, when he came back to his feud after a long military activity. Most of the sculptures were finished by 1563: the identification of the real author of sculptures and architectures is still a matter of discussion. The quality of the figures is surely of a remarkable level and suggest the presence of one or more professional sculptor or architect supervising the work.

At present these sculptures are affected by alteration processes connected with the environmental thermohygrometric conditions. Their surface is often completely covered by biological patinas (mosses, lichens) giving rise to a velvet layer which sometimes prevents the exact comprehension of the sculptures, the anatomic details and the inscriptions. These biological patinas keep the materials beneath wet for a long time and therefore promote their alteration processes.

When the rock is rich in lapilli and rock fragments, "Peperino" shows a special kind of degradation which puts in evidence these inclusions while the surface takes a pseudoalveolar aspect. In the long run these processes will cause the statues to mingle again with the rocks they had been carved out.

Anyway "Peperino" is a rock that consolidated in superficial conditions, close to the subaerial ones; for such a reason this material shows a fairly good durability. This good resistence to alteration is connected with a strong formability and this is why it has been used since ancient times as free stone and dressed stone.

Viterbo and the surrounding villages have been built largely with this kind of rock that, due to its yellowish colour on alteration, gives to the houses and monuments a sort of warm tonality.

We have studied the present conditions of this material and its degradation processes with the aim of giving a contribution to the restoration of the Bomarzo artifacts.

2. METHODS AND MATERIALS

In order to have a set of data adequate to understand the alteration processes characterizing the sculptures it has been necessary to sample both weathered and unweathered material. We drew 11 samples of weathered material from the statues while the unweathered rock was sampled from four quarries on the outskirts of the Park. Each quarry provided two samples. From one of them we also collected some weathered material to compare with the one from the Park.

The following analyses were made on all samples:

- thin section petrographic study by optical microscope

- determination of the principal mineralogical composition by XRD

- determination of the mineralogical composition of the clay portion ($<4u$) by XRD

- determination of the major elements chemical composition by XRF

- determination of physical characteristics: density, bulk density, open porosity, imbibition coefficent, pore-size distribution by helium porosimeter and mercury porosimeter

- SEM observations and analyses of some patinas.

3. GEOLOGIC SETTING OF "PEPERINO"

"Peperino" is defined petrographically as a riodacitic ignimbrite. It belongs to the Mount Cimino volcanic complex, in the surroundings of Viterbo, north of Rome.

Volcanites from M. Cimino are quite similar to the alkali-calcic tuscan volcanites and consolidated in an age interval which ranges from 1,9 to 1,4 m.y. ago according to the following succession:

1) riodacitic domes

2) riodacitic ignimbrite (Peperino)

3) trachytic and latitic lavas

4) latitic and olivin- trachytic lavas

These mutual relationships are not always simple and univocal.

Riodacitic domes form particular hills and surround M. Cimino like a circle.

Riodacitic ignimbrites are placed in a fan shaped plateau which spread for an extension of 10-12 km with respect to the volcanic vent (M. Cimino). The thickness of the ignimbrite flow is rather variable; from few tens up to some hundreds m. according to the morphology. Probably this thickness is due to several ignimbrite flows as shown by some ash intercalations and sharp changes in the welding degree.

Trachytic-latitic lavas are due to a volcanic episode restricted to the slopes of M. Cimino and they partly cover domes and ignimbrites. These lava-flows are very thick and this most likely depends on the high viscosity of the lava which had no possibility to spread out.

Latitic and olivin-trachytic lavas represent the last volcanic episode of M. Cimino. They spread out from the top of the volcano and probably were characterized by high fluidity compared to the previous ones, as shown by the low thickness of the lavas-flows and the long distance reached.

4. EXPERIMENTAL RESULTS

4.1 Thin Section Petrographic Study

The analysis of unweathered material shows a rock characterized by a porphyritic structure with a percent of phenocrysts ranging from 35 % to 60 % . We found in order of decreasing abundance, plagioclases, sanidine, biotite, iperstene, augite, scarce olivine. Plagioclases are of andesine- labradorite type often with a chipped shape. Sanidine has always a chipped shape with some rounded edges. Iperstene and augite are mostly idiomorphic. Biotite often shows a coloured halo characterized by a lower pleochroism and sometimes partial hematization phenomena. Some biotite crystals appear strongly expholiated as a consequence of the stresses suffered during the eruption. Lapilli are really abundant and show a characteristic fluidal glassy structure. Minor amounts of rock fragments are present like metamorphic rocks rich in spinels, monzonitic rocks, limestones and siliceous rocks.

In weatherd rocks phenocrysts look quite similar to the unweathered ones. Plagioclases and sanidine are mostly unweathered with no mark of sericitization phenomena. Also pyroxenes are mostly unweathered but show serpentinization phenomena when they are present in the outer surface (Figure 2) and sometimes along the fractures in not superficial phenocrysts. Biotite too does not show differences with respect to the one of unweathered samples. On the contrary, the glassy groundmass shows some differences; along the surface there is often a devetrification with the glass changing in chlorite and sometimes in serpentine. Inside the material these phenomena are restricted to narrow regions concerning just a little portion of the rock.

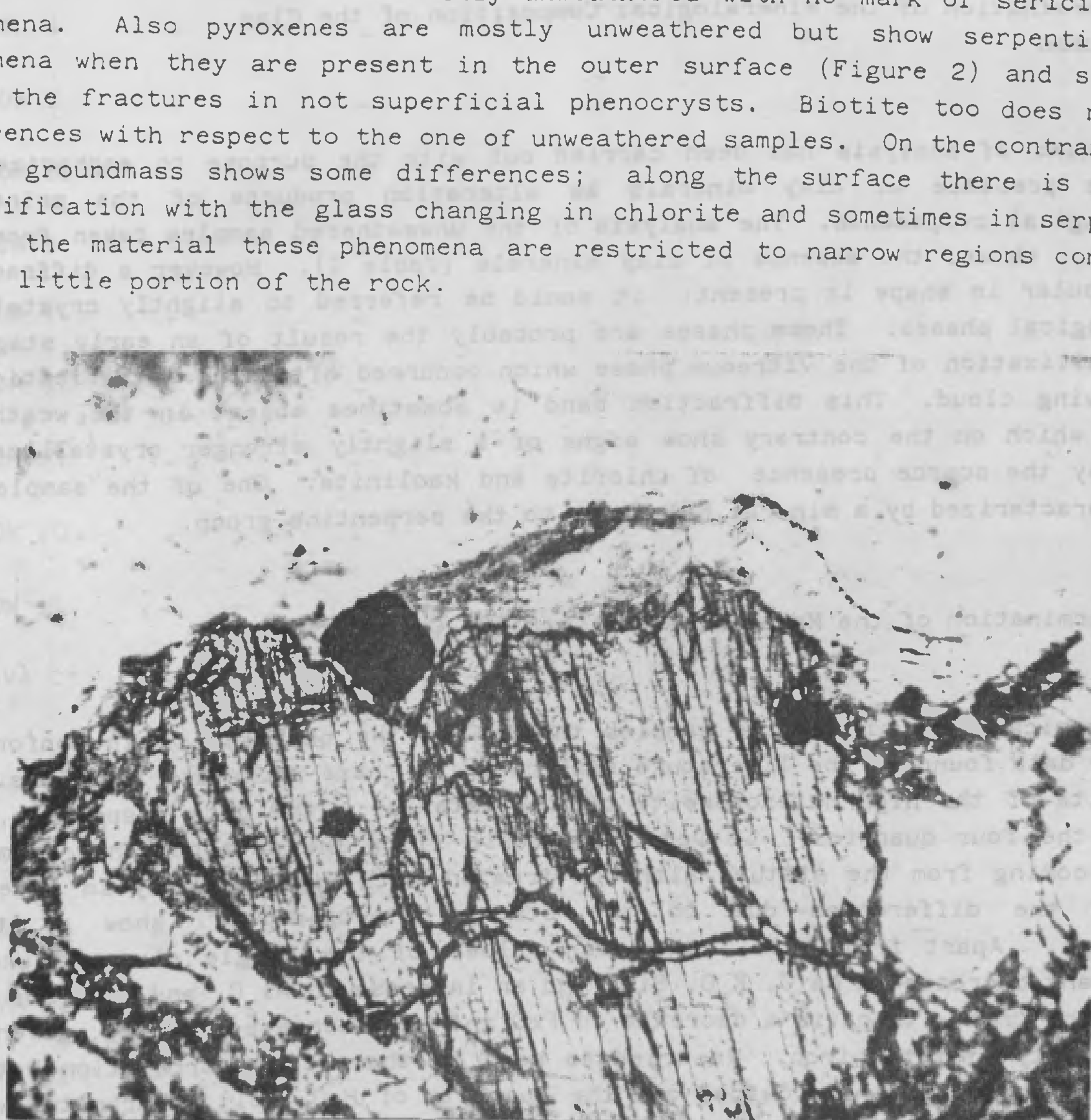


Fig. 2 - 10 X, nicols ⊥. Thin section photography of a pyroxene lying in the outer surface and affected by serpentinization phenomena.

4.2 Determination of the Principal Mineralogical Composition

This kind of analysis confirmed the thin section observations. The principal mineralogical components are: plagioclase of andesine-labradorite composition, K-sanidine, biotite, pyroxenes (augite and iperstene). The weathered material has an identical composition and this means the absence of significant quantity in alteration compounds.

4.3 Determination of the Mineralogical Composition of the Clay Portion

This kind of analysis has been carried out with the purpose to emphasize the possible presence of clay minerals as alteration products of the principal mineralogical components. The analysis of the unweathered samples taken from the quarries, showed the absence of clay minerals (Table I). However a diffraction band tabular in shape is present: it could be referred to slightly crystalline mineralogical phases. These phases are probably the result of an early stage of recrystallization of the vitreous phase which occurred after the lithification of the glowing cloud. This diffraction band is sometimes absent in the weathered samples which on the contrary show signs of a slightly stronger crystallization marked by the scarce presence of chlorite and kaolinite. One of the samples is also characterized by a mineral belonging to the serpentine group.

4.4 Determination of the Major Elements Chemical Composition

The chemical analysis of the samples taken from the quarries is in conformity with the data found in the literature that classify these rocks as riodacites.

In spite of the high heterogeneity of the material, the data dispersion, as regards the four quarries, is very low (Table II). The data obtained from the samples coming from the statues although treated with high accuracy in order to minimize the differences due to the strong heterogeneity, show a strong dispersion. Apart from this, the mean values of the single elements show a significant decrease in Na_2O, K_2O, SiO_2 and an increase in Al_2O_3 and H_2O. For what it concerns iron, there is a decrease in FeO and an increase in Fe_2O_3, given the same quantity of total iron. We tried to see if there is a correlation between the quantity of the single oxides and the quantity of H_2O (LOI), parameter which can be directly related with the rock alteration degree. A good correlation came out especially as regards Na_2O and SiO_2 (Figure 3 and 4) while for the other elements, the value dispersion did not allow us to draw any significant curve even if some correlations may be recognized. On the whole we may affirm that the alteration process involved a leaching of alkalis and SiO_2 and a relative increase in Al_2O_3. The iron, in connection with the present conditions of alteration, does not show a significant mobility, even if its increasing oxidation is evident.

TABLE I. Mineralogical Composition of the Clay Portion

	Chlorite	Kaolinite	Serpentine	Tabular diff. band
BOM 1	+	−	−	+
BOM 2	+	−	−	+
BOM 3	−	−	−	+
BOM 4	−	−	−	+
BOM 5	+	−	−	−
BOM 5b	−	−	−	−
BOM 6	−	+	−	−
BOM 7	+	−	−	+
BOM 8	+	−	−	−
BOM 9	−	−	−	+
BOM 10	−	−	−	−
BOM 11	−	−	−	+
CAVA C*	−	+	+	+
CAVA A1	−	−	−	+
CAVA A2	−	−	−	+
CAVA B1	−	−	−	+
CAVA B2	−	−	−	+
CAVA C1	−	−	−	+
CAVA C2	−	−	−	+
CAVA D1	−	−	−	+
CAVA D2	−	−	−	+

BOM: weathered samples; CAVA: unweathered samples;
CAVA C*: weathered sample from quarry C.

TABLE II. Major Elements Chemical Composition
(mean values of weathered and unweathered samples)

	weathered samples		unweathered samples	
	$\bar{X}$	S	$\bar{X}$	S
H_2O	2.69	1.04	0.96	0.16
Na_2O	1.79	0.14	2.07	0.04
MgO	2.05	0.28	2.36	0.16
Al_2O_3	17.34	1.04	16.48	0.04
SiO_2	60.08	1.32	61.68	0.16
P_2O_5	0.31	0.08	0.24	0.01
K_2O	4.99	0.23	5.24	0.06
CaO	4.14	0.65	4.58	0.09
TiO_2	0.78	0.04	0.81	0.03
MnO	0.09	0.02	0.08	0.00
FeO	3.06	0.26	3.52	0.25
Fe_2O_3	2.93	0.29	2.32	0.16
Fe tot.	5.56	0.37	5.49	0.09

$\bar{X}$: mean
S : standard deviation

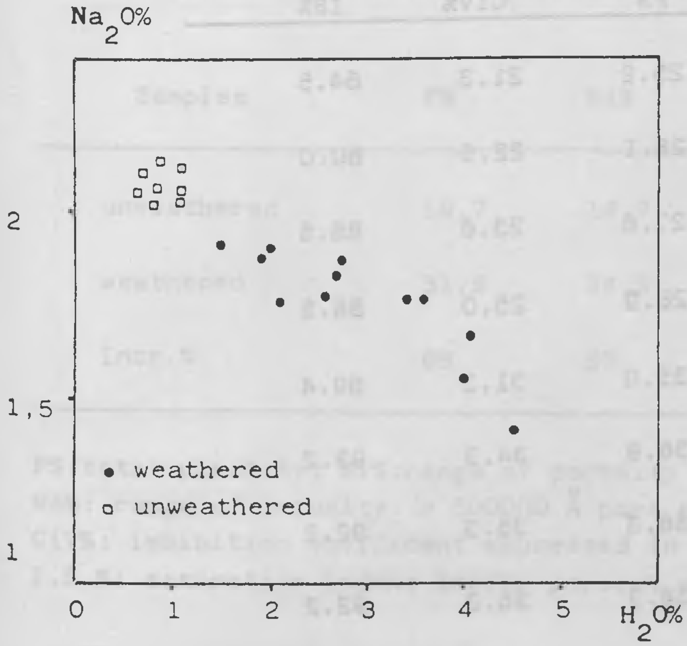


Fig. 3 - Percent of Na_2O plotted versus H_2O for each sample.

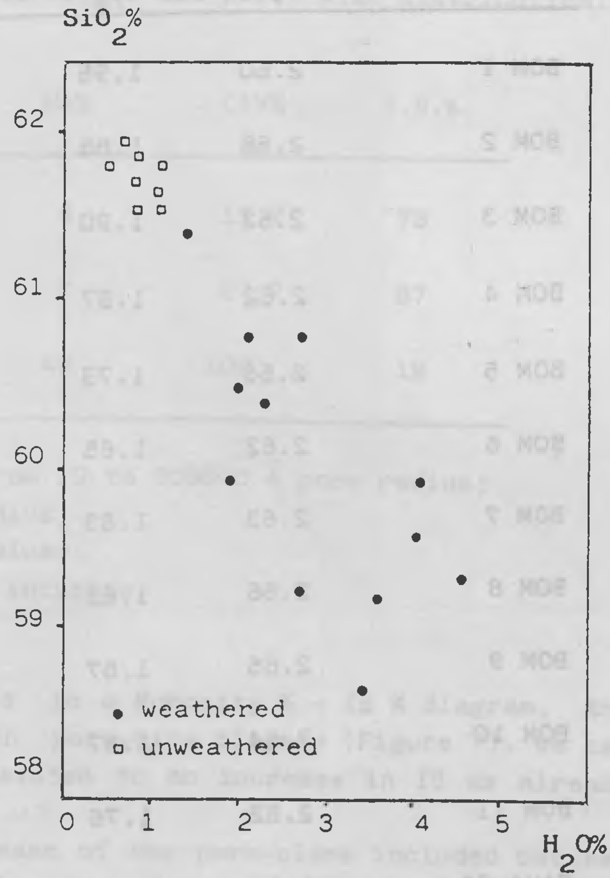


Fig. 4 - Percent of SiO_2 plotted versus H_2O for each sample.

4.5 Physical Characteristics

The study of the physical characteristics as well as the chemical analysis, involved some problems due to the high heterogeneity of the rock. In order to minimize these differences, we analized at least three samples of each specimen. The data showed in Table III therefore are to the mean values . A comparision between the two groups of samples (weathered and unweathered) emphasize, as expected, the higher dispersion in the values of weathered samples and the logical variations of some parameters as a consequence of the alterative processes . In particular, if we consider porosity and imbibition coefficent, we observe that an increase in total porosity equal to 68 % is not reflected in a similar increase in imbibition coefficent which has risen by 100 % (Table III and IV). If we relate these two parameters, we observe that with the increasing porosity the samples are sited closer to IS=100% (Figure 5).

These data can be better understood if we take in consideration the histogram of the pore-size distribution in the range 10-500.000 Å (Figure 6). The change in porosity and in the pore-size distribution are in fact the parameters more closely related to the water absorption and hence to the decay processes. Weathered samples are characterized by an increase in porosity equal to 80 % (Table IV) and, within these limits, by a higher increase in the 10^3 and 10^5 Å pores size range.

TABLE III. Physical Characteristics

	γ	γs	P%	CiV%	IS%
BOM 1	2.60	1.95	25.2	21.3	84.5
BOM 2	2.58	1.86	28.1	22.5	80.0
BOM 3	2.63	1.90	27.6	23.6	85.5
BOM 4	2.62	1.87	28.9	25.0	86.5
BOM 5	2.66	1.73	35.0	31.3	89.4
BOM 6	2.62	1.65	36.8	34.3	93.2
BOM 7	2.63	1.63	38.3	35.3	92.2
BOM 8	2.66	1.63	38.3	35.3	92.2
BOM 9	2.65	1.67	36.7	34.7	94.5
BOM 10	2.64	1.87	28.8	25.5	88.5
BOM 11	2.52	1.76	29.9	19.8	66.2
CAVA C*	2.62	1.97	24.8	22.9	92.4
$\bar{X}$	2.62	1.79	31.5	27.7	87.2
S	0.04	0.13	5.1	6.1	7.9
CAVA A1	2.67	2.10	21.2	15.5	73.1
CAVA A2	2.66	2.13	19.9	14.2	71.3
CAVA B1	2.66	2.18	17.7	12.4	70.0
CAVA B2	2.65	2.15	18.8	13.5	71.8
CAVA C1	2.65	2.14	19.2	14.3	74.7
CAVA C2	2.66	2.19	17.6	13.0	73.8
CAVA D1	2.61	2.21	15.1	10.5	69.5
CAVA D2	2.66	2.11	20.4	16.3	79.7
$\bar{X}$	2.65	2.15	18.7	13.7	73.0
S	0.02	0.04	1.9	1.8	3.2

γ: density; γs: bulk density; P%: open porosity; CiV%: imbibition coefficent expressed in volume; IS%: saturation index.

TABLE IV. Summary of the Physical Characteristics and pore- size distribution.

Samples	P%	Mi%	Ma%	CiV%	I.S.%
unweathered	18,7	14,7	5	13,7	73
weathered	31,5	24,5	7	27,7	87
Incr.%	68	80	40	102	19

P%:total porosity; Mi%:range of porosity from 10 to 500000 Å pore radius;
Ma%: range of porosity > 500000 Å pore radius;
CiV%: imbibition coefficent expressed in volume;
I.S.%: saturation index; Incr%: percent of increase.

In order to show these changes we plotted in a Porosity % - IS % diagram, the porosity values of each sample subdivided in pore-size classes (Figure 7). We can observe that an increase in porosity is related to an increase in IS as already showed in Figure 5.

Furthermore it is to be noticed the increase of the pore-class included between 10^4 and 10^5 Å as a function of IS, while the other classes do not show any remarkable increase. Therefore we could infer that this pore-class is the one that mostly contribute to the water absorption and especially to keep this water inside the structure.

Density (γ) shows only a little decrease in weathered samples. This means that alteration compounds could not form in significant amount but also that the recrystallisation of glassy phase did not took place, as confirmed by the clay portion analysis.

4.6 SEM Observation and Analysis of Some Patinas

During sampling we observed that the rock surface , relative to compact lichen coverings, showed, for a thikness of about 1.5 mm, a darker colour and a traslucent appearence with a coherence even greater with respect to the underlying material. In order to verify the composition of this patina, we made some sections that have been observed by SEM and analized by the electron microprobe.

The patina showed a compact structure and a more homogeneous appearence than the underlying rock (Figure 8), while the microprobe analysis showed a slight increase in Fe (Figure 9) and P with respect to the other major elements.

All these observations support the hypotesis of a contribution of lichens in the formation of this patina. Acidic compounds produced by their metabolism may have caused a transformation of the primary glassy structure and a concentration of the iron as reported in the literature as due to some kinds of lichens.

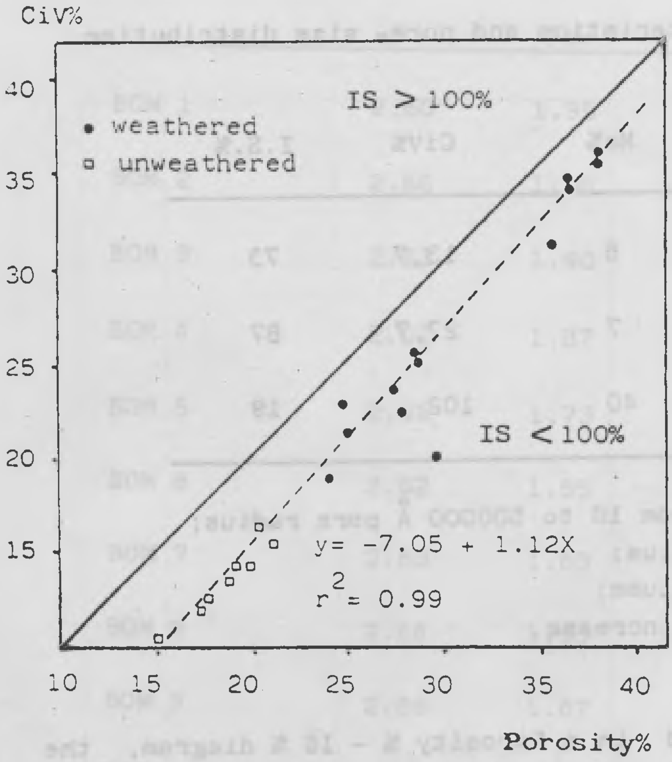


Fig. 5 - Imbibition coefficent (CiV%) plotted versus porosity for each sample . The continuous line divides the samples characterized by saturaction index (IS) < and > 100% respectively.

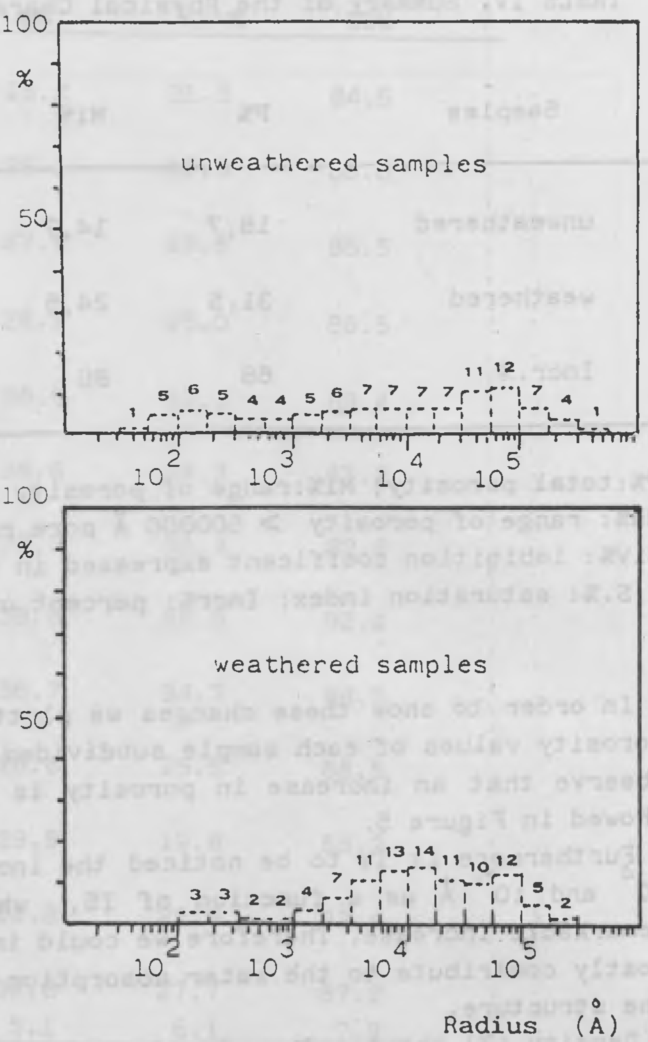


Fig. 6 - Pore-size distribution relative to microporosity in weathered and unweathered samples.

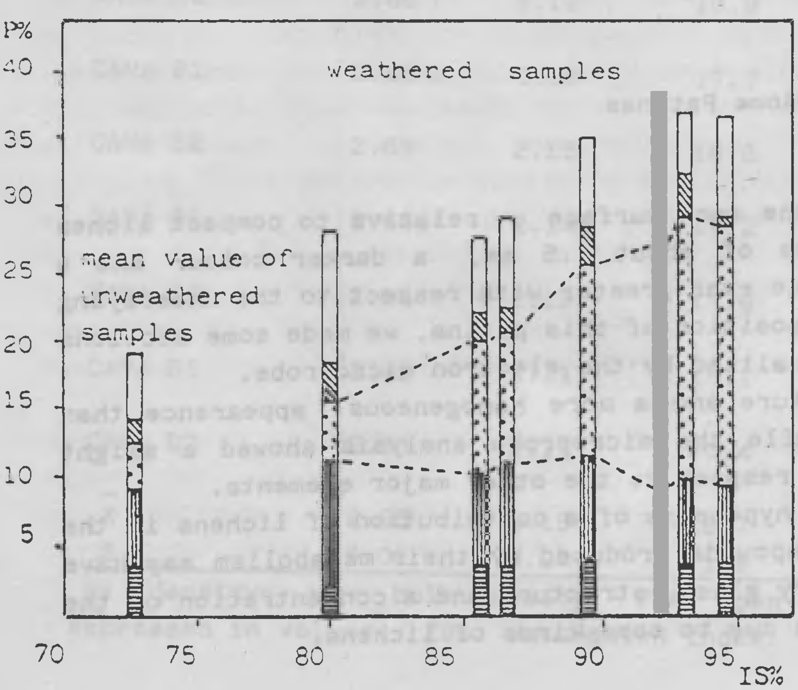


Fig. 7 - Porosity (P%) plotted versus saturation index (IS%). The porosity values of each sample have been subdivided in the portion relative to the different pore-size classes.

- pore-size $<10^3$ Å;
- pore-size $10^3 - 10^4$ Å;
- pore-size $10^4 - 10^5$ Å;
- pore-size $10^5 - 10^6$ Å;
- pore-size $> 10^6$ Å.

Weathered samples have been selected in order to avoid superimposition in the diagram.

Fig. 8 - SEM microphotography of the patina (20 X). It is possible to see the compact structure and the more homogeneous appearence with respect to the underlying rock.

Fig. 9 - Iron distribution obtained by Xray microanalysis relative to the area showed in Fig. 8. The surface (1.5 mm thick) shows a little increase in Fe. The other spots correspond to biotite crystals.

5. CONCLUSIONS

The evidence gained from centuries on the old monuments indicates that "Peperino" has a good durability and decays only in particular conditions. We may explain these characteristics considering that this rock solidified in almost subaerial conditions from of a vitreous matrix which "sealed" all the minerals and the xenoliths. Therefore it is a rock that is close to the equilibrium with the chemical-fisical conditions of the subaerial environment. All the data collected and particulary the comparision between weathered and unweathered samples, has given us the possibility to verify the durability of "Peperino" and in the meantime to observe how the rock alteration goes on.

The crystalline phases seldom show signs of alteration and they seem like protected , "sealed" by the vitreous matrix which on the contrary shows a few signs of alteration with devitrification phenomena concentrated in spots. The result of this process is expecially the formation of chlorite which can be detected in little quantities through the clay mineral analysis.

The analysis of the major elements confirms that the alteration mainly concerns the vitreous matrix as shown by the depauperation in alkali metals. This is surely due to the leaching of the glass since the minerals rich in alkalis (sanidine and plagioclase) do not show any sign of alteration.

The study of the physical characteristics has shown in weathered samples a remarkable increase in porosity which is mainly due to the growth of a precise pore-class as a consequence of the hydrolysis of the vitreous matrix.

The ability of the stone to retain the water inside the material can be well correlated with the development of this pore-class.

On the whole, the material of the Bomarzo Park shows a slight degree of alteration. However it seems that the present conditions can not warrant a further good conservation since the material has developed a structural change which may lead to a faster alteration process.

6.REFERENCES

1.Battisti, E.; "L'antirinascimento" Garzanti, 1989.

2.Bettini, G.; " Bomarzo, guida al parco dei mostri" Plurigraf Narni, 1988.

3.Bianchetti, P.L.; Lombardi, G.; "Study of the degradation of tuff blocks used in the roman temple of Cibeles (Rome,Italy)" in the Proceedings of the Fourth International Congress on the Deterioration and Preservation of Stone Objects, Louisville, 1982.

4.Calvesi, M.; "La prova della selva stregata" Art e Dossier Giunti Marzocco Firenze, November 1989, n. 40.

5.Caner, E.N.; Türkmenoğlu, A.G.; "Deterioration of basalts from a hittite archaeological site, Karatepe, Turkey" in the Proceedings of the Vth International Congress on Deterioration and Conservation of Stone, Losanne, 1985, vol. I.

6.Caner, E.N.; Türkmenoğlu, A.G.; Göktürk, H.; Demirci, Ş.; Böke, H.; "Examination of surface deterioration of Gröeme Tuffs for the purpose of conservation" in the [Supplement to the] Proceedings of the VIth International Congress on Deterioration and Conservation of Stone, Toruń, 1988, [vol. II].

7.Corazza, A.; Conti, C.; Filetici, M.G.; Lombardi, L.; Rava, A.; Torraca, G.; "On the conservation of tuff stone; studies on treatment methodology" in the Proceedings of the Congress on "Conoscenze e sviluppi teorici per la conservazione di sistemi costruttivi tradizionali in muratura", Bressanone, 1987.

8.Deer, W.A.; Howie, R.A.; Zussman, J.; "Rock forming minerals" Longman, 1963.

9.Hatsagortsian, Z.; "Durabilité des tufs volcaniques et des basaltes" in the Proceedings of the VIth International Congress on Deterioration and Conservation of Stone, Toruń, 1988, vol. I.

10.Illustrative notes of Geological Map of Italy, sheet 137 Viterbo, Geological Survey of Italy.

11.Jackson, T.A.; Keller, W.D.; "A comparative study of the role of lichens and inorganic processes in the chemical weathering of recent Hawaiian lava flow" Americal Journal of Science, 1970, vol.269, pp. 446-466.

12.Jones, D.; Wilson, M.L.; "Chemical activity of lichens on mineral surfaces. A review" Int. Biodetn. Bull. , 1985, vol. 21 (2), pp. 99-104.

13.Lipman, P.W.; Christiansen, R.L.; Van Altstine, R.E.; "Retention of alkalis by calc-alckalic rhyolites during crystallization and hydration" The American mineralogist, 1969, vol. 54.

14.Rossi Manaresi, R.; Pellizer, R.; "The volcanic tuff of the archaeological monuments in Cochasqui, Ecuador: cause of decay and effectiveness of conservation treatements" in the Proceedings of the 3rd International Congress on Deterioration and Conservation of Stone, Venezia, 1979.

15.Sersale, R.; Frigione, G.; "Sul recupero di manufatti architettonici in tufo giallo napoletano" in the Proceedings of the Congress on "Manutenzione e conservazione del costruito fra tradizione e innovazione", Bressanone, 1986.

16.Zielinski, R.A.; Lipman, P.W.; Millard jr, M.T.; "Minor-elements abundances in obsidian, perlite and felsite of calc-alckalic rhyolites" American Mineralogist, 1977, vol.62, pp. 426-437.

17.Williams, M.E.; Rudolph, E.D.; "The role of lichens and associated fungi in the chemical weathering of rock" Mycologia, 1974, vol. 66, pp. 648-660.

ACKNOWLEDGEMENTS

The authors wish to thank Doctor Giovanni Bettini, owner of the Park, who gave the possibility to carry out this work.

The evidence gained from centuries on the old monuments indicates that [illegible] conditions [illegible] rock [illegible] in almost [illegible] the [illegible] and the xenoli[illegible] to the equilibrium [illegible] the chemical-fisic[illegible] conditions of the subaerial environment. All the data col[illegible] between weathered and unweathered samples, has given us the possibility to verify the durability of "Peperino" and [illegible] and they seem like protected, [illegible] matrix which on the contrary shows a few signs of alteration with [illegible] phenomena concentrated in spots. The [illegible] which can be detected in little quantities through the clay mineral analysis.

The analysis of [illegible] confirms that the alteration mainly concerns [illegible] in alkali metals. This is surely due to [illegible] in alkalis (sanidine and plagioclase) do not show [illegible]

The study of the physical characteristics has shown in weathered samples a [illegible] growth of a precise [illegible] can be well [illegible]

On the whole, the material of the Bomarzo Park shows a slight alteration. However it seems that the present conditions can not warrant a further [illegible]

1.[illegible]

2.[illegible]

3.[illegible] blocks used [illegible] International [illegible] Objects, [illegible]

4.Calvesi, M.: "La prova della [illegible]" [illegible] Giunti Marzocco Firenze, November 1989, n. 40.

5.Caner, [illegible] archeological [illegible] in the Proceedings of the [illegible] International Congress on Deterioration and Conservation of Stones, [illegible]

DETERIORATION OF SOME VOLCANIC ROCKS FROM EGYPT

F. M. HELMI

Conservation Department, Faculty of Archaeology,
Cairo University, Giza, Egypt

ABSTRACT

Deterioration of some volcanic rocks from Egypt were investigated using x-ray diffraction, atomic absorption, thin section analyses, and scanning electron microscopy. In the present work, the mechanisms of deterioration due to the role or water, change in temperature, and ultraviolet radiation exposure are discussed. A comparative study of basic and acidic volcanic rocks is presented including the degree of crystallinity as a parameter in the deterioration process. Water-repellent silicon resins materials are very important for conservation of volcanic rocks.

RESUMEN

La deterioración de algunas rocas volcánicas de Egipto fue estudiada utilizando difracción de rayos x, absorción atómica, secciones delgadas y microscopía electrónica de barrido. En el presente trabajo se discuten los mecanismos de deterioro debido a los efectos del agua, cambios de temperatura y exposición a radiación ultravioleta. Se hace un estudio comparativo de rocas volcánicas básicas y ácidas incluyendo el grado de cristalinidad como uno de los parámetros en el proceso de dete-rioro. Resinas de siliconas hidrófugas son materiales muy importantes para la conservación de las rocas volcánicas.

1. INTRODUCTION

Volcanic rocks are igneous ones, formed by solidification of lavas on the surface of earth's crust, either on land or on ocean's bottom. They consist of glassy non-crystalline materials or from microcrystall--ine minerals or from both two. They differ from plutonic igneous rocks in texture and structure, in their high relatively content of water in the non-crystalline portion, and in high percentage of ferric to ferr--ous ions due to atmospheric oxidation factors.

Ancient Egyptians used some volcanic rocks since Neolithic,predy--nastic, and through Dynastic periods, such as basalt, andesite,obsid--ian, porphyrites, and tuffs.Basalt was widely utilized in making anc--ient vessels, sarcophagues, statues, in constructing parts of Temples in paving Temples's roads. On the other hand, andesite was used in ha--rd stone working. Remains of this rock were found in old quarries of granite and quartzite in Aswan,and in Gebel-El Ahmer respectively. Where obsidian was well known in the manifacture of weapons,spear-hea--ds,amulets,beads,scarabs,eyes of statues and sarcophagues,and small vessels.Porphyrite was widely used in making vessels,pots,and sarcoph--agues.All these volcanic rocks are existed in Egypt, at Eastern des--ert , Fayoum, Aswan, and Sinai(1).

The aim of the present work is to study deterioration mechanisms of naturally deteriorated volcanic rocks and also through artificial weathering. So,to find out the suitable materials for their conserva--tion.

2. EXPERIMENTAL

2.1 Samples

Eight different volcanic rocks from Egypt were investigated. They include basalt,dolerite,pyroclastic tuff,pumice,green tuff,obsidian, rhyolite,and greyish black tuff. Also,two naturally deteriorated bas--alt samples from Ne-Weser-Rah Temple (5th Dynasty),at Abu-Sir,Egypt were also studied.

2.2 X-ray Diffraction Analysis

The samples were ground in an agate mortar to a fine powder,pre--ssed in the specimen holder,and then mounted in a Philips x-ray dif--fractometer. The operating conditions were: Generator CuKα radiation (1.5418Å),with Ni filter,40 Kv,20 mA current tube,speed: 0.1,chart:5 range:1×10^3,time constant:1,and slit:0.1.

2.3 Thin Section Analysis

The volcanic rock samples were sectioned,mounted on microscopic slides. The constituting minerals of each rock were identified using a Leitz polarizing microscope.

2.4 Atomic Absorption Analysis

Obsidian cubic sample was immersed in deionized water for two months. The washing water was examined for the presence of Na,K,Fe, Mg,Ca ions.

2.5 Artificial Weathering

The rock samples were cutted into small cubes $3Cm^3$,dried in an oven at 105°C till constant weight.Then they were submitted to wet-dry cycles,immersed in distilled water in a covered beaker at 65°C for 4 hour, then dried at 65°C for the same period,followed by exposure to U.V. radiation (λ= 254 nm) for 12 hour. Ultra- violet radiation exp--osure was stopped after 420 hour,and was substituted by immersion in distilled water till 60 cycles.

2.6 Scanning Electron Microscopy Examination

SEM examination was carried out on four rock samples: basalt,obsi--dian,rhyolite,and greyish black tuff,which were showed visual alterat--ions after artificial weathering. The specimens were fixed on specimen holders by an adhesive material containing silver,then coated with gold.

3. RESULTS

3.1 Basalt

X-ray diffraction data of basalt (Fig.1),showed the existence of the following minerals:Augite (Au) Ca,Fe,Mg SiO_3 (3-0623), Anorthite (An) $CaAl_2Si_2O_8$ (12-301),and Grunerite (Gr) $(Fe,Mg)_7Si_8O_{22}(OH)_2$ (17-745). Where XRD data of a naturally deteriorated basalt sample from Ne-Weser-Rah Temple,Abu-Sir (Fig.1) showed the absence of Grunerite. Thin section analysis of basalt (Fig.2), declared crystal of augite in a matrix of calcic plagioclase feldspars.

After 60 cycles of artificial weathering,the surface of basalt cube became pitted,and reddish brown material filled these pits which consisted of hematite Fe_2O_3,and geothite FeO(OH).

SEM examination of the artificial weathered sample is shown in Fig.3,which is clearly seen the effect of dry wet cycles and U.V. exposure in breaking the surface,forming cracks and pits,and alterat--ion of its constituting minerals (light colour).

3.2 Andesite

X-ray diffraction data of andesite (Fig.4) showed that it cons--ists of Oligoclase (Ol) $0.71NaAlSi_3O_8.0.29CaAl_2O_8$ (9-456),Augite (Au) Ca,Fe,Mg SiO_3 (3-0623),Grunerite (Gr) $(Fe,Mg)_7Si_8O_{22}(OH)_2$(17-745) and traces of Kaolinite (Ka) $Al_2Si_2O_5(OH)_4$ (14-164).Thin section an--alysis Fig.5 clarified large crystals of plagioclase feldspars in a matrix of ferromagnetic minerals. Artificial weathering of andesite did not show any alteration in its appearance.Its cubic surfaces were still smooth without neither pits nor change in colour.

3.3 Pyroclastic Tuff

X-ray diffraction data of this tuff(Fig.4)verified that it con--sists of Quartz (Q)α-SiO_2 (5-0490),Andesine (Ad) $0.62NaAlSi_3O_8.0.38CaAl_2O_8$ (10-359),and traces of kaolinite (Ka) $Al_2Si_2O_5(OH)_4$ (14-164). Thin section analysis showed fine crystals of quartz and pla--gioclase feldspars and some alterations to clay minerals(Fig.6.). Artificial weathering did not affect on appearance of this tuff.

3.4 Pumice

X-ray diffraction analysis of pumice(Fig.4)showed that is nea--rly amorphous ,there are very small peaks,which is an indication to nucleation of micro-crystallites of most probably quartz and feldspar minerals.Thin section analysis of pumice Fig.7 declared the vesicular texture characteristic to this rock in a glassy mat--rix.Artificial weathering led to the appearance of a brownish ma--terial at the surface which consisted of iron oxides.

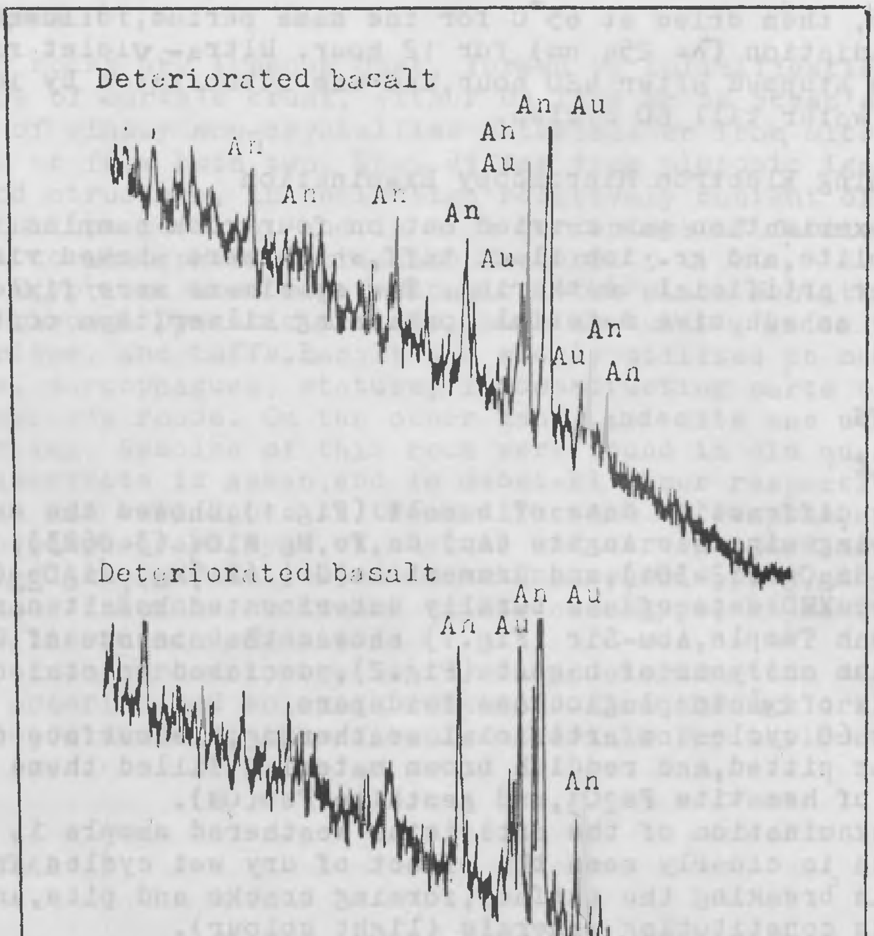


Fig. 1 X-Ray diffraction patterns of basalt and deteriorated basalt samples from Ne-Weser-Rah Temple Abu-Sir. (Au) augite, (An) anorthite, (Gr) grunerite.

Fig. 2 Thin-Section photograph of basalt (Xnicols) showed crystal of augite in a matrix of calcic plagioclase feldspars, 6.3X.

Fig. 3 SEM micrograph of basalt after artificial weathering,pits and cracks at the surface and alteration of minerals 2000X.

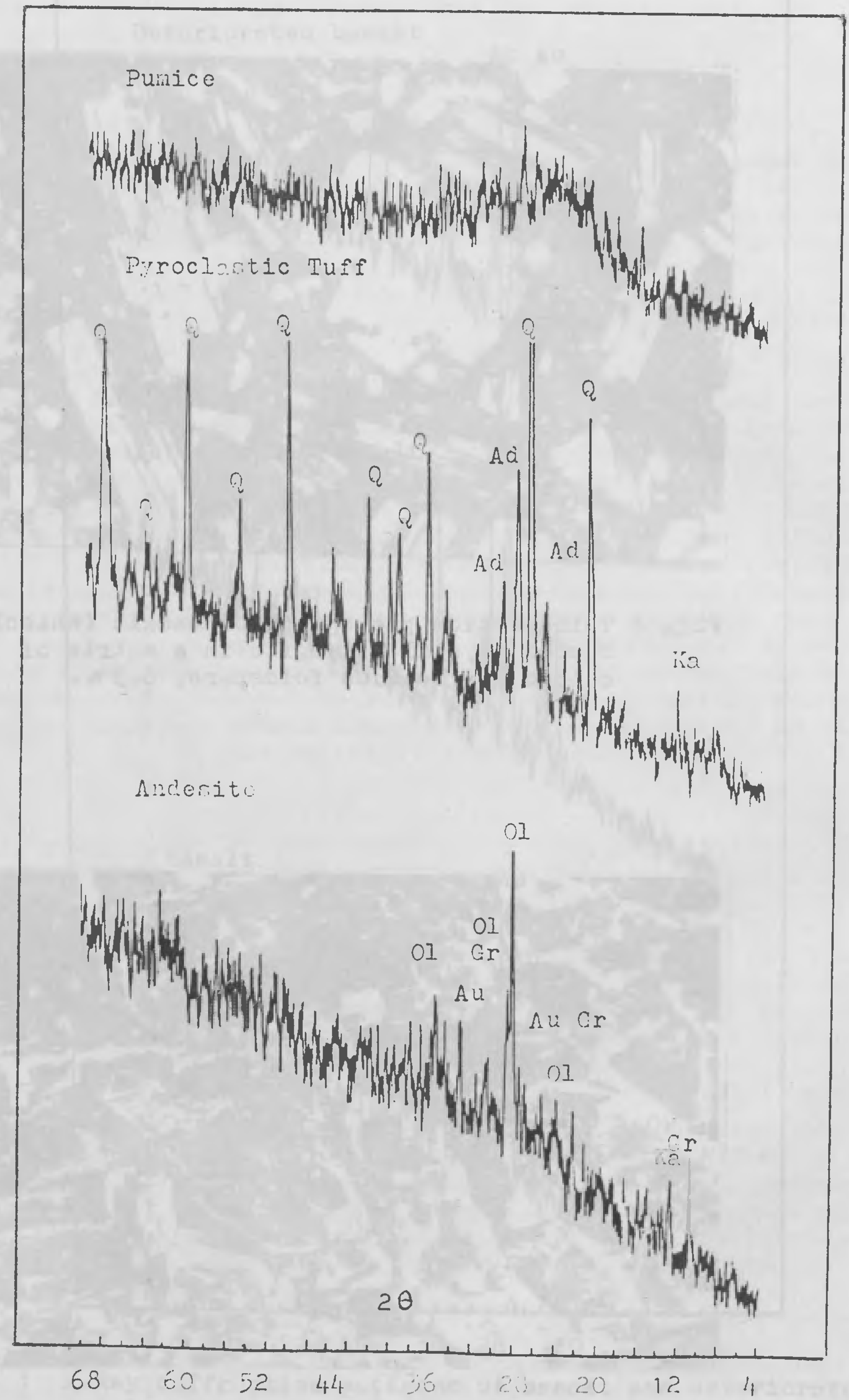


Fig. 4 X-Ray diffraction patterns of andesite, pyroclastic tuff, and pumice. (Ol) oligoclase, (Au) augite, (Gr) grunerite,(Ka) kaolinite, (Q) quartz, (Ad) andesine.

Fig. 5
Thin section photograph of andesite (xnicols) clarified large crystal of plagioclase felds. in a matrix of ferromagnesian minerals. 6.3 X

Fig. 6
Thin section photograph of pyroclastic tuff (xnicols) showed crystals of quartz and feldspars, also some alterations to clay minerals. 6.3 X

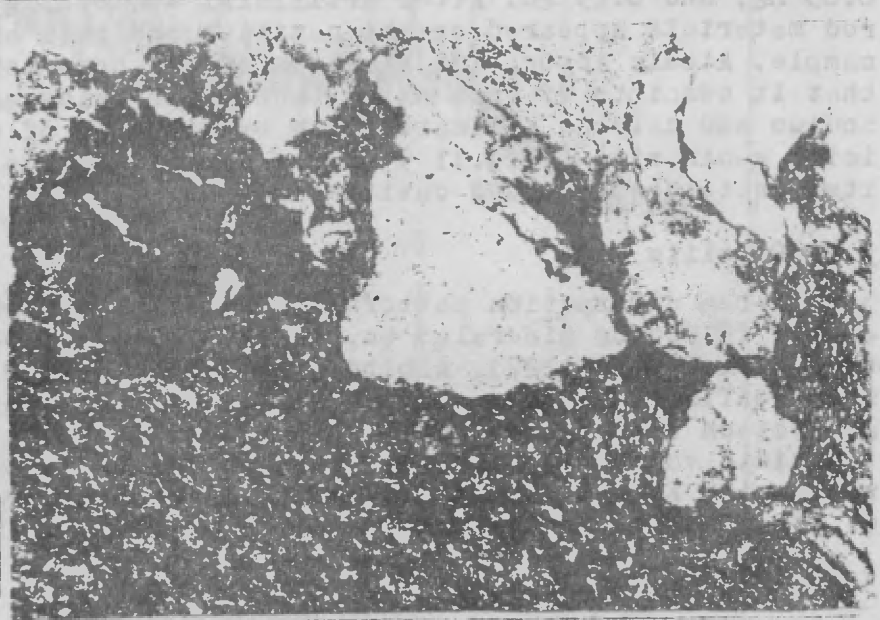
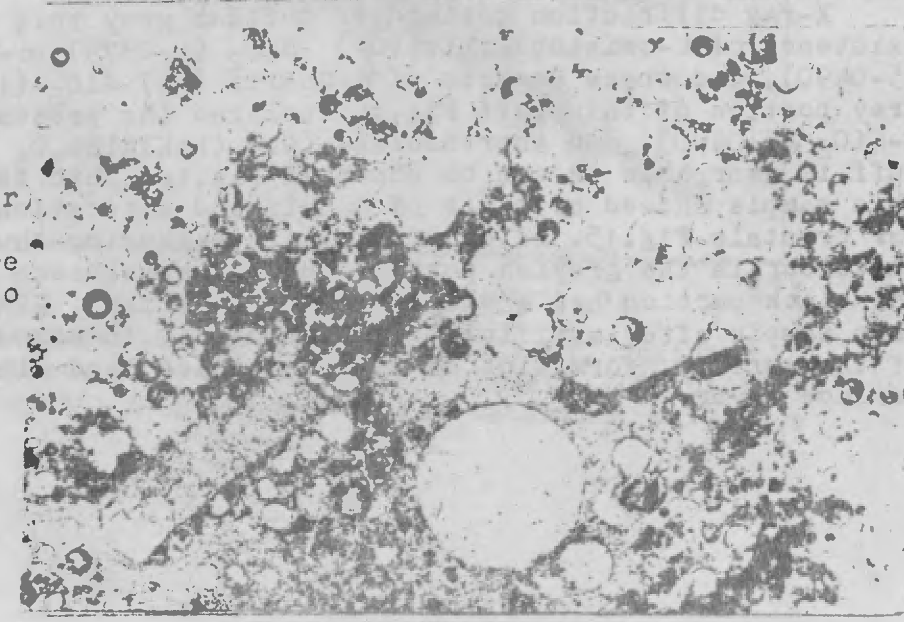


Fig. 7
Thin section photograph of pumice (polarizer) declared the vesicular texture characteristic to this rock in a glassy matrix. 6.3 X



3.5 Green Tuff

X-ray diffraction data of this sample Fig.8 showed the existence of the following minerals: Quartz (Q α-SiO_2 (5-0490), sepiolite (Sp) $Mg_4Si_6O_{15}(OH)_2.6H_2O$ (26-1226), and traces of biotite (B) $K(Fe,Mg)_3AlSi_3O_{10}(OH)_2$ (2-0045), muscovite (M) $KAl_2(Si_3Al)O_{10}(OH)_2$ (7-042), Kaolinite (Ka) $Al_2Si_2O_5(OH)_4$ (14-164). Thin section analysis of green tuff (Fig. 9) declared fine crystals of quartz, sepiolite in the ground mass, biotite and muscovite with strong interference colours. Artificial weathering on this tuff showed a slight change in colour, from green to pale grey, and appearance of very fine fissures.

3.6 Obsidian

X-ray diffraction analysis of obsidian demonstrated that it consists mainly of glassy material has a few small dispersed peaks which indicate the nucleation and recrystallization of minerals, (See Fig. 8). These data were confirmed by thin section analysis (Fig.10) which declared few crystals of quartz and altered feldspars. Atomic absorption analysis of the washing water of obsidian after two months showed the existence of the following elements: 0.15 Na, 0.05 K, 0.15 Ca, 0.05 Mg, and 0.25 Fe. After artificial weathering white and brownish red materials appeared on the cavities and pits at the surface of the sample. Atomic absorption analysis of the brownish material showed that it consists of iron oxide, where the white material consists of sodium and calcium silicates. SEM examination of obsidian after artificial weathering (Fig.11) showed disintegration and alteration of its constituents around cavities and holes.

3.7 Rhyolite

X-ray diffraction pattern of rhyolite Fig.8 showed the existence of the following minerals: Quartz (Q) α-SiO_2 (5-0490), Sanidine (S) $(NaK)AlSi_3O_8$ (19-1227), Albite (Al) $NaAlSi_3O_8$ (10-393). These results were confirmed by thin section analysis Fig.12 which declared quartz and potash feldspar minerals in a spherulitic texture characteristic to acidic volcanic rocks. SEM examination of rhyolite after artificial weathering Fig.13 showed alteration (light colour) and disintegration of the constituting minerals.

3.8 Grey and Black Tuffs

X-ray diffraction pattern of whitish grey tuff Fig.14 showed the existence of α-cristoballite (Cr) SiO_2 (4-0379), α-Quartz (Q) α-SiO_2 (5-0490), and trace amounts of β-Quartz (BQ) SiO_2 (11-252). Where the grey portion of this tuff Fig.14 declared the presence of Quartz (Q) α-SiO_2 (5-0490), and anorthoclase (An) $(NaK)AlSi_3O_8$ (9-478). The black tuff is amorphous as can be shown in Fig.14. Thin section analysis of this sample showed crystals of quartz and alteration in potash feldspar crystals Fig.15. After artificial weathering there was a change in colour in the greyish portion and the appearance of cracks, where the black portion had a slightly pitted surface. SEM examination of this sample after artificial weathering Fig.16 showed deterioration of the surface, formation of pits and holes, and alteration in the surface layer.

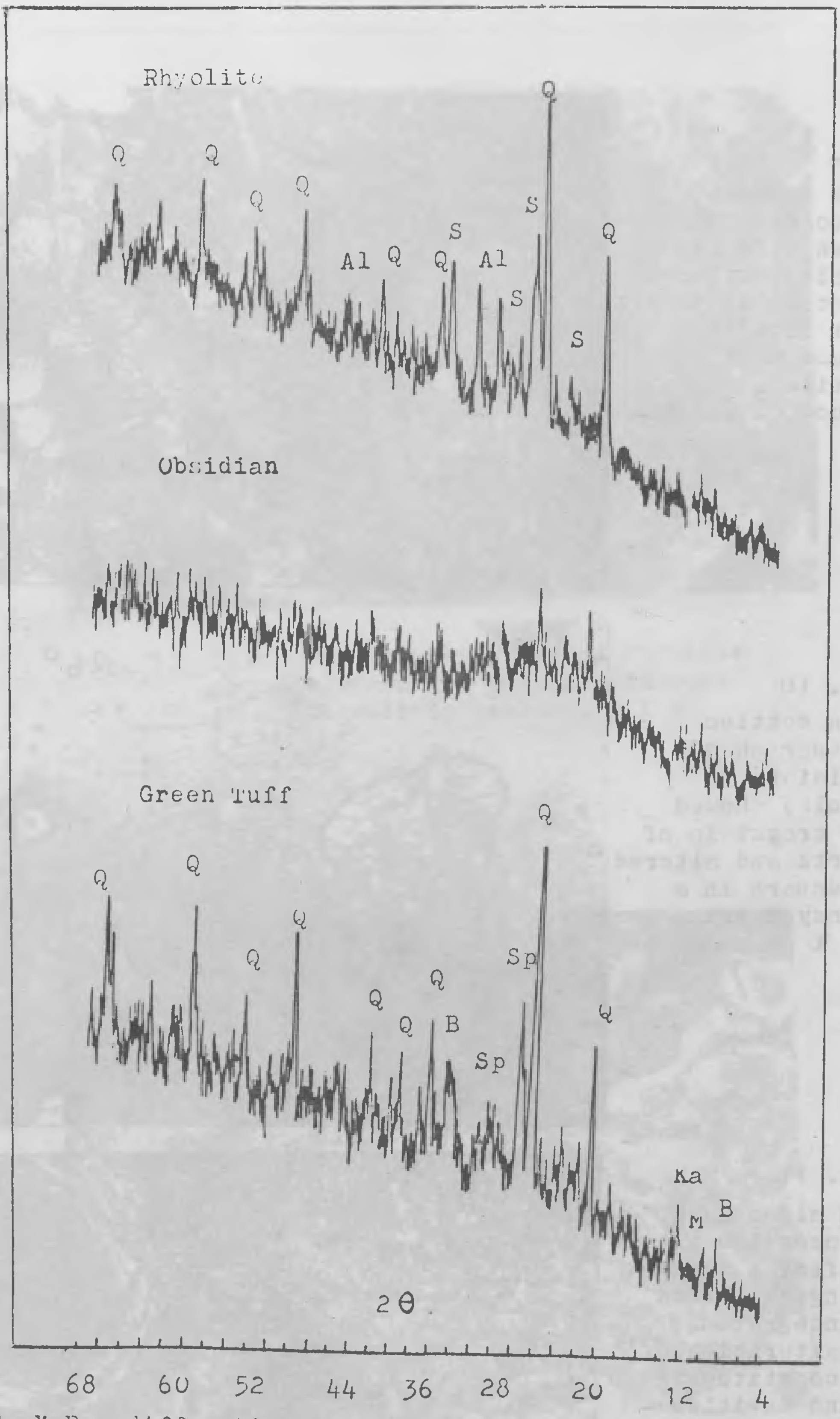


Fig. 8 X-Ray diffraction patterns of green tuff, obsidian, and rhyolite. (Q) quartz, (Sp) sepiolite, (B) biotite, (M) muscovite, (K) kaolinite, (S) sanidine, (Al) albite.

Fig. 9
Thin section photograph of green tuff (X nicols) declered crystals of quartz sepiolite in a ground mass of biotite and muscovte. 6.3 X

Fig. 10
Thin section photograph of obsidian (X nicols) showed few craxstals of quartz and altered feldspars in a glassy matrix. 6.3 X

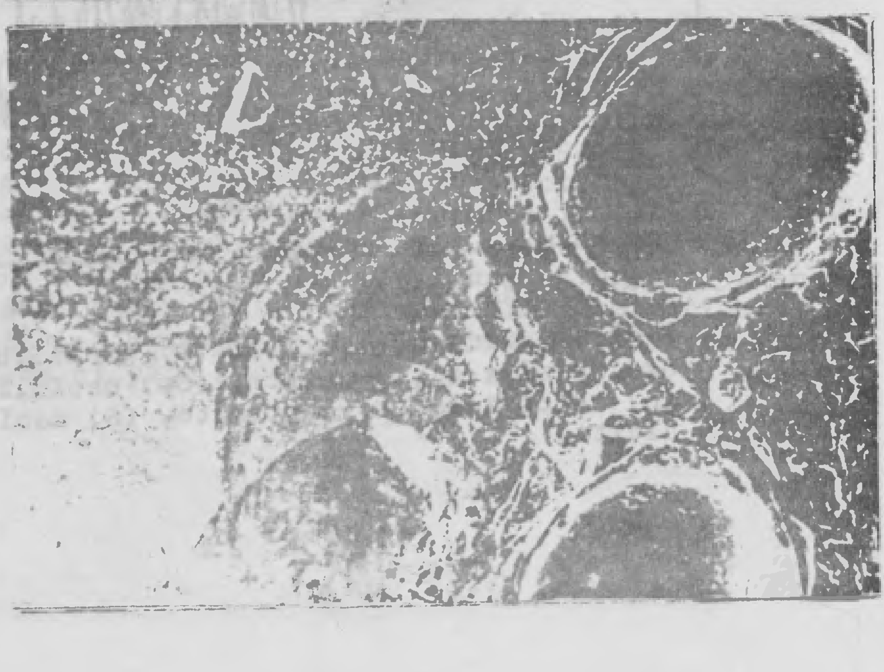


Fig. 11
SEM micrograph of obsidian after artificial weathering clarified disintegration and alteration of its constituents around cavities and holes. 200 X.

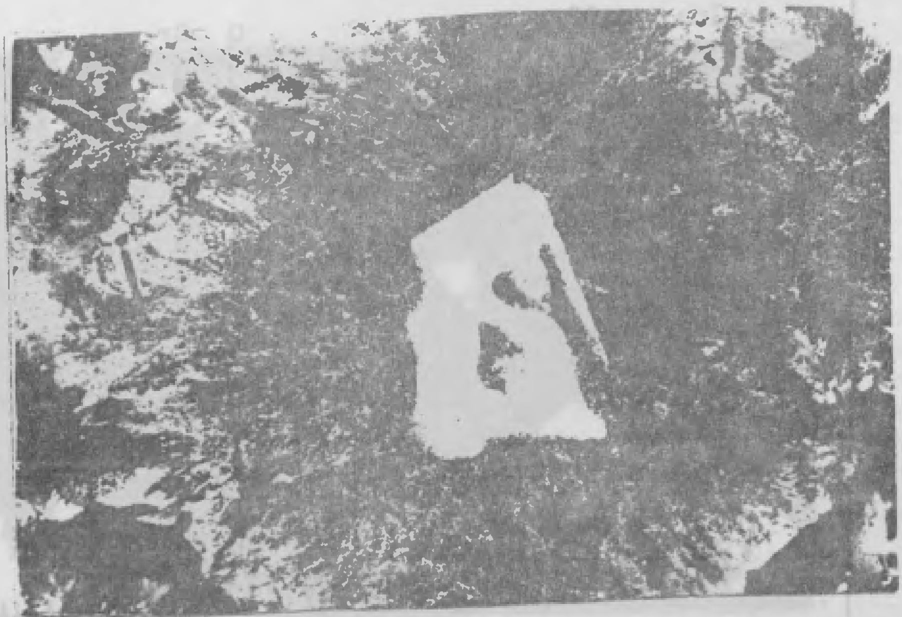


Fig. 12 Thin section photograph of rhyolite showed quartz and potash feldspars in a spherulitic texture. 6.3 X (X nicols)

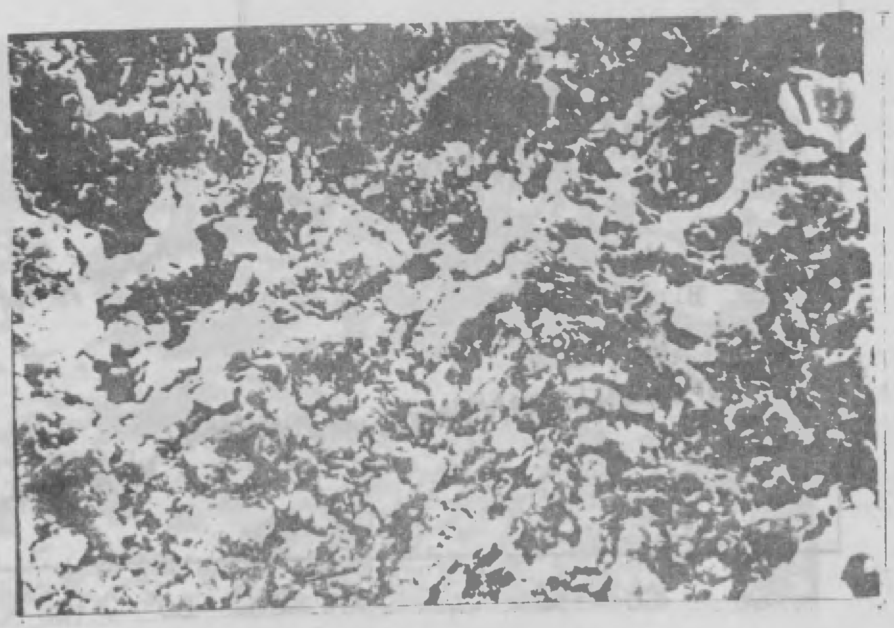


Fig. 13 SEM micrograph of rhyolite after artificial weathering showed alterations (light colour) and disintegration of minerals. 2000 X

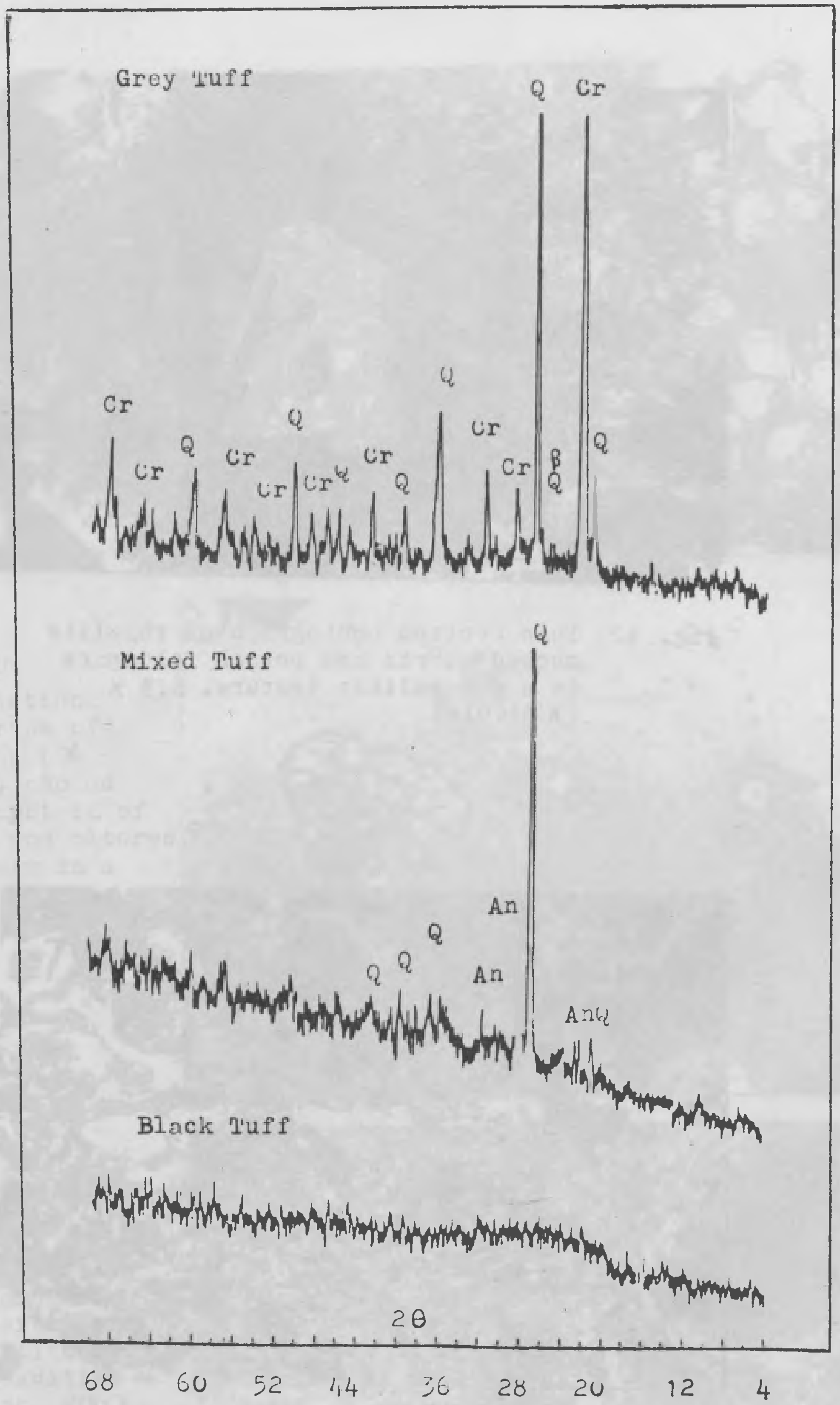


Fig. 14 X-Ray diffraction patterns of black and grey tuffs. (Cr) cristoballite, (Q) α -quartz, (β Q) β-quartz, (An) anorthoclase.

Fig. 15 Thin section photograph of greyish black tuff declared crystals of quartz and alteration of potash feldspars. 6.3 X (X nicols)

Fig. 16 SEM micrograph of greyish black tuff after artificial weathering showed det rioration of the surface and alterations. 1000 X

4. DISCUSSION

Deterioration process of volcanic rocks in Egypt is due to chemical and physical weathering. The process became more rapidly in the presence of cavities, fissures, and cracks in the rocks. Volcanic tuffs have a large water content in their non-crystalline portion , which were cooled suddenly from lavas. Devitrification phenomenon of volcanic rocks was occured through geological periods which led to the formation of minerals i.e. the more stable crystalline state. Devitrification of glass is very low under normal conditions, but it may occured in a relatively more short time in the presence of circulating solutions. Volcanic rocks have an additional factor of deterioration which is devitrification giving rise to the formation of new minerals by time i.e. change in colour.

At Ne-Weser-Rah Temple, Ab-Sir, Egypt, water is the dominant deterioration factor of basalt in addition to the variation in temperatures between day and night . This area has an arid desert climate, in the early morning the relative humidity is very high leading to condensation of water droplets on the surface of basalt. The chemical weathering of basalt is a dissolution process of the constituting silicate minerals which causes undesirable discolouring of the ferromagnesian minerals leading to their alteration. The colour of basalt was changed from almost black to pale brownish grey. Exfoliation of the surface layer is very clear in site accompanied by the presence of brown friable material between the separated bands. Exfoliation was due to physical weathering i.e. different thermal expansion of the constituting minerals. After applying artificial weathering on basalt pits coated with brown iron oxides were appeared on the surface which assured the dissolution and leaching process specially iron from its minerals. SEM photomicrograph declared disintegration and alteration of basalt at the surface. X-ray diffraction patterns of weathered basalt showed the appearance of Grunerite mineral (iron magnesian hydroxide silicate) and decrease in the percentage of augite mineral which confirmed that deterioration process initiated by dissolution of ferro-magnesian minerals.

In case of obsidian which is consisted of almost glass , devitrification will play an important role in the deterioration process. It was found that it was rapidly altered after artificial weathering. There was leaching of iron,calcium,sodium , and trace amounts of potassium and magnesium from the glass matrix. This was confirmed by atomic absorption analysis and by the formation of brown and white materials in the holes and cavities at the surface of the sample. The same phenomenon was occured in pumice which is consisted also of nearly glass. Brown precipitate of iron oxides appeared at the surface of the sample after artificial weathering.

Comparison between the rate of deterioration for basic and acidic volcanic rocks after artificial weathering declared that basic rocks seem to be more deteriorated than acidic ones. This may be probably due to the presence of large amounts of ferromagnesian minerals. The appearance of pits was more occured on the surface of basalt (basic) than on rhyolite (acidic). On the contrary discolouring of basalt was less than that of rhyolite. The degree of crystallinity in volcanic rocks is an effective factor in the deterioration process. The crystalline rocks may take longer time than the glassy ones in deterioration. The developing of cracks and susceptibility to disintegration and break were occured more rapidly in glassy rocks than in the crystalline cases.

Deterioration of basalt may be originated through microveins in their structure. The results showed the importance of salt crystallization with the presence of water (2). The formation of iddingesite on olivine is one of the processes of deterioration (3). Plagioclase feldspars and biotite grains were found to be used as indicators for the depth of alteration (4).

The author believes that deterioration of volcanic rocks initiated by alteration i.e. dissolution of both plagioclase, potash feldspars; mica (biotite,muscovite); ferromagnesian minerals (augite,olivine...). It depends on the composition of the rock and its constituting glassy material and minerals. The mechanism of deterioration of microcrystalline acidic volcanic rocks is similar to that of granite (5). This in addition to the effect of variation in temperatures and U.V. in disintegration process.

5. CONCLUSIONS

The present work showed that deterioration process of volcanic rocks is due essentially to the presence of water even in the absence of salts. Disintegration of the surface layer is caused by large variations in temperatures which led to exfoliations,cracks specially in the glassy rocks. Devitrification of glassy rocks plays an important role in the formation of new minerals i.e. stable crystalline state, giving rise to change in colour at the surface. Application of water repellent materials is very impotant for conservation Archaeological volcanic rocks to minimize the effect of water which is the main source of deterioration. These materials will form a non-polar protective layer on the rocks surface prevent them from deterioration.

6. REFERENCES

1. Lucas , A.; "Ancient Egyptian Egyptian Materials and Industries"; 3rd ed.,Edward Arnold Ltd.,London,1948.
2. Caner, E.N.; Türkmenoglu, A.G.; in Proceedings of the Vth International Congress on Deterioration and Conservation of Stone, Lausanne, 1985, Vol.1, pp.411-420.
3. Eggleton, R.A.; Clays and Clay Minerals 32, No.1, 1984, pp. 1-11.
4. Caner, E.N.; Turkmenoglu, A.G., Gökturk, H., Demirci, S., Böke, H. ; in Proceedings Supplement of the VIth International Congress on Deterioration and Conservation of Stone; Torun, 1988, pp. 287-302.
5. Helmi, F.M.; in Proceedings of the Vth International Congress on Deterioration and Conservation of Stone, Lausanne, 1985, pp. 421-429.

4. DISCUSSION

their structure. ...

ation with the presence of water (12). ...

olivine is one of the ...

which were cooled suddenly from lavas. ...

depth of alteration (4).

The author believes that ...

At Ab-Ghorab Temple, Ab-Sir, Egypt ... basalt in addition ... and night. This area ... climate, ... the relative humidity ... water droplets ...

5. CONCLUSIONS

... diffraction patterns of weathered basalt showed the appearance of Brunerite mineral (iron.magnesian hydrous silicate) and decrease in the percentage of augite ...

6. REFERENCES

DETERIORATION INDUCED BY LICHENS ON VOLCANITE OF THE VULSINI COMPLEX (CENTRAL ITALY)

O. SALVADORI, D. PINNA* and G. C. GRILLINI+

Laboratorio Scientifico, Soprintendenza per i Beni Artistici e Storici di Venezia, 30131 Venice, Italy
*Soprintendenza per i Beni Artistici e Storici di Bologna, 40126 Bologna, Italy
+Fondazione "Cesare Gnudi", 40126 Bologna, Italy

ABSTRACT

The results of an investigation on eight crustose lichen species and one foliose species grown on volcanic tuff from the area of Civita Bagnoregio (Central Italy) are given. The observations of thin sections coupled with electron microprobe and XRD analysis allowed the identification and localization of weathering products produced by lichens. The most important effect of the lichen growth is the removal of calcium from the substrate to form weddellite accumulated in the thalli in different quantities and location depending on the species involved. Fungal hyphae penetrate deeply into the tuff. The relationship between fungal hyphae and rock often causes the detachment of some millimeters of stone under the central part of the thallus.

RESUMEN

Se presentan los resultados obtenidos en una investigación sobre ocho especies de líquenes crustáceos y una foliosa desarrollados sobre toba volcánica del área de Civita Bagnoregio (Italia central). Las observaciones de secciones delgadas junto con análisis con sonda electrónica y difracción de rayos x, permitió la identificación y la localización de los productos de alteración producidos por los líquenes. El efecto principal del crecimiento del líquen es la remoción del calcio del sustrato y la formación de weddelita que se acumula en los talos en cantidades variables y en diferentes localizaciones dependiento de las especies. Las hifas de los hongos penetran profundamente en la toba, y esta acción produce muchas veces el desprendimiento de algunos milímetros de piedra bajo la parte central del talo.

1. INTRODUCTION

The role of lichens in the physical and chemical deterioration of stone has been discussed by many authors and is now generally accepted (1,2,3,4,5,6).

Lichens have different deteriorative effects on stone depending on the species and the kind of rock involved. Limestone is the substrate which has been most thoroughly investigated (7), while few studies regarding other stone, such as volcanic tuffs (8), have been carried out.

Most authors consider that the deteriorative aspect connected with lichen growth is the most significant, however the hypothesis that in some cases the lichen can form a protective covering effective in limiting the action of other degrading agents, requires further investigations.

This work is part of a wider study on the deteriorative effects of lichen species on different stone and the identification of the more harmful species for the purpose of deciding if and how they should be removed.

The specific objective of the present work was to investigate the effects of lichen growth on a volcanite of Central Italy: a tephritic-phonolitic ignimbrite. The samples were taken in the area of Civita Bagnoregio, located between Lake Bolsena and the Tiber valley (Fig.1) (9) "where extensive Quaternary alkaline-potassic volcanic units, related to the Vulsini volcanic group , overlie a thick Pliopleistocenic, mainly marine clastic, series" (10). Civita Bagnoregio "is built on a high cliffed rock ("rupe"), where compact volcanics overlie an easily-erodible clayey basement"(10).

Eight lichen crustose species and one foliose species , among the most frequent in the area, were investigated in order to evaluate their weathering ability.

2. MATERIALS AND METHODS

The rock is a volcanite, yellow or reddish or greyish in colour. It is classified as tephritic-phonolitic ignimbrite ("Tufo rosso a scorie nere" Auct.), "one of most characteristic products of a major fissural volcanic activity which led to the effusion of huge pyroclastic flows and lavas, starting from about 0.4 M.a. ago" (9).

Rock specimens were sampled from both an active quarry and natural outcrops.

The rock is characterized by a clastic texture, scarcely cemented, formed of scoriae, blackish pumices, xenoliths of lava and phenoclasts dipped in a microgranular groundmass formed of glassy fragments. The phenoclasts are represented by sanidine, clinopyroxenes of the augitic type, leucite frequently analcimized, biotite with rare crystals of nepheline and labradoritic plagioclases. Iron oxides and hydroxides are present as secondary minerals.

In addition, the rock includes: a) portions of basaltic and/or andesitic lava-rocks formed of plagioclases, pyroxenes and some olivine; b) black and grey vitreous pumices with vescicular texture and high porosity; c) portions of lava with pseudofluidal texture with vitreous bands which often are closed forming flattened vitreous vesicles (11,12,13).

Two zeolites are also present, in varying proportions, in the glassy matrix: chabazite and less abundant phillipsite. Zeolites seem to be "a very common product of autopneumatolitic and weathering processes" (10), responsible for lithification.

No clay minerals are found in the samples examined; this excludes, for the present, the neoformation of clay minerals from feldspars, volcanic glass and zeolites.

Lichen specimens were sampled from natural outcrops and then identified. For the study of the effects of lichen growth on stone, some of the more frequent species were taken into consideration: *Caloplaca flavescens* (Huds.) Laund., *Caloplaca teicholyta* (Ach.) Steiner, *Diploicia canescens* (Dicks.) Massal., *Diploschistes actinostomus* (Ach.) Zahlbr., *Lecanora muralis* (Schreb.), *Lecidea fuscoatra* (L.) Ach., *Ochrolechia parella* (L.) Massal. and *Parmelia loxodes* Nyl., the only foliose species.

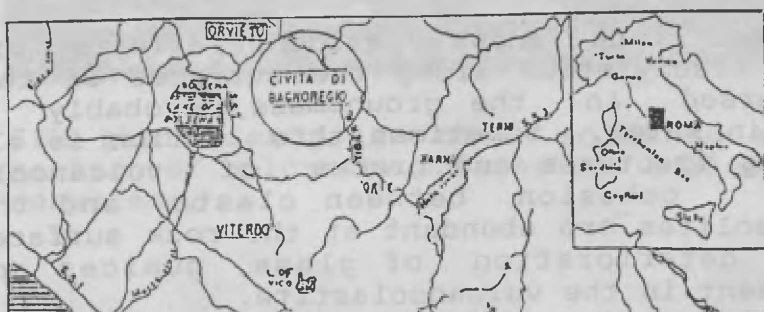


Fig.1 - Map of Central Italy, showing the sampling area of Civita Bagnoregio.

Thin sections were prepared and examined by light and polarizing microscopy. Before preparation of the thin sections, the samples were fixed in glutaraldehyde 3% in 0.1 M phosphate buffer at pH 6.8 for 2 hours at 4 C, dehydrated in an ethanol series and embedded in epoxy resin.

The colonized stone as well as the stone without lichens were scraped, powdered and examined with a Philips 1710 diffractometer using CuK radiation.

The XRD analyses were carried out on both unoriented and oriented clay samples.

Mineralogical determination of the clay minerals was carried out on the < 2 m fraction, obtained by sedimentation.

Portions of the lichen-covered stone were fractured, coated with Au and examined with a Philips 505 scanning electron microscope . Polished cross sections were analysed with electron microprobe analysis, for Ca, Si, Fe, Al and K.

3. RESULTS

The exposed rock shows evident effects of mechanical erosion and lisciviation along the surfaces of the clasts and pumices immersed in the groundmass, probably due to the action of rain water. Sometimes this action is also performed in depth along fractures and cracks of vulcanoclastite, thus reducing the cohesion between clasts and the vitreous groundmass. Zeolites are abundant at the rock surfaces, probably due to the deterioration of glass, pumices and siliceous fragments present in the vulcanoclastite.

The results of X-ray diffraction analysis of the rocks colonized by lichens and the lichen-free rocks were essentially the same except for the presence, in different quantities and not for all samples, of weddellite.

The results for the various lichen species studied can be summarized as follows:

- *Caloplaca flavescens* (Huds.) Laund.

The observations of thin sections showed the thallus penetrating within the substrate and wrapped around sanidine crystals that are rather corroded. Pyroxenes located near the thallus also are severely damaged and in strict contact with fungal hyphae. Large quantities of weddellite were detected by XRD analyses.

- *Caloplaca teicholyta* (Ach.) Steiner

Fungal hyphae penetrate as much as 1.5 mm into the substrate. Abundant weddellite is present and located mainly in the medulla rather than in the upper cortex, as confirmed by electron microprobe analyses.

- *Diploicia canescens* (Dicks.) Massal.

The thallus shows a medulla with a loose texture and does not seem to penetrate into the vulcanoclastite. Weddellite is present in small amounts and accumulated only on the thallus surface as in Fig.2 and 3.

- *Diploschistes actinostomus* (Ach.) Zahlbr.

The thallus shows a particular way of growth: it penetrates in small portions among the superficial fractures of the

Fig.2 - SEM photomicrograph of a polished cross-section of volcanite covered by *Diploicia canescens*.

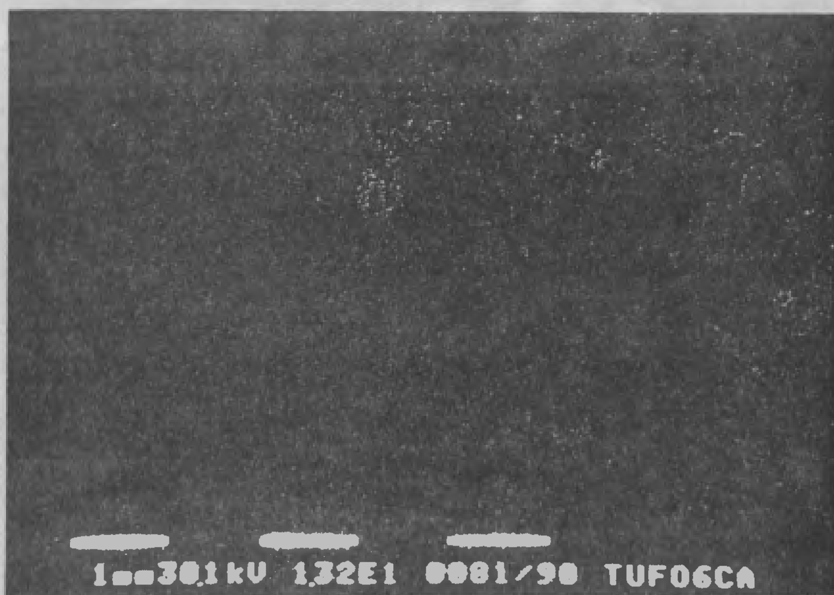


Fig.3 - As in figure 2, but showing the distribution of Ca accumulated only in the surface layer of the thallus.

Fig.4 - Micrograph of a thin section showing the complete adhesion of *Diploschistes actinostomus* to the substrate formed of blackish pumices, glassy fragments, phenoclasts of augite and sanidine (N //, 43x).

Fig.5 - Micrograph of a thin section showing the large amount of calcium oxalate (weddellite) accumulated in the thallus of *Diploschistes actinostomus* (N+, 43x).

groundmass and, in this way, it is able to remove small portions of stone (Fig.4 and 5). Microprobe analysis showed a small accumulation of Si in the thallus. The accumulation of calcium oxalates (weddellite) in the lichen is abundant and limited to the medullar zone.

- *Lecanora muralis* (Schreb.) Rabenh.

This species contains considerable weddellite distributed in the medulla and on the upper cortex. Brown hyphae, not belonging to the thallus, are present in the rock-lichen interface; the significance of these hyphae, observed also in other cases (unpublished data), will be the subject of a future investigation.

- *Lecidea fuscoatra* (L.) Ach.

Fungal hyphae penetrate among the vitreous pomices and wrap some highly deteriorated augitic phenoclasts . The highest depth of penetration into the stone (4-5 mm) among all the lichens considered was found for this species (S.E.M. observations). No accumulation of elements is present in the thallus.

- *Ochrolechia parella* (L.) Massal.

The thallus is rather thick, penetrates up to 1.5 mm in depth and is wrapped around highly corroded pyroxene crystals. Microprobe analysis did not show any accumulation of Ca in the

Fig.6 - Micrograph of a thin section showing *Parmelia loxodes* adhering to the substrate only by rhizines (N //, 108x).

lichen. Only in this lichen silicon is present in the same amount as in the stone. No silicon mineral compounds were detected in the thallus (XRD analysis).

- *Parmelia loxodes* Nyl.

As for all foliose lichens, adhesion to the substrate is ensured by the rhyzines, and thus occurs to a lesser extent than in the crustose types. Nevertheless some weddellite is observed in the surface layer (Fig. 6).

4. DISCUSSION AND CONCLUSION

All the species considered show the fungal hyphae penetrating in the vulcanoclastite more deeply than in other kinds of substrates, on the average 1.5 - 2 mm, up to a maximum of 5 mm in *Lecidea fuscoatra*. The ability to penetrate the tuff is facilitated by the high porosity and the heterogeneity of this stone: hyphae break into the microgranular groundmass and vitreous pumices while the phenoclasts (such as sanidine and pyroxene) and plagioclases are often surrounded by the mycobiont but not penetrated (Fig.7).

The presence of some of the species examined could initially form a sort of protection from the degrading effects of water, as has already been observed on very porous substrates (unpublished data).

In the case taken into consideration, the deep penetration of the fungal hyphae into the rock causes the detachment of some millimetres of stone which adhere to the lower surface of the lichen. This phenomenon may be due to different phenomena involving the central part of the thallus, i.e., the oldest part and may be related to the proliferation and crowding of apothecia (14) or to the fact that sometimes this central part of the thallus is the first part to die and detach (15).

The most important result of chemical deterioration induced by lichens seems to be the production of calcium oxalate. The same crystalline phase, weddellite ($CaC_2O_4 \cdot 2H_2O$), was always identified.

The ability of *Caloplaca* genus to produce calcium oxalate is confirmed. In fact, both the species considered (*C. flavescens* and *C. teicholytha*) accumulate large quantities of weddellite.

The analytical studies showed that *Diploschistes actinostomus* and *Lecanora muralis* have withdrawn calcium from the stone, concentrating it in the thallus (Fig.8). The effect of these two species and the localization of oxalates in their thalli have already been studied on other substrates, Muggia sandstone (16) and Pietra Serena (17), and the results obtained correspond with those described here.

In *Diploicia canescens* and *Parmelia loxodes* oxalate is present only in the surface layer of the thallus (18).

Iron oxides present at the rock surface do not seem to be caused by the action of lichens but rather are the result of natural decay. A role of lichens in the surface enrichment in iron of volcanic tuff and basalt has been demostrated by some authors (19,20,21). In our samples no preferential accumulation of iron oxides was noted in relation to the presence of lichens.

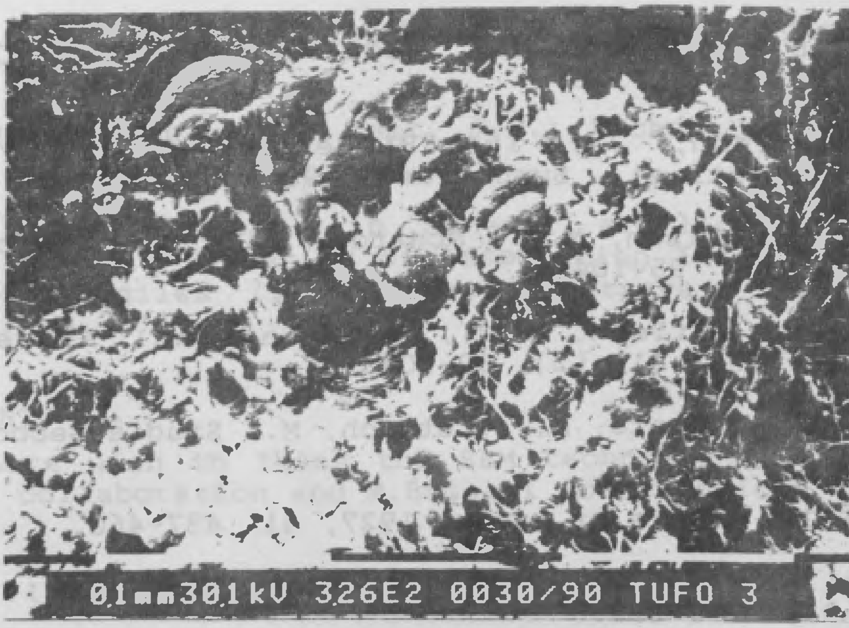


Fig.7 - SEM photomicrograph showing fungal hyphae of *Lecidea fuscoatra* penetrating in the substrate.

Fig. 8 - SEM photomicrograph showing crystals of weddellite in the thallus of *Diploschistes actinostomus*.

5. REFERENCES

1. Ascaso, C.; in "Surface physiology of lichens"; Vicente, C., Brown, D.H., Legaz, M.E., Eds.; Universidad Complutense, Madrid, 1984, 87-113.

2. Bech-Anderson, J.; in "Biodeterioration 6/ 6th Int. Biodeterioration Symposium", 1984, 126-131.

3. Jones, D.; Wilson, M.J.; McHardy, W.J.; Journal of Microscopy 1981, 124, 95-104.

4. Jones, D.; Wilson, M.J.; International Biodeterioration Bulletin 1985, 21 (2), 99-104.

5. Nimis, P.L.; Monte, M.; Tretiach, M.; Studia Geobotanica 1987, 7, 3-161.

6. Fry, E.J.; Annals of Botany 1927, 41, 437-460.

7. Ascaso, C.; Galvan, J.; Rodriguez-Pascal, C.; Pedobiologia 1982, 24, 219-229.

8. Charola, A.E.; Lazzarini, L.; in "Wiener Berichte über Naturwissenchaft in der Kunst, 1987-1988, 4/5, 392-401.

9. Jacobacci, A.; Bergomi C.; Centamore, E.; Malatesta A.; Malferrari N.; Martelli, G.; Pannuzi, L.; Zattini, N.; "Note illustrative della Carta Geologica d'Italia. Fogli 115 - 122 - 130."; Servizio Geologico d'Italia, 1970.

10. Lombardi, G.; Mattias, P.; in AIPEA 7th International Clay Conference, Bologna and Pavia, 1981.

11. Nappi, G.; Ottaviani, M.; in Proceedings of the 5th International Congress International Association of Engineering Geology, Buenos Aires, 1986, pp. 455-464.

12. Nappi, G.; Chiodi, M.; Rossi, S.; Volponi, E.; Boll. Soc. Geol. It. 1982, 101, 327-342.

13. Nappi, G.; De Casa, G.; Volponi, E.; Boll. Soc. Geol. It. 1979, 98, 431-445.

14. Seaward, M.R.D.; Lichenologist 1988, 20 (3), 291-295.

15. Hawksworth, D.L.; Hill, D.J.; "The lichen-forming fungi", Blackie Ed., Glasgow and London, p.158.

16. Salvadori, O.; Lazzarini, L.; "Lichens deterioration on stones of Aquileian monuments", Botanika Chronika (in press).

17. Pallecchi, P.; Pinna, D.; in Proc. 6th Intern. Congr. on Deterioration and Conservation of Stone, Torun, 1988, Supplement, 39-47.

18. Wadsten, T.; Moberg, R.; Lichenologist 1985, 17 (3), 239-245.

19. Jackson, T.A.; Keller, W.D.; American Journal of Science 1970, 269, 446-466.

20. Jones, D.; Wilson, M.J.; Tait, J.M.; Lichenologist 1980, 12, 277-289.

21. Wilson, M.J.; Jones, D.; in "Minerali argillosi ed ossidi di ferro del suolo"; Meeting of Association Internationale pour l'etude des argiles (Italian Group), Stresa e Valsesia, 1985, pp.57-65.

AKNOWLEDGEMENTS

The authors wish to thank the SEM technician D. Zanella for his valuable collaboration and M.Bulgari for technical assistance.

Ascaso, C. in "Scanning Electron Microscopy of Lichens"; Vicente, C., Brown, D.H., Legaz, M.E. (eds.): Universidad Complutense, Madrid, 1984, 87-113.

3. Gehrmann-Andersen, ... in "Biodeterioration 6, Int. Biodeterioration Symposium" 1986, 126-131.

4. Jones, D.; Wilson, M.J.: International Biodeterioration Bulletin 1985, 21 (2), 99-104.

5. Mäkie, ...; Hente, ...; Tremisch, ...: Studia geobotanica 1987, ...

6. Fry, E.J.: Annals of Botany 1927, 41, 437-460.

7. Ascaso, C.; Galvan, J.; Rodriguez-Pascual, C.; Pedobiologia 1982, 24, 219-229.

8. Charola, A.E.; Lazzarini, L.: in "Wiener Berichte über Naturwissenschaft in der Kunst, 1987-1988, 4/5, 392-401.

9. Jacobacci, A.; Bergomi, C.; Centamore, E.; Malatesta A.; Malferrari N.; Martelli, G.; Pannuzi, L.; Zattini, N.; "Note illustrative della Carta Geologica d'Italia. Fogli 118 - 122 + 130."; Servizio Geologico d'Italia, 1970.

10. Lombardi, G.; Mattias, P.: in AIPEA 7th International Clay Conference, Bologna and Pavia, 1981.

11. Nappi, G.; Ottaviani, M.: in "Proceedings" of the 5th International Congress International Association of Engineering Geology, Buenos Aires, 1986, pp. 455-464.

12. Nappi G.; Chiodi, M.; Rossi, P.; Volponi, E.; Boll. Soc. Geol. It. 1982, 101, 327-342.

13. Nappi, G.; De Casa, G.; Volponi, E.; Boll. Soc. Geol. It. 1979, 98, 431-445.

14. Seaward, M.R.D.; Pedobiologia 1986, 30 (5), 291-295.

15. Hawksworth, D.L.; Hill, D.J.: "The lichen-forming fungi", Blackie Ed., Glasgow and London, p.158.

16. Salvadori, O.; Lazzarini, L.: "Lichens deterioration on stones of Aquileian monuments" Botanika Chronika (in press).

17. Pallecchi, P.; Pinna, D.: in Proc. 6th Intern. Congr. on Deterioration and Conservation of Stone, Torun, 1988, Supplement, 29-47.

4. TRATAMIENTOS

TREATMENTS

ESTUDIO DE CONSOLIDACION DE LA FACHADA DE LA IGLESIA DE SANTO DOMINGO DE POPAYáN, COLOMBIA, LABRADA EN TOBA VOLCANICA

L. A. USECHE

Centro Nacional de Restauración de Obras de Arte,
Instituto Colombiano de Cultura, COLCULTURA, Bogotá, Colombia

RESUMEN

La portada de la Iglesia de Santo Domingo, así como muchos otros monumentos importantes de Colombia, incluída el área arqueológica de San Agustín, fueron tallados en tobas volcánicas. Estas rocas presentan un deterioro muy marcado, dadas sus condiciones físicas y su naturaleza mineralógica.

El portalón sufrió daños importantes en el terremoto de 1983. Se desmontó y se realizaron los estudios presentados en el siguiente trabajo. Se tienen en la actualidad rocas tratadas según los resultados del presente trabajo a la intemperie con el objeto de hacer un seguimiento de la efectividad de los tratamientos propuestos.

ABSTRACT

The portal of the Church of Santo Domingo, as well as many other important monuments of Colombia, including the archaeological area of San Agustín, were carved out of volcanic tuffs. These rocks show a pronounced deterioration due to their physical state and mineralogical nature.

The portal suffered largely during the earthquake of 1983. It was then taken apart and studies carried out. These are described in the present paper. Some of the specimens, treated according to the results of the study, are still being field-tested to evaluate the effectiveness of the proposed treatment.

La Iglesia de Santo Domingo de la ciudad de Popayán se constituye en uno de los Monumentos más queridos por la comunidad; sitio obligado de paso y visita, dada su ubicación y su proximidad con el Claustro de la Universidad del Cauca.

Su portada, ampliamente comentada y admirada por los críticos e historiadores del arte, es de caracter macizo, abigarrada decoración a base de elementos vegetales, con columnas platerescas, friso convexo de inspiración " Palladiana ", que la convierten en una obra notable, en donde se combinan lo arcaico y lo barroco.

Se terminó de labrar en 1714 en una toba volcánica, roca ampliamente utilizada en la ciudad de Popayán como material de construcción de fachadas.

El portalón sufrió lamentables pérdidas en el terremoto de 1983, que empeoraron su ya deteriorada condición.

El propósito del estudio es tratar de determinar un consolidante que llene poros y grietas de esta roca, para devolverle parte de su resistencia mecánica, y preveerle futuros deterioros.

Se midieron constantes físicas a roca testigo, como densidad de volumen, resistencia a la compresión, porosidad y absorción de agua.

Se escogieron algunos productos comerciales consolidantes y se trataron con ellos probetas de roca, usando diferentes concentraciones y tiempos de inmersión. Luego de los tratamientos se midieron de nuevo las propiedades físicas para determinar la efectividad de los mismos.

Vista frontal del Portalón antes del terremoto.

INTRODUCCION

La toba volcánica ha sido muy utilizada en la ciudad de Popayán como material de construcción de fachadas, casas, e iglesias antiguas que involucran tallas en piedra; ésto debido principalmente a que este tipo de roca se halla ampliamente distribuído en la región. Tobas volcánicas se encuentran en un radio de unos 20 a 50 km de distancia alrededor de la ciudad de Popayán.

Estudios geológicos de la zona hablan de rocas pertenecientes a la formación Popayán de naturaleza conglomerática, porosas y permeables, rocas volcánicas y depósitos fluvio-lacustres, flujos de lava, flujos de lodo volcánico y tobas (1) (2) (3).

En " El Deterioro de la Fachada de la Iglesia de San Francisco de Popayán (4) se realizaron análisis petrográficos comparativos de rocas extraídas de las canteras cercanas a Popayán y que son actualmente trabajadas por los artesanos locales, con muestras tomadas de la fachada en mención, resultando ser de la misma composición.

Las tobas volcánicas por su naturaleza geológica y su composición, son porosas, permeables y por lo tanto fácilmente meteorizables.

La portada de la Iglesia de Santo Domingo de Popayán fué labrada sobre roca de ésta clase; hoy en día se encuentra en avanzado estado de meteorización.

El propósito de este estudio es de tratar de determinar un consolidante que llene poros y grietas de esta roca, en orden a devolverle parte de su resistencia mecánica, lo cual previene en gran parte su completa desintegración; este material consolidante prevendría también deterioros posteriores.

En la actualidad existe una amplia gama de productos comerciales que están siendo estudiados y probados en Norte América y

Europa, con miras a resolver serios problemas de desintegración de sus monumentos y prevenir futuros deterioros (5) (6) (7) (8). Estos productos abarcan resinas sintéticas de diferentes composiciones químicas y clases que van desde resinas, epóxicas, acrílicas, poliuretanos, hasta las más novedosas en este campo como son las siliconas de diversas especificaciones (9) (10) (11) (12).

Ninguno de los productos arriba enunciados poseen todas las ventajas que requeriría un preservativo de problemas tan específicos, pero, dentro de un rango altamente aceptable hay algunos que se comportan de manera óptima, y las desventajas que involucran tienen fácil solución, esto depende obviamente del tipo de roca y su estado de deterioro (7).

Vale la pena enfatizar que si el grado de deterioro de una roca es muy alto ningún producto por óptimo que sea la salva de su desintegración total.

Se concluyó, que las resinas a base de ésteres de etilo son las más apropiadas para el problema que nos ocupa, ya que restituyen de manera significativa las propiedades mecánicas de la roca, sin cambiar su apariencia.

Desde Enero de 1989, y hasta la actualidad, se tienen colocadas a la intemperie, muestras de roca del portalón tratadas con resinas de los ésteres de etilo. Su comportamiento al medio agresivo es excelente.

CARACTERISTICAS PETROGRAFICAS Y CAUSAS DE DETERIORO

En el estudio de las causas del alarmante estado de meteorización de la roca, con la cual se talló la portada de la Iglesia de Santo Domingo, se hizo un análisis macroscópico sobre muestra de mano; se trata de un material friable, desmoronable a simple presión con los dedos. Su porosidad secundaria (poros, grietas y microfisuras) debida a lixiviación de minerales, es alta como se observa en la Fig 1. Los poros y grietas de mayor tamaño se encuentran rellenos con un material negro, de consistencia bituminosa.

No se observan en ella zonas diferenciables de porosidad, o sea que su meteorización es homogénea; no se quiere indicar con esto que su composición tambien lo sea, ya que como se dijo antes, se encuentran zonas rellenas de sustancia negra, que abarcan aproximadamente un 20% de la muestra.

La alteración comienza generalmente con la devitrificación del vidrio para dar material túrbido débilmente birrefringente de color pardo; si continúa el proceso de alteración, el vidrio es reemplazado por sustancias verdosas que se oxidan a color castaño y luego a un material resinoso negro engañosamente semejante al betún ". (3) (12)

El análisis microscópico en sección delgada de esta roca altamente alterada corrobora las características arriba enunciadas. Este reportó la siguiente composición porcentual mineralógica :
olivinos 23% - biotita 1.8%, piroxeno 5%, plagioclasa 2%, matriz 55%, porosidad primaria 10%, porosidad secundaria 5% (Pradilla Alejandro - Geólogo).

En las secciones pulidas se puede apreciar claramente el estado de disgregación de los minerales, así como su alteración. También se observan claramente las grietas rellenas en algunos casos con el material negro, y la alta porosidad, debida a la lixiviación de los óxidos de hierro, las biotitas, y otros minerales que otrora hacían parte de su estructura.

Fig. 1. Muestra de roca de la portada. Se observan grandes grietas, rellenas de material negro. No hay zonas diferenciables en porosidad. (Ampliada 5 veces).

PARTE EXPERIMENTAL

Ensayos Preliminares :

Los siguientes son los productos utilizados para los ensayos preliminares, realizados sobre terrones de muestra alterada : Paraloid, Mowilit, Primal, Limes Tone (hidrofugante), Resina Silicona (Silicato de etilo) W - 6789 - OH, y W - 5937 - H, Resina Epóxica (Toch 8004).

Las muestras se sumergieron totalmente en los productos anteriores,a tiempos diferentes de inmersión; posteriormente se hicieron mediciones de densidad y absorción.

Tratamientos Finales :

Los resultados de los ensayos preliminares nos permitieron preseleccionar los productos que parecían los más adecuados para este problema.

Aunque los resultados preliminares con el Paraloid no fueron totalmente satisfactorios, este producto se ensayó finalmente para obtener sus datos evaluativos.

El método de aplicación que se escogió fué la inmersión total, ya que por el estado de disgregación de la muestra, se debía garantizar su total impregnación. Además como la efectividad de un tratamiento de consolidación depende fundamentalmente del consolidante y del método de aplicación, para obviar esta última variable todas las muestras se trataron igual (inmersión total).

Todos los tratamientos que se describirán abajo, y que numeraremos de 1 a 9, se realizaron sobre paralelepípedos, desafortunadamente no regulares, debido a lo meteorizado de la muestra. Fig.

CARACTERISTICAS FISICAS :

Fueron determinadas por las siguientes propiedades físicas :

Densidad de Volumen : Masa por unidad de volumen aparente; el volumen fué determinado por peso hidrostático de la muestra saturada con agua, a presión atmosférica.

Porosidad (n): El total de poros abiertos fué determinado por el método de kobe basado en la evaluación del volúmen de aire que llena los poros de interconexión de la roca. Es expresado como porcentaje del volúmen aparente de la roca.

Resistencia a la Compresión (q) : Fué determinada sobre paralelepípedos aplicando la carga en la dirección de la dimensión mayor, expresada en kg/cm^2 .

Agua de Absorción : Determinada por medidas de la masa de agua absorbida por la muestra previamente secada a 110°C hasta peso constante, en 24 horas de inmersión a presión atmósferica. Expresada como porcentaje de la masa seca.

TABLA 1.

Propiedades Físicas de la Toba Volcánica

Densidad de volúmen	(g/cm^3)	1.299
Resistencia a la Compresión	(kg/cm^2)	12.9
Porosidad	(%)	47.4
Absorción de agua	(%)	36.6

TABLA N°2

	PRODUCTOS EVALUADOS						
	Paraloid	Mowilith	Primal	Limes-tone	Silicona W-H	Silicona W-OH	Epóxica
Naturaleza química	Polimeros de ésteres acríli cos y metacrilatos.	Polivinil acetatos	Emulsión Acrílica	Silicona	Silicato de etilo	Silicato de etilo	Resinas Epóxicas
Designación Comercial	Paraloid	Mowilith sólido	Primal	Limes-tone	Wacker-H	Wacker-OH	Tooch 8004
Solventes	Xilol-thiners toluol	acetona acetato de amilo	agua	-	alcohol etílico	alcohol etílico	acetona cetonas
Gravedad específica	1.00	Aprox. 1.17	-	-	Aprox. 0.9	Aprox. 0.94	
Aspecto del residuo	Película transparente	Película transparente	Película lechosa	Película transparente	Residuo vitreo translucido	Vitreo translúcido	Película amarillenta
Viscosidad	470 a 770 40% sólidos	110 a 150 Viscosímetro	-	-	60 seg con copa DIN de 2 mm.	42 seg con copa DIN de 2 mm.	-
Características Comerciales sobresalientes	incoloro, Buena protección duración resistencia al agua, ácidos y vapores.	incoloro adhesivo hunectante (Nota: no está indicado como consolidante	Durable resistecia al agua	Hidrofugante evita manchas de ollín y otras, evita hongos (Nota : no está indicado como consolidante,	incoloro. Consolidante de rocas resistente hidrorepelente. Alta duración	incoloro. Consolidante rocas. hidrorepelente. Alta duración	Múltiles usos : adhesivo. Consolidante. Alta resissistencia a la compresión. Oscurece el sustrato.

Probeta de trabajo. Ampliación 5 veces.

Los tratamientos que se realizaron finalmente fueron los siguientes :

1. Solución de Paraloid B-72 al 5% en thiner. La muestra se sumergió durante 10 días.

2. Solución de Paraloid B-72 al 10% en thinner. Sumergida durante 10 días.

3. Primal al 30% en agua. La muestra se sumergió durante 10 días.

4. Wacker OH. Pura. (W 6789 OH). Sumergida la muestra durante 2 días.

5. Wacker H. Pura. (W 5937 H). Se sumergió durante 1 día.

6. Este ensayo se realizó haciendo una pre-consolidación con Wacker OH. (W 6789 OH) como sugieren los productores. La muestra se sumergió en resina W 6789 OH durante 1 día, luego se saco, se dejó escurrir y se sumergió en resina W-5937H, durante dos días.

7. Resina epóxica Toch 8004 de Texement, diluída en proporción 1:2 con acetona. para hacerla más fluída. La inmersión se realizó durante 3 horas.

8. Este ensayo se efectuó con resina W-5937 H pura. , utilizando un mayor tiempo de inmersión, 5 días.

9. Ensayo con resina Primal al 30% en agua, durante tres días.

Efectos Estéticos :

En lo que concierne a los efectos estéticos de las impregnaciones se hicieron observaciones visuales con las muestras tratadas comparándolas con el testigo.

El producto que contiene resina epóxica causa oscurecimiento marcado de las muetras tratadas : esto es natural ya que la solución es amarilla.

Las muestras tratadas con Primal en la concentración del 30% dejan sobre la superficie una película ligeramente rosada. Esto se puede obviar fácilmente disminuyendo la concentración del producto.

Los productos que contienen resina silicona W-5937 cambian la apariencia oscureciendo ligeramente.

La resina silicona W - OH 6789 cambia la apariencia pero en menor proporción que la anterior.

Los datos se observan en la Tabla 4.

TABLA N° 3

Tratamiento	Porosidad	Resistencia a la Compresión
N°	n (%)	q (kg/cm²)
1	42.5	8.09
2	42.4	12.41
3	44.4	48.64
4	36.5	21.32
5	21.0	32.80
6	14.2	51.00
7	22.6	83.67
8	10.7	22.88
9	46.1	14.24
Testigo	47.4	12.87

TABLA N° 4

Tratamientos N°	Absorción de Agua	Densidad Aparente	Peso inicial	Peso Final	Incremento de peso
	(%)	g/cm²	(gr)	(gr)	(%)
1	32.9	1.292	20.4622	20.7489	1.40
2	31.0	1.368	17.0494	17.6663	3.61
3	31.5	1.410	21.6156	21.9650	1.62
4	25.7	1.421	17.2206	19.0799	10.80
5	8.2	1.450	21.7960	23.6050	8.30
6	9.7	1.459	20.8332	22.8591	9.72
7	14.3	1.583	27.1606	30.9950	14.10
8	6.8	1.579	21.0883	23.2397	10.2[illegible]
9	35.9	1.283	25.8143	27.5782	6.83
Testigo	36.4	1.301	-	-	-

CONCLUSIONES Y RECOMENDACIONES

Por los resultados obtenidos de los ensayos efectuados en el Laboratorio, nos es posible resumir las características peculiares de cada uno de los productos evaluados como sigue :

- El Paraloid a la concentración que se probó (5% y 10 %) no tiene efectos consolidantes sobre este tipo de roca, no limita la entrada de agua, ni aumentan sus propiedades mecánicas. Este producto no cambia la apariencia de la roca y es completamente reversible.

- El Primal tiene muy buen efecto consolidante, y buena capacidad fortalecedora de la estructura, pero no protege óptimamente a la roca contra la entrada de agua.

  Usado a la concentración de 30% forma una película brillante de color ligeramente rosado sobre la superficie de la roca.

  El Primal es excelente consolidante pero siempre y cuando no esté sometido a cambios drásticos de humedad, ni en contacto prolongado con el agua.

- El tratamiento hecho con la resina epóxica tiene un excelente poder consolidante, también buena capacidad fortalecedora, y adecuada penetración. Presenta dos inconvenientes que son, el pronunciado oscurecimiento alterando sustancialmente la apariencia de la roca, y su irreversibilidad.

- El tratamiento 8, con resina del tipo silicona (mezcla de silicato de etilo y alkyltrialkoxisiliano) tiene buena penetración, buena capacidad de consolidación, protege contra la entrada de agua, y aumenta la resistencia mecánica de la roca.

  El tiempo inmersión está en relación directa con la mayor absorción de resina por parte de la roca, esto hace que el consolidante llene más poros disminuyendo la capacidad de absorción de agua, y la porosidad efectiva de la roca.

La menor resistencia a la compresión de este tratamiento comparada con los tratamientos 5 y 6 desvirtúa solo parcialmente lo dicho anteriormente, ya que como se mencionó en el parágrafo correspondiente a la medida de resistencia a la compresión, ésta, no es absolutamente exacta ya que en ella intervino la variable roca que por las características de las probetas no pudo ser eliminada.

Comparando los tratamientos 5, 6, y 8 podemos afirmar que los tres cumplen con el propósito de llenar los poros y grietas, protegen contra el agua y aumentan la resistencia a la compresión de esta roca.

De los tres el que menos cambia la apariencia es el 6, los otros la alteran ligeramente, oscureciéndola.

Una desventaja que posee este producto es su irreversibilidad y su no capacidad cementante de los granos que pueden estar sueltos sobre la superficie de la roca.

Estos productos tienen además un secado lento (aproximàdamente 2 meses)

- El método de aplicación más efectivo para esta clase de roca es la inmersión total, con ella se garantiza penetración. Entre más tiempo se deje la roca sumergida mayor es la absorción de resina por parte de ésta.
- Una generalización de estos resultados a escala mayor debe hacerse una vez realicen pruebas sobre los bloques que van a ser tratados.
- A pesar de que los tratamientos con resina del tipo silicona arrojaron resultados positivos , no se puede afirmar nada sobre la duración de estos tratamientos, pero se recomienda hacer seguimientos y análisis periódicos con el fin de detectar cualquier signo de

deterioro posterior al tratamiento.

CONSIDERACIONES FINALES : (*)

- Las resinas W - H y W - OH son las ideales para este tipo de problemas.

- Sus inconvenientes : el costo, la importación.

- No se necesitaría inmersión total, percolocación podría ser.

- Se puede usar solo W - H y asegurar que la roca quede embebida.

- Oscurece ligeramente .

- Es conveniente hacer las juntas muy bien para que no penetre humedad.

- Proteger el portalón periódicamente con hidrofugante (Limes Tone)

- Si no se tiene el dinero se podría pensar en otro tratamiento más barato pero que no garantiza más de 10 años.

- Aun así es mejor consolidar con algo que dejarla así, ya que estructuralmente los bloques son débiles por la clase de roca y su meteorización.

- En el estudio de Coyasqui en el Ecuador realizado en Italia con roca similar aconsejan el mismo tratamiento.

- En la actualidad se tienen a la intemperie muestras de roca consolidadas con W-H y W-OH, y sus resultados son excelentes ya que no han sido alteradas por la lluvia, ni la contaminación.

(*) Estas consideraciones finales se recogieron después de cpnsultar los resultados de este estudio con diferentes especialistas de todo el mundo, que nos han visitado o que hemos tenido la oportunidad de ver en Stone Conservation Course en Venecia, en España etc.

BIBLIOGRAFIA

1. ABIGAIL, Orrego L. : " Observaciones Geológicas sobre la formación Popayán. Hacia el Este del Caserío " El Placer ". Ingeominas - Dirección Regional de Popayán II E - 21.

2. ABIGAIL, Orrego L. : " Geología y ocurrencias Minarales de la parte Oeste del Cuadrangulo N - 6 Popayán " . Ingeminas Dirección Regional de Popayán, II E - 18

3. WILLIAMS, H. Turner, Francis, Silver On. : " Petrografía " Compañía Editorial Continental S. A. México 1979.

4. RODRIGUEZ, Dario : " El Detrioro de la Fachada de la Iglesia de San Francisco de Popayán ". Centro Nacional de Restauración. Bogotá 1980.

5. J. SRAMEK, M. Kralova. : " Stability of some Polymers used for treatment of stone against U. V. Radiation and SO_2 ataack " Preprints of the Contributions to the International

6. FURLAN V, R. Pancella. : Propriétes d' un gres tendre traité avec des silicates d' ethyle et un polymere acrylique. Preprints of the Contributions to the International Symposium. Bologna. 1981.

7. ROSSI, Manaresi, : Effectiveness of Conservation Treatments for the sandstone of Monuments in Bologna. Preprints of the Contributions to the International Symposium. Bologna 1981.

8. SLEATER, Gerald A. : " Stone Preservatives " Center for Building Technology. National Bureau of Standards. Washington. 1977.

9. ROSSI M, Pellizzer R. : " The Volcanic Tuff of the Archaeological Monuments in Cochasqui, Ecuador : Cause of Decay and Effectiveness of Conservation Treat ments ". Centro per la Conservazione delle Sculture all'aperto. Bologna. Instituto di Mineralogía e Petrografia, Universitá di Siena.

10. MUNNIKENDAM R.A. : " The Combination of low Viscosity Epoxy Resins and Siliconesters for the Consolidation of Stone ". Central Research Laboratory for Objetcs of Art and Science Amsterdam.

11. MARCHESINI, L. Biscontin, G. : " Essai de Protection et de Consolidation sur la Facade en Terre Cuite d' une Eglise " Instituto di chimica Industriale, Université di Padova.

12. KERR. Paul. : " Mineralogía " Mc Grow - Hil New York, 1969. 3a Edición. Mc Graw Hill. New York 1979.

INTERACTION BETWEEN VOLCANIC TUFF AND PRODUCTS USED FOR CONSOLIDATION AND WATERPOOFING TREATMENT

M. LAURENZI TABASSO, A. M. MECCHI* AND U. SANTAMARIA

Istituto Centrale per il Restauro, 00184 Roma, Italy
*CNR, Istituto Conservazione delle Opere Monumentali, Italy

ABSTRACT

Volcanic tuffs were commonly used in many Italian regions, because of their availability and workability. Their durability, on the other hand, is rather poor, and therefore conservation treatments need to be applied. Researches on the interactions betwen tuff and the products used for consolidation and waterproofing are therefore necessary.
The present paper gives the results obtained with four different systems, all having a consolidating action and a water-repellent effect, applied to blocks of a volcanic tuff obtained from the remains of an etruscan wall in the area of Cerveteri, to the north of Rome.
The products studied were: a methylmethacrylate monomer, a polymethylmethacrylate, a methylphenylpolysiloxane and a mixture of ethylsilicate and methylsilane.

RESUMEN

Las tobas volcánicas fueron frecuentemente utilizadas en muchas regiones italianas, debido a su disponibilidad y su fácil elaboración. Por otra parte, son poco durables y en consecuencia, muchas veces necesitan tratamientos de conservación. Es preciso, por lo tanto, investigar las interacciones entre la toba y los productos utilizados para su consolidación e hidrofobización.
Este trabajo presenta los resultados obtenidos con cuatro sistemas diferentes, todos ellos con acción consolidante e hidrorepelente, aplicados a bloques de toba volcánica provenientes de los restos de una muralla etrusca en el àrea de Cerveteri, al norte de Roma.
Los siguientes products fueron estudiados: un monómero de metilmetacrilato, un polymethylmetacrilato, un metilfenilpolisiloxano y una mezcla de silicato de etilo y metilsilano.

1. INTRODUCTION

Volcanic tuff is commonly found in many parts of the world, and is often used in building because it has a low quarrying cost and is easy to work.

In the Lazio region of Italy, there is a considerable amount of ignimbrite stone which was widely used by the Etruscans and Romans. This tuff, light and easy to work, is not very long lasting. In antiquity, this problem was dealt with by coating walls with plaster, which generally no longer survives.

The archeological remains which have survived up to our time generally owe their conservation to the fact that they were buried up to the time of discovery. Once they were uncovered, however, they feel the effect of environmental factors and deteriorate rapidly.

The urgent conservation problems for this material are complex due to the presence of reactive minerals such as zeolites and to the very high porosity. Moreover, large structures are often involved (city walls, remains of buildings etc.) situated at ground level and difficult to protect from the damp.

Under these circumstances, the need to use consolidation and waterproofing products has led to research on the interaction between these products and the stone, so as to identify the most suitable type of treatment with the fewest possible drawbacks.

In the present study several products for consolidation and protection were applied to volcanic tuff; the most significant chemical and physical properties were then monitored before and after treatment, so that the interaction between the stone and the different products could be analysed. The same properties were also examined after samples had been subjected to artificial aging.

2. EXPERIMENTAL PROCEDURES

2.1 Petrographic features of tuff

The blocks of tuff used came from the Cerveteri archeological area and belonged to an Etruscan building which has now been completely destroyed. This stone, commonly referred to as "tufo rosso a scorie nere (red tuff with black cinders)" is actually a reddish-yellow lithoid tuff with black cinders of irregular size and shape spread out in as micropumice. The stone is an ignimbrite from the volcanic regions of Sabazia and Cimino to the north of Rome.

The matrix is deep yellow-brown, because of iron oxides and iron compounds; there are extensive fractures and holes. The phenocrystals include: sanidine, analcime derived from alteration of leucite, occasional plagioclase, pyroxene (diopsidic), occasional biotite and olivine with signs of weathering.

X Ray diffractometer analysis shows chabazite (and phillipsite), and indications of extensive zeolitization, which took place during the diagenesis.

The vitreous mass of the cinders contains perfectly clear sanidine crystals with occasional leucite crystals, which are usually analcimized. The cavities may contain small groups of pyroxene, plagioclase and magnetite crystals.

2.2 Products and treatments

Two different systems were tried with silicon based products (an ethyl-silicate + silane and a polysiloxane) and two methacrylate polymers (one applied as a monomer and polymerized in situ, and the other applied in solution).
Most of the products used in recent decades for treating stone belong to these groups.
The following were tested:

1) T: Tegovakon V, made by Goldschmidt A.G., an ethyl-silicate dissolved in organic solvents (dry residue about 34% by weight) used for consolidation + Tegosivin HL 100 made by Goldschmidt A.G., defined by the manufacturer as a low molecular weight modified siloxane, solvent-free, and applied for waterproofing.

2) S: Rhodorsil 11309, made by Rhone Poulenc, a methyl-phenyl-polysiloxane dissolved in 1,1,1 trichloroethane (10% weight/volume).

3) PMMA: Paraloid A21 LV, made by Rohm & Haas, a low viscosity polymethylmethacrilate in 1,2 dichloroethane (10% weight/volume).

4) MMA: Methylmethacrylate monomer mixed at 10% in SNIATRON 1629 polyester resin made by SNIA BPD.

The various types of treatment were applied on 27 cm cube shaped tuff samples. One of these cubes was kept untreated as a control sample. These sizes, rather unusal for a laboratory testing, were adopted in order to reproduce, as far as possible, the conditions met with in treating monuments. They also allowed for a better assessment of the penetration depth and the distribution of the treatment products. The samples were dry weighted before and after treatment, and the ultrasonic velocity was measured as well.
The first three treatments were applied according to the following method.
Each sample, completely wrapped with a tight gauze-cotton-gauze cover, is placed inside polyethilene tank on supports to keep the sample raised off the bottom.
The covering is soaked with a solution applied by slow dripping from infusion needles imbedded in the cotton. The excess solution, collected on the bottom of the tank, can rise up by capillarity through the portions of the covering touching the tank bottom (Fig. 1).
For PMMA and S the treatment lasted four days.
For the system T, at first ethyl-silicate was applied for seven days and then, after 21 days to allow the hydrolisis and the precipitation of silica, the methyl silane was applied, with the same modalities, for five days.
Methacrylate treatment was carried out by dipping the entire sample into the monomer solution; a patented polymerization method was used. This treatment was carried out in the laboratory of Italcementi S.p.A. in Colleferro, under the management of Prof. A. Rio (1).
The 27 cm pieces were then cut into 5 cm cubes, with the position on the original block being recorded. The measurements described in 2.3 were performed for these samples. They were then

aged with the procedures described in 2.4. After aging, the same measurements were repeated.

2.3 Measurements

The measurements performed were intended to indicate the interaction between the stone and the products used, especially with regards to the structural and mechanical properties, the behaviour in relation to water (liquid and vapour) and the colour. All the measurements were performed on both treated and untreated samples, before and after artifical aging. In order to assess the penetration depth and distribution of the different products in the tuff, all the measurements (except weight and ultrasonic velocity measurements) were made with a distinction between the samples of the outer "shell" (0-5 cm) and the internal ones (5-10 cm). The former was conventionally indicated as layer N° 1.

Internal samples were registered according to the horizontal layer of origin: the layer labelled N° 2 is between 5 and 10 cm from the upper surface; N° 3 is between 10 and 15, and N° 4 is between 15 and 20 (Fig. 2). Layer N° 5 is considered equivalent to N° 1.

a) Porosity

A Mercury Porosimeter was used, in accordance with Doc. NORMAL 4/80 (2).

The results are given as integral open porosity P%. The porosimetric distribution was calculated by measuring the volume of pores with a radius r < 1000 Å, 1000 Å < r < 10000 Å, 10000 < r < 100000 Å and with r > 100000 Å.

b) Ultrasonic velocity

This was measured in accordance with Doc. NORMAL 22/86 (3) using equipment supplied by the C.E.B.T.P. at St. Rémy Les Chevreux (France); the measurements were performed by the C.N.D. Soc. (Controlli non Distruttivi) in Rome. In order to take into account the irregularity of the tuff the measurements were taken on the 27 cm blocks, both before and after treatment.

c) Ultimate compressive strength

An INSTRON dynamometer with a load increase velocity of $8.3 \cdot 10^{-3}$ mm/sec was used for measurements. The results are given as ultimate compressive strength (KN/cm^2). The measurement was carried out on a minimum of 3 for each set of samples.

d) Water absorption by capillarity

This was measured in accordance with Doc. NORMAL 11/85 (4) on homogeneous groups of 5 samples. The results are given as capillarity coefficient C.A. ($g/cm^2\ s^{\frac{1}{2}}$) and maximum absorption M^{∞} (asymptotic value of the quantity of water absorbed in g/cm^2).

e) Water absorption by total immersion

This was measured in accordance with Doc. NORMAL 7/81 (5) on homogeneous groups of 5 samples. The results are shown as imbibition coefficient C.I.% .

f) Drying index (D.I.)

This was measured in accordance with Doc. NORMAL "Drying Index", to be published shortly, on homogenous groups of 5 samples, considering a drying time of 120 hours.

g) Permeability to water vapour

This was measured in accordance with Doc. NORMAL 21/85 (6) on homogenous groups of 3 samples, all from the external layer (N°1).

After artificial aging, the same number of samples could not always be prepared due to the acquired fragility of the tuff. In these cases (which will be identified) measurement is only approximate.

h) Colour

The colour of the external surface of layer N° 1 was measured by using the Munsell Soil Charts. Measurement refers only to the matrix without taking into account the large particles and black cinders. The results are expressed as H (hue), V (value) and C (Chroma).

2.4 Artificial aging

The artificial aging was carried out in two steps; the first with freeze-thaw cycles and the second with exposure to salt fog.

First stage. The samples were immersed in deionized water until saturation; then they were sealed in polyethylene bags with 20 ml of deionized water. These samples were then submitted to 50 freeze-thaw cycles in a climatic chamber; the cycle was as follows: 2 h at +15°C; from +15°C to -15°C in 1/2 hour; 2 h at -15°C, from -15°C to +15°C in 1/2 h.

Second Stage. The samples dried at 60°C were immersed into the following solution:

30 g/l Na_2SO_4

15 g/l NaCl

5 g/l $NaNO_3$

H_2SO_4 up to pH 4.5:

The saturated samples were then submitted to six dry-wet cycles as follows:

a) 4 hours in a salt fog chamber at 25 ±/2°C with a spray solution of the same type previously used.

b) 20 hours in a climatic chamber under 4 UV germicide lamps Philips TUV 15 WG15TO, total intensity = 300 lux, at a 50 ± 2°C.

After these six cycles, the samples were washed with tap water and finally with deionized water to wash away the soluble salts.

For each of the products tested, 10 samples from the outer layer were aged.

3. RESULTS

All the results reported in the tables are average values; as the standard deviation is not significant due to the reduced number of samples, the semidispersion was calculated:

(val max - val min) / 2.

Even if it is not given in the tables, this semidispersion was taken into account, when evaluating the experimental results.

3.1 Methylmethacrylate monomer

Table I and Fig. 3, 4, 5, 6, show the results obtained with samples treated with the methacrylate monomer. This data allows us to draw the following conclusions:

a) Amount of products absorbed and depth of penetration.
The increase in sample weight after treatment was 15% . All the measurements performed indicate that a satisfactory amount of the product also reaches the internal part of the sample, showing that the penetration reaches at least 13.5 cm.

b) Homogeneity of distribution
The comparison of the amount of water absorbed by capillarity and by total immersion of the samples, both for the outer "shell" and for the internal areas, shows that the outer layer always has a slightly higher absorption level.
This is almost certainly due to the fact that during treatment there is a slight loss of monomer due to its rather high vapour pressure. This causes a reduction of the consolidating material in the outermost layers, which consequently tend to be less hydrophobic that the inner layers.

c) Structural properties
The porosity P% decreases considerably both in the inner and outer layers, to an average level of around 16%. Lack of homogeneity in results from external layers is due to the inherent irregularities in the tuff rather than to non homogeneous distribution in the pores of the stone.
With regards to porosimetric distribution, the polymer material preferentially tends to fill pores with a radius of 1000 - 10000Å. Once the cavities having a radius >100 μ (not detectable before treatment with the technique used) were filled, the formation of pores in the 100000 - 300000Å range was triggered.
These results are in good agreements with those published by other Authors (7) on a Neapolitan Yellow Tuff.
In accordance with the porosimetric data, ultrasonic measurement also indicated a considerable reduction of internal porosity: the velocity of sound more than doubled after treatment.

d) Mechanical properties
The value of the compressive strength was increased by more than tenfold for all the samples measured. The slight differences measured between internal and external layers are probably due more to the uncertainties of the measurement method than to the irregular distribution of the product or the characteristics of the tuff.
These results too agree with those of the already cited paper (7).
Artifical aging of the samples led to a reduction in the compressive strength (around 30%), but these levels are still much higher than in untreated tuff.
As for the effects of artifical aging, it should also be added

that there was no breakage of any of the samples treated with MMA.

e) Behaviour of the samples to water

As pointed out previously, samples from the internal layers absorb less water than the outer layers. This is especially obvious after an assessment of the C.A. value (affected by the first minutes of contact of the sample surface with water) and the C.I. value (which represents the maximum quantity of water absorbed by full immersion at atmospheric pressure).

After aging, the C.A. is the parameter most affected, although it is still less than 1/10 of the value of untreated stone. This can be explained by the fact that capillary absorption, for the outer samples, occurs through the original outer layers which have the least consolidating product and are more prone to aging.

The flex in the capillary absorption curve before aging (Fig. 3) indicates that treatment provides excellent waterproofing only during the first minutes; water absorption then speeds up for a certain amount of time, slowing down as it nears saturation.

Finally, as for the permeability to vapour and drying characteristics (Fig. 6 and the D.I. value), it can be pointed out that although the tuff is much less permeable to vapour, it still dries much more easily than the untreated stone.

f) Colour

Treatment causes a colour change in the tuff, apparent to the naked eye; the colour becomes redder, darker and less saturated.

3.2 Polymethyl-methacrylate

Table II and Fig. 7, 8, 9, 10, 11, shows the results obtained with Paraloid A21 LV polymethyl-methacrylate by Rohm & Haas. The following observations can be made.

a) Amount of product absorbed and depth of penetration

The quantity of product absorbed amounts to 13.6% in weight, i.e. only slightly lower than the value obtained with methacrylate monomer. A comparison between the results of untreated samples and those of samples in between 5 and 10 cm, shows that the product penetrated to a depth of 10 cm. The porosity value P% measured in the very core of the initial sample is slightly under the minimum value recorded for untreated tuff. It can thus be concluded that some of the product reached the core.

b) Homogeneity of distribution

Assuming that for each treatment with a waterproofing product, the reduction in the amount of water absorbed by the sample depends directly on the amount of product present in this sample, a comparison of the absorption data allows for an excellent assessment of the distribution. All the results of these measurements indicate clearly that the samples of the external layer are more hydrophobic and therefore contain more PMMA.

Moreover, when samples of between 5 and 10 cm from different layers are compared, the results depend on their position in the original block (Fig. 11).

It can be observed that the 2nd layer absorbs more than the 4th layer; this 4th layer is comparable with the 1st one in terms of capillary absorption, while has an even lower C.I. On the basis of this comparison, it can be concluded that polymer distribution is not very homogeneous. In the upper part of the original block, the product tends to stop at between 0 and 5 cm, while in the lower part there is a positive effect from the capillary absorption of the product through the pieces of gauze traling in the resin solution.

On the other hand, the 3rd layer has a C.I. value twice as high as the 4th layer. This can be explained by the hypothesis that the capillary penetration effect does not go beyond 10 cm. The high level of solution viscosity (n = 8.0 cSt) may be the reason both for the low rate of capillary rising and the difficulties in migrating from the 1st layer by gravity, or by horizontal transport.

c) Structural properties

The values of P% measured on samples pertaining to different positions in the original cube generally suggest the same considerable lack of homogeneity in distribution already hypotized (especially enhanced are the discrepancies of values obtained with the internal samples).

In any case, the results show values near the lower P% limit for untreated tuff, or even slightly higher. Despite the lack of homogeneity in these values, the histograms of the porous distribution show that the PMMA tends to fill pores with a radius between 10000 and 100000 Å.

Together with the relatively slight decrease in porosity, the increase in ultrasonic velocity is also slight, though still better than in untreated tuff.

d) Mechanical properties

The ultimate compressive strength is doubled by treatment, both in the outer shell and in the samples in between 5 and 10 cm.

Unlike the water absorption figures, there are no significant differences in compressive strength as regards the position in the original block. One can thus conclude that any lack of homogeneity in distribution of PMMA at levels high enough to influence water absorption will have no effect on compressive strength.

A possible interpretation of this phenomenon is that the PMMA has an excellent "adhesive" power, and that a small amount is therefore sufficient to bring about a considerable improvement in mechanical resistance. Since the product has less waterproofing impact, when the percentage of the product in the sample falls under a certain threshold, the effect on the quantity of water absorption is strongly reduced.

e) Behaviour of samples to water

Water absorption is considerably lower than in untreated tuff. As mentioned in point b), the maximum reduction is shown for the samples from the outer layer, especially the ones from the lower area.

The greatest differences with untreated samples are in capillary absorption (C.A. is reduced to about 1/100) while the completed immersion figures are lower (C.I. is reduced to a maximum of 1/6). After aging, there is no worsening in the samples except for the C.A. value, which however is still considerably lower than for untreated tuff.

As for the behaviour to water vapour, although permeability is a good deal lower, the rather low D.I. values compared to the untreated tuff indicate that, thanks to the waterproofing acquired in the treatment, the samples dry at a relatively fast rate.

f) Colour

Treatment with PMMA produces a slight change in the colour, which is slightly redder, darker and less saturated.

With aging, the tone comes back to yellow as in untreated tuff.

3.3 Methyl-phenylpolysiloxane

Table III and Fig. 12, 13, 14, 15, 16, shows the results obtained with methyl-phenyl polysiloxane produced by Rhone-Poulenc, Rhodorsil 11309. The following obervations can be made.

a) Amount of products absorbed and depth of penetration

The amount of product absorbed after treatment amounts to only 12% . A comparison of the porosity P% and water absorption for samples taken from the outer layer and the inner layers shows that the product definitely reaches the core of the original stone block, although, as in the case of the PMMA, the most of product is detected in the area between 0 and 5 cm from the surface.

b) Homogeneity of distribution

Here too, the homogeneity of distribution of the product can be assessed by the degree of waterproofing of the tuff. A comparison of the C.A., M$^{\infty}$ and C.I. values for the different layers shows that the concentration of the product is lower from the upper surface (and from the lateral surfaces in general) inward. The highest amounts of product are in the lower layer (5th and 4th), falling towards the 3rd level, and, of course, in the 2nd level.

In this case, too, there is a positive effect from capillary absorption, while there is a lower rate of horizontal movement or percolation from above. Irregularity in distribution, however seems lower than with PMMA, and this may be due to the much lower viscosity (η = 1.08 cSt) of the polysiloxane solution compared to the methacrylate resin.

c) Structural properties

The integral open porosity P% of the treated samples is only slightly lower than for untreated tuff, especially for the internal samples. The P% for the core sample is the lowest of all the levels measured, but it should be recalled that the heterogeneity of the stone could unduly influence these results.

In agreement with these results, the very slight increase in ultrasonic velocity seems to indicate that treatment has not produced a very good filling of the cavities in the tuff.

d) Mechanical properties

The ultimate compressive strength is only affected by the treatment of the outer layer, where most of the product accumulates. Values for the internal areas are comparable to untreated tuff. The pre-treatment values are also observed for external samples after artificial aging.

Considering that compressive strength is related to the adhesive properties of the consolidation product, results seem to show that for Rhodorsil 11309 these properties are not ideal for this type of stone. A detectable improvement of the compressive strength is only possible if the product concentration exceeds 12% (average value shown for the whole initial sample, and therefore

certainly lower than the concentration in the external shell).
This experimental result agrees closely with the ones obtained in other types of highly porous stone (8, 9).

e) Behaviour of samples to water
All the water absorption figures (C.A., M∞, C.I.) are sharply reduced after treatment. Hydrophobicity of Rhodorsil 11309 is very high, even for samples from the area between 5 and 10 cm from the surface and from the 2nd layer. This means that even low quantities of the product are enough to produce a considerable effect, given the excellent waterproofing qualities of this product.
It should also be pointed out that the treated samples remain very permeable to vapour, and dry more quickly than untreated samples.

f) Colour
The only effect of the treatment is a slight darkening and lower saturation level. These features persist after the aging treatment.

3.4 Ethyl-silicate + siloxane

Table IV and Fig. 17, 18, 19, 20, shows the results obtained from treatment with Tegovakon V Ethyl-silicate and Tegosivin HL 100 silane, both manufactured by Goldschmidt. The following observations can be made.

a) Amount of product absorbed and depth of penetration
The increase in sample weight after treatment was 15%. The penetration depth obtained with ethyl silicate can be assessed on the basis of compressive strength; water absorption rates are only slightly affected by this treatment, also in view of the high porosity level of the tuff. On the other hand, it is unlikely that the silane could bring about a decisive improvement of the mechanical properties, since the manufacturer is marketing the product only as a water repellent.
Since there is a considerable increase in the compressive strength in both the inner and outer layers, it is possible to infer that ethyl-silicate reached the core of the original block.
As for the penetration depth of the waterproofing product, the outer shell is mainly involved; samples to a depth of between 5 and 10 cm show M∞ and C.I. values very near to the ones for untreated stone. Only the C.A. value remains considerably lower, and this can be interpreted as due to a rather poor quantity of waterproofing silane, which can only delay the initial penetration of water in the capillary network.

b) Homogeneity of distribution
The measurements taken do not allow for an assessment of the distribution of the ethyl-silicate. As for the silane, the water absorption measurements do not show differences among the inner layers which, as it has already been stated, are only slightly affected by the product.

c) Structural properties
The P% for the samples from different parts of the original stone block are very near to the levels for untreated tuff. This result is an obvious contrast to all the other results, especially

with the increase in weight and the improvement of compressive strength and ultrasonic velocity.

Since number of porosity measurements are too extensive to attribute the discrepancy to the lack of homogeneity in the stone or to experimental errors, two hypotheses can be made. Either the treatment has affected very small pores (smaller than 50 - 100Å) outside of the range of the technique used, or, on the contrary, there has been a partial coating of cavities larger than 100 μ. These cavities were not measurable before the treatment and therefore did not affect the P% . Due to the treatment their radius should have been reduced so that they became measurable and could increase the value of P% .

It is obvious that the two hypotheses do not exclude one another, but both require experimental confirmation. The first hypothesis, which seems the more probable taking into account the chemical nature and the molecular weight of the ethyl-silicate, requires the study of the possible interaction between monomeric structures such as orthosilic acid produced by the hydrolysis of the ethyl-silicate, and minerals such as chabazite contained in the tuff. This would verify if the silica can penetrate in the zeolite crystalline lattice.

If this phenomenon can take place, and leads to a fall in the cationic exchange capacity of the minerals, this would also mean a considerable reduction of the deterioration process that normally occurs in these minerals and in the stone containing them (10).

d) Mechanical properties

As previously stated, there is a considerable improvement in the compressive strength for both internal and external layers. This effect is probably due especially to the affinity between the product of the silicate hydrolysis and the silicates contained in the tuff.

It is significant that the ultimate compressive strength after aging is still higher than in untreated tuff, although the values are rather scattered.

It should be observed on the other hand,that artifical aging produced breakage in 20% of the samples, which, of course, could not be used for the measures.

e) Behaviour of samples to water

Waterproofing properties increase considerably only in the external layers, especially with regards to capillary absorption (which, actually, is measured through the outermost layer of the samples).

Drying rates of the samples are similar to the untreated tuff, although permeability to vapour is considerably lower.

f) Colour

Treatment had very little influence on the tuff colour; it was slightly darker, and with slightly less saturation.

4. CONCLUSION

Considering the overall results, the use of samples which are much larger than those generally used for laboratory tests has proved especially effective.

This enabled us to reduce, or even eliminate, the influence of the inherently heterogenous nature of the tuff on the results of the experiment, since some of the measurements were taken before the tuff was cut into smaller cubes.

The treatment with the different products of blocks of stones of the same size generally used for ancient buildings has also ensured a good assessment of the possibilities of penetration and distribution homogenity. The results obtained are all the more significant when we consider that, apart from the methacrylic monomer, the application technique used in the study can be used for architectural features on building sites as well.

The comparison of the results of the 5 cm cubes from different positions in the original blocks gave a clearer understanding of interaction between the products and the stone showing the variations of the measured parameter as a function of the amount of absorbed product.

The different effects of the four consolidating and protective treatments were also stressed as a function of their chemical and physico-chemical properties.

It was shown that all the treatments improved the durability of the tuff, despite the initially poor state of preservation due to its long exposure to weathering. With reference to that it should be noted that after artificial aging, the untreated samples were so damaged as to make some of the measurements impossible.

Out of the four tested treatments, methylmethacrylate monomer gave the most interesting results: all the measured properties improved after the treatment, and the improvement remained even after the aging. Considering that the aging process involved considerable temperature fluctuations, it may be said that the differences in linear thermal expansion coefficient between the polymer and the stone, though high, are not so large as to trigger a breakdown of the "compound". This is probably due to the fact that consolidation was obtained with a quantity of product, comparable to those used for other types of treatment, high enough to increase the mechanical strength, but still leaving empty spaces to allow thermal expansion; moreover the product has no tendency to form a surface layer, and penetrates very deeply into the sample.

If treatment with methacrylic monomers has many advantages, the application technique should nevertheless be improved. Systems should be found which are suited to the needs of architectural restoration sites, while trying to reduce the chromatic effects on this type of stone.

A comparison between the PMMA and the methyl-phenyl polysiloxane also gives interesting information. All the results clearly show that the former has better adhesive than waterproofing properties, while the latter is an excellent waterproofing material but has only a slight effect on the mechanical resistance of the tuff. The consequence from the practical point of view is that more research is advisable to study the behaviour of mixtures of acrylic and silicone resins or, even better, for acrylic-silicone co-polymers, looking for products with suitable viscosity and surface tension in order to improve the penetration capacity of the solution used for treatment.

It might also be interesting to study the mixtures of methacrylic and vynilic monomers with silanic functions to get the co-polymer inside the stone (11).

Another aspect that we think should be studied is the interaction between tuff and ethyl silicate.

The hypothesis as to the orthosilicic acid interacting with the zeolithic minerals by penetrating the crystalline structures requires both theoretical and experimental testing. If confirmation is forthcoming, it could prove to be a useful tool for improving the mechanical properties and for slowing down the weathering process in the stones containing these minerals.

6. REFERENCES

1. Rio, A.; Cernia, E.M.; J. of Polymer Sc., Macromolecular Rewiew, (1974), 9, pp. 127-162.

2. Doc. NORMAL 4/84; Distribuzione del volume dei pori in funzione del loro diametro, C.N.R.-I.C.R., Roma, 1980.

3. Doc. NORMAL 22/86, Misura della velocità di propagazione del suono, C.N.R.-I.C.R., Roma, 1987.

4. Doc. NORMAL 11/85, Assorbimento d'acqua per capillarità - Coefficiente di assorbimento capillare, C.N.R.-I.C.R., Roma, 1986.

5. Doc. NORMAL 7/81, Assorbimento d'acqua per immersione totale - Capacità di imbibizione, C.N.R.-I.C.R., Roma, 1981.

6. Doc. NORMAL 21/85, Permeabilità al vapor d'acqua, C.N.R.-I.C.R., Roma, 1986.

7. Aurisicchio, S.; Evangelista, A.; Nicolais, L.; Rivista Italiana di Geotecnica, 1985, XIX, 2, pp. 89-100.

8. Laurenzi Tabasso, M.; Santamaria, U.; Preprints of the Vth Int. Congress on Deterioration and Conservation of Stone, Lausanne 25-27 Sept. 1985, pp. 697-707.

9. Rhone-Poulenc, Personal communication.

10. Lewin, S.Z.; Charola, A. E.; X-Ray powder diffraction investigation of the monumental stone of the Castel dell'Ovo, Naples, Italy, Advances in X-Ray Analysis, vol. 22, Plenum Press, New York, 1979 (?), pp. 169-180.

11. He, H.W.; Widmaier, J. M.; Herz, J.E.; Meyer, G.C.; Polymer, (1989), vol. 30, Feb., pp. 364-368.

ACKNOWLEDGEMENTS

Authors wish to thank Dr. P. Bianchetti for the petrographical description of tuff, Dr. D. Adami for the collaboration in the editing and Mr. G. Venturi for the valuable help in carrying out the experimental measurements.

TABLE I. Results of measurements for the samples treated with MMA

	bw		aw
	Ext.layer	Int.layer	Ext.layer
Water absorption by capillarity, M_∞ (g/cm^2)			
UT	1.8	-	-
MMA	0.4	0.3	0.6
Water absorption by capillarity C.A. · 10^{-3} (g/cm^2·sec$^{1/2}$)			
UT	47	-	-
MMA	2	0.9	3.6
Water absorption by full immersion C.I. - Imbibition coeff. (ΔM/M %)			
UT	34.2	-	-
MMA	11.2	9.5	11.7
Compressive strength (KN/cm^2)			
UT	0.16	-	-
MMA	1.87	1.78	1.33

	bw	aw
Drying Index		
UT	0.26	-
MMA	0.21	0.20
Water vapour permeability (g/m^2·24h)		
UT	370	-
MMA	130	150 (2)
Colour measurements		
UT	10YR 6/6-6/5	
MMA	7.5YR 4/2-4/3	7.5YR 4/2

Ultrasonic velocity (m/sec) (3)	
before treatment	1172
after treatment	2410

Weigth increase (%): 15

Integral open porosity, before weathering (P%) (1)			
	Ext.layer	Int.layer	Core
UT	22-39	-	-
MMA	16	19-10	16

bw = before weathering; aw = after weathering
UT = untreated

(1) Minimum and maximum values.
Core is the center of the 27 cm cube.

(2) Measure carried out on one sample.

(3) Average value of the three directions parallel to the surface of the 27 cm cube.

TABLE II. Results of measurements for the samples treated with PMMA

	bw		aw
	Ext.layer	Int.layer	Ext.layer
Water absorption by capillarity, M∞(g/cm²)			
UT	1.8	-	-
PMMA	0.2	1.0-0.7-0.2 (1)	0.25
Water absorption by capillarity C.A. · 10^{-3}(g/cm²·sec½)			
UT	47	-	-
PMMA	0.6	5.6-0.3-0.3 (1)	2.1
Water absorption by full immersion C.I. - Imbibition coeff. (Δ M/M %)			
UT	34.2	-	-
PMMA	12.7	18.0-21.6-7.0(1)	9.0
Compressive strength (KN/cm²)			
UT	0.16	-	-
PMMA	0.37	0.37	0.36

	bw	aw
Drying Index		
UT	0.26	
PMMA	0.23	0.12
Water vapour permeability (g/m²·24h)		
UT	370	
PMMA	260	240 (3)
Colour measurements		
UT	10YR 6/6-6/5	-
PMMA	7.5 YR 5/4	10YR 5/2-4/2

Ultrasonic velocity (m/sec) (4)	
before treatment	1037
after treatment	1425

Weight increase (%): 13.6

Integral open porosity, before weathering (P%) (2)			
	Ext.layer	Int.layer	Core
UT	22-39	-	-
PMMA	21	19-26	19

bw = before weathering; aw = after weathering
UT = untreated

(1) The values are related to the 2^{nd}, 3^{th}, 4^{th} layer.

(2) Minimum and maximum values.
Core is the centre of the 27 cm cube.

(3) Measure carried out on one sample.

(4) Average value of three directions parallel to the surface of the 27 cm cube.

TABLE III. Results of measurements for the samples treated with S

	bw Ext.layer	bw Int.layer	aw Ext.layer
Water absorption by capillarity, $M\infty$ (g/cm^2)			
UT	1.8	-	-
S	0.2	0.6-0.1 (1)	0.1
Water absorption by capillarity C.A. $\cdot 10^{-3}$ ($g/cm^2 \cdot sec^{\frac{1}{2}}$)			
UT	47	-	-
S	0.5	2.9-0.5 (1)	0.4
Water absorption by full immersion C.I. - Imbibition coeff. ($\Delta M/M$ %)			
UT	34.2	-	-
S	8.4	15.9-7.5-6.3 (2)	9.2
Compressive strength (KN/cm^2)			
UT	0.16	-	-
S	0.31	0.17	0.17

	bw	aw
Drying Index		
UT	0.26	-
S	0.19	0.13
Water vapour permeability ($g/m^2 \cdot 24h$)		
UT	370	-
S	360	320 (4)
Colour measurements		
UT	10YR 6/6-6/5	
S	10YR 4/2-4/4	10YR 4/2

Ultrasonic velocity (m/sec) (5)	
before treatment	1141
after treatment	1201

Weight increase (%): 12

Integral open porosity, before weathering (P%) (3)	Ext.layer	Int.layer	Core
UT	22-39	-	-
S	20	23.5	18

bw = before weathering; aw = after weathering
UT = untreated

(1) The values are related to the 2^{nd} and 4^{th} layer.

(2) The values are related to the 2^{nd}, 3^{th}, 4^{th} layer.

(3) Minimum and maximum values.
Core is the center of the 27 cm cube.

(4) Measure carried out on one sample.

(5) Average value of the three directions parallel to the surface of the 27 cm cube.

TABLE IV. Results of measurements for the samples treated with T

	bw		aw
	Ext.layer	Int.layer	Ext.layer
Water absorption by capillarity, M_∞ (g/cm^2)			
UT	1.8	-	-
T	0.5	1.5	1.2
Water absorption by capillarity C.A. · 10^{-3}(g/cm^2·sec^{½})			
UT	47	-	-
T	1	5.4	4
Water absorption by full immersion C.I. - Imbibition coeff. (Δ M/M %)			
UT	34.2	-	-
T	28.6	31.2	28
Compressive strength (KN/cm^2)			
UT	0.16	-	-
T	0.36	0.40	0.26-0.46 (1)

	bw	aw
Drying Index		
UT	0.26	-
T	0.27	0.24
Water vapour permeability (g/m^2·24h)		
UT	370	-
T	260	340 (3)
Colour measurements		
UT	10YR 6/6-6/5	-
T	10YR 5/3-5/4	10YR 5/2

Ultrasonic velocity (m/sec) (4)	
before treatment	1692
after treatment	1837

Weight increase (%): 15

Integral open porosity, before weathering (P%) (2)			
	Ext.layer	Int.layer	Core
UT	22-39	-	-
T	30-41	32-36	28

bw = before weathering; aw = after weathering

UT = untreated

(1) Minimum and maximum values.

(2) Minimum and maximum values.
Core is the centre of the 27 cm cube.

(3) Measure carried out on one sample.

(4) Average value of the three directions parallel to the surface of the 27 cm cube.

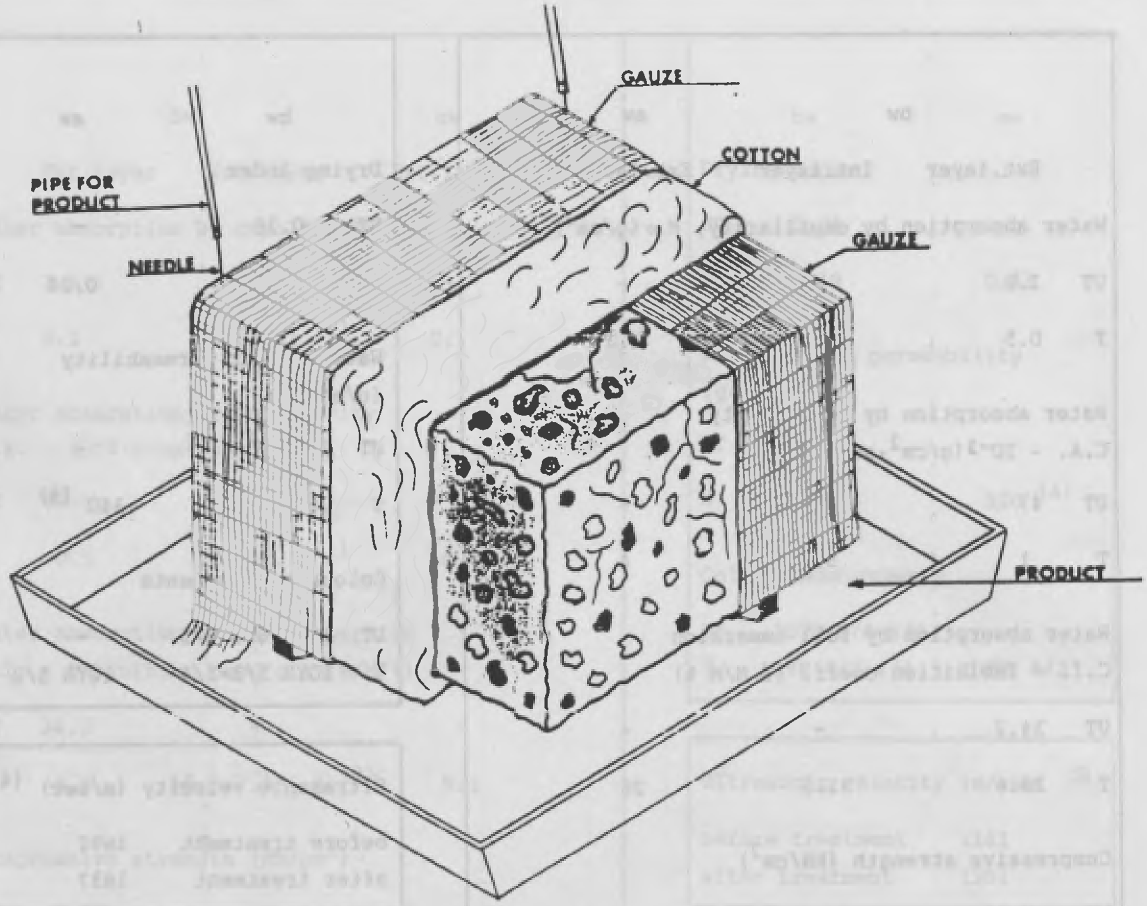


Fig. 1 - Method of treatment for PMMA, S and T

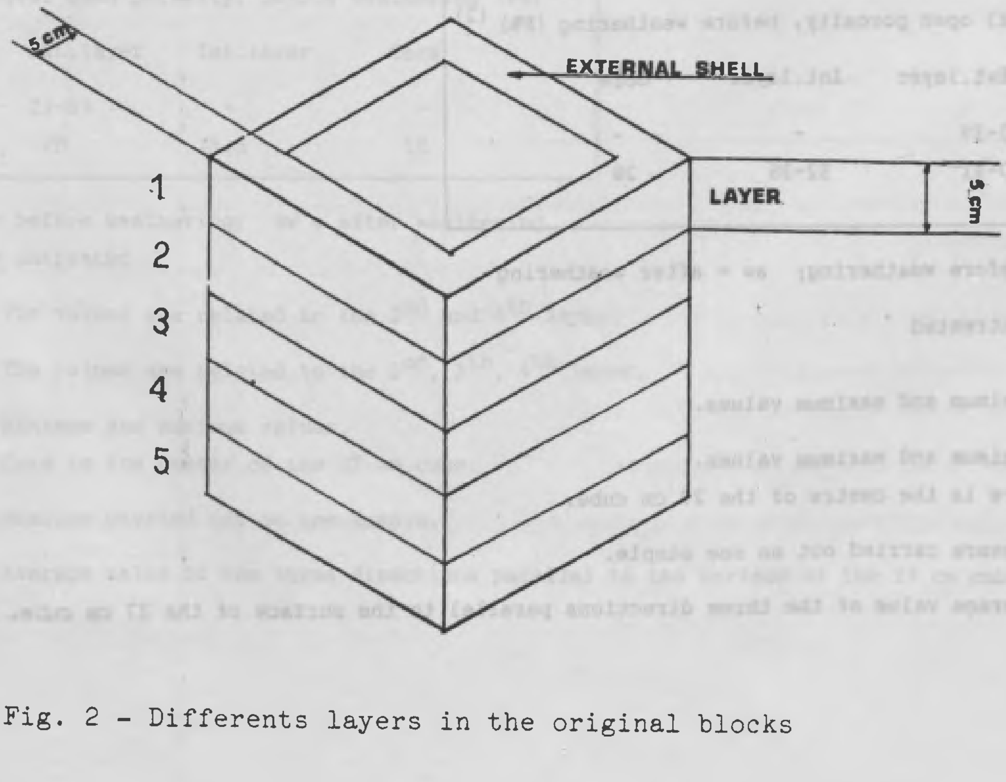


Fig. 2 - Differents layers in the original blocks

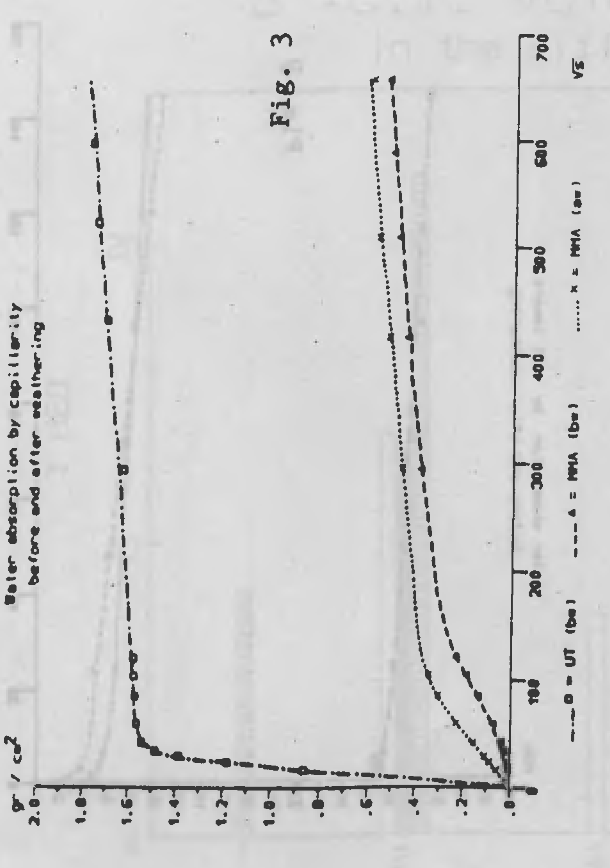


Fig. 3

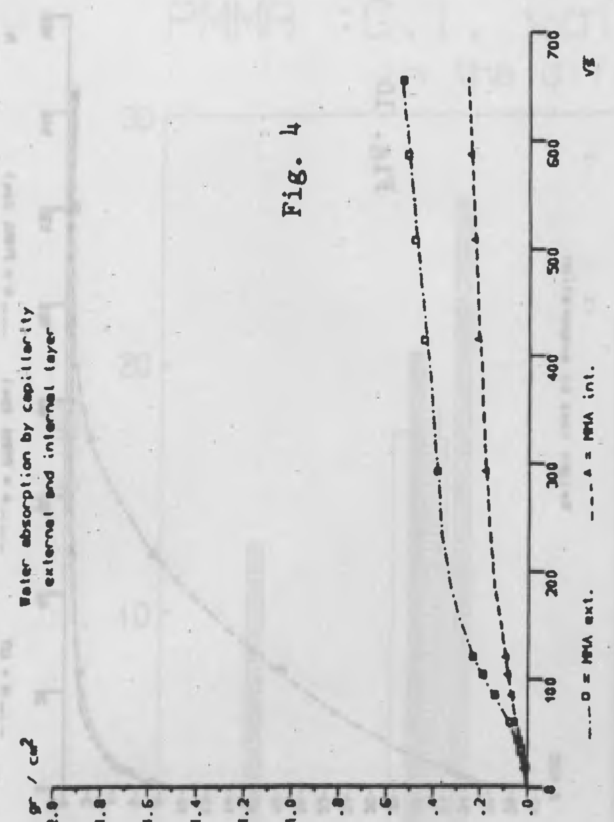


Fig. 4

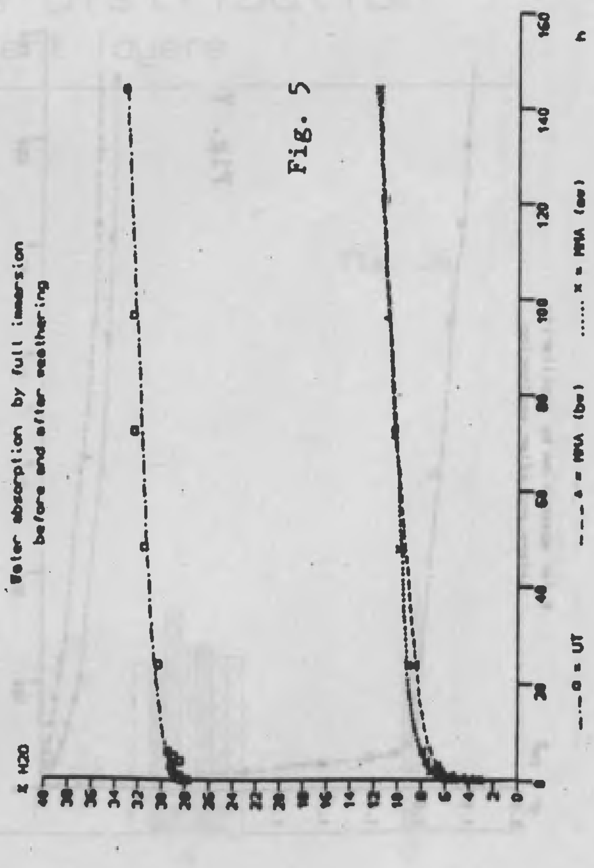


Fig. 5

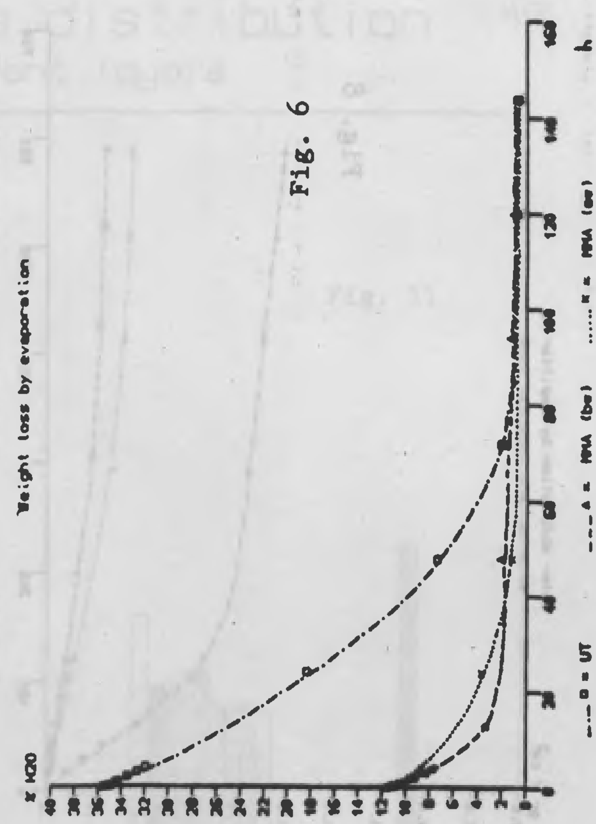


Fig. 6

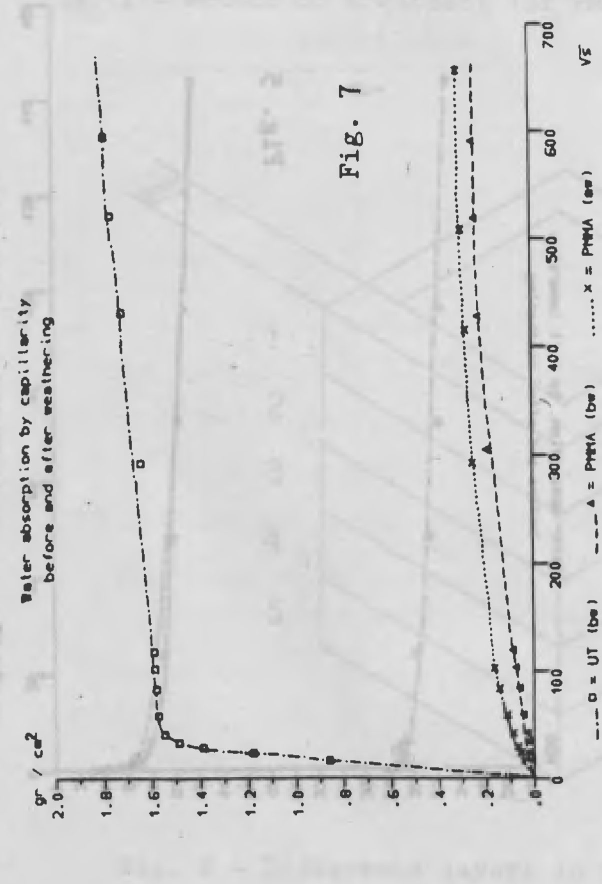


Fig. 7

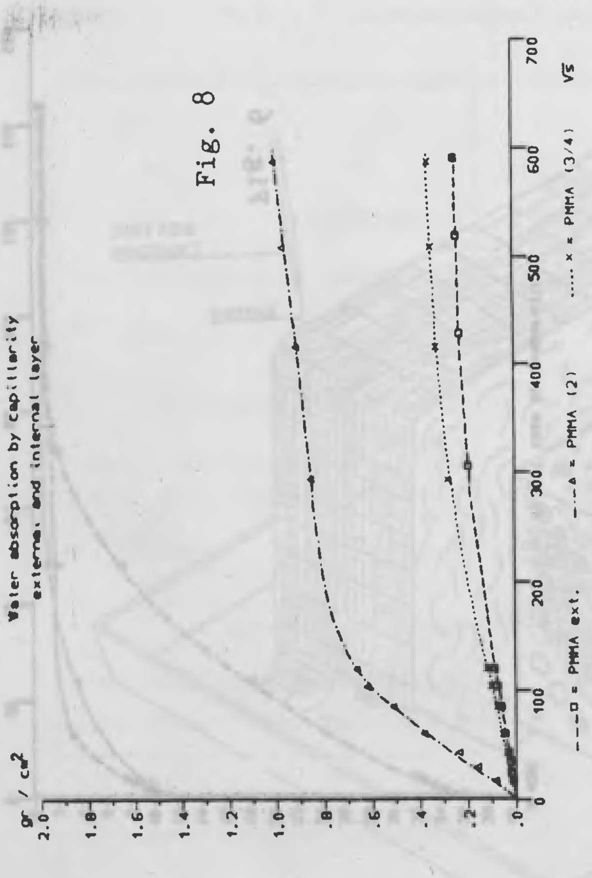


Fig. 8

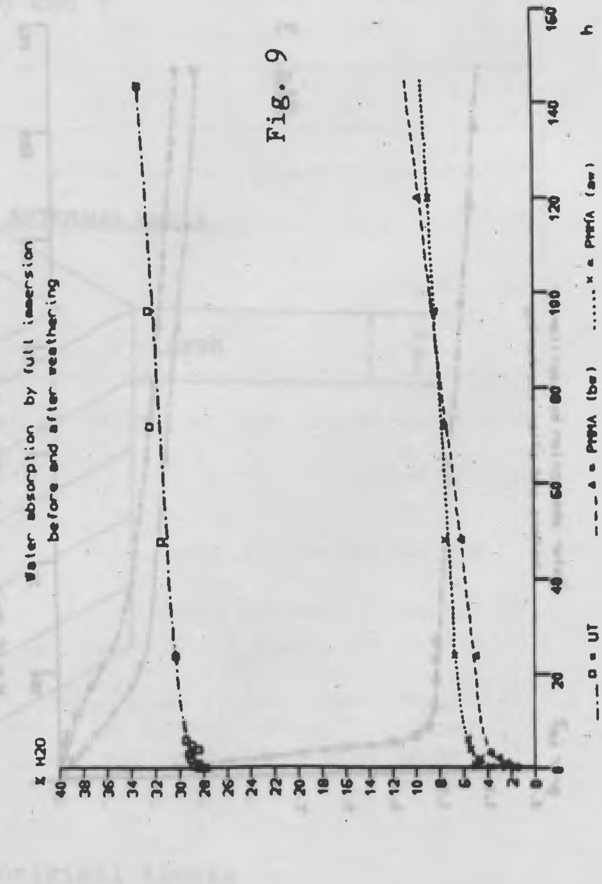


Fig. 9

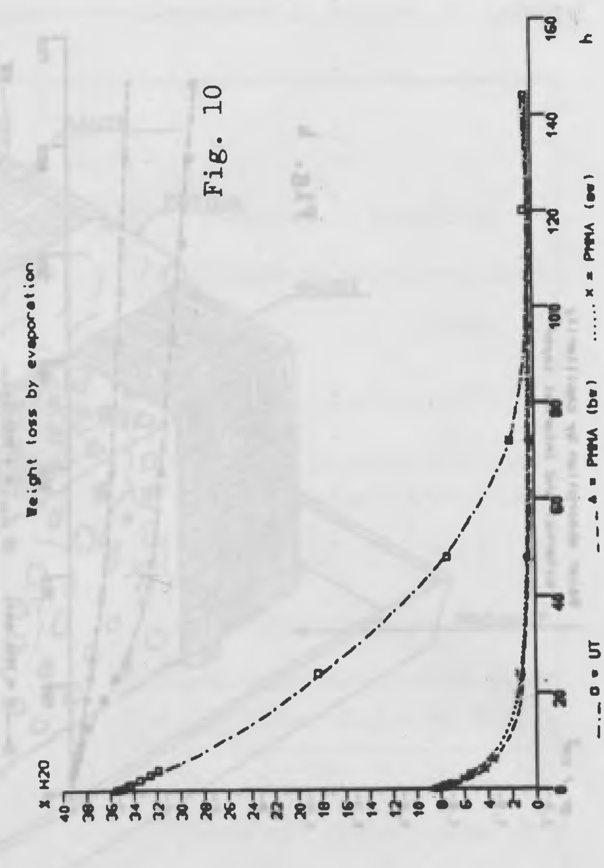
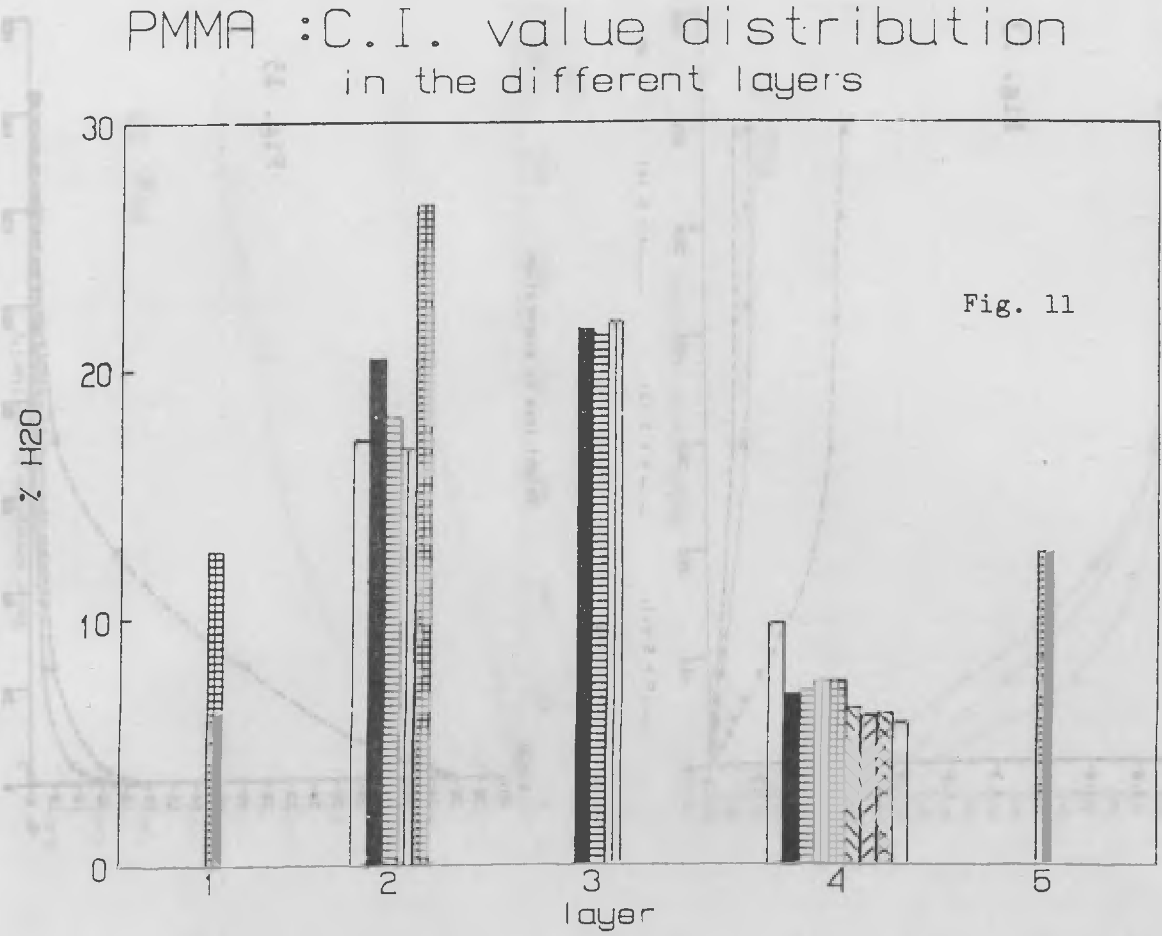
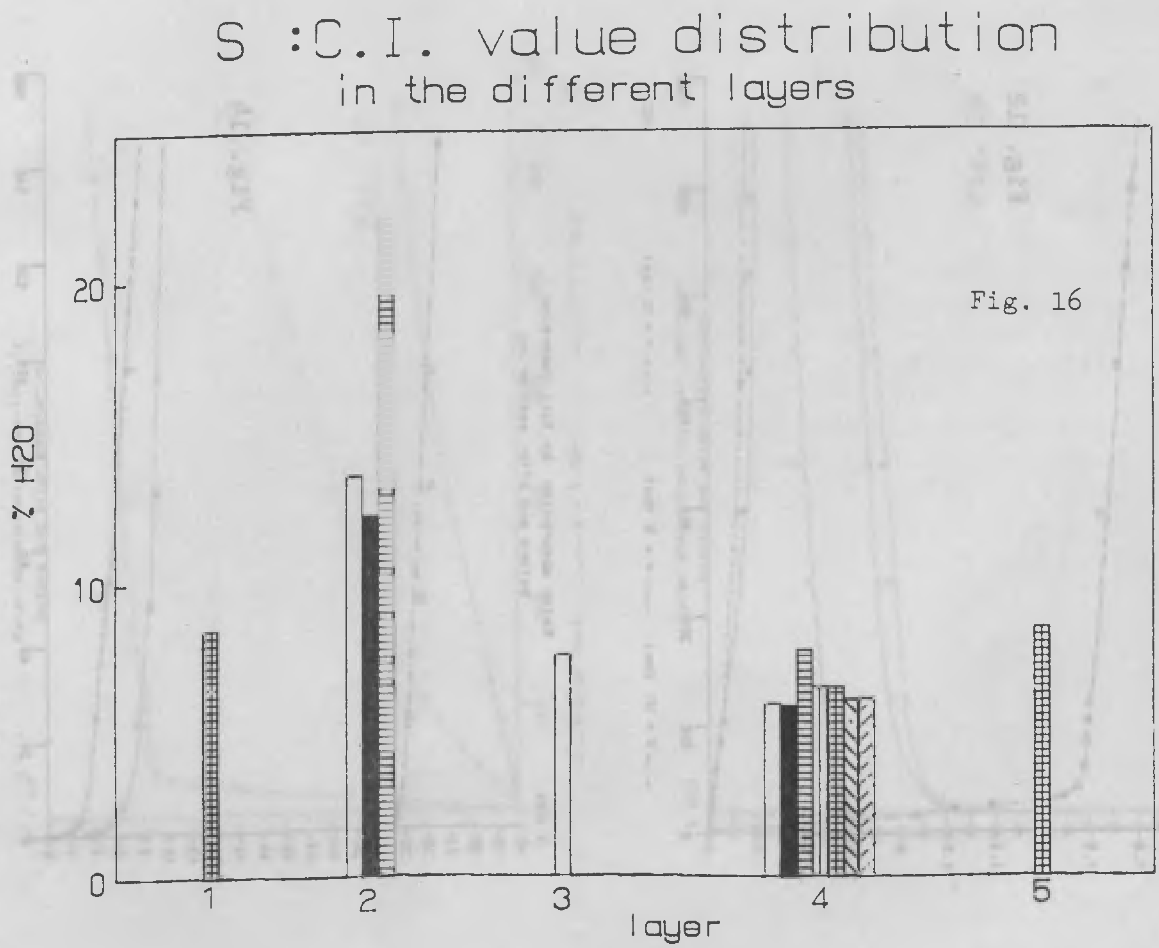


Fig. 10


PMMA :C.I. value distribution
in the different layers
30
20
10
0
% H2O
1
2
3
4
5
layer
Fig. 11


S :C.I. value distribution
in the different layers
20
10
0
% H2O
1
2
3
4
5
layer
Fig. 16

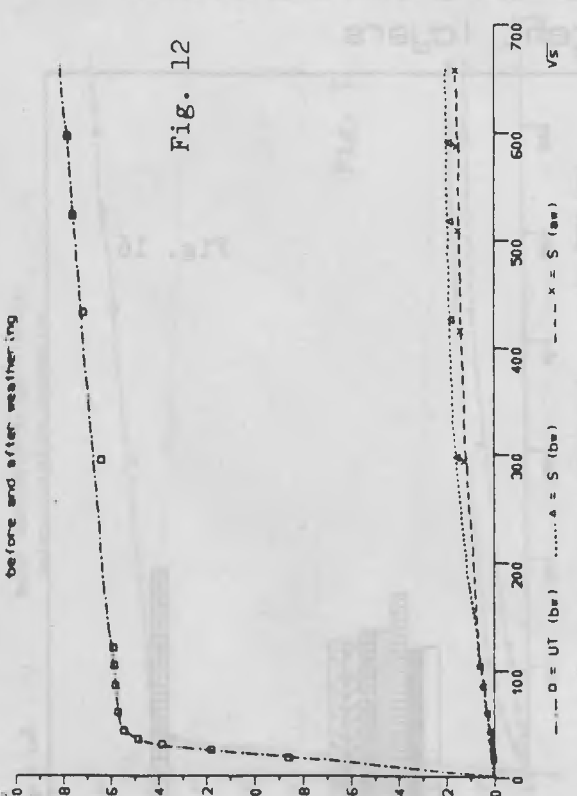


Fig. 12

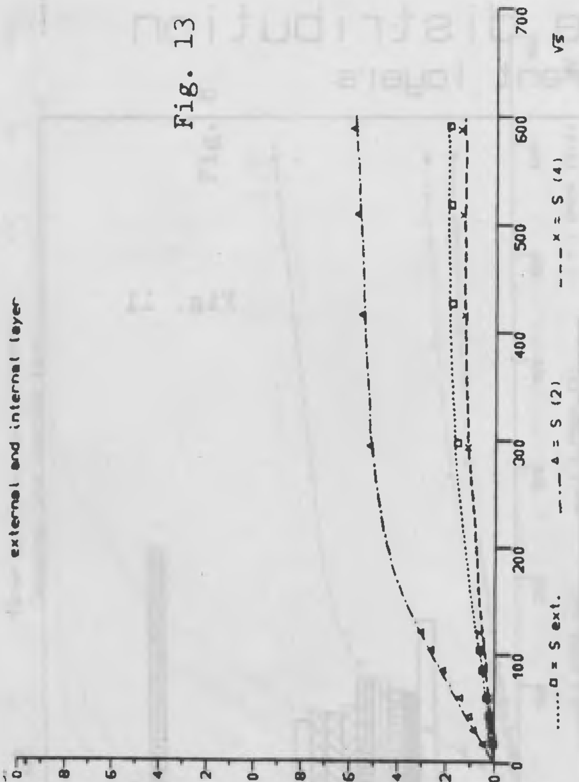


Fig. 13

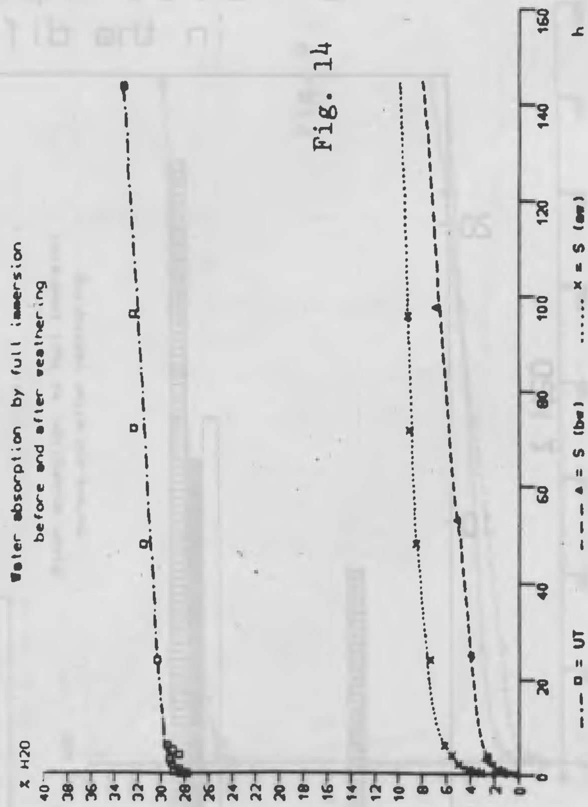


Fig. 14

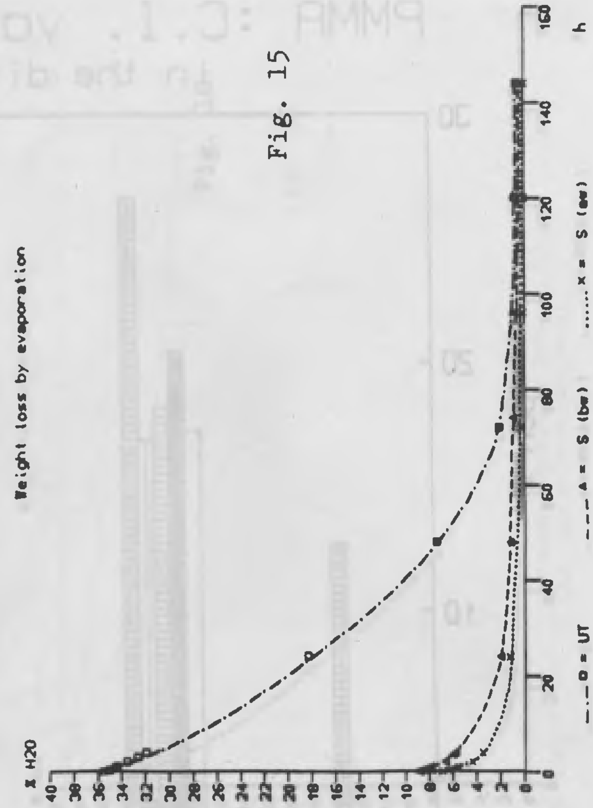


Fig. 15

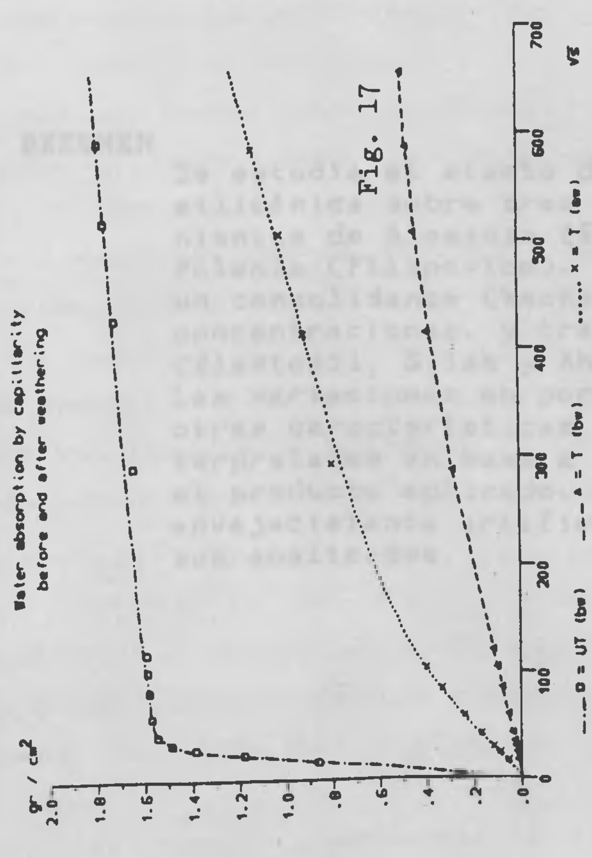


Fig. 17

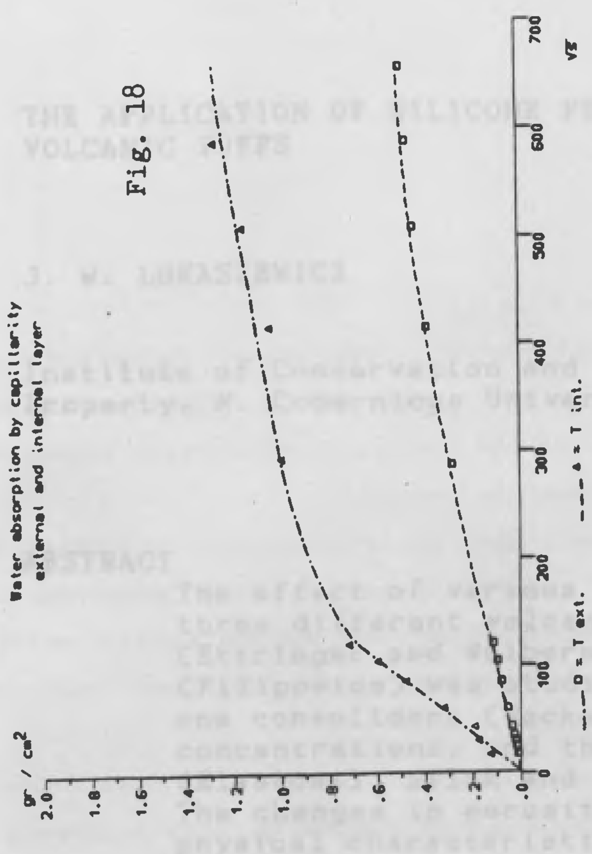


Fig. 18

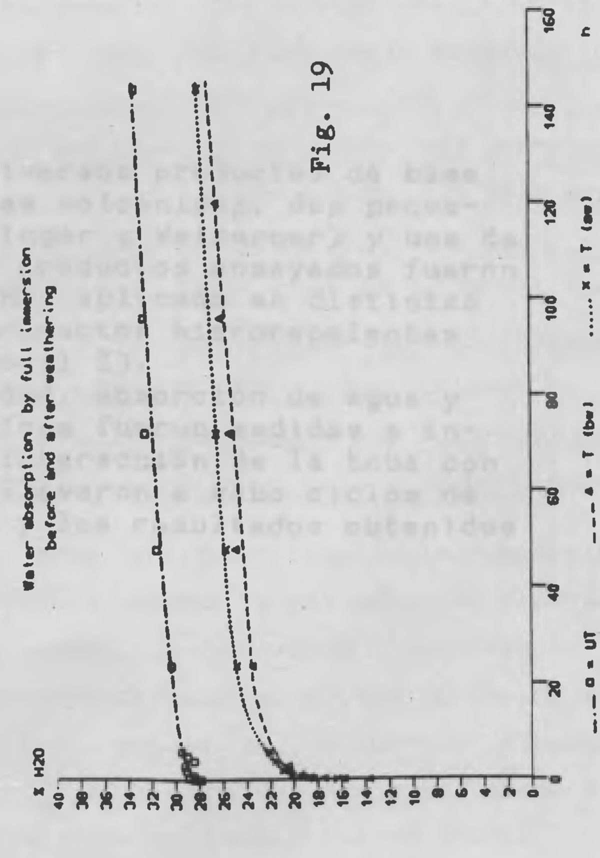


Fig. 19

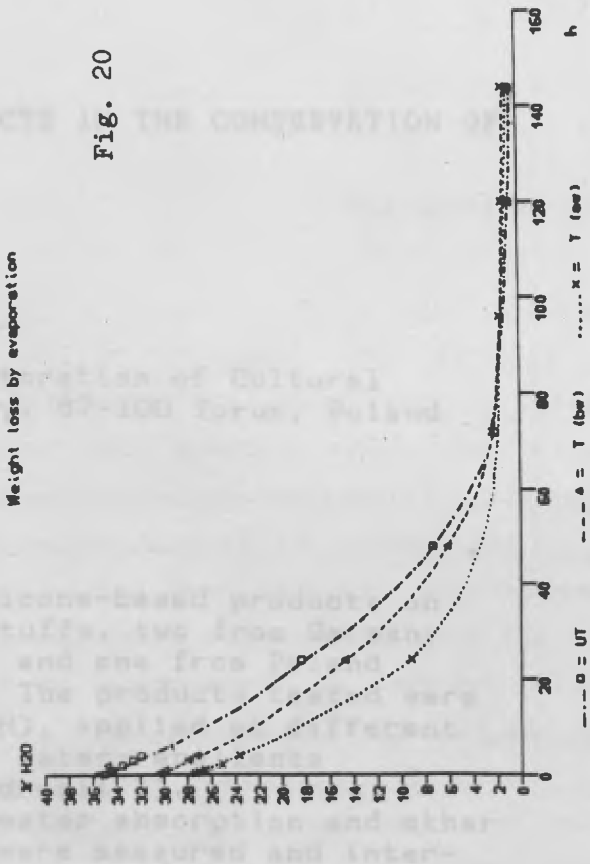


Fig. 20

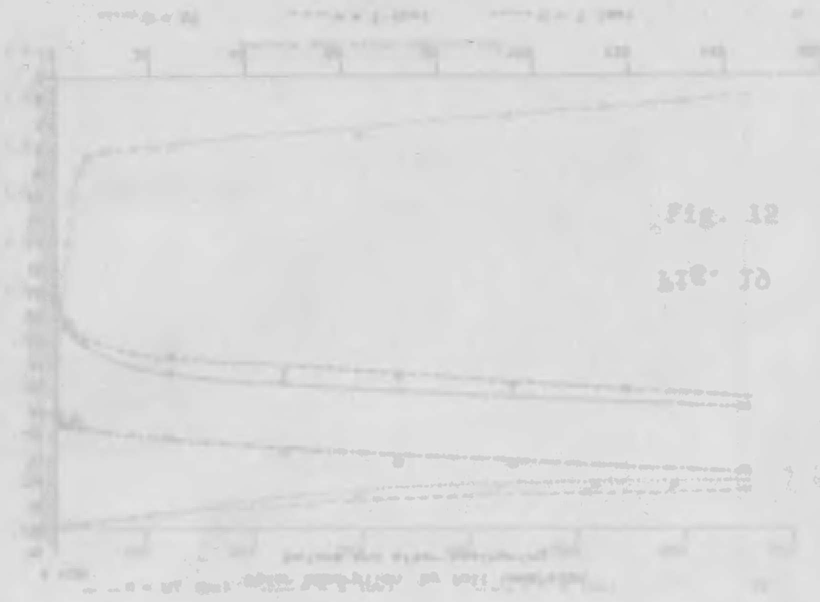


Fig. 12

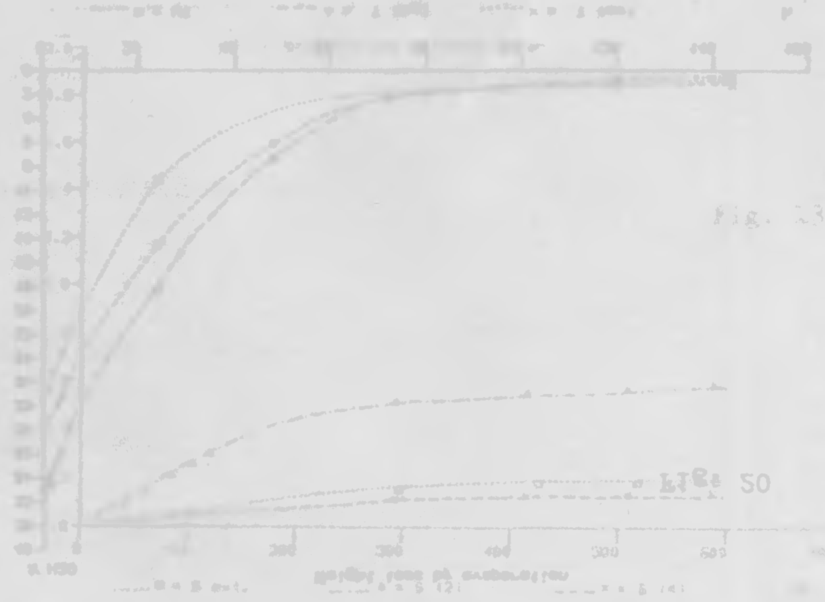


Fig. 13

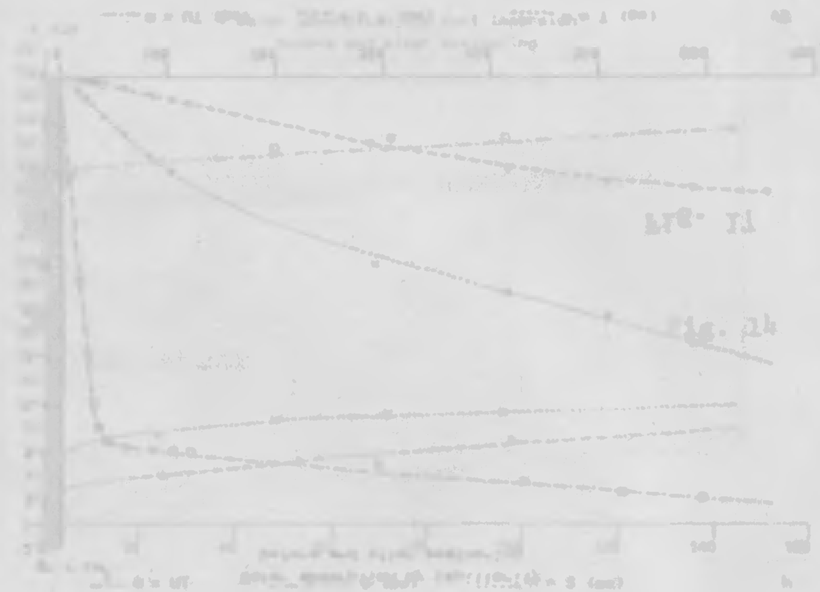


Fig. 14

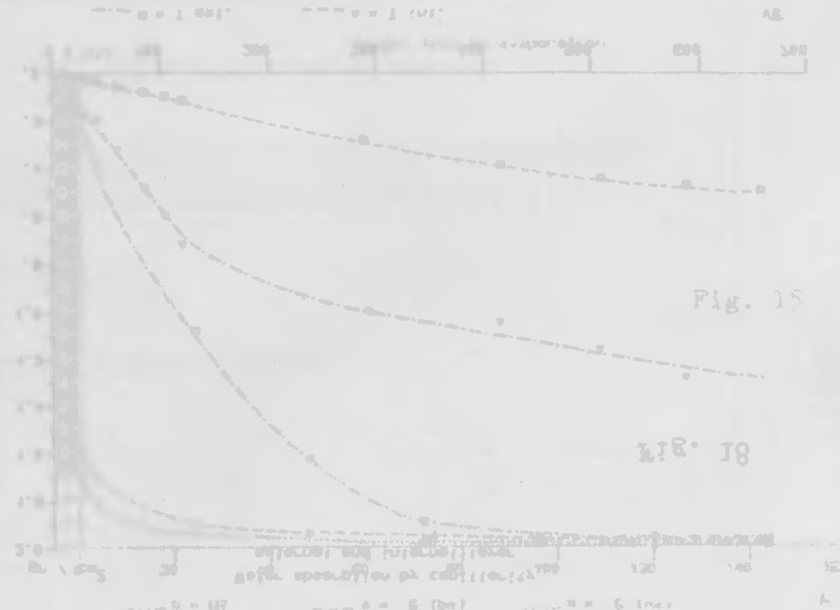


Fig. 15

THE APPLICATION OF SILICONE PRODUCTS IN THE CONSERVATION OF VOLCANIC TUFFS

J. W. LUKASZEWICZ

Institute of Conservation and Restoration of Cultural Property, N. Copernicus University, 87-100 Torun, Poland

ABSTRACT

The effect of various silicone-based products on three different volcanic tuffs, two from Germany (Ettringer and Weiberner) and one from Poland (Filipovice) was studied. The products tested were one consolidant (Wacker OH), applied at different concentrations, and three water-repellents (Elastosil, Silak and Ahydrosil Z).
The changes in porosity, water absorption and other physical characteristics were measured and interpreted on the basis of the tuff/applied product interaction. Artificial weathering cycles were also carried out and the results obtained are discussed.

RESUMEN

Se estudia el efecto de diversos productos de base silicónica sobre tres tobas volcánicas, dos provenientes de Alemania (Ettringer y Weiberner) y una de Polonia (Filipovice). Los productos ensayados fueron un consolidante (Wacker OH), aplicado en distintas concentraciones, y tres productos hidrorepelentes (Elastosil, Silak y Ahydrosil Z).
Las variaciones en porosidad, absorción de agua y otras características físicas fueron medidas e interpretadas en base a la interacción de la toba con el producto aplicado. Se llevaron a cabo ciclos de envejecimiento artificial y los resultados obtenidos son analizados.

1. Introduction

Stone Giant figures from Easter Island are executed in andesitic volcanic tuff. On the basis of investigations carried out by W. Domaslowski /1/ the main destructive factors have been found to be : rain water, high relative humidity, temperature variations and microorganisms.

The action of the above mentioned agents is promoted by mineralogical composition, texture and structure of volcanic tuffs. Clay minerals present in the rock paste swell under the action of water and can be rinsed which leads to a decrease in compactness of the surface layers of the rock and finally, to the effect of powdering.

Unequal heating of tuffs results in shearing stress. It has been found out /2/ that the Giats from Easter Island are unequally heated during sunny days. The temperature of sun-exposed fragments rises significantly, while that of the shadowed ones remains close to ambient. For example, at ambient temperature of 28°C, the temperature of sun-heated stone attains 70°C, while the temperature of stone in skade does not exceed 36-38°C.

Even more important difference in temperature, i.e. larger stress, occurs between the superficial and the deeper layers of stone, which is proved by its high moisture content.

In spite of long periods of drought, humidity at the depth of 1 - 3 cm was found to be very high. Obviously, this is also a result of high water vapor absorption by clay minerals.

Tensions resulting in stone fissuration originate from a different thermal expansion of each component of a volcanic tuff as debris of volcanic and sedimentary rocks, cement-rock paste. This results in a decrease of rock cohesion, disintegration and crumbling away of volcanic and sedimentary rock fragments as well as powdering of cement-rock paste.

The contribution of microorganisms can not be neglected in the formation of deposits due to biochemical decomposition of aluminosilicates. The deposits, usually grey-black in colour, strongly absorb sun radiation, in consequence of which the stone surface heats very distinctly.

Though Easter Island is surrounded by the salted Pacific Ocean (salt contents up to 3,5%), no harmful effect of water soluble salts has been stated on tuffs deterioration /3/.

Similarly, P. L. Bianchetti, G. Lambarchi, G. Mencci /4/, in their investigations of tuff blocks used in the Roman temple of Cibeles, did not find any action of chemical agents, among which water soluble salts (due to their low percentage) on the process of stone decay.

To sum up, the essential problem concerning tuffs conservation appears to be consolidation limited to superficial layers which have lost their cohesion due to cement rinsing.

Consolidation should be followed by an efficient protection against the action of water vapour and liquid water.

Investigations of the Giants from Easter Island /5/ showed a decreased cohesion of certain areas of surface layers which require consolidation. Deeper stone fragments demonstrate high hardness and mechanical strength.

Therefore, main stress has been put in the present work on determination of efficiency of tuffs protection against water and water vapour after they had been heated with orthosilicic acid esters.

As consolidant an alcoxysiloxane product Steinfestiger OH has been chosen (product of Wacker-Chemie, Germany). This product is characterized by good penetration capacity even into fine-porous stone. According to S. Z. Lewin and P. M. Schwartzbaum /6/, alcoxypolysiloxanes may cross link aluminosilicate layers due to the reaction of their -OH grups with these of partly hydrolyzed alcoxysiloxanes.

The formation of typical chemical bounds between -OH groups from polysiloxanes and clay minerals is not always possible, e. g. because of the distance between -OH groups /7/. However, a hydrogen reaction may be expected between the minerals and consolidant. As a result, a rapid amelioration of mechanical strength is noticed.

As water-repellents, also silicone products were chosen because of their great chemical affinity with stone consolidant applied, as well as satisfactory water-repellent properties and a rich commercial offer.

2. Materials

2.1. Tuffs

Investigations were carried out on 3 types of tuffs of different mineralogical coposition and properties. Tuffs from the quarries at Ettringer and Weiberner (Germany) and Filipowice (Poland) were used.

The E t t r i n g e r tuff is a fineporous rock (percentage of pores of r < 10^4 A^0 equals 60% of total pore volume - Table 1), yellow-beige in colour. Volcanic glass is the basic component of rock paste, except for this, clay minerals are present (probably illites recorded by X-ray diffraction) as well as SiO_2 - minerals. Rock debris have been identified to be feldspars, micas or olivines /8/.

The W e i b e r n e r tuff is coarseporous rock (percentage of pores of r > 10^4 A^0 exceeds 73% of total pore volume), grey-brown in colour. Coarse debris of sedimentary and volcanic rocks are present (d = 1-2 cm). Rock paste consists mainly of volcanic glass of ball structure and clay minerals probably illites. Debris of sedimentary rocks consist mainly of mudstones and fineporouse sandstones, while these of volcanic rocks comprise feldspares, oliwines, quartz and amphiboles.

The F i l i p o v i c e tuff represents a crumbly phase of acidic volcanic eruptions, compound in a sedimentary way with deeper conglomerates. Its mineralogical composition consists mainly of feldspars, quartz, biotites, calcite and enallogene rock debris. It is a fineporous rock (the percentage of pores of r < 1000 A exceeds 50% of total pore volume), violet-pink in colour with irregularly distributed white spots.

Certain physical properties of the tuffs examined are given in Tablel.

2.2 Consolidants

Tuffs were consolidated with alkoxysiloxane product of Wacker-Chemie (Germany) - Steinfestiger OH in commercial solution and with ethyl alcohol 1 : 1 in the case of fineporous tuffs (especially Ettringer and Filipowice, Fig. 1, Table 1).

Commercial product is an about 75% solution of tetraetoxysilane oligomeres in methylethylketone. Under the action of water adsorption in the pores of stone and water vapour from the atmosphere it subjects hydrolytic polycondensation which results in polysiloxane gel formation. The gel forms new binder in disintegrated stone, which improves its mechanical strength. The rise in mechanical strength depends directly on the structure of stone under consolidation /9/.

2.3. Water-repellents

Both untreated and preconsolidated (SF OH) tuffs were subjected to water repellent treatment.

5% solution of methylphenylsilicone resin Silak M11 was applied in xylene and white spirit (product of Zaklady Chemiczne of Nowa Sarzyna, Poland) and a 5% solution of silicone caoutchouc Elastosil E 41 in white spirit (product of Wacker-Chemie, Germany).Elastosil E 41 is a 90% solution of methypolysiloxanes with silanol groups in toluene. These groups are blocked by acetic acid and form unstable esters. At the presence of humidityit subjects a rapid polycondensation leading to the formation of cross linked polymer of high water-repellent properties.

In order to compare the efficiency of various products, tuffs were impregnated with methylsiloxane resin Ahydrosil Z (product of Instytut Chemii Organicznej, Poland). Ahydrosil Z is a two-component product, whose component A is an 10% solution of methylpolysiloxane resin in xylene and white spirit, while the component B is a cross-linking factor, added in a quantity equal to 1% of component A.

The properties of consolidant and water repellent solutions are given in Table 2.

3. Consolidation

Samples (4 x 1 x 8 cm^3) dried to constant mass at ambient conditions, were impregnated by capillarity whith solutions of Steinfestiger OH.

Table 3 reports the time of capillary rise of these solution and water.

The consolidant solutions show a lower rate of penetration that of water. Stone structure is the decisive factor as far as the rate of penetration is concerned. Solutions penetrate easily into a coarseporouse tuff as "Weiberner". Water rises to the height of 7 cm within 40 minutes, while the respective time for concentrated SF OH is 2,5 h and 2 h for a diluted solution. Both water and cosolidant solutions penetrate into a fineporous tuff "Filipowice" at a very low rate. After 24 h, the solutions attained the height of 4 cm, while water that of 5 cm.

All samples destinated for further investigations were impregnated by capillary rise, being immersed in consolidant to the depth of 1 cm by the 1 x 8 cm side. Three hours later, the samples were reversed upside down and left over 21 hours. In this way, a very high degree of stone impregnation was achieved (Table 3).

Taken out of impregnant, the samples were cured in a climatic chamber at RH = 75% /10/ in order to facilitate and speed up hydrolytic polycondensation of SF OH. Six weeks later, the samples were removed from the chamber and dried at abient conditions (temperature 20 - 22° C, RH=40-50%). The drying rate of consolidated tuffs is a function of their structure (Table4).

The rate of evaporation of solvent and by-products of hydrolytic polycondensation (ethanol and water) was the highest from the coarseporous tuff "Weiberner", and lower from fineporous "Ettringer" and "Filipowice". It is interesting that the samples mass of appeared constant as soon as 4 days after removal from climatic chamber and did not decrease during 3 subsequent weeks. A relatively high contents of gel in the stone porous it to contain significant percentage of solvents.

Samples were not dried at a higher temperature as this kind of treatment appears rather difficult to be executed "in situ". Moreover, gel contains more free -OH groups they can react with water repellent product applied, which in consequence, would considerably improve the tuffs resistance to the action of water.

4. Water protection

Both consolidated and untreated samples were impregnated with water repellent products by capillarity for 24 h. A part of natural samples was impregnated with Ahydrosil Z. Methylsilicone resin subjected hardening in the pores of stone under the action of a crosslinking agent. The product received improves mechanical strenght of stone and renders it water repellent. As it results from table 5, precondensation of stone with SF OH considerably reduces its absorption capacity of water repellents. The decrease of absorption is the most pronounced for samples impregnated with SF OH in commercial condensation. Untreated samples showed the highest absorption capacity. The type of water repellent solutions and the texture of stone material are of some importance. A solution of Elastosil E 41 penetrated with difficulty being characterized by the highest viscosity (Table 2). Satisfactory impregnation of all tuffs was achieved with the use of Silak M 11 and Ahydrosil Z.

Among the rocks examined, the "Weiberner" tuff was the most easy to impregnate. Although, due to preconsolidation, the highest polysiloxane gel quantity was introduced into its pores, the decrease of its absorption capacity was the least among those of the tuffs examined. This effect results from the coarseporous texture of this stone.

5. Properties of tuffs after consolidation and water-repellent treatment

Tuff samples impregnated with water-repellent were dried in laboratory conditions (temp. 20-22°C, RH=40-55%) for 2 weeks, then under vacuum at the temperature of 50°C.

5.1. Open porosity

Impregnation with both consolidants and water repellents reduced open porosity of all samples (Table 6). The effect was the most pronounced for the "Filipowice" samples reaching 46%. This kind of tuff is characterized by a fineporous texture (Table 1), the percentage of pores r<1000A amounts 70%. Therefore the resins introduced occlude the pores and considerably reduce the porosity. As concern the tuff "Weiberner", its natural porosity has not been changed much by the consolidation treatment.

A distinct effect of the type of product applied on the change in open porosity was noticed. Preconsolidation with SF OH in commercial concentration resulted in the highest reduction in porosity. The effect was less important for a diluted product and the least for the samples treated with Ahydrosil Z.

The changes observed are proportional to the amount of product introduced, i.e. to the concentration of impregnants (Table 2).

All the samples preserved their porosity, thus being able to be treated again it necessary.

5.2. Hygroscopicity

Evaluation of hygroscopicity and water absorption capacity allows to determine the efficiency of protective treatment of tuffs against water vapour and liquid water. Application of the methylsiloxane resin Ahydrosil Z proved the most efficient as far as a reduction in vapour absorption is concerned (Table 7). Similar protection was achieved with the use of a Silak M11 solution without preconsolidation. Tuffs treated with Elastosil E 41 showed a little higher hygroscopicity.

The highest hygroscopicity, even higher than that of untreated samples, is recorded for all tuffs preconsolidated with SF OH in commercial preparation. This is due to a high content of highly sorptive polysiloxane gel in the pores of stone (up to 7%) /11/. The water repellents applied, because of their low concentration, did not significantly reduce adsorption of water vapour.

5.3. Water absorption

The water repellents examined provide a satisfactory protection of tuffs against the action of liquid water (Table 6).

All samples treated with water repellents, both preconsolidated and natural, showed a much lower water absorption (by 88-58%) than that of untreated stone.

Similarly to the results of hygroscopicity examination, the lowest water absorption was noticed for tuffs treated with Ahydrosil Z, a little higher for the ones treated with Silak M 11 and caoutchouc E 41 without and after preconsolidation whith a diluted SF OH solution. The highest water absorption was recorded for tuffs consolidated with SF OH in commercial preparation.

6. Resistance of tuffs after artificial ageing

Easter Island with her area 180 km^2 is situated among the Pacific Ocean, 3500 km of Chile.

The neighborhood of the Ocean and the location of the Island in the subtropical zone determine climatic conditions with heavy rainfalls up to 1000 mm per year. Air humidity remains extremely high, both in July and in January and equals about 80%. Insulation of this region is also very high, due to which air temperature ranges from 20 to 30°C. Temperature exceeds 25°C during about 300 days ayear /12/, which as already mentioned, results in heating of stone surface /13/.

If we are able to provide a more or less efficient protection of stone against the action of water, we have no means to fight with the temperature. Therefore, except basic standard properties of consolidated ageig test was also performed. Samples were impregnated with water at 25°C for 6 hours and heated at 105° for 18 h. In the course of the test, visual changes in the stone surface as well as water absorption were recorded.

6.1. Aspect of stone

Table 8 presents changes in the aspect of all samples. The tuff "Ettringer" revealed to be extremely low resistant to the action of water and heating. As soon as after 2 cycles the surface began to powder, after 4 cycles the samples cracked and decayed after 6 cycles. Thus, consolidation and water protection did not render the "Ettringer" tuff resistant artificial ageing.

The samples treated with Ahydrosil Z, in spite of fine fissure (after 6 - 7 cycles) remained compact after 9 cycles. Similar behaviour showed the samples preconsolidated with SF OH in both commercial preparation and diluted solution before water protection whith Silak M 11 as well as those treated with caoutchouc E 41. Deterioration developed the most rapidly in the samples preconsolidated with SF OH solution and water protected with E 41 and in those treated uniquely with Silak M 11.

The surface of other tuffs did not show any remarkable changes after as so many as 20 cycles of artificial ageing.

6.2. Water absorption

Tabele 9 shows the variation in water absorption of tuffs during ageing. Absorption of untreated "Weiberner" and "Filipowice" tuffs remained unchanged after ageing. The same tuffs subjected to consolidation and water protection showed a slight increase in water absorption after 2 cycles. Further ageing cycles had no effect on water absorption. This is probably due to violent dehydration of polysiloxane gel during heat treatment at 105°C. As for the "Ettringer" tuff, its water absorption rised violently from 15 to 23% after as few as 2 cycles, which resulted from the formation of micro- and then macro-fractures.

Artificial ageing also caused an increase in water absorption of samples, both consolidated and water protected. The rise in water absorption was accompanied by a decrease in mechanical strength and in consequence by stone powdering.

The extremely poor resistance of the "Ettringer" tuff to the action of water and heat-treatment will be investigated in future.

7. Conclusions

The investigations carried out allow us to state that:

1. The efficiency of water protective treatment is conditioned mainly by the texture of tuff. The tuffs, the texture of which is close to that of "Weiberner", are prove to impregnation and the introduction of imprenant solutions does not meet any obstacles. Within a few hours, the object may be impregnated by capillarity to the depth of over 10 cm. In the case of fine-porous texture, the penetration of solutions is very slow. The introduction of consolidant or water repellent to the depth of several cm reveals difficult.
2. All water repellents applied, considerably reduced water absorption capacity and hygroscopicity of tuffs and can be successfull used in the conservation practice.
3. Preconsolidation with alcoxypolysiloxane gel followed by a water repellent treatment does not provide a total of tuffs against water and water vapour.
4. If the state of the object requires consolidation, it is advised to accomplish it with the use of a solution of methysiloxane resin (Ahydrosil Z),

which except structural hardening, also provides the best protection from water and water vapour.

8. References

1. W. Domasłowski, Problemetyka konserwatorska kolosów z Wyspy Wielkanocnej, Ochrona zabytków, 1985, 2, p. 92,
2. W. Domasłowski, Problematyka ... p. 95,
3. W. Domasłowski, Problematyka ... p. 95,
4. P. L. Bianchetti, G. Lombardi, C. Meucci, Study in the Degradation of Tuff Blocks Used in the Roman Temple of Cibeles (Rome, Italy), Deterioration and Preservation of Stone Objects, Fourth International Congress, Louisville, Jully 7-9, 1982, p. 33, 36,
5. W. Domasłowski, Problematyka ..., p. 87,
6. S. Z. Lewin, P. M. Schwartzbaum, Investigation of the Long-Term Effectiveness of an Ethyl Silicate-Based Consolidant on Mudbinck, International Symposium and Training Workshop on the Conservation of Adobe, Lima-Cusco, Peru, 10-12 September 1983, p. 78,
7. R. Snethlage, Steinkonservierung 1979-1983, Arbeitshefte des Bayerischen Landesamtes für Denkmalpflege, 22, 1984, p. 115-116,
8. Petrographic analysis of thin slices was performed by mgr M. Ziółkowska, Institute of Geography, N. Copernicus University, Toruń, Poland,
9. W. Domasłowski, J. W. Łukaszewicz, Possibilities of Silica Application in Consolidation of Stone Monuments, VI th International Congress on Deterioration and Conservation of Stone, Toruń 12-14.09.1988, pp. 571-573,
10. A. E. Charola, G. E. Wheeler. G. G. Freund, The influence of Relative Humidity in the Polymerization of Methyl Trimetoxy Silane, Adhesives and Consolidants Congress in Paris, 2-8 September 1984, IIC London, p. 178,
11. W. Domasłowski, J. W. Łukaszewicz, Possibilities ..., p. 574,
12. D. Martyn, Klimaty kuli ziemskiej, PWN, Warszawa, 1987, p. 42-69,
13. W. Domasłowski, Problematyka ..., s. 95.

Table 1

Physical properties of tuffs examined

Nº	Property	Type of tuff		
		Ettringer	Weiberner	Filipowice
1.	Bulk density (g/cm³)	1,85-1,91	1,48-1,59	1,95-2,12
2.	Absorption by weight (%)			
	water	14,8-15,9	21,4-22,3	7,9-9,1
	white spirit	10,2-12,3	18,1-19,1	6,1-6,5
3.	Open porosity (%)	25,9-30,5	33,6-36,8	16,8-18,0
4.	Volume of open pores (cm³/g)			
	50<r<75000 A	0,1723	0,2986	0,1168
5.	Pore size distribution (%)			
	50<r<100 A	1,5	-	-
	100<r<1000 A	11,0	7,5	51,5
	1000<r<10 000 A	46,5	19,0	32,0
	10 000<r<75 000 A	41,0	73,5	16,5

Table 2

Properties of consolidants and watter-repellents

Nº	Product	Concentration (%)	Solvent	Dencity (g/cm³)	Viscosity (mPa.s)
1.	Steinfestiger OH (SF OH)	75	methyl ethyl ketone	0,9575	1,25
2.	Steinfestiger OH (1:1)	37	methyl ethyl ketone ethanol		
3.	Elastosil E41 (E41)	5	white spirit	0,7824	4,80
4.	Silak M11 (M11)	5	white spirit	0,8014	1,89
5.	Ahydrosil Z (A Z)	10	mixture of organic solvents	0,8164	2,64

Table 3

Rate of capillar rise and absorption capacity of Steinfestiger OH and water in tuffs

N°	Tuff	Solution	Time of capilar rise to the height of 1 cm	2 cm	3 cm	4 cm	5 cm	6 cm	7 cm	Absorption of solution (%)
1.	Ettringer	SF OH	22'	1h54'	-	-	-	-	**	11,2-13,4
		1:1	7'15"	56'	3h	-	-	-	*	11,0-11,9
		H_2O	6'28"	28'	1h02'	1h45'	3h	4h20'	-	14,8-15,9
2.	Weiberner	SF OH	3'28"	12'18"	30'20"	47'30"	1h10'	-	2h28'	26,4-29,6
		1:1	2'19"	7'40"	15'46"	-	44'	1h27'	1h57'	19,1-27,3
		H_2O	1'01"	3'13"	7'47"	13'49"	19'48"	30'10"	41'23"	21,4-22,3
3.	Filipowoce	SF OH	4'18"	2h21'	-	24h				6,7- 7,4
		1:1	6'50"	3h25'	-	24h				6,5- 7,3
		H_2O	6'	1h15'	4h15'	-	22h			7,9- 9,1

* after 24 hours impregnated to the height of 7 cm
** after 24 hours impregnated to the height of 9,5 cm

Tabele 4

Drying rate of tuffs consolidated with Steinfestiger OH

N°	Tuff	Solution	Absoption of solution (%)	Percentage of polysiloxane gel after curing in climatic chamber *	during drying 24 h	4	7	14	21 days
1.	Ettringer	SF OH	12,5	8,0	4,9	4,4	4,4	4,6	4,5
		1:1	11,5	4,1	2,3	2,2	2,25	2,4	2,4
2.	Weiberner	SF OH	24,1	14,7	9,8	9,2	9,4	9,3	9,2
		1:1	20,6	7,0	4,6	4,4	4,5	4,5	4,45
3.	Filipowice	SF OH	6,9	4,7	3,0	2,8	2,7	2,7	2,7
		1:1	6,9	2,9	1,9	1,7	1,77	1,84	1,8

* samples impregnated with SF OH and SF OH diluted in alkohol (1:1) were cured in climatic chamber by RH=75% for 6 weeks in order to promote hydrolytic polycondensation

Table 5

Absorption of water-repellent products in tuffs

Nº	Type of tuff	Percentage of polysiloxane gel	Water-repellent	Absorption capacity (%)	Decrease in absrption (%)
1.	Ettringer	5,17	E 41	5,7	44,0
		2,38		8,1	20,6
		-		10,2	-
		4,46	Silak M11	7,9	28,8
		2,30		9,0	18,9
		-		11,1	-
		-	Ahydrosil Z	12,9	-
2.	Weiberner	8,89	E 41	13,4	32,7
		4,7		15,5	22,1
		-		19,9	-
		9,6	Silak M11	14,4	26,2
		4,4		15,1	22,1
		-		19,9	-
		-	Ahydrosil Z	19,2	-
3.	Filipowice	2,7	E 41	2,9	54,4
		1,9		3,6	36,8
				5,7	-
		2,9	Silak M11	3,7	47,9
		1,8		4,2	40,8
		-		7,1	-
		-	Ahydrosil Z	6,1	-

Tabele 6

Open porosity and water absorption of tuffs after impregnation with consolidant and water-repallent products

Nº	Type of tuff	Consolidant	Water-repellent	Open porosity(%)	Decrease in open porosity (%)	Water absorption (%)	Decrease in water absorption(%)
1.	Ettringer	SF OH	E 41	19,3	36,9	6,5	57,8
		1 : 1		21,5	29,7	5,9	61,7
		-		25,8	15,6	5,2	66,2
		SF OH	Silak M11	20,8	32,0	3,9	74,7
		1 : 1		23,4	23,5	2,7	82,5
		-		24,1	21,2	5,2	66,2
		Ahydrosil Z		22,0	28,1	2,4	84,4
		-	-	30,6	-	15,4	-
2.	Weiberner	SF OH	E 41	27,7	24,7	5,2	76,5
		1 : 1		27,6	25,0	4,0	81,7
		-		33,0	10,3	4,2	80,7
		SF OH	Silak M11	29,5	19,8	4,5	79,4
		1 : 1		29,8	19,0	3,4	81,7
		-		33,0	10,3	3,4	84,4
		Ahydrosil Z		31,2	15,2	2,9	86,7
		-	-	36,8	-	21,8	-
3.	Filipowice	SF OH	E 41	10,5	41,3	2,2	74,1
		1 : 1		13,2	26,3	2,4	71,8
		-		-	-	4,5	47,1
		SF OH	Silak M11	9,5	46,9	1,8	78,8
		1 : 1		10,8	39,7	1,3	84,7
		-		-	-	3,6	57,6
		Ahydrosil Z		-	-	0,97	88,6
		-	-	17,9	-	8,5	-

Tabele 7

Higroscopicity of tuffs treated with silicone water-repellents

N°	Type of tuff	Consolidant	Water-repellent	Higroscopicity (%) after 48 hours	after 7 days
1.	Ettringer	SF OH	E 41	2,50	4,07
		1 : 1		1,78	2,39
		-		1,51	1,97
		SF OH	Silak M11	1,97	2,76
		1 : 1		1,44	1,76
		-		1,01	1,26
			Ahydrosil Z	0,94	1,20
		-	-	2,23	2,83
2.	Weiberner	SF OH	E 41	2,59	3,85
		1 : 1		2,23	2,72
		-		0,85	1,11
		SF OH	Silak M11	1,01	1,75
		1 : 1		0,92	1,33
		-		0,53	0,80
			Ahydrosil Z	0,54	0,97
		-	-	1,62	2,23
3.	Filipowice	SF OH	E 41	1,34	1,79
		1 : 1		1.08	1,53
		-		0,97	1,42
		SF OH	Silak M11	0,72	1,29
		1 : 1		0,44	0,77
		-		0,46	0,82
			Ahydrosil Z	0,32	0,72
		-	-	1,15	1,77

Tabele 8

Changes of aspect of tuffs subjected to consolidation and water-repellent treatment in the course of ageing

Nº	Type of tuff	Consolidant	Water-repellent	Ageing cycles 1	2	3	4	5	6	7	8	9	10	11	12	13
1.	Ettringer	SF OH	E 41	0	0	0	*	**	***							
		1 : 1		0	0	0	*	**	***							
		-		0	0	0	0	*	*	*	*	**	***			
		SF OH	Silak M11	0	0	0	0	*	*	*	**	***				
		1 : 1		0	0	0	0	*	*	**	**	***				
		-		0	0	0	0	*	*	*	**	**	***			
			Ahydrosil Z	0	0	0	0	0	*	*	**	**	***			
		-	-	0	0	0	*	**	***							
2.	Weiberner	SF OH	E 41	0	0	0	0	0	0	0	0	0	0	0	0	0
		1 : 1		0	0	0	0	0	0	0	0	0	0	0	0	0
		-		0	0	0	0	0	0	0	0	0	0	0	0	0
		SF OH	Silak M11	0	0	0	0	0	0	0	0	0	0	0	0	0
		1 : 1		0	0	0	0	0	0	0	0	0	0	0	0	0
		-		0	0	0	0	0	0	0	0	0	0	0	0	0
			Ahydrosil Z	0	0	0	0	0	0	0	0	0	0	0	0	0
		-	-	0	0	0	0	0	0	0	0	0	0	0	0	0
3.	Filipowice	SF OH	E 41	0	0	0	0	0	0	0	0	0	0	0	0	0
		1 : 1		0	0	0	0	0	0	0	0	0	0	0	0	0
		-		0	0	0	0	0	0	0	0	0	0	0	0	0
		SF OH	Silak M11	0	0	0	0	0	0	0	0	0	0	0	0	0
		1 : 1		0	0	0	0	0	0	0	0	0	0	0	0	0
		-		0	0	0	0	0	0	0	0	0	0	0	0	0
			Ahydrosil Z	0	0	0	0	0	0	0	0	0	0	0	0	0
		-	-	0	0	0	0	0	0	0	0	0	0	0	0	0

0 - no changes,
* - micro-crackes,
** - macro-crackes,
*** - completely decayed

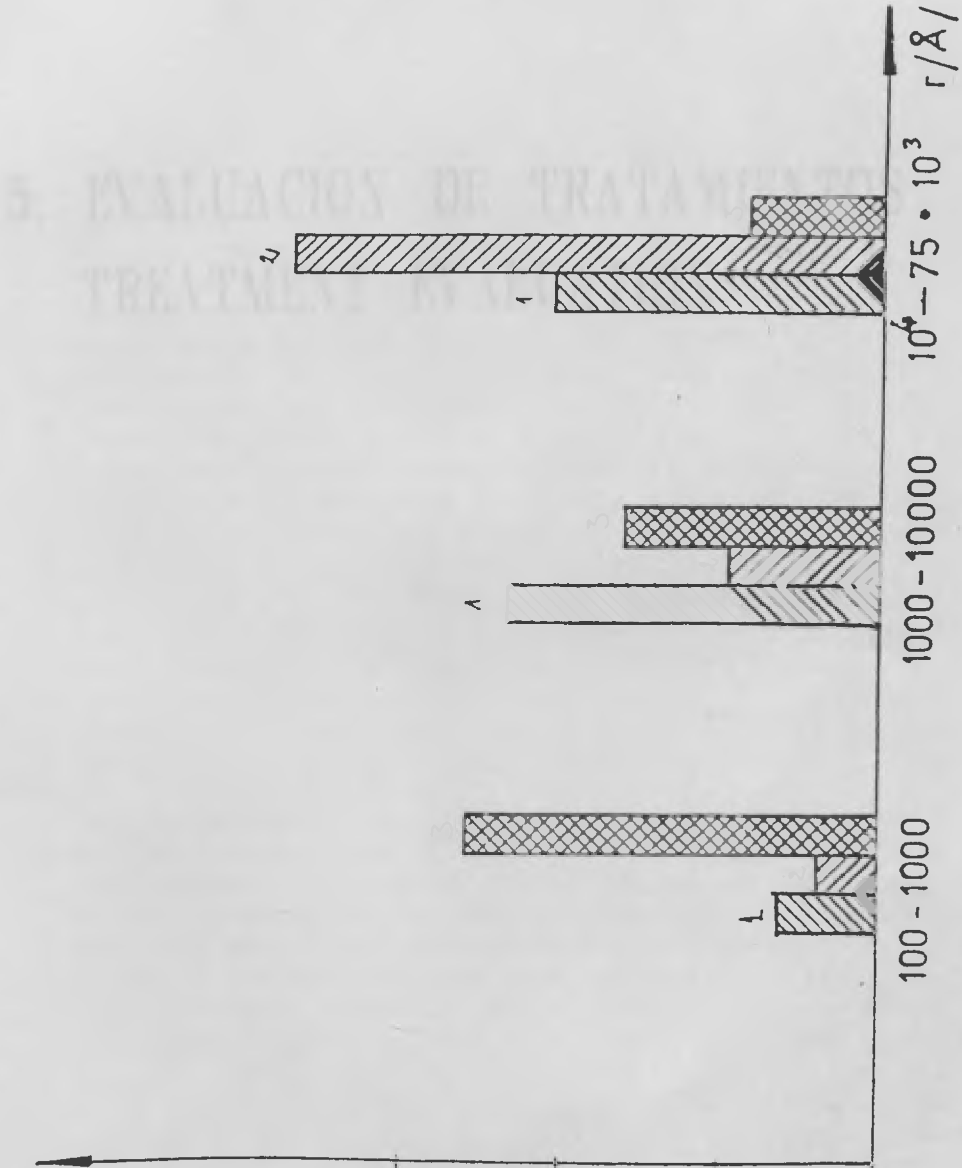
Tabele 9

Changes in water absorption capacity of tuffs after ageing

N°	Type of tuff	Consolidant	Water-repellent	Water absorption (%) befor	after 2	6	10	20 ageing cycles
1.	Ettringer	SF OH	E 41	6,5	15,0	-	-	-
		1 : 1		5,9	13,5	-	-	-
		-		5,2	10,4	14,9	16,2	-
		SF OH	Silak M11	3,9	8,3	10,7	10,6	-
		1 : 1		2,7	5,2	5,8	6,1	-
		-		5,2	5,1	-	-	-
			Ahydrosil Z	2,4	4,7	4,9	-	-
		-	-	15,4	23,1	-	-	-
2.	Weiberner	SF OH	E 41	5,2	6,6	6,6	6,5	6,4
		1 : 1		4,0	5,0	5,0	4,8	4,6
		-		4,2	4,0	4,1	3,8	3,8
		SF OH	Silak M11	4,5	5,3	5,5	5,8	5,5
		1 : 1		3,4	5,5	5,1	3,9	4,1
		-		3,4	5,1	4,5	3,2	3,0
			Ahydrosil Z	2,9	3,7	3,3	3,4	2,9
		-	-	21,8	21,4	22,1	21,7	21,5
3.	Filipowice	SF OH	E 41	2,2	3,1	3,2	3,3	3,2
		1 : 1		2,4	2,8	2,9	3,0	2,8
		-		4,5	4,7	4,5	4,2	4,6
		SF OH	Silak M11	1,8	2,3	2,2	2,2	2,3
		1 : 1		1,3	1,8	1,7	1,7	1,7
		-		3,6	1,5	1,4	1,3	1,3
			Ahydrosil Z	0,97	1,03	0,91	0,97	0,97
		-	-	8,5	8,4	8,2	7,9	8,0

Fig. 1 Pore size distribution

1 - Ettringer
2 - Weiberner
3 - Filipowice



Tabele 9

Changes in water absorption capacity of tuffs after ageing

Nº	Type of tuff	Consolidant	Water-repellent	Water absorption (%) befor	after 2	6	10	20 ageing cycles
1.	Ettringer	SF OH 1 : 1	E 41	6,5	15,0	-	-	-
				5,9	13,5	-	-	-
		-		6,2	10,4	14,9	16,2	-
		SF OH 1 : 1	Bilak Mil	3,9	8,3	10,7	10,6	-
				2,7	5,2	5,8	6,1	-
		-		5,2	5,1	-	-	-
			Abydrosil I	2,4	4,7	6,9	-	-
		-		15,4	23,1	-	-	-
2.	[illegible]	[illegible]	[illegible]	[illegible]	6,6	6,6	6,5	6,4
				[illegible]	5,0	5,0	4,8	4,6
		-		4,2	4,0	4,1	3,8	3,8
		SF OH 1 : 1	Bilak Mil	4,3	5,3	5,5	5,8	5,5
				3,4	5,5	5,1	3,9	4,1
		-		2,4	5,1	4,5	3,2	3,0
			Abydrosil I	3,0	3,7	3,3	3,4	[illegible]
		-		[illegible]	[illegible]	12,1	11,7	[illegible]
3.	[illegible]	SF OH 1 : 1	E 41	3,2	[illegible]	[illegible]	[illegible]	3,2
				2,4	2,8	[illegible]	3,0	2,8
		-		4,5	[illegible]	[illegible]	4,2	4,6
		SF OH 1 : 1	Bilak Mil	1,8	[illegible]	2,2	2,2	2,3
				1,3	[illegible]	1,7	1,7	1,7
				[illegible]	[illegible]	1,4	[illegible]	[illegible]
			Abydrosil I	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		-		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

5. EVALUACION DE TRATAMIENTOS
TREATMENT EVALUATION

ASSESSMENT OF THE EFFICIENCY OF CONSERVATION TREATMENTS APPLIED TO VOLCANIC TUFFS BY RADIOACTIVE LABELLING

J. SRAMEK and T. NISHIURA*

State Institute for Restoration, 118 00 Prague 1, Czechoslovakia
*Tokyo National Research Institute of Cultural Properties, Tokyo 110, Japan

ABSTRACT

The interactions of stone surfaces with a corrosive atmosphere can be followed by labelling stone samples with radioactive Krypton 85 in a low energy plasma beam. The decrease of radioactivity is related to the corrosion speed and measures the durability of stone in that atmosphere. It can be applied to evaluate differences between treated and untreated samples and betwen diverse treatments. The corrosion resistance of three basic types of Japanese tuffs in an atmosphere with a high content of sulfur and nitrogen oxides is studied. The results show clearly that the examined tuffs corrode easily and that the speed of corrosion depends on pollutant concentration, relative humidity and pore structure. It was found that treatments with acrylic copolymers were more efficient in preserving the tuff than treatments with siloxanes.

RESUMEN

Las interacciones entre superficie de piedra y atmósfera corrosiva se pueden seguir por marcado de la piedra con kripton 85 radioactivo en haz de plasma de baja energía. La disminución de la radioactividad depende de la velocidad de corrosión de la piedra y mide su durabilidad en esa atmósfera. Esto se puede aplicar para evaluar las diferencias entre piedras tratadas y no tratadas y entre distintos tratamientos. Se investigó la resistencia a la corrosión de tres tipos de tobas japonesas en atmósferas con alto contenido de óxidos de sulfuro y nitrógeno. Los resultados demuestran que la velocidad de corrosión depende de la concentración de contaminantes, la humedad relativa y la estructura porosimétrica. Los tratamientos con copolímeros acrílicos se probaron más eficaces como protectores de la toba que los tratamientos con siloxanos.

1. INTRODUCTION

It is known that the labelling of the crystalline substances can be carried out with accelerated ions which impact on the surface producing changes within the lattice, atomic interactions and trapping of these ions (1, 2, 3). When atoms of inert gases are used with relatively small energy (hundreds of eV), no mechanical damage to the surface layers occurs. Usually, there are also no chemical reactions under these conditions because they need much higher impacting energy. The trapped ions are located in interstitial places with their depth of distribution depending on the original energy of the incident ions, and, on the physical and chemical conditions on the surface. Non-crystalline substances, e.g. organic or amorphous ones do not capture the impacting ions.

It has been found that stones can be labelled in the same way like metals or glasses and the radioactive 85 Krypton appeared to be very convenient for this purpose. The radioisotopes of inert gases are generally used because they enable to follow the process of labelling simply: measurement of radioactivity gives the measure of incident ions. The work with 85 Krypton which has the half-life 10.3 years makes it easy to work in most common laboratories with no special precautions.

In practice, it is therefore possible continuously and at the same time with great precision to detect all the processes leading to the release of trapped ions in the stone sample, e.g. corrosion interactions of the stone sample with an atmosphere containing higher amounts of pollutants. In this work, the samples of three types of Japanese tuffs were labelled by 85 Krypton and then the changes of gained radioactivity were investigated under conditions in which the stone samples were placed into a continuous flow apparatus where the artificially prepared air contained higher amount of sulfur dioxide or nitrogen monooxide. As well, the relative humidity was possible to maintain on a given level because already during the previous experiments it was found that the marble corrosion by sulfur dioxide is strongly affected by R.H. conditions (3, 4).

It is clear that the radioactivity decrease during the gas--solid interaction of labelled stone sample covers many particular processes including diffusion, sorption, the entire reaction, the re-diffusion of krypton atoms back to the gas phase, etc. and that only relatively similar substances can be investigated and compared. The examined tuffs were found to be partly similar each to other, regarding their chemical composition and pore structure and so it would be believed that the measured differences are to be related to the individual characteristics of the tuffs and could be generalized also to the other types of tuffs,taking into account the immense scale of tuffs with respect to their mineralogical composition and pore structure.

Immediately, after the labelling the tuff sample loses around 30 % of initially gained radioactivity but afterwards the radioactivity becomes almost stable with a decrease in radioactivity about 5 % a week. From indirect measurements and calculations (5) it arises that about 10 upper atomic layers are reached under the given conditions. This is the disadvantage of the labelling process because sometimes this very surface of the stone can be reacted out quickly. On the other hand it was proved that higher energies of the impactiong krypton atoms create changes within the crystals, mostly meaning the dehydration or better losses of crystal water. The advantage of the stone labelling beside the following the speed of interaction is that the labelled sample can be consequently treated with materials that do not react with stone lattice. The siloxanes or acrylic copolymers appeared not to change substantially the radioactivity and thus, they enable to investigate the decrease in radioactivity of treated/untreated stone samples and to evaluate the conservation efficiency of these materials.

The basic problem of this secondary use of labelled stone samples, it means to cover them with a conservation material, is how much the re-diffusion of trapped krypton ions back to the gas phase is influenced by the eventual formed films. The results show, nevertheless, that when using the usual conservation conditions, i.e. concentrations of conserving materials, then there is always a decrease in radioactivity when exposing the stone sample into a corrosive atmosphere. It corresponds also with the S.E.M. images of treated samples where never a complete covering with a film was found. In this case the measurements are taken just in order to compare relatively the effect of the particular treatment with the other one.

2. EXPERIMENTAL

2.1 Apparatus for 85 Krypton labelling

The labelling of the tuff surface by radioactive 85 Krypton was carried out in a glass vacuum apparatus shown in Figure 1.

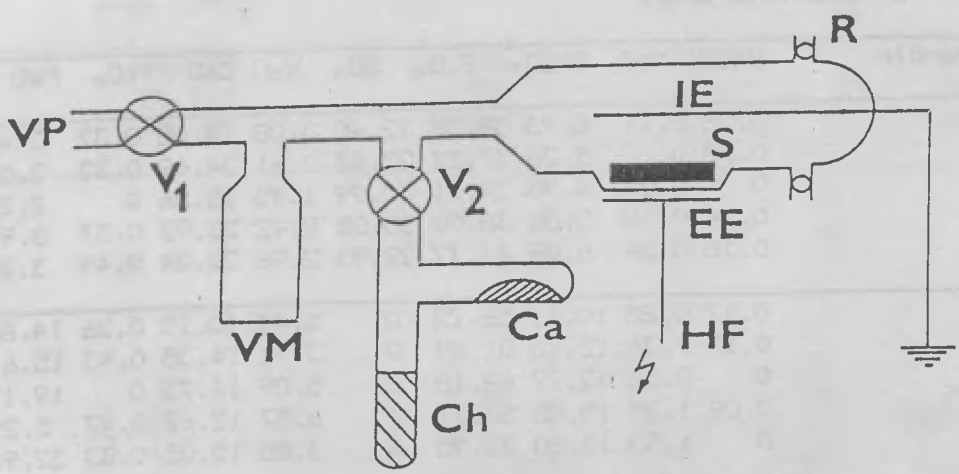


Fig. 1 - Schema of the experimental set-up for the tuff sample labelling by radioactive 85 Krypton in high frequency plasma discharge

S- stone sample, IE, EE - internal resp. external electrode, R - rubber rings, HF - high frequency source, V - vacuum valves, VP - vacuum pump, Ch - charcoal for adsorbing surplus of krypton gas, Ca - metallic calcium for gas cleaning

After evacuating to approximately 1 Pa, krypton containing roughly 5 % of radioactive isotope 85 Kr is filled in up to preasure of 12 Pa, and the external electrode under the sample is charged with a HF-voltage of peak value of 15 kV from a TESLA transformer. The procedure is repeated several times and then the free krypton atoms together with the gas impurities which are also released during the ion impacting on the surface are adsorbed on activated charcoal at the boiling point of liquid nitrogen and cleaned before reuse by metallic calcium heated to 800 - 900 °C.

Using the given type of discharge and preasure of tens of Pa the radioactive 85 Kr ions gain relatively low energy plasma and penetrate only into the most upper (around 10) atomic layers of the stone. The radioactivity and its eventual changes during any interaction is then measured by a GEIGER-MULLER Counter as a number of radioactive decays per time.

2.2 Tuff samples

The three types of Japanese tuffs were examined:
1) "OHYA", the tuff from quarries in Toshi Prefecture, near Nikko, commonly used in facades in Tokyo and Kanto
2) "NARA", the tuff removed about 10 km Western of Nara in the viscinity of Budhas reliefs carved into this type of tuff
3) "ECHIZEN", the tuff from Fukui Prefecture, used in facades, sometimes called in Japan the janstony-tuff

For labelling purposes the tuffs samples of 5 - 7 x 10 x 20 mm size were cut, polished and washed with distilled water. The Table 1 summarizes the typical EDAX analysis of 5 chosen points of their largest areas that were also in these particular cases later labelled.

TABLE I. The example of EDAX analysis of 5 chosen points within the surface of examined tuffs

Tuff sample	Na_2O	MgO	Al_2O_3	SiO_2	SO_3	K_2O	CaO	TiO_2	FeO
"OHYA"	0.26	0.11	8.93	59.38	12.40	3.08	13.05	0.37	2.42
	0.08	0	5.26	37.37	27.83	2.61	24.48	0.32	2.06
	0	0.14	4.96	34.21	30.99	1.93	25.56	0	2.22
	0.24	0.16	5,80	38.08	25.08	2.42	23.92	0.37	3.94
	0.10	0.24	6.08	41.77	22.93	2.96	22.24	0.49	3.21
"NARA"	0.17	0.85	10.11	58.22	0	5.44	10.15	0.26	14.80
	0.17	1.26	12.73	51.69	0	3.76	14.35	0.43	15.61
	0	0.56	12.27	48.18	0	5.09	14.73	0	19.17
	0.09	1.80	15.45	57.71	0	6.57	12.62	0.47	5.29
	0	1.33	13.50	32.95	0	3.88	15.05	0.33	32.96
"ECHIZEN"	0	1.76	19.30	61.02	0	6.68	0.44	0	10.80
	1.30	0	19.37	70.76	0	6.34	0.26	0.27	1.84
	0	1.52	17,27	61.06	0	5.67	0.51	3.82	10.15
	0	7.56	19.76	38.04	0	1.31	1.92	0.31	31.11
	0	3.09	23.34	50.52	0	7.51	0.20	0	15.34

Even taking into account that the data in Tab. I have very small statistical value, it is clear that the three tuffs differ each from other as far as the content of basic elements and their compounds, oxides, carbonates, and possibly in the case of "OHYA" tuff sulfates is concerned. It can be calculated that the "OHYA" contents about half of the mass of calcium minerals in the form of gypsum. The other types, namely the "NARA" and "ECHIZEN" have not any amount of gypsum within the sound tuff, but differ mostly in calcite content. This was also proved by the TG and DTG analysis. It should be expected that the most corrodable mineral by sulfur oxide is calcite event. iron oxide and from that point of view it was interesting to follow the particular behaviour of the tuffs in interaction with corrosive atmosphere.

2.3 Porometric characteristics of examined tuffs

From the point of view of interpretation of the radioactivity changes of labelled stone samples it is always important to know much about the pore structure of examined stone because not only the interaction of gas phase with stone is influenced by pore structure, but also the releasing of trapped krypton atoms undergoes diffusion processes dependent on pore size. So, the pore size distribution, specific surface area and other porometric data of examined tuffs were measured, everything by means of Micromeritics Auto-pore instrument, Model 9200 V2.03. As it can be seen from Table II and Figures 2, 3, resp. 4, the tuffs differ relatively each from other, but all the three samples possess quite a high specific surface area.

TABLE II. The porometric data of examined tuffs

Tuff sample porosity	Specific surface area (m^2/g)	Bulk density (g/cm^3)	Skeletal density (g/cm^3)	Porosity (%)
"OHYA"	24.973	1.496	2.217	64.23
"NARA"	20.717	1.428	2.157	56.53
"ECHIZEN"	15.054	1.960	2.752	38.83

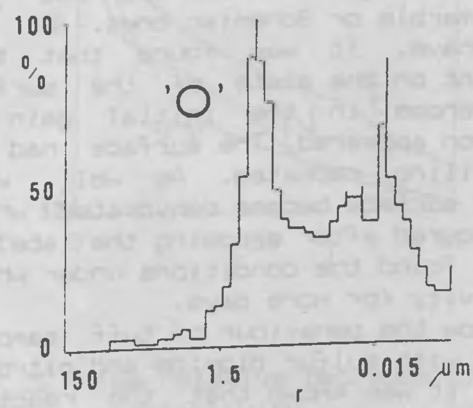


Fig. 2 - Pore size distribution of the "OHYA" tuff

(average pore radius = 0.0174 micrometers)

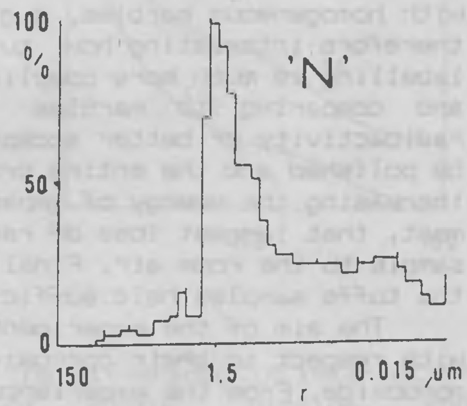


Fig. 3 - Pore size distribution of the "NARA" tuff

(average pore radius = 0.0228 micrometers)

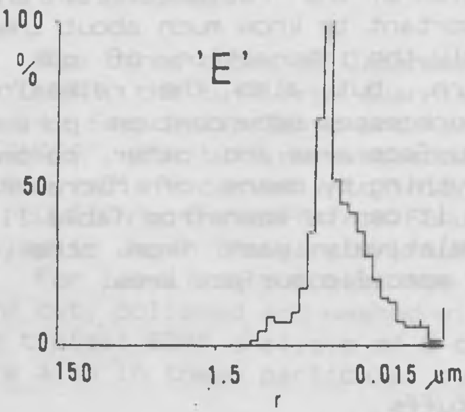


Fig. 4 - Pore size distribution of the "ECHIZEN" tuff

(average pore radius = 0.0195 micrometers)

The "OHYA" and "NARA" tuffs are closer in specific surface area and total porosity but the average pore diameter differs strongly. On the other hand the "OHYA" and "ECHIZEN" tuffs are very close each other in the average pore diameter, but the difference in total porosity and thus, in specific surface area is substantial. From these data it can be expected that the "OHYA" would react much easier with the gas phase than the other tuffs. The speed of gas-solid interactions are namely generally of first order to the total surface reacting. As well, one should expect that independently on chemical composition of the surface the re-diffusion of released krypton atoms will proceed smoothly in the case of "OHYA" tuff.

3. RESULTS

The previous experiments with stone labelling were carried out just with homogeneous marbles, e.g. the Carrara marble or Bohemian ones. It was therefore interesting how tuffs would behave. It was found that tuff labelling is much more complicated, dependent on the state of the surface and comparing to marbles larger differences in the initial gain of radioactivity or better acceptance of krypton appeared. The surface had to be polished and the entire process of labelling repeated. As well, when increasing the energy of impacting ions the surface became dehydrated which ment, that largest loss of radioactivity occured after exposing the labelled sample to the room air. Finally, there were found the conditions under which the tuffs samples held sufficient radioactivity for more days.

The aim of the experiments was to follow the behaviour of tuff samples with respect to their corrosive interaction with sulfur dioxide and nitrogen monooxide. From the experience with marbles it was known that the reaction strongly depends on relative humidity and therefore all the experiments were carried out by three different R.H. The concentrations of sulfur and nitrogen oxides in continuous flow set-up were increasing from 125 to 300 ppm. The firstly mentioned concentration enabled to measure within the time of at maximum two hours, which was found the period with high reproducibility. The lower concentrations do not give repeatable results, apparently caused by difficulty in holding the constant flow and concentrations of these reactive gases, and clearly, due to the fluctuation of all the processes within the very surface of stone, i.e. above all the diffusion to the surface, sorption conditions, and re-diffusion of released krypton atoms. The gas flow was maintained at 40 ml/min, and the R.H. was adjusted by bubbling the pre-air through water. The R.H. was always measured by freezing the air at the temperature of solid carbon dioxide. The exact amount of sulfur dioxide was determined by titration after absorbing in alkaline solution (3).

The second aim of the experiments was to distinguish the preservation efficiency of eventual conservation materials that could be used for treatment of rocky carved sculptures in tuffs in Japan. The problems with maintaning these monuments in the recent changed climatic conditions which include even the air pollution are serious and large scale research and practical work has been done (e.g. 6, 7, 8). Beside the sheltering constructions to protect these sculptures it is often necessary to consolidate their surface and to prevent further influence of water (9). Thus, the labelling experiments had to be used also for evaluating the preservation effect of the most common types of stone conservation materials, namely of siloxanes and acrylates.

3.1 Corrosion of tuffs with sulfur dioxide and nitrogen oxides

The experiments clearly showed that all the examined tuffs are easily corroded with both oxides. As it is seen from Figure 5 and 6 the radioactivity starts to decline immediately after the sulfur or nitrogen oxide comes into the contact with the surface of stone. In the behaviour of all the three tuffs there were apparent the differences connected with pore structure and chemical composition of the very surface. The "OHYA" and "NARA" tuffs react with the highest speed which corresponds probably with

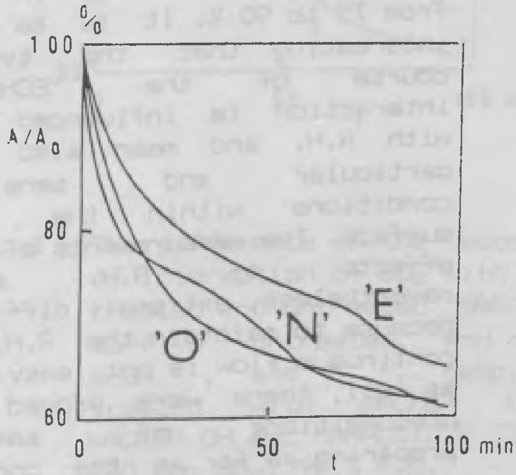


Fig. 5 - The relative decrease of radioactivity on examined tuffs in time (125 ppm of SO_2, "E" -Echizen, "N" - Nara, "O" - Ohya tuff, 85 % R. H.)

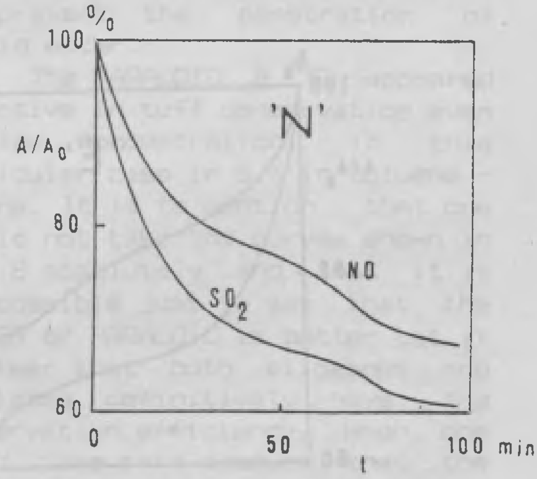


Fig. 6 - The difference in interaction of sulfur dioxide and nitrogen monooxide on "Nara" tuff sample (125 ppm of SO_2 and of NO, resp., 85 % R.H.)

their high specific surface area and probably calcite content. It is also interesting the course of radioactivity decrease in the case of "NARA" tuff which appeared as well by the "ECHIZEN". It is supposed in both cases that the explanation could be connected with the high content of iron oxides which are not only reactive with both sulfur and nitrogen oxides but due to their catalytic properties in heterogeneous oxidation reactions they are expected to be responsible for the entire oxidative transformation within stone surface, and thus a change in reaction mechanisms in the course of surface gas-solid interactions.As well, the sorption properties of amorphous iron oxides are well known and strong reaction with both oxides must occure. The presented curves in all the figures in this work are representable for all the measurements and the course of such a radioactivity decline was found, nevertheless, in each experiment.

The Fig. 6 shows that nitrogen oxide is also active in interactions with tuffs. Already at this point it is to be mentioned that its reactions with all the samples occured only under high R.H., in general above 80 %R.H. Similarly to the sulfur dioxide experiments also these ones were rerodučable which was maintained with the fact that after use the sample of tuff was washed with distilled water, re-polished and used for further labelling again. In that way it was supposed one could eliminate the expected heterogenity in particular tuff samples.

3.2 The influence of relativive humidity on corrosive reaction

Already during the experiments with marbles it was found that the R.H. plays important role in these types of interactions. In general, even in this very corrosive media, i.e. the concentrations more than hundreds ppm, the entire reaction does not proceed in lower R.H. than around 50 %. How strong effect has the relative humidity on tuff reaction with gaseous oxides is actually apparent from the Figure 7 which represents the change in R.H. from 75 to 90 %. It is as well interesting that the typical course of the "ECHIZEN" interaction is influenced even with R.H. and mean also very particular and sensitive conditions within the tuff surface. The measurements of the effects of R.H. were, nevertheless, extremely difficult because to maintain the R.H. in continuous flow is not easy and as well, there were proved the preconditions of samples preparing as far as the contact with different relative humidity is concerned. It is clear that adsorbed water, resp. its exact form is one of the most important factors in the corrosive interactions. Thus, the samples were always pre-worked in the same way.

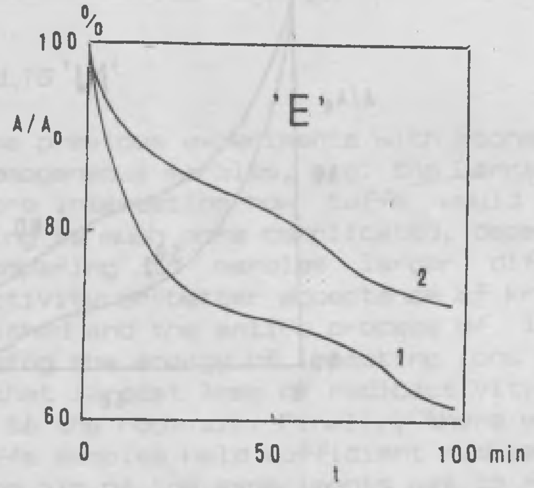


Fig. 7 - The influence of R.H. on the corrosive interaction of "ECHIZEN" tuff (1 - 90 % R.H., 2 - 75 % R.H., 150 ppm SO_2)

3.3 The preservation efficiency of conservation materials on tuffs

The use of labelling in the experiments with treated/untreated samples is not simple because during the conservation treatment could be formed the films that could prevent the re-diffusion of released krypton atoms and hence the radioactivity would stable - if actually the corrosive agents could penetrate such films. Both cases were proved not to occure. The three used conservation materials, namely WACKER H, WACKER OH and PARALOID B 72, resp., were found active in tuff conservation but only as far as the lowering of the corrosive interaction is concerned. It was always proved that under used conditions of high concentrations of pollutants in gas phase there is always an interaction even with the treated samples with mentioned materials. As well, the S.E.M. pictures proved that there are no regular films on the treated surfaces - which should be not acceptable actually from the point of view of water vapour equilibriom with stone surroundings - and, thus that the labelling can be used for following the differences between the treated and untreated stone, when treated in the same way as in practical work. The basic results in this connection are apparent from Figure 8 where it is clear in the case of "NARA" tuff that the treatment as it is carried out in practice only slows the interactions with stone surface. As far as the difference between the hydrophobic and hydrophilic materials is concerned, i.e. both WACKER materials, it was again proved that at least from the point of view of gaseous interactions there is no special effect on stone corrosion. The sulfur dioxide penetrates both conserved surfaces in the same speed and it seems that use of hydrphobic materials is justified only on areas where it is necessary to prevent the penetration of liquid water.

The PARALOID B 72 appeared effective in tuff conservation even in low concentration, in this particular case in 5 % in toluene - xylene. It is to mention that one should not take the curves shown in Fig. 8 absolutely and that it is not possible just to say that the WACKER or PARALOID is better but it is clear that both siloxanes and acrylates definitively have the conservation efficiency. When one would take into account that the measured reasults precisely prove the effect of these materials then their use should prolong the state of stone in substantial way - with respect to the gaseous reactions. In any case, the interactions with stone occured - the radioactivity decreased and it seems that these materials are adhesed strongly to the surface when the radioactivity changed so slowly. One should not expect in this connection that the effect is just due to the mechanical strengh of this materials on the surface that prevents the break of the lattice and hence the releasing of the trapped krypton atoms.2

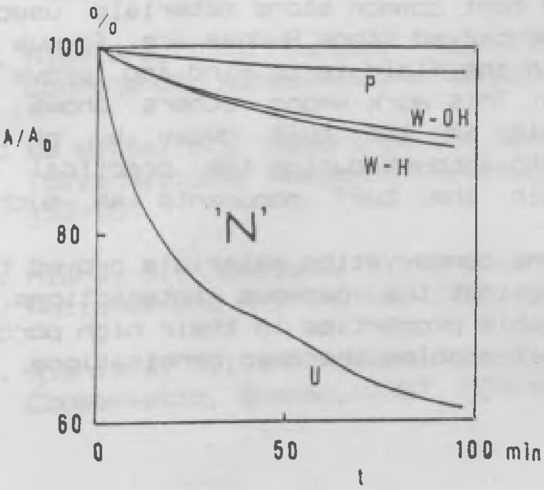


Fig. 8 - The difference in the speed of interaction of SO_2 with treated and untreated "NARA" tuff (U - untreated, W-H -, W-OH -, and P -, resp., treated with WACKER H, WACKER OH and PARALOID B 72. 130 ppm SO_2, 90 % R.H.)

4. DISCUSSION

The stone labelling gives the picture of integral processes that occur within the labelled stone surface in the course of its interaction with surroundings, e.g. with corrosive gases like in this particular case with sulfur dioxide and nitrogen oxide. Naturally, it is not possible to use only this method in the studies of stone corrosion and conservation but when combined with other techniques the radioactive labelling could supply the research field with comparative data as it enables to follow the same stone samples in different conditions.

The three types of Japanese tuffs appeared to be easily corroded and one should expect that any polluted air with content of sulfur or nitrogen oxide will negatively effect their surface. It is apparently the high porosity and the content of calcite and other minerals that react with reactive gases which makes the tuffs so vulnerable to the reactive atmosphere. Surely, this work gives only one of the whole comples conditions why tuffs erode and corrode but it has been proved that the tuffs from the point of view of corrosive reaction could be compared with porous limestones - with all the aspects of problems with historical monuments made from these stones.

In Japan the tuffs are one of the most common stone materials used in history for carving the sculptures. The carved stone Budhas are famous and one of the basic goals of scientists in the field is to find and prove the best conditions for their preservation. This work among others shows that water, better R.H., plays important role in the tuff decay by polluted atmosphere and that one should take into account during the practical work to lower the content of water within the tuff monuments as much as possible.

The both most common types of stone conservation materials proved to be effective in stone preservation even against the gaseous interactions. In that connections the tuffs have favourable properties in their high porosity and even the pore size distribution that enables the deep penetrations.

5. CONCLUSIONS

The three types of Japanese tuffs, namely "OHYA", "NARA", and "ECHIZEN", resp., were found to be easily corroded by sulfur dioxide or nitrogen monooxide when being present in polluted atmosphere. This was proved by experiments in which the samples of the mentioned tuffs were labelled by radioactive 85 Krypton and exposed to the conditions with different concentrations of the gases and relative humidity. From the measurements one can conclude that it is the pore structure and contents of minerals which easily react with used gases which makes the tuffs so vulnerable.On the other hand, both examined types of conservation materials, namely siloxane types WACKERs and acrylate type PARALOID, prove to be effective in the conservation of tuffs.

ACKNOWLEDGEMENTS

The authors are greatly indebted to Dr. S.Miura of the Tokyo National Research Institute of Cultural Properties, to Dr. M. Sawada of the Nara National Cultural Properties Research Institute, to Dr. J.Rathousky and the whole staff of the Research Laboratory at the State Institute for Restoration, Prague, and to Dr. E.Rykl of the Geological Institute, Prague, for their valuable help and advices.

Dr. J.Sramek uses this opportunity to express his thanks again to the Japan Society for the Promotion of Science, resp. to Dr. H. Kida, Director General of the JSPS, for enabling him the fellowship at the Tokyo National Research Institute of Cultural Property.

REFERENCES

1. Jech, C.; Int. J. Appl. Radioact. Isot. 1965, 8, 179 -185

2. Jesenak, V.; Valtyni, I.; Isotopenpraxis , 1969, 5, 259

3. Sramek,, J; Perina, V.; in Proceedings of the Int. Congress on Deterioration and Protection of Stone Monuments, Lausanne, 1986, 553-560

4. Sramek, J.; in Proceedings of the Technical Congress 89, Conservation of Historical Monuments, Their Role in Modern Society, Prague, 1989, 212-221

5. Jech, C.; in Proceedings of the 2nd U.N. International Conferenece, Peaceful Uses of Atomic Energy, New York, 1958, 183

6. Nishiura, T.; Fukuda, M.; Miura, S.; in Proceedings of the IIC Conference, Adhesives and Consolidants, London, 1984, 156-159

7. De Witte, E.; "Report on the conservation of Usuki stone Budhas", in Tokyo National Research Institute of Cultural Properties, Tokyo , 1985, 152-157

8. Miura, S.; Tomizawa, T.; and Ishikawa, R.; Scientific Papers on Japanese Antiques and Art Crafts, 1982, 27, 38-42

9. Nishiura, T.; in Proceedings of the 8th Meeting of ICOM Committee for Conservatio, Sydney, 1987, 509-511

the research field with [illegible] stone samples in different conditions.

The three types of Japanese [illegible] one should expect that any polluted air with content of sulfur or nitrogen [illegible] apparently the high [illegible] with reactive gases which makes the tuffs so vulnerable to the reactive [illegible] complex conditions [illegible] point of view of corrosive reaction could be compared with porous limestones [illegible] made from these stones.

In Japan the tuffs are one of the most common stone materials used in [illegible] carved [illegible] are famous and [illegible] prove the best conditions for their preservation. This work among others shows that [illegible] the tuff decay by polluted [illegible] the practical work [illegible] the content of water within the tuff monuments as much as possible.

[illegible] conservation materials proved to be effective in stone preservation [illegible] interactions. In these connections the tuffs have favourable properties in their high porosity [illegible]

5. CONCLUSIONS

The three types of Japanese tuffs, namely "OYA", "[illegible]", and "[illegible]", resp., were found to be easily corroded by sulfur dioxide or nitrogen monoxide when being present in polluted atmosphere. This was proved by experiments in which the samples of the mentioned tuffs were labelled by [illegible] and exposed to the atmosphere with different [illegible] of the gases and relative humidity. From the results one can deduce that it is the pore structure and contents of [illegible] which easily react with used gases which makes the tuffs so vulnerable. On the other hand, both examined types of conservation materials, namely [illegible] type and acrylic type (PARALOID) proved to be effective in the conservation of tuffs.

ACKNOWLEDGEMENTS

The authors are greatly indebted to Dr. [illegible] of the Tokyo National Research Institute of Cultural Properties, to Dr. [illegible] of the Nara National Cultural Properties Research Institute, to Dr. [illegible] and the whole staff of the Research Laboratory at the State Institute for Reconstruction, Prague, and to Dr. [illegible] of the Geological Institute, Prague, for their valuable help and advice.

Dr. [illegible] uses this opportunity to express his thanks also to the Japan Society for the Promotion of Science, [illegible] Director General of the [illegible] enabling him the [illegible] at the Tokyo National Research Institute of Cultural Properties.

A NEW CONCEPT FOR PRESERVATION OF POROUS NATURAL STONES

H. R. SASSE and D. HONSINGER

Institut für Bauforschung, T.U., 5100 Aachen, FRG

ABSTRACT

The study deals in the first part with the development of criteria for the performance of stone treatment systems and for the assessment of the effectivenes of stone protecting materials. The assessment of the effectiveness of new impregnation materials was based on the comparison of the results of physical tests carried out on treated and untreated samples. A number of important criteria, which are to be optimized, have been quantitatively and qualitatively evaluated. The laboratory tests cover measurements on polymer properties, porous material properties and impregnated porous material properties. The main aim of this project is to develop new and highly effective stone protecting and strengthening materials in collaboration between different scientific institutes and the chemical industry.

RESUMEN

El trabajo describe en su primera parte el desarrollo de criterios para la perfomance de sistemas de tratamientos de piedra y para la evaluación de la eficiencia de materiales protectores. La evaluación de la eficiencia de nuevos materiales de impregnación fue basada en la comparación de los resultados de ensayos físicos llevados a cabo en muestras tratadas y no-tratadas. Varios criterios importantes, que aún necesitan ser optimizados, han sido evaluados cuali- y cuantitativamente. Los ensayos de laboratorio abarcan medidas de las propiedades de los polímeros, de los materiales porosos, y de los materiales porosos tratados. El objetivo fundamental de este proyecto es el de desarrollar materiales efectivos de consolidación y de protección para la piedra en colaboración con otros institutos científicos y la industria química.

1 INTRODUCTION

Deterioration or damage of weathered structural stone members and sculptures in the form of crusts, surface scaling, exfoliations and granular disaggregations is most usually a result of atmospheric influences. In addition to naturally caused weathering processes anthropogenic detrimental influences have increased. Mainly sandstones as well as volcanic tuffs are susceptible to considerable weathering processes and the conservation of these types of rock, which are characteristic for very many old buildings and monuments in Germany and other countries, causes serious problems.

Despite the intense efforts of curators, restorers, and architects, in many cases the actual losses of cultural and historic material cannot be prevented sufficiently applying the available substances and procedures. At best is can be slowed down.

The present paper is ment to be an example for the techniques used for checking the effectiveness of the consolidating and protecting treatments. These techniques already existing in interdisciplinary fields are specifically modified and adapted to practical stone works.

New concept means new fundamental theoretical model and new types of polymeric materials. The combination of both has given very promising results in the protection and the structural consolidation of porous natural stones like sandstone as well as volcanic tuffs. New types of polymeric materials do not only mean absolutely new materials but also logically developments of marketable stone protecting materials.

2 TERMINOLOGY OF STONE CONSERVATION

Stone conservation differentiated according to their functional outfit can be defined by the extremes "hydrophobic impregnation" and "bulk sealing", Fig. 1.

Film-forming impregnation causes coating of the internal pore surfaces and therefore protection against chemical or biological attacks without considerable changing the pore structure.

Hydrophobing treatment means a particular technique of impregnation reducing the capillary water absorption properties /1,2/.

A special kind of impregnation causing protection in addition to structural consolidation was first presented in /3/. An integral compound between polymer and stone as well as an "isolating" separation of the mineral substance from harmful environmental influences will achieve these two aims, without negative changes of the building material properties.

Sealing means filling of pore channels in the border areas of the structural member or sculbture. The external surfaces get covered by a surface-layer with a loss of water vapour permeability.

Sealing of the complete bulk volume by acrylic resin is a special technology. It necessitates stationary equipment and is limited therefore to relatively small sculptures and elements, which can be transported to the laboratory.

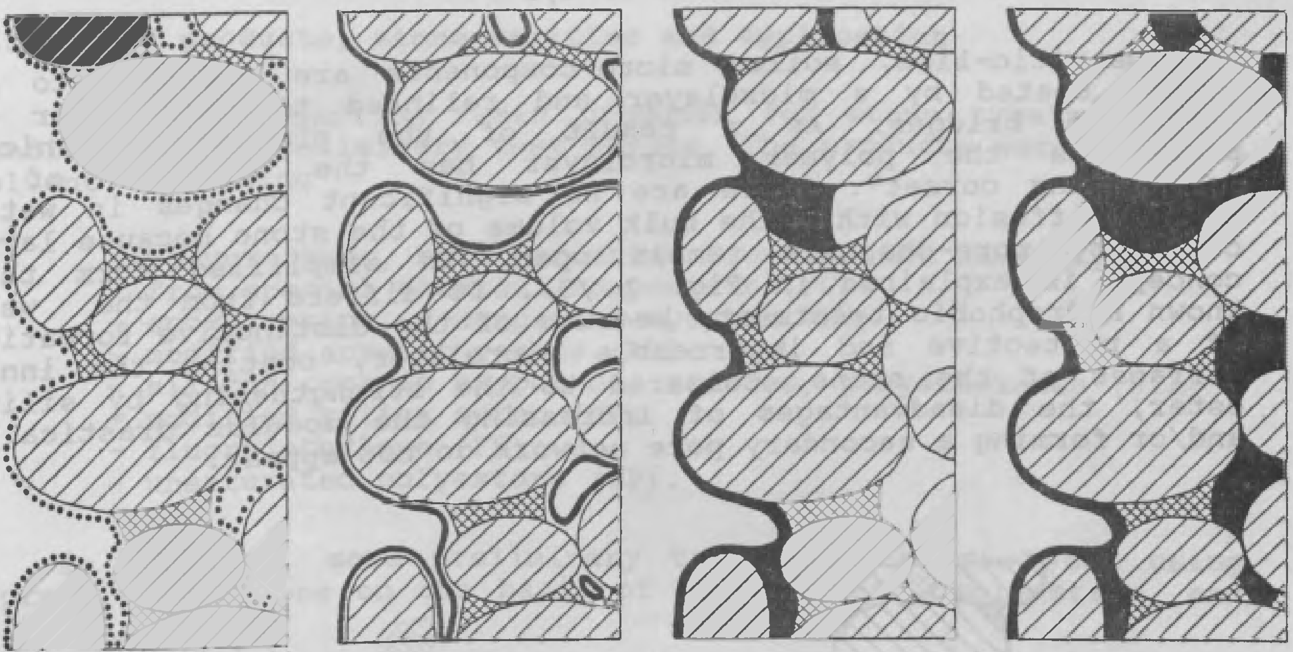


Fig. 1: Schematic presentation: terminology of stoneimpregnation

3 TECHNOLOGICAL REQUIREMENTS, CONCEPT FOR STONE PROTECTION AND CONSOLIDATION

As a base for the research activities a "catalogue of requirements" for protective agents has been elaborated in interdisciplinary cooperation /4/. The technical demands can be summarized into four main criteria:

- aesthetics of natural stone surface
- effectiveness and durability of protective means
- building site usability
- compatibility with ecological demands.

These main criteria are specified in detail by several subcriteria. The subcriteria are discussed in /4/.

The so called "supporting corset" model is understood as a protecting and strengthening polymer microlayer, coating the internal pore surfaces of the stone. The microlayer is supposed to be

- water repellent (hydrophobic) and water resistant
- impermeable against water
- restraining the water vapour diffusion
- resistant against chemical and biological agents
- capable of elastic deformation through a wide range of temperature (-30°C to 80°C).

Detritic-like, soiled micro-components are expected to be evenly coated by a microlayer and relinked to each other by polymeric bridges. As a result of the planned mechanical properties the polymer microlayer has the function of a "supporting corset". There are no significant changes in water vapour diffusion within the bulk volume of the stone because large capillary pore-channels remain open. In simplified form this concept is explained in Fig. 2 /5/. It differs from the well known hydrophobic treatment, because of the distinctive formation of a protective and impermeable microlayer, coating the inner surfaces of the stone. Compared to the strengthening by silica ester, the disadvantages of increasing the modulus drastically and/or forming a secondary pore network do not appear.

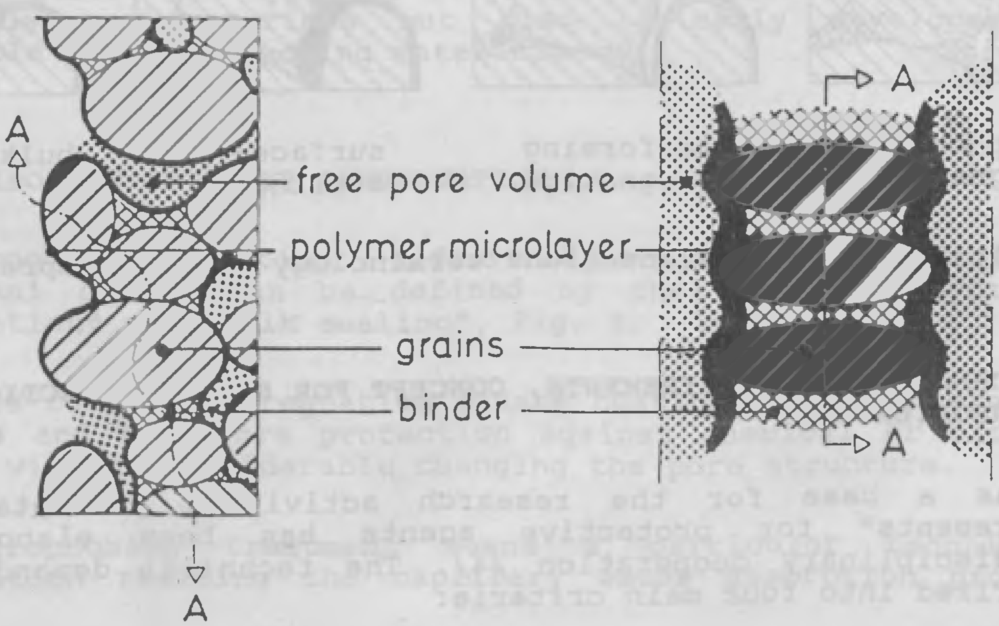


Fig. 2: The "supporting corset", protective polymer microlayer coating the pore walls

4 EXPERIMENTAL INVESTIGATIONS

4.1 Aims

On the basis of the technological requirements, effectiveness tests for existing products have been carried out. In an iterative process, specifications were elaborated as a basis for developments of new polymer stone treatment systems which are able to protect natural stone monuments against harmful atmosphericals and to strengthen the microstructure.

4.2 Tested products, stone varities and application

About 150 reaction resin products for stone treatment were studied during preliminary test series. The products were based on solvent containing

- polyurethane, both hardening from ambient humidity and from special chemical components (PUR)
- epoxy resins, 2-component systems (EP)
- modified acrylic resins (AY)
- silicon organic compounds, silanes, polysiloxanes (SIL)
- modified silica ester (SE)
- fluoro ethylene (FE)
- unsaturated polyesters (UP).

In addition, some preliminary tests were carried out using hydrous dispersions on the basis of polyurethane, polyesters, and acrylic resins.

Resins dissolved in a mixture of organic solvents may have very low viscosities and can be use successful for deep impregnation of materials with low and with high porosity. Suitable stone treatment materials must have:

- viscosity coefficient less than about 10 mPa*s
- moderate surface tension (higher than about 20 mN/m and lower than 30 mN/m)
- moderate interrelation between polar and unpolar groups inside the resin molecule (in relation to the polarity of the stone)
- low average molecular weight
- low reactivity, very slow increase of viscosity
- low solvent content.

Substrates were different types of sandstones and tuff, representative for German stone monuments. Three different quarry sandstones and one quarry tuff were selected for their typical features, such as mineral content, pore structure and colour. The treatments were carried out on

- Ebenheider Sandstone (EH)
- Obernkirchener Sandstone (OK)
- Sander Schilfsandstone (SS)
- Weiberner Tuff (WB).

The samples had the dimension of 5cm x 5cm x 10cm. In order to simulate the situation of a large element, treated and weathered from the surface, an 1.0 mm EP sealing was applied around the sample lateral faces. The front and back sides (5cm x 5cm) remained free. The samples were exposed to different climates (8°C/60% R.H., 23°C/50% R.H., 28°C/95% R.H.) until reaching constant humidity. Some properties of the samples are summerized in table I.

Table I: Properties of the untreated sandstones

Stone-type	density [g/cm^3]	maximum capillary water content [wt-%]	water absorption coefficient [Kg/m^{2}t$^{1/2}$]	porosity [Vol-%]	average pore radius [μm]	specific surface [m^2/g]	water vapour diffusion factor [g/m^{2}d]
1	2	3	4	5	6	7	8
EH	2,59 - 2,73	7,99	2,439	17,3 - 20,9	3,5	2,44 - 4,10	82
OK	2,66 - 2,69	6,75	1,670	16,4 - 19,0	2,0	1,29 - 1,32	71
SS	2,64 - 2,71	7,99	1,001	19,6 - 19,9	1,9	4,49 - 7,30	91
WB	2,26 - 2,40	27,59	6,904	41,6 - 44,0	0,7	10,04 -10,1	178

Products were applied by capillary absorption. The sample surface of 5cm x 5cm was immersed to 0,5cm depth into the impregnation liquid under atmospheric pressure. The level was kept constant. After four hours of sucking time the samples were left at laboratory climates 8°C/60% R.H., 23°C/50% R.H., 28°C/95% R.H. in order to achieve hardening of the polymer. After one month the samples were weighted again to determine the residual amount of impregnation material in the stone.

5 SELECTED TEST RESULTS

5.1 Penetration depth test

The penetration tests were carried out by different methods /5/. Dependent on stone variety, weathering grade, and physical properties of the liquid agents, penetration depths from some mm up to 70 mm have been achieved. The correlation between penetration depth and viscosity or surface tension respectively have been illustrated in /6/. In this case the different climates have no significant influence on the penetration depths of the protective liquids. The influence of polarity has not been clarified yet.

5.2 Suction of water and drying behaviour

Suction of water is understood as water absorption in result of capillary or adsorptive forces when wetting surfaces without external pressure. The polymer treated surface was immersed into water and suction was vertically upwards. The time related increase of weight was measured until reaching constance of weight and was reported in percent of the maximum capillary water content of the untreated specimens.

The drying behaviour is important because liquid water sometimes accumulates behind the treated zone due to condensation, cracks, or rising damp. Drying behaviour was determined after suction of water for 28d by measuring the weight during the drying process under 23°C/50% R.H.

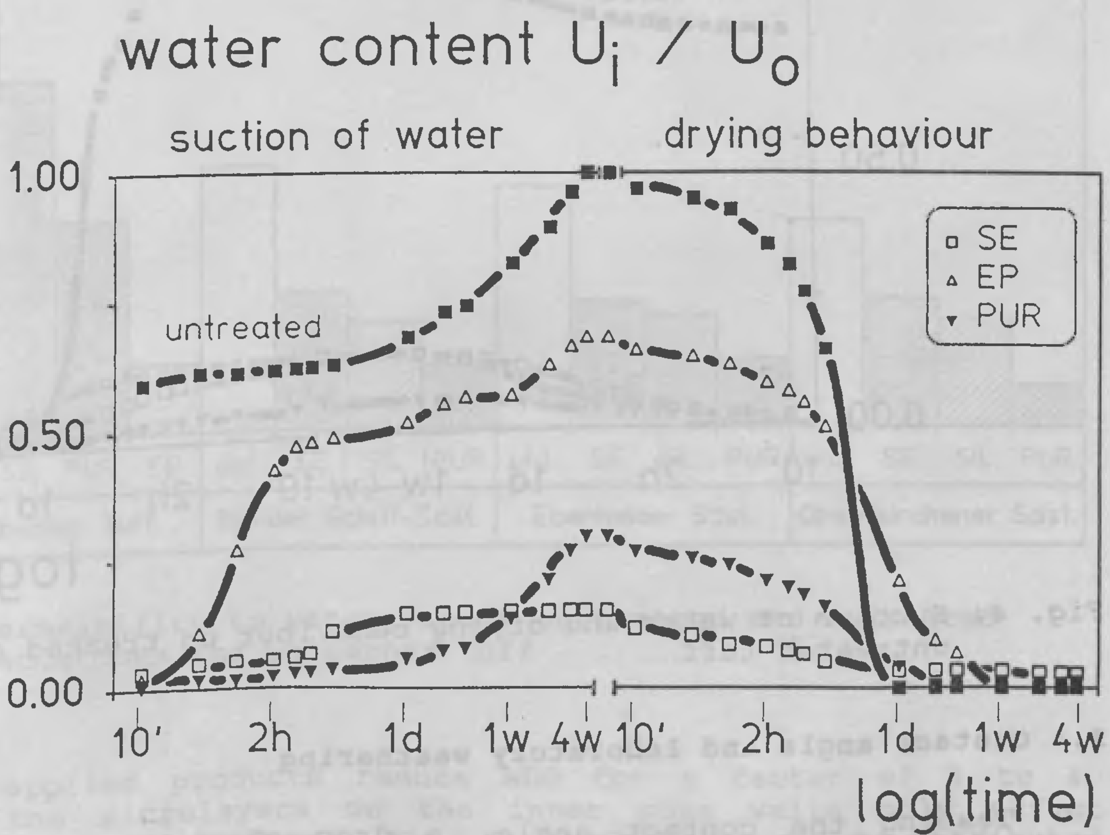


Fig. 3: Suction of water and drying behaviour on treated and on untreated sandstone

The graphs in Fig. 3 demonstrate the time related water absorption and -desorption processes of non treated and polymer treated stone samples. Compared to the untreated rock, drying velocities of the successfully treated samples are considerably reduced. The samples treated with modified silica ester show a significantly hydrophobic character throughout the whole time of exposition. Samples treated with polyurethane show a moderate rise of water sorption after 7d, meaning that after that time of exposition the hydrophobic, water repellent effect is lost. As a principle it is advantageous to have shorter desorption (drying) times than adsorption times. This property was not met by the selected polymer systems.

The graphs in fig. 4 show suction of water and drying behaviour on tuff with a similar characteristic. The difference lies in the fact that in the case of water suction there is no loss of the hydrophobing effect.

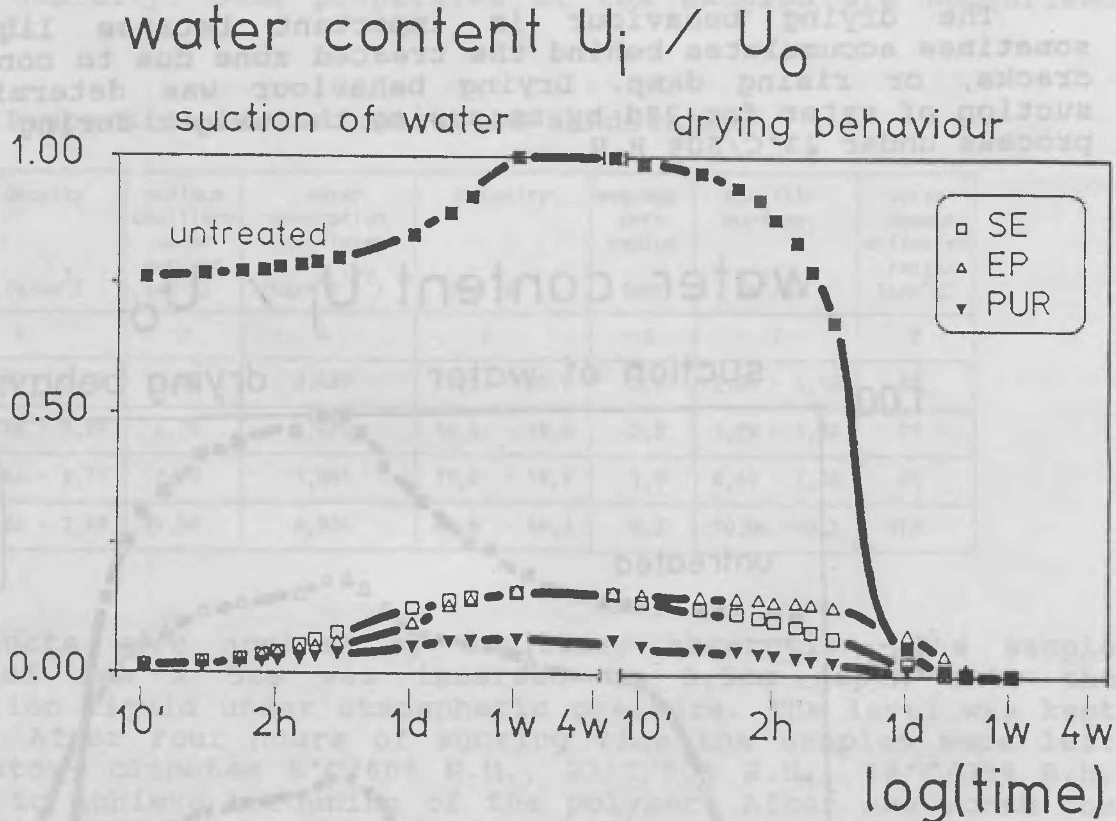


Fig. 4: Suction of water and drying behaviour on treated and on untreated tuff

5.3 Contact angle and laboratory weathering

Testing the contact angle, a drop of water of a defined volume is deposited on a horizontally adjusted rock surface. Using a goniometer microscope the contact angle can directly be determined. Above 90° degrees, a surface can be defined as hydrophobic. Laboratory weathering tests allow a comparative evaluation of the durability of the different products. As a result of exposure the polymer microlayers at the macro surface are partly destroyed, leading to an activation of the surface energy, and thus to smaller contact angles. These surfaces can be wetted, but no suction of water into the capillary system is possible /5/.

5.4 Water vapour diffusion

The polymer treated stone volume is expected not to act as a barrier against the flow of water vapour. This is especially important for moisture exchange processes between the building structure and the surrounding atmosphere. Density of water vapour flow (WDD) was tested according to DIN 52615 /7/. The treated samples had a cross section of 50mm x 50mm and a thickness of 10 mm. The test was carried out according to the so called "wet cup method"

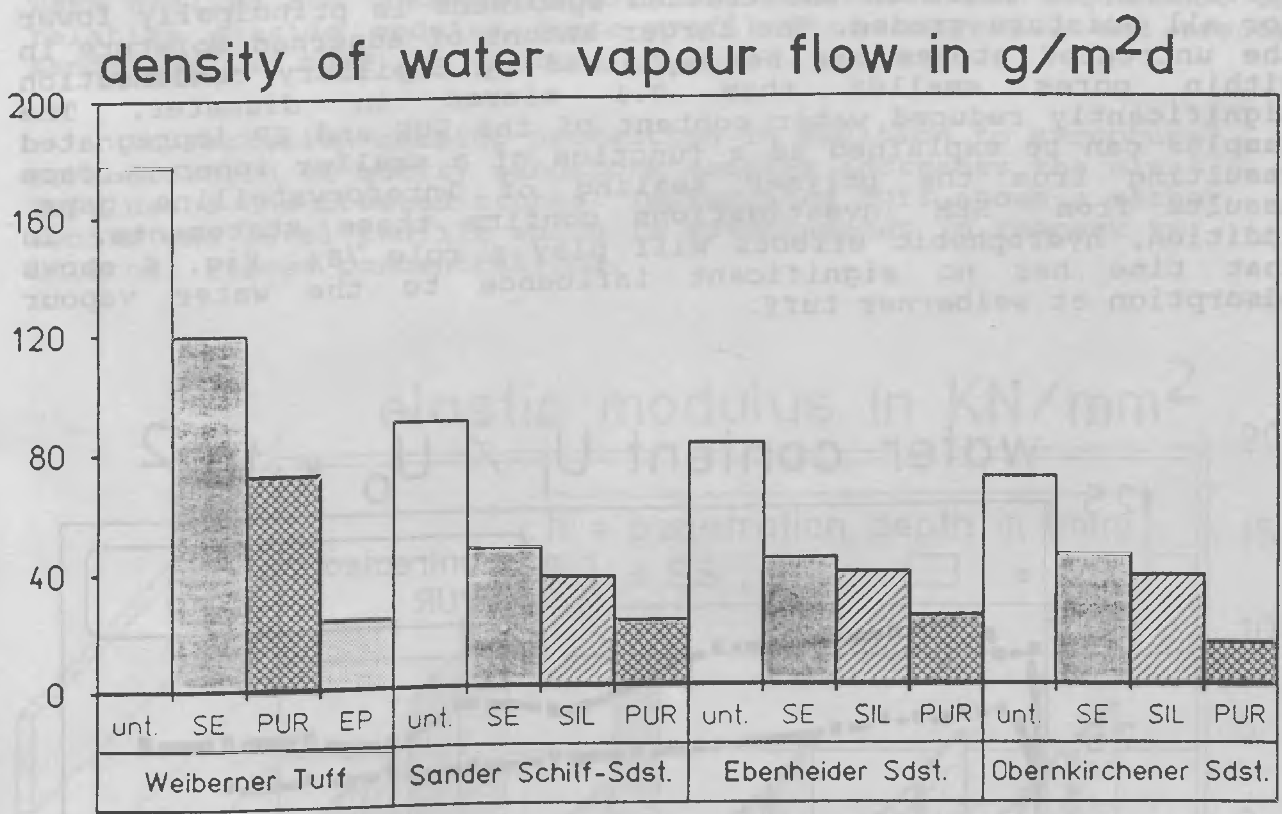


Fig. 5: Permeability to water vapour on treated and untreated sandstones and weiberner tuff

The applied products reduce WDD for a factor of 3 to 4, although the microlayers on the inner pore walls only affect porosity in the desired way, Fig. 5. The results can be attributed to the moderate hydrophobic effects of the products, inducing a reduction of the adhesive moisture. Due to that fact transportation of water molecules within the pore system is reduced. In this case surface diffusion and capillarity only moderately attribute to the diffusion of water vapour. The results of WDD tests seem tolerable but the product's hydrophobic features should nevertheless be optimized.

5.5 Water vapour adsorption

The isotherm of sorption characterizes the amount of moisture being adsorbed on the inner surfaces. Hydrophobing treatments effect a reduction of water adsorbing capacity of the stone. This should be aimed by sealing pores which do not contribute essentially to the moisture transport mechanisms of the stone.

Water vapour sorption was tested using 50mm x 50mm x 10mm sized samples. At 23°C relative humidities of 22%, 43%, 56%, 85% and 92% were selected. Compared to the untreated samples the adsorption of water on the treated specimens is principally lower for all moisture grades. The larger amount of adsorbed moisture in the untreated stones can be explained by capillary condensation within pores smaller than 0.1 micron in diameter. The significantly reduced water content of the PUR and EP impregnated samples can be explained as a function of a smaller inner surface resulting from the polymer sealing of intercrystalline gaps. Results from SEM investigations confirm these statements. In addition, hydrophobic effects will play a role /8/. Fig. 6 shows that time has no significant influence to the water vapour adsorption at weiberner tuff.

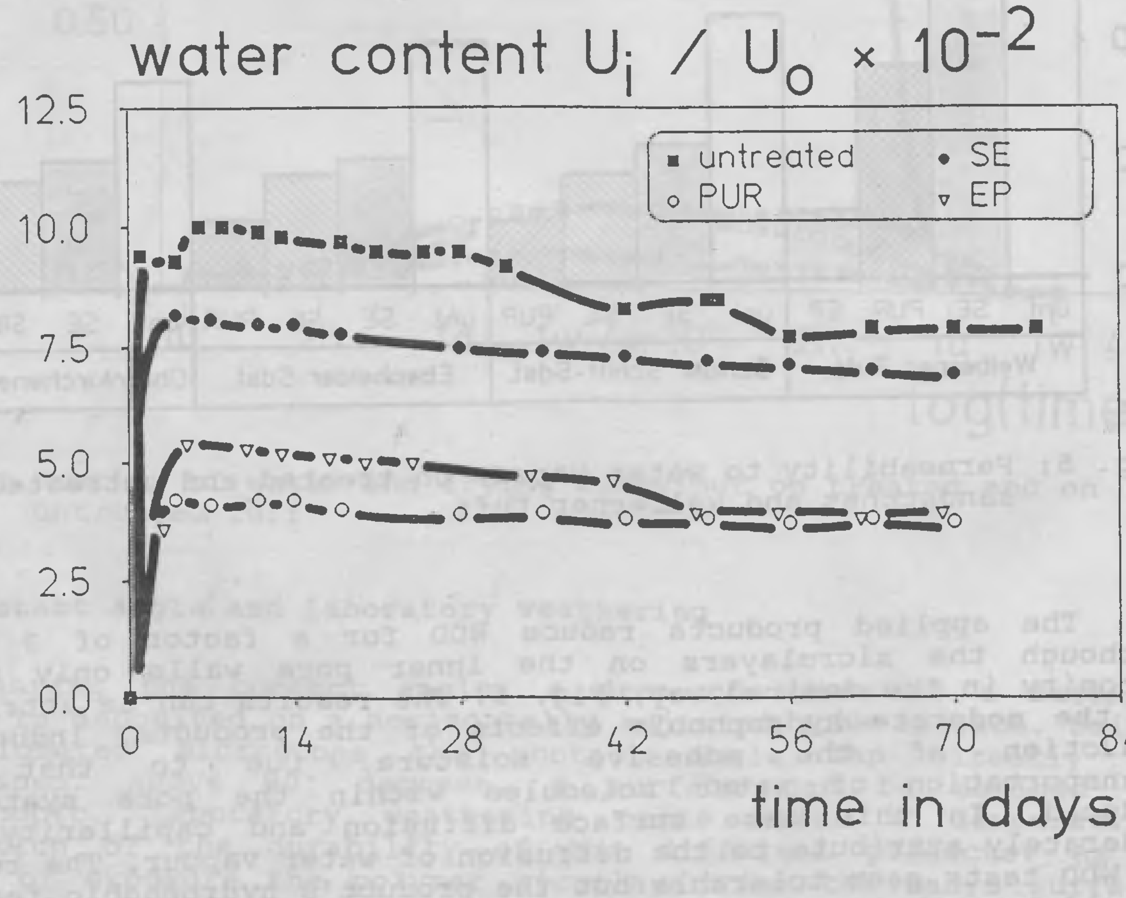


Fig. 6: Time related water vapour adsorption of tuff exposed to climate 28°C / 92% R.H.

5.6 Biaxial flexural strength and elastic modulus

The strength of decayed border areas has to be increased, if necessary, so that occurring internal stresses can safely be beared. A remarkable increase of the elastic modulus is not desired in order to prevent thermic and hydric induced internal stresses. Strength and elastic modulus measurements, before and after treatment, are therefore central to the assessment of any consolidant. Such measurements are very difficult to perform (due to changing of properties with the distance from the surface), therefore a technique proposed by Wittmann and Prim /9/ was tried instead. This test procedure allows to determine the relative strength and the relative elastic modulus in depth-profiles. From the original samples (5cm x 5cm x 10cm) cylinders of 4cm diameter were drilled and these were cut into slices of 4mm thickness. The relative elastic modulus depth-profiles of untreated and treated sandstone and tuff are plotted in fig.7.

Impregnation causing protection in addition to structural consolidation of quarry sandstone samples increases the elastic modulus of the treated stones. Impregnated tuff shows a rather smooth and level profile which is advantageous in respect to internal stress concentrations.

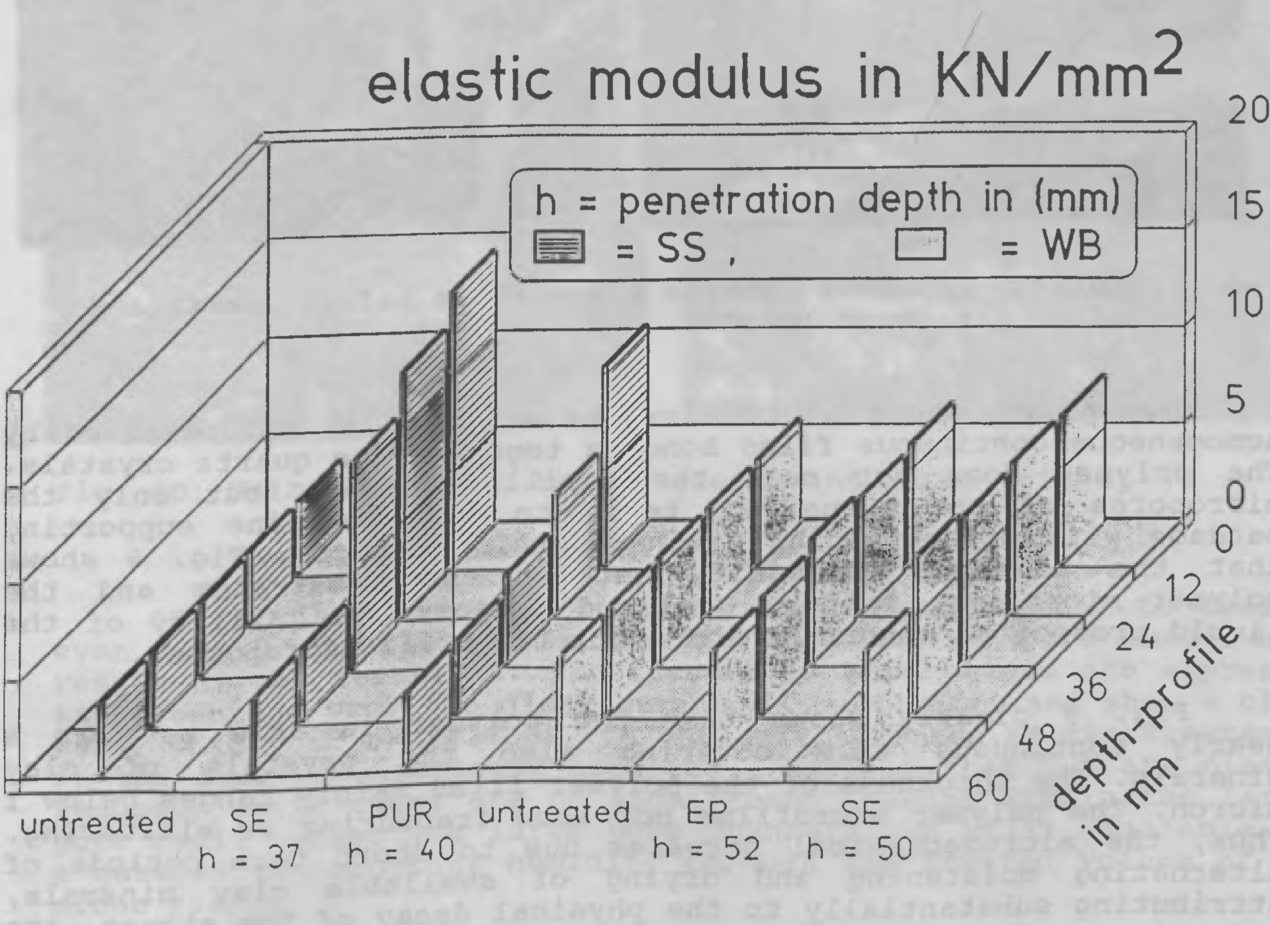


Fig. 7: Relative elastic modulus depth-profiles before and after polymer treatment of sandstone and tuff

5.7 Investigation on the pore structure

The description of the pore structure is a very important requirement for the assessment of impregnation treatments /10/. The most important requirement for studying the formation of the polymer corset at bulk surfaces and cracked sections, on which the main interest is focused, is to recognize structure features in sufficiently small areas with the aid of the scanning electron microscope (SEM) /11/. In addition, an EDX-analyzer equipped with an ultra thin aluminium window was used for the detection of the carbon content within the coating films. The recognized thicknesses of the polymer microlayer range between nanometers (nm) and some microns (μm), depending upon local geometric situations and type of stone /12/. Using specially developed sample preparation methods, the topography of the inner surface features can be studied down to nanometer structures /13/.

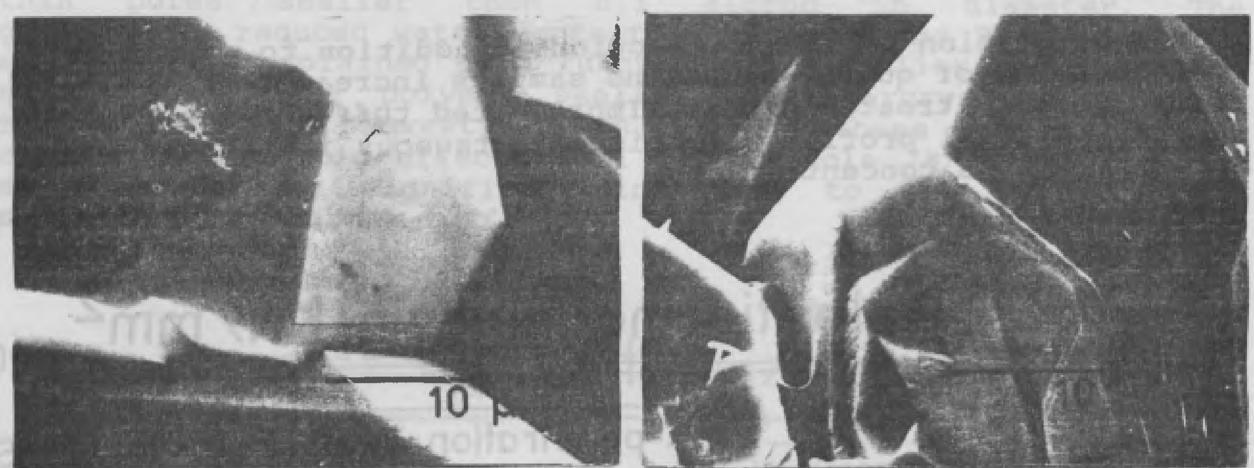


Fig. 8: Quartz crystals inside a sandstone before (left) and after treatment (right)

The visual shape of the treated samples is characterized by homogeneous continuous films bonding together the quartz crystals. The polymer does not seal the capillary pores, but only the micropores of the stone. It tends to leave a fine supporting bandage with strengthening grain-to-grain contacts. Fig. 8 shows that the adhesive capability between the substratum and the polymer microlayer is very good and moreover the ability of the liquid product to penetrate and completely fill micropores .

Fig. 9 clearly shows that the polymer is able to form a nearly continuous film covering also the crystals of clay minerals. The thickness of the polymer films mainly ranges below 1 micron. The polymer microfilms not show fracturing or blistering. Thus, the micromechanical stresses due to short term periods of alternating moistening and drying of swellable clay minerals, attributing substantially to the physical decay of the stones, are reduced to a great extend.

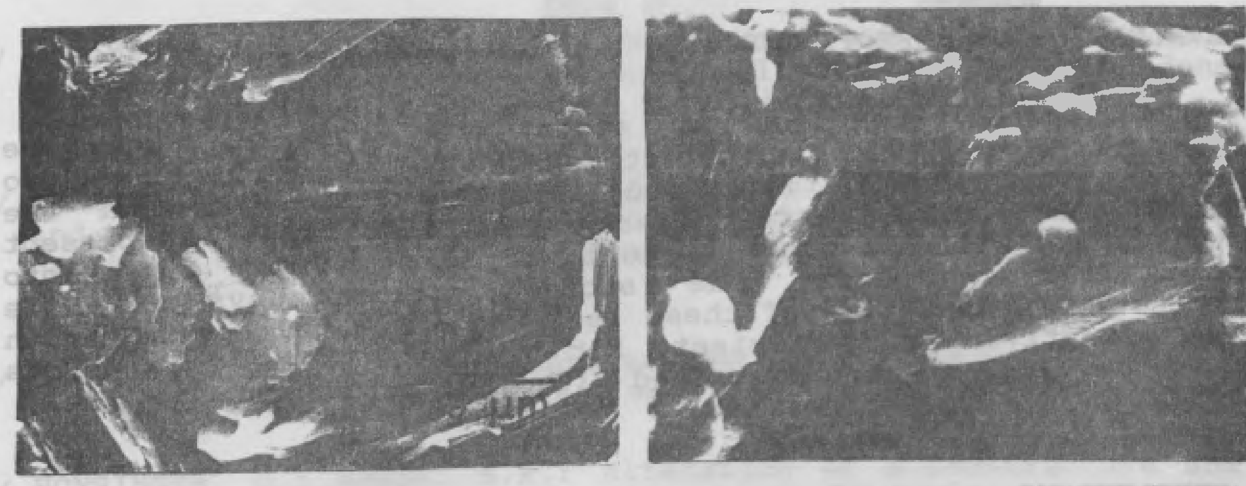


Fig. 9: Vermicular stacks, the characteristic structure for kaolinite, before (left) and after (right) treatment

The resin forms a microlayer well connected with each other and bridging the micropores also in tuff structures, fig. 10.

Fig. 10: Weiberner tuff, before (left) and after (right) treatment

SEM studies are supported by mercury-porosimetry to measure even slight changes within the distribution of pore radii as a result of the treatment. Differences in pore volume are expressed as percentage over the distribution of pore radii and show a clear mark, which can be related to the effectiveness of the treatment. In the case of sandstones pore radii smaller than 5μm are clearly reduced, while there are no significant changes within the larger pore radii ranks. The large pore channels are still available for a gaseous transport of humidity through the treated volume of the stone /14/.

6 EVALUATION OF EFFECTIVENESS

The effectiveness of a stone treatment can only be characterized by multiple effectiveness features. In order to carry out a computer supported, quantitative evaluation the effectiveness, criteria are differentiated into ranks. At present status only 7 effectiveness criteria of about 20 are taken into account for optimizing the stone treatment systems. The quantitative intensities of these features allow the determination of an effectiveness coefficient. For the most promising products further developments are discussed with the producers /5/.

7 CONCLUSIONS

The results received hitherto show that several polymer systems met the technological demands which are discussed in this study. In fact these types of polymers have not yet been in use for strengthening and protecting of natural stone. Some epoxies and polyurethanes show good penetration into the stone and form nearly continuous microlayers covering the mineral pore walls. They do not seal capillary pores but only the micropores of the stone. They tend to form a fine supporting bandage and do not drastically effect the modulus or the colour, moreover they give strength and protection including increased water repellent property. On the basis of these results a selection of the most effective products was made and several test products seem to be worth for further development. In connection with the chemical industry these products will be developed and tested in a more sophisticated way. Of these, studying the polymer treated stone under natural weathering conditions and in short time laboratory simulation tests will be the most important future investigations.

8 REFERENCES

/1/ SNETHLAGE, R.: Steinkonservierung. Forschungsprogramm des Zentrallabors für Denkmalpflege 1979-1983, Bayerisches Landesamt für Denkmalpflege München, Arbeitsheft 22, München 1984

/2/ WEBER, H.: Steinkonservierung. Der Leitfaden zur Konservierung und Restaurierung von Naturstein. Expert Verlag, Sindelfingen 1985

/3/ SASSE, H. R.: Neuartige Konzepte für den Schutz gefährdeter Natursteinbauten. Symposium über Steinzerfall. Bild der Wissenschaft, Bonn, 15. April 1988

/4/ SASSE, H. R.: Polymere als Schutzstoffe für Naturstein. Bautenschutz und Bausanierung Sonderausgabe, (1) 1987, S.65-88. 1. Statusseminar des BMFT, Mainz, 17./18. Dez. 1986

/5/ HONSINGER, D.; SASSE, H.R.: Neue Wege zum Schutz und zur Substanzerhaltung von Sandsteinoberflächen unter Verwendung von Polymeren. Bautenschutz und Bausanierung, Heft 6, 1988

/6/ HONSINGER, D.; FIEBRICH, M.: Polymers for consolidation and preservation of natural stone. Proceedings.- 2nd International Conference on Engineering Materials. Bologna, 19.-23.06.1988

/7/ DIN 52615 11.87. Wärmeschutztechnische Prüfungen. Bestimmung der Wasserdampfdurchlässigkeit von Bau- und Dämmstoffen

/8/ HONSINGER, D.; SASSE, H.R.: Alteration of microstructure and moisture characteristics of stone Materials due to impregnation. In: Proc. V th International Conference on Durability of Building Materials and Components. Brighton, U.K. 7.- 9.11.1990

/9/ WITTMANN, F.H.; PRIM, R.: Mesures de l'effet consolidant d'un produit de traitement. In: Materiaux et construction (RILEM), 16 (1983), Nr.94. S 235-242

/10/ROSSI-DORIA, P.: Pore Structural Analysis in the Field of Conservation. State of the Art and future Developments, Proceedings. RILEM/CNR International Symposium. Principles and Applications of Pore Structural Characterization, Milan 1985

/11/HONSINGER, D.: Die Bedeutung von Strukturuntersuchungen im Elektronenmikroskop für die Qualitätssicherung von imprägnierten Sandsteinen. In: Tagungsband, 14.Vortragsveranstaltung des Arbeitskreises "Rasterelektronenmikroskopie in der Materialprüfung", 25.-27.04.1990. Berlin 1990

/12/HONSINGER, D.; NEISEL, J.: Strukturuntersuchungen an imprägnierten Sandsteinen. Ibac- Kurzbericht Nr. 17. Selbstverlag Institut für Bauforschung, RWTH Aachen. Aachen 1990

/13/BURCHARD,W.-G.; CLOOTH, G.; SASSE, H. R.; HONSINGER, D.: Rasterelektronenmikroskopische Strukturuntersuchungen an polymergetränkten Naturwerksteinen als Hilfsmittel zur Wirksamkeitsbeurteilung von Schutzmaßnahmen. In: Beiträge zur elektronenmikroskopischen Direktabbildung von Oberflächen 20 (1987). 20. Kolloquium des Arbeitskreises für elektronenmikroskopische Direktabbildung und Analysen von Oberflächen (EDO)

/14/HONSINGER, D.: Mikrogefügeuntersuchungen als Hilfsmittel für die Wirksamkeitsbeurteilung von Steinschutzmaßnahmen. Ibac-Kurzbericht Nr. 15. Selbstverlag Institut für Bauforschung, RWTH Aachen. Aachen 1989

/5/ HONSINGER, D.; SASSE, H.R.: Neue [illegible] zum Schutz und zur Substanzerhaltung von Sandsteinoberflächen unter Verwendung von Polymeren. Bautenschutz und Bausanierung, Heft 5, 1988

/6/ HONSINGER, D.; PIETSCH, M.: Polymers for consolidation and preservation of natural stones. Proceedings 2nd International Conference on Engineering Materials, Bologna, 19.-23.06.1988

/7/ DIN 52615 11.87 Wärmeschutztechnische Prüfungen; Bestimmung der Wasserdampfdurchlässigkeit von Bau- und Dämmstoffen

/8/ HONSINGER, D.; SASSE, H.R.: Alteration of microstructure and moisture characteristics of stone Materials due to impregnation. In: Proc. V th International Conference on Durability of Building Materials and Components, Brighton, UK, 7.-9.11.1990

/9/ WITTMANN, F.H.; PRIM, P.: Mesures de l'effet consolidant d'un produit de traitement. In: Matériaux et constructions (RILEM), 16 (1983), Nr. 94, S. 235-242

/10/ ROSSI-DORIA, P.R.: Pore Structural Analysis in the Field of Conservation: State of the Art and future Developments. Proceedings of International Symposium "Principles and Applications of Pore structural Characterization", Milan 1985

/11/ HONSINGER, D.: Die Bedeutung von Strukturuntersuchungen im Elektronenmikroskop für die Qualitätssicherung von imprägnierten Sandsteinen. In: Tagungsband 11. Vortragsveranstaltung des Arbeitskreises "Rasterelektronenmikroskopie in der Materialprüfung", 15.-17.04.1990, Berlin 1990

/12/ HONSINGER, D.; WEISEL, J.: Strukturuntersuchungen an imprägnierten Sandsteinen. Ibac-Kurzbericht Nr. 17. Selbstverlag Institut für Bauforschung, RWTH Aachen, Aachen 1990

/13/ BURCHARD, W.-D.; LOOS, G.; SASSE, H. R.; HONSINGER, D.: Rasterelektronenmikroskopische Strukturuntersuchungen an polymergetränkten Naturwerksteinen als Hilfsmittel zur Wirksamkeitsbeurteilung von Schutzmaßnahmen. In: Beiträge zur elektronenmikroskopischen Direktabbildung von Oberflächen 20 (1987). 20. Kolloquium des Arbeitskreises für elektronenmikroskopische Direktabbildung und Analyse von Oberflächen (EDO)

/14/ HONSINGER, D.: Mikrogefügeuntersuchungen als Hilfsmittel für die Wirksamkeitsbeurteilung von Steinschutzmaßnahmen. Ibac-Kurzbericht Nr. 15. Selbstverlag Institut für Bauforschung, RWTH Aachen, Aachen 1989