LAVAS AND VOLCANIC TUFFS

PROCEEDINGS OF THE INTERNATIONAL MEETING

Easter Island, Chile, October 25–31, 1990

ICCROM

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Proceedings of the International Meeting
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FOREWORD

These Proceedings of the International Meeting on Lavas and Volcanic Tuffs, held on Easter Island in 1990, are a very interesting example of an approach to dealing with the conservation of cultural heritage, an approach that attempts to take into account all aspects of the problem.

The many experts from various nations, with broad-based experience from having studied problems in similar stones, brought their knowledge to the analysis of the particular problems found on Easter Island. This gave that enterprise a systematic approach and allowed for a global outlook.

The initiative taken in relation to Easter Island offered a good opportunity to study, thoroughly and extensively, these volcanic materials. These have been the subject of fewer studies than other kinds of stone, although stones of volcanic origin are equally widespread and have been used extensively as building materials for many of the constructions that form the world's cultural heritage.

These Proceedings bring together current knowledge of lavas and volcanic tuffs, their deterioration and conservation problems. As studies from many different countries, climates and environments are included it gives an opportunity to compare the behaviour of similar materials in different situations. The value of this publication is enhanced by the inclusion of a systematic literature survey on the topic, and by the careful editing that the contributed papers received to ensure a uniform style to the presentations and to improve their readability. The inclusion of papers concerning the history of the Rapa Nui people and present-day problems in the management of the Rapa Nui National Park give the framework for any preservation project on the Island.

The Recommendations that resulted from the meeting clearly outline the strategies that are needed to carry out a preservation project: a comprehensive conservation programme and measures regarding training and site management and control. Within these, maintenance is a key issue, and I wish to underline its importance in the long-term preservation of cultural heritage. In our field of stone conservation we have seen a lot of effort put into conservation procedures, but many of these efforts have been wasted because the appropriate maintenance was not available. The stress that this nascent programme puts on the importance of a multidisciplinary approach – including issues such as local development and tourism, and the support of long-term maintenance from the outset – can serve as an example to the world.

Paola Rota Rossi-Doria

Director
Istituto Conservazione Opere Monumentali
Consiglio Nazionale delle Ricerche

Lecce, Italy, May 1992

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 *moai*, 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 objeto 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 realizó a fines de octubre de 1990 en la Isla de Pascua, permitió no sólo discutir los actuales trabajos, sino, proyectar hacia el futuro nuevas tareas de investigación, así como también un plan concreto de acciones 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, noviembre de 1990

INTRODUCTION

The present volume has been prepared on the basis of the pre-prints published for the International Meeting on Lavas and Volcanic Tuffs, held on Easter Island in October 1990. It also includes papers that were received after the deadline for the pre-print publication, together with the conclusions and recommendations that were drafted during the meeting.

The meeting resulted from a 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.

The aim of the meeting, and of the competition that preceded it, was to encourage the study of lavas and volcanic tuffs. The interest in the topic arose from the conservation problems posed by the monumental statues and unique petroglyphs of Easter Island, which were carved from these types of stones. Worldwide, the deterioration and conservation problems associated with such stones had not been studied as thoroughly as those of other types, such as marble or sandstone.

Even though a fairly large number of papers have been published on this subject, no unifying effort had previously been made to bring them all together and compare information and experiences. As a result, the field had been covered only patchily. The present volume was intended to provide an overview. The literature review summarizes previous publications; the deterioration, treatment, and treatment evaluation sections give state-of-the-art information based on recent and current studies. Finally, the Easter Island section brings together not only technical studies but also the background information that is a necessary pre-requisite for the formulation of any conservation programme to be carried out on the island.

During the meeting, guidelines for the development of such a conservation programme were discussed. The need for a comprehensive approach, the importance of preservation measures and the long-term maintenance of sites was stressed. The final conclusion was that an adequate framework for the protection of petroglyphs and other archaeological artifacts, the long-term maintenance of the sites and training of personnel to deal with the visitors to the island were all felt to be essential if conservation treatments of the monumental stone heritage were to be successful. The development of such a comprehensive plan represents a new step in approaches to the preservation of cultural heritage.

A. Elena Charola

Editor

New York City, April 1992

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Part One

LITERATURE REVIEW

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

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ABSTRACT

A literature review reveals that conservation studies of volcanic stonework have focused on tuffs, which exhibit serious deterioration. Other volcanic rocks used for monuments or sculpture are basalt, scoria, andesite, dacite, rhyolite and trachyte. Important examples include the statues on Easter Island, the Buddhist shrine of Borobudur in Java, the churches at Göreme in Turkey and Lalibela in Ethiopia, 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.

1.1 INTRODUCTION

Some of the world's most spectacular monuments, including those at Easter Island, Borobudur in Java, Göreme in Turkey, and Lalibela in Ethiopia, are made of volcanic stone, and have shown themselves to be vulnerable to deterioration. Nevertheless, compared to other types of stone, volcanic stone has been little reported on in the stone conservation literature. In a tally of papers on stone weathering and conservation and given at congresses, 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 paucity 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

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the Study of the Preservation and Restoration of Cultural Property) reports or studies stemming from their projects prove to be an important source of information on such monuments. The purpose of this paper is to review the literature to date so as to provide a basis for further study.

The Conservation Information Network (CIN), the library of ICCROM, Rome, the Conservation Analytical Laboratory of the Smithsonian Institution in Washington, 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, and if a particular publication is difficult to find, copies are available through the Center.

1.1.1 Geology

Igneous rocks are those which derive 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, with larger grains, are volcanic breccia and agglomerates. Most of these are far too friable and soft to be used for stonework.

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. In general, acid rocks are lighter in colour than basic rocks, which contain dark-coloured 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 4-32 mm in diameter) tuff.

1.1.2 Weathering

Volcanic rocks, which form at high temperatures, are not chemically stable at ambient temperatures in the presence of water, which is the principal agent of alteration. Metal ions are gradually 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 surface areas and tend to hold water. Thus they usually deteriorate more rapidly than dense rocks such as basalt. As a general rule, the glassy portions of rocks weather more rapidly than crystalline portions because of the greater instability of the glass. However, it must be noted that the weathering of volcanic rocks is relatively slow compared to the aqueous dissolution of carbonate rocks. Moreover, volcanic rocks are not very susceptible to attack by air pollutants such as the sulphur dioxide that is so damaging to calcareous rocks.

1.1.3 Uses

Volcanic rocks have been used for both buildings and sculptures. While they tend not to take a polish or fine detail like marble, they can 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 implications for treatment, especially cost. At Borobudur, for example, there are 33 100 relief blocks and nearly 500 sculptures. At Easter Island there are approximately 1 000 colossal heads exposed to the open air. Important volcanic monuments such as the churches at Lalibela and Göreme, the rock-cut Buddhas in Japan, and the caves in India, are not only large, but they have difficult problems associated with the fact that they were carved *in situ* rather than constructed using cut stone blocks. 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].

1.1.4 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 favour for use on less porous rocks such as marble, they have been successfully applied to tuff. Monomer methylmethacrylate, polymerized *in situ*, has also performed well 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 when dealing with tuff and other volcanic rocks located in tropical areas. Removal of soiling is rarely an issue for volcanic stones in the same way as it is for limestone, marble or sandstone. Repair of structural problems, like cracks, are in particular discussed in the case of monuments cut *in situ*.

This 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 geographical location. Characteristics of the rocks, their deterioration, and conservation treatments are then summarized. For the convenience of the reader, a list of the commercial products mentioned in the text is given at the end of the paper, including the name of the manufacturer and the components in so far as they are known.

1.2 TUFF

Of all the volcanic building and sculpture stones, tuff has been written about most extensively. 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 vary 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, together with subsequent alterations. For 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 because of their capacity for ion exchange they have implications for both deterioration and treatment. Vesicles left from the gases which propelled the pyroclasts produce open porosity as high as 50%, with concomitant high water absorption potential. 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" is unambiguous and so can be useful in preventing confusion.

1.2.1 Easter Island

Considering that concern for the heritage of this island brought about the conference, it is appropriate to begin with the *moai* or colossal statues of Easter Island. Most of these approximately 1 000 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]. Some statues are known to be made out of other rock. The two statues in the village were carved out of an alkaline trachyte, apparently from the Poike volcano [5]. Two of the statues located at Tahai are made from a scoria, but not that of Puna Pau [5]. At Ahu Vinapu II there is a standing statue of red scoria, supposed to represent a female which originally had two heads [6]. Probably the best known statue is the one now in the British Museum in London, called Hoa Haka Nana Ia – "the wave breaker." That moai is carved from basalt, and used to stand in the ceremonial village of Orongo [7; 8].

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 photographs taken using scanning electron microscopy (SEM). 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 [9], later summarized in a Polish article with an English abstract [10], 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 that there is need for stone consolidation. Laboratory testing of the capillary uptake of white spirit, *Wacker OH*, *Wacker H* and a 20% solution of epoxy resin was carried out on samples of the rock [9]. 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 statues selected for treatment [11] and the December 1986 treatment of one of them located at Hanga Kio'o are described [4; 12; 13]. After surface cleaning, consolidation with *Wacker OH* (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).

1.2.2 Italy

The extensive tuff deposits found in central Italy were used by the ancient Etruscans and Romans for building material, as well as by medieval artisans. Etruscan tombstones [14] and subterranean tombs [15; 16] made of tuff have been studied. Tuff from an Etruscan wall at Bolsena [17] and a building at Cerveteri [18; 19] have been used in testing. Types of tuff used by the Romans, their quarry sources, use in buildings and typical sizes and shapes are well described in a book by Roberto Marta [20]. The Romans' use of tuff commenced with the founding of the city and continued to the time of Augustus (ca 30 BC), when the embellishment of buildings with marble was encouraged instead. Tuffs from ancient monuments in the Forum and throughout Rome [21; 22; 23; 24; 25; 26; 27; 28], at Ostia Antica (the historic port of Rome) [23; 29; 30], at Capua [31], and at Caprarola [23] have been included in studies. Samples from the church of Sta Maria Maggiore in Viterbo [22], the twelfth-century Castel dell'Ovo in Naples [32; 33; 34] and the fifteenth-century Capitoline Palace in Rome have also been studied [35].

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 [28]. Alarming deterioration of the Castel dell'Ovo in Naples is attributed to the presence of sea salts and wind erosion [32; 33; 34]. 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 Italian Patent 932873 of Nov. 11, 1972) mixed with 10% *Sniatron* showed the best performance. These were compared with samples consolidated with a polymethylmethacrylate solution [18] and with *Tegovakon V* followed by application of a water repellent, *Tegosivin HL 100* [19]. *Wacker H* and *Wacker OH* were tested on samples from the Temple of Cibeles [28]. Samples of stone from the Castel dell'Ovo were tested with five products [33]. *Rhodorsil 10336* proved the best in accelerated weathering tests, followed by a mixture of 1 part *Paraloid B-72* at 30% in organic solvents, 1 part *Dry Film 104* silicone resin, and 8 parts trichloroethane. *Wacker H*, *Rhodorsil XR-893*, and *Product 460* proved unsatisfactory. *EP 2101*, a cycloaliphatic epoxy resin, showed even distribution and good penetration in SEM photographs of test samples [24]. The *EP 2101*-impregnated Viterbo tuff of a Roman aqueduct 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 [17]. Treated samples showed improved performance under artificial 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 [16; 21; 22; 23; 30; 31]. Tests with *Fluometuron*, *Clorobromuron*, *Terbutryn* and *Vancide 51* on 15 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 crustaceous (crustose) or powdery lichens [30]. 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 [14]. *Lito 7* was also included in cleaning materials tested on tuff samples quarried at Viterbo [36]. *AB 57* showed slightly stronger action than the *Lito 7* or the *Contrad 2000*.

The deterioration and treatment of a recently excavated tuff wall of the Crypt of Balbus is reported [25]. 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 AC 33* [35].

1.2.3 Hungary, Germany and Austria

The use of volcanic rock, and tuff in particular, is little remarked upon in Europe other than in Italy. 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 [37; 38]. 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 were found which mention tuff from Germany, in both cases used in the early sixteenth century. The deterioration of a local porphyritic tuff used for the north portal sculpture of the Schlosskirche at Karl-Marx Stadt (now renamed Chemnitz) is the subject of discussions about the possible application of epoxy resins [39]. Restoration of a polychromed sacrament house made of Weibern tuff in the Church of St Martin at Linnich is described, repairing damage occurring during the Second World War [40].

A tuff used for a portion of the Linz Cathedral in Austria, constructed in 1938, was examined with ultraviolet fluorescence microscopy to determine the location of gypsum [41]. Gypsum proved to be unevenly distributed at various depths, without correlation between amount and extent of damage.

1.2.4 Turkey

One of the world's most spectacular tuff sites is the lunar-like landscape on the Anatolian plateau at Göreme in Cappadocia. More erosion-resistant, cone-shaped rocks were formed adjacent to conduits for escaping gases. These cones 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 Government of Turkey [35; 42; 43; 44; 45]. The stone is identified as dacitic lapilli tuff [45]. Laboratory analyses have been carried out both on weathered samples from the St. Barbara Church [43] and on freshly quarried stone [45]. 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 [43]. Lichen growth produces exfoliation of the stone. Fissuring of the stone, as it permits the entry of water, is perhaps the most serious hazard for the decorated interiors of the churches [42].

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 on site [42]. *Vinavil*, applied as a surface coating, sloughed off. Application of a 3 cm-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 [35]; 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 [43]. 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* [45]. 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 [35; 42].

The properties of a green dacitic tuff from the eastern end of the Marmara Sea (Karamursel) used in Istanbul during the sixth century for walls of Hagia Sophia and Hagia Eirene are described [46]. Records of sixteenth-century orders have been found, but the quarries are no longer functioning.

1.2.5 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 has been analysed. The principal deterioration phenomenon is loss of cohesion of the matrices, especially in the more coarser-grained samples [47].

1.2.6 Countries of the former Soviet Union

Tuff has been widely used as a cut stone up to the present day in Armenia, with monuments from the fourth to the twelfth centuries cited [48; 49]. Five tuffs have been studied in the laboratory: quaternary tuffs from Ani, Artik, Erevan, and Burakan; and a 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 – all cut into a vertical cliff [50]. 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 organosilicates were tested as consolidants. The best results were achieved with the organosilicates, with a deposition layer 5-8 mm in depth when applied in the field. Application of a polyethyl hydrosiloxane water repellent was recommended.

1.2.7 Japan

Considerable work has been done in Japan on the deterioration and treatment of tuffs. A few publications are in English [51; 52; 53; 54; 55], but most are in Japanese with English abstracts. The focus of the work has been the treatment of Buddhas dating from the eighth to the nineteenth centuries and cut into cliffs. These are located at Usuki [56], at Hakone in Kamto District [51], in Ohita prefecture [51; 57], and in the caves of Oya Temple [51; 58; 59; 60] in Tochigi Prefecture [61; 62]. Tuff used for two historic structures in the city of Otaru has also been studied [63].

The Oya Temple tuff is identified as a zeolite-bearing acidic stone, with sodium nitrate salts ($NaNO_3$) found on the surface [58]. Neutron activation studies found high calcium contents in the surface crust and aluminum enrichment in heavily deteriorated portions of Ohita stone [57]. Freeze/thaw cycles are thought to provide a major contribution to the deterioration of Japanese tuffs [51; 63]. The effects of freeze/thaw cycles on Oya tuff have been measured with acoustic emission [59]. The crystallization of salts (mainly gypsum) from ground water is also considered a major factor [53; 64]. The biodeterioration of tuffs has also been studied [63].

The alkoxysilane *SS-101*, which is water repellent, produced the best consolidation results in laboratory testing [66]. A variety of tests were conducted on samples, some of which were artificially aged with freeze/thaw cycling [54; 61; 62; 67; 68]. 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 *Tegovakon V* followed by *Tegosivin HL-100*, were also subjected to sodium sulphate crystallization cycling [64]. Colour changes were measured after treatment with the *SS-101* and artificial aging [52].

Methyl(triethoxy)silane solutions have been used in the field since 1976 [53]. 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 100 cm into the rock; these are subsequently filled with stainless steel bars, epoxy, and stone powder.

As a less expensive alternative, investigations were done on samples impregnated with solutions of potassium silicate and lithium silicate, and compared to samples impregnated with *Paraloid B-72* and *SS-101* [55]. 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 means of protecting rock-cut Buddhas from freeze/thaw damage [53; 60].

1.2.8 India

In India a pyritic volcanic tuff was carved to decorate the Josgeshwari Caves near Bombay [69; 70; 71]. The deterioration of these caves, with growth of gypsum exudations from the hydrolysis of the pyrite, is described.

1.2.9 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 [72]. 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 into cliff faces [73]. More recently the rock was used by US Work Projects Administration 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 [74]. The rock measures over 50 m in length, and it is fissuring because of loss of support due to 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 [75]. 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 [76]. 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 in the construction and decoration of Spanish colonial cities since the early days of colonization[73].

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 Cochasquí, Ecuador [77; 78]. 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 [73].

1.3 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-coloured minerals and the light-coloured plagioclase are common. Basalt tends to be dense and massive, but it can also be vesicular.

1.3.1 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, Ellora, Elephanta, Karla, Bhaja, Pitalkhara and Kanheri [69; 70; 71; 79; 80]. These rocks are mineralogically similar, mainly labradorite and enstatite-augite, and occur in both vesicular and non-vesicular forms [70].

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 [80]. 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 [70]. 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 [69]. Removal of soluble salts with moist paper pulp has been carried out at Elephanta and Kanheri [80]. 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.

1.3.2 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 [81]. Basalt samples, presumably from Portugal, are included in studies of igneous rocks by Delgado Rodrigues [82, 83]. The thickness of the weathered crust on Bohemian basalts has been correlated with age [84]. Basalt from Mayen/Eifel and Londorf/Hessen are among the stones used in the construction of the Cathedral of Cologne [85; 86]. 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.

1.3.3 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 [87]. 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 both for rustic buildings made of field stones and for massive structures with sculptural relief, from the Bronze Age onwards [88]. The foundations of the ancient Greek city of Locri in Calabria, Italy, were constructed of basalt from Mount Etna, a fact confirmed by recent petrographical and geochemical studies [89]. No reports have been found on the deterioration or treatment of these stones.

1.3.4 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 [90]. They are generally in good condition.

1.4 SCORIA

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

1.4.1 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 [91] was 25% and water absorption was 12%, while the 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 from 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 1920s: 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, the churches were treated with a tetraethyl orthosilicate consolidant by Lewin [92].

1.5 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 grey, green, or red. Phenocrysts of light-coloured sodic plagioclase and dark-coloured biotite, hornblende and pyroxene are common. The rock is named from the Andes Mountains, where it is common.

1.5.1 Borobudur

This world-famous Buddhist monument was erected in central Java around AD 800. While the rock is most often referred to as an andesite and is included in the andesite section here, its composition is actually intermediate 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 [93] and begun in 1973, with an entire issue of *Studies in Conservation* devoted to the subject [94; 95; 96]. 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 artificial mound that had been weakened by infiltrating rainwater [97]. In order to carry out structural repairs, the bulk of the monument was disassembled [94; 95], and a new drainage system and concrete supports were installed. Thorough study of the stone and its deterioration were carried out prior to treatment [98; 99; 100]. 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 [98; 101]. Salts from old cements have also caused damage through deposition and efflorescence [99]. An excellent account of the historical documentation, including many direct quotations about past treatments of the monument, is given in one of the articles [98]. 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) [95; 99]. Crustaceous lichens were to be removed with a mixture of *AB 57* and clay. It was later reported that *Hyamine 3500* had been used to prevent the regrowth of algae and protolichens [101]. A 1% solution of *Hyvar X-L* had been used to eradicate and prevent the growth of mosses.

1.5.2 Greece and Egypt

In the ancient world, rocks now known as green antique porphyry and red antique porphyry were highly prized. The term porphyry comes from Mount Porphyrites 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 colour and was designated an imperial stone, used in Rome from the first century BC [20]. 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 [102]. 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* in Italian. The stone was used in Rome from the first century AD [20]. It is one of the stones used in Venice, and is considered one of the most resistant to weathering and air pollution, and in most cases it is shiny and perfectly preserved [102]. In only a very few instances has a partial, superficial fading been found.

1.5.3 Central America

Andesite was used for the colossal Olmec heads at San Lorenzo, La Venta, Laguna de los Cerros, and Tres Zapotes in Mexico [103]. 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 between AD 400 and 800, was built of a greenish andesite [104; 105]. 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 an abundant microflora. Particular concern about the deterioration of the hieroglyphic staircase is reported. The staircase is currently covered with a tent [106]. Tests with commercial ethyl silicates as consolidants were started in 1985. In January 1977 removal of biological material was carried out with *Clorox* (commercial hypochlorite bleach), diluted 1:5 in water, followed by sodium perborate (5% aqueous solution) a day later [107]. 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 [105].

Andesite is identified as the stone used for the staircases and patio floors at Templo Mayor in Mexico City [76], as well as for sculptures from Tenochtitlan, such as the colossal Jaguar prominently displayed in the Museo Nacional de Antropologia in Mexico City [90]. Most of the Aztec andesite sculptures are covered or have been moved indoors since excavation, and they are in good condition.

1.5.4 Armenia

Andesite from Khendzorout and Kapoutan in Armenia has been studied in the laboratory [47; 48]. Deterioration near soil level caused by 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.

1.6 DACITE

Dacite (>63% silica) has the same general composition as andesite, but with less calcic plagioclase and more quartz.

1.6.1 Armenia

Dacite from Karnout in Armenia has been studied in the laboratory [47; 48]. Salt damage is noted on a temple at Karnout.

1.7 RHYOLITE

Rhyolite is an acid rock (>66% silica) and is characteristically white, grey, or pink. It commonly contains a few phenocrysts, typically of quartz and alkali feldspar, in a glassy to cryptocrystalline groundmass.

1.7.1 Quirigua, Guatemala

At the humid, lowland site of Quirigua, different types of biological growth found on altars and stelae made of both sandstone and rhyolite [107] have been identified. A programme 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 [108; 109]. The sculptures are currently protected from rainfall by thatched roofing.

1.8 TRACHYTE

Trachyte (>58% silica) is a light-coloured, intermediate-to-acidic rock which contains potassium feldspar and minor mafic minerals (biotite, hornblende or pyroxene) as the main components.

1.8.1 Europe

Trachytes, from Drachenfels/Siebengebirge and from Stenzelberg (Berkum and Wolkenburg), were used during the early stages of construction of the Cathedral of Cologne [88; 89]. 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 [110].

A local trachyte from the Euganean Hills was used as a building material in Venice from the tenth to thirteenth centuries [111]. It was used as a damp-proof course in the city, and it is still quarried today. Epoxy resin (*EP 2101*) consolidation of a lion sculpture in Padua, made of Euganean trachyte, is reported [24].

1.9 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 crustaceous 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.

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APPENDIX - MATERIALS

The following list of products mentioned in the text gives (in parentheses) the company name 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 also been listed.

AB 57: a mixture of ammonium bicarbonate, sodium bicarbonate, di-sodium EDTA, *Desogen*, and carboxymethylcellulose.

Araldite CY 230 & Epomait B-002 (Ciba-Geigy): epoxy resin and hardener, used at 25% in toluene.

Araldite XG 40 & XG 41 (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 [Commercial household bleach.]

Conservare H: see *Wacker H.*

Conservare OH: see *Wacker OH.*

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].

Dry Film 104 Silicone Resin (General Electric): a polyalkal(methyl)siloxane resin, 70% in mineral spirits.

Elastosil E 41 (Wacker-Chemie): a silicone-rubber water repellent.

EP 2101 and *K 2102*: 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 AC-33 (Rohm & Haas): aqueous acrylic resin emulsion.

Product 460: a siliconate-acrylic copolymer in water.

Rhodorsil XR-893 (Rhône Poulenc): a partially condensed polymethyl(phenyl)-siloxane, used with toluene (final solution 15% solids).

Rhodorsil 10336 (Rhône 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% solids).

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 (Wacker-Chemie): tetraethyl orthosilicate monomers and dimers, 75% in methylethylketone, acetone, and dibutyltindilaurate.

Wacker H (Wacker-Chemie): tetraethyl orthosilicate and methyl(triethoxy)silane.

Wacker 090 (Wacker-Chemie): an oligomeric alkylalkoxysiloxane mixture. [Version *090 L* = concentrated; *090 S* = ready to use]

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 tratamineto utilizado más frequentemente, pero poco se sabe de su eficacia a largo plazo. Los monumentos tallados *in situ* presentan problemas particularmente difíciles.

RESUME

Un examen de la bibliographie montre que l'étude de la conservation des oeuvres en pierre volcanique s'est concentrée sur les tufs, lesquels présentent importantes détériorations. Les autres roches volcaniques utilisées dans les monuments ou les sculptures sont le basalte, la scorie, l'andésite, la dacite, la rhyolite et la trachyte. Parmi les exemples importants figurent les statues de l'Ile de Pâques, le temple bouddhiste de Borobodur, les églises de Göreme et Lalibela, les bouddhas taillés dans la roche au Japon et les cavernes du plateau du Deccan en Inde. L'application de consolidants a été le traitement le plus fréquemment testé mais son efficacité à long terme est mal connue. Les monuments taillés *in situ* présentent des problèmes particulièrement difficiles à traiter.

KURZFASSUNG

Eine Literaturrecherche zeigt, daß sich Konservierungsstudien an vulkanischen Gesteinen hauptsächlich auf Tuffe konzentrieren, die die schwerwiegensten Schäden aufweisen. Andere Vulkangesteine mit bildhauerischer Verwendung sind Basalt, Gesteinsschlacken, Andesit, Dazit, Rhyolith und Trachyt. Wichtige Beispiele stellen die Statuen der Osterinsel, der Buddhistische Schrein in Borobodur, die Kirchen in Göreme und Lalibela, die steingeschnitzten Buddhas aus Japan und die Höhlen des Deccan-Plateaus in Indien dar. Die am häufigsten getestete Behandlung ist diejenige mit Festigungsmitteln, über deren Langzeitverhalten jedoch wenig bekannt ist. Monumente, die aus dem anstehenden Gestein gearbeitet sind, stellen dabei besondere Anforderungen.

Part Two

DETERIORATION

VOLCANIC TUFFS: THE DESCRIPTION AND QUANTITATIVE RECORDING OF THEIR WEATHERED STATE

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ABSTRACT

For many centuries volcanic tuffs from western Germany have been used in the construction of important historic buildings. These have suffered severe weathering damage, calling for immediate preservation actions. The effectiveness of these actions depends on accurate knowledge of the causes and state of the damage. By mapping the building using a classification scheme of tuff weathering forms it is possible to make an objective and reproducible description of the damaged condition. The results of mapping a minster from the Middle Ages are given. 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.

2.1 INTRODUCTION

Tuffs from the Rhine area have been put to diverse uses as a natural stone for over 2 000 years. The stone has been employed in the form of bricks for masonry construction, and in large blocks for the bases of buildings. More rarely, tuffs have been used for sculptures and decorative architectural elements.

Today, Rhenish tuff no longer has great importance as a building stone. The quarries, however, are still operative and provide material for restoration work, as well as some new building. The Rhenish tuffs were used extensively 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

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buildings were constructed out of tuff. Most of these buildings are at present in poor condition, requiring prompt preservation measures. The effectiveness of such measures depends in the first place on having information on the relevant rock properties.

The results of systematic work on tuff buildings – known as building mapping – are presented. In this work the visible weathered condition of the stone is recorded quantitatively, and the most important characteristic properties 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 on-site investigations at the buildings with results from the laboratory, conclusions can be drawn as to weathering processes and the factors that cause them.

2.2 SAMPLE MATERIAL

The Quaternary Rhenish tuffs [1] occur in the Laach volcanic area, west of Koblenz on the Rhine. Various phases of volcanic activity can be identified 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 three petrographical types:

- coarse-grained Selbergittuffs
- fine-grained Selbergittuffs, and
- 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 regions mentioned above. Studies were also carried out at many historic buildings constructed with tuff 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 characteristic petrographical 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.

2.3 METHODOLOGY

In order to be able to characterize, in a reproducible manner, the state of damage of stone-built historic buildings according to phenomenological criteria, investigations were carried out at the building [2]. This allowed a facade map to be constructed of the natural stone varieties used for the building, and the damage suffered by them.

As a first step, all natural stones in the building were noted and documented. They were differentiated according to standard petrographical classification schemes. Next, the distribution was mapped of the natural stone varieties identified in the masonry. Lithological mapping such as this provides an overview of the natural stones used in the building.

In the second stage, the apparent weathering forms on all accessible areas of the building were registered photographically and described in detail. Such documentation allows an exact comparison of weathering forms at one site with those already registered at other monuments, all of which are continuously catalogued using photographs 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 followed as the next step. The results of both the lithological mapping and the mapping of the weathering forms were either recorded on large photographs or on existing building plans. The nature and accessibility of the buildings, as well as the purpose of the study, determine the degree of precision of the mapping. For instance, only the main weathering forms were recorded during cursory mapping. In contrast, during the detailed mapping, all of the information on each stone was recorded on a stone-by-stone basis. Additionally, the dominant weathering forms were recorded, using the criteria of type, extent and intensity.

The aim of the petrological investigations was to record the mineral composition and porosity characteristics of the various 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 were recorded. X-ray diffraction investigations provided 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 was investigated. Microscopy is used to directly record pores with a radius between 3 μm and 1 000 μm. Mercury porosimetry facilitates the calculation of pore throat radii between 0.0019 μm and 250 μm and additional porosity values.

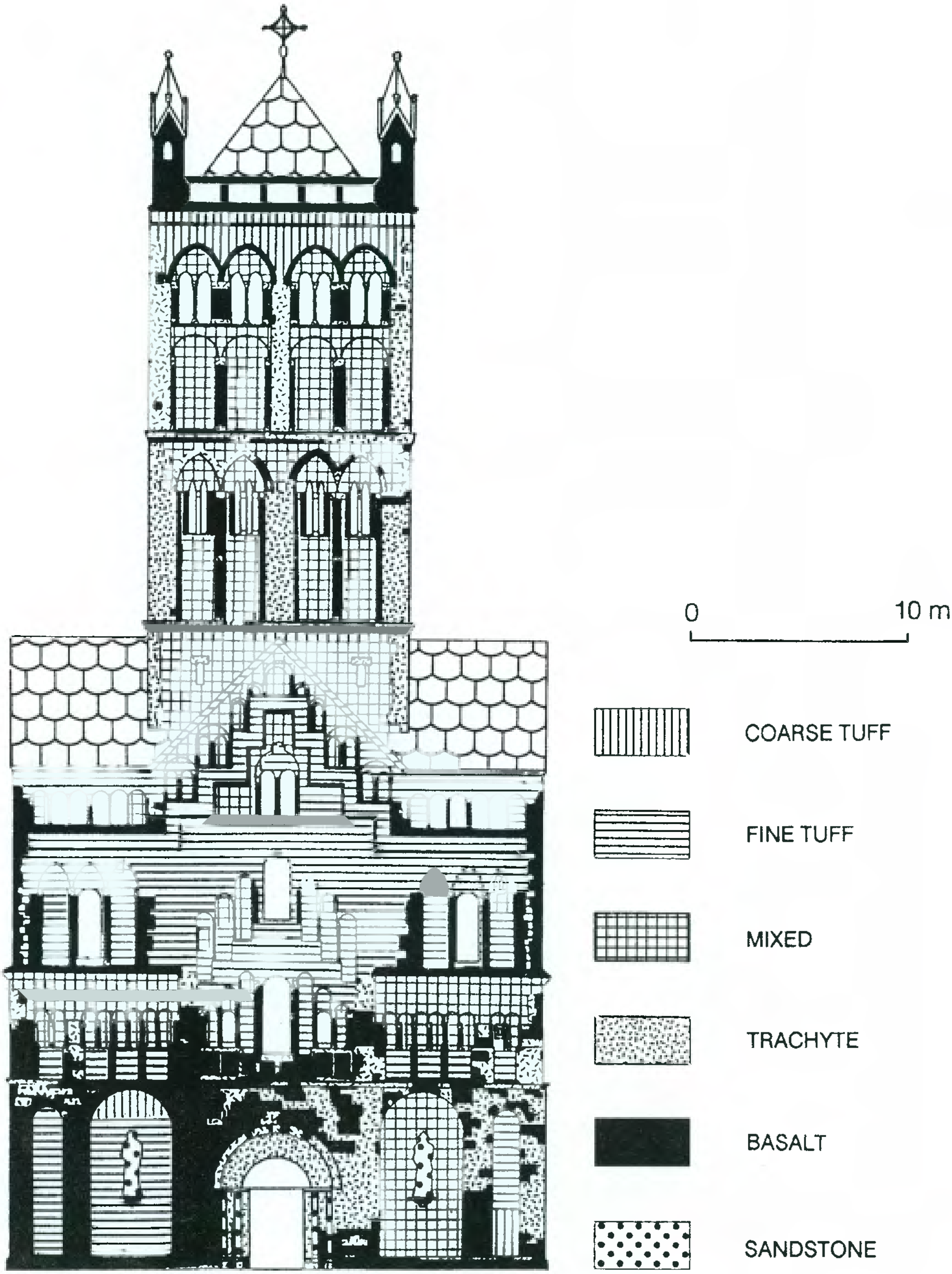

Figure 2.1 **Lithological mapping.**
West facade of the St. Quirinus Minster, Neuss.

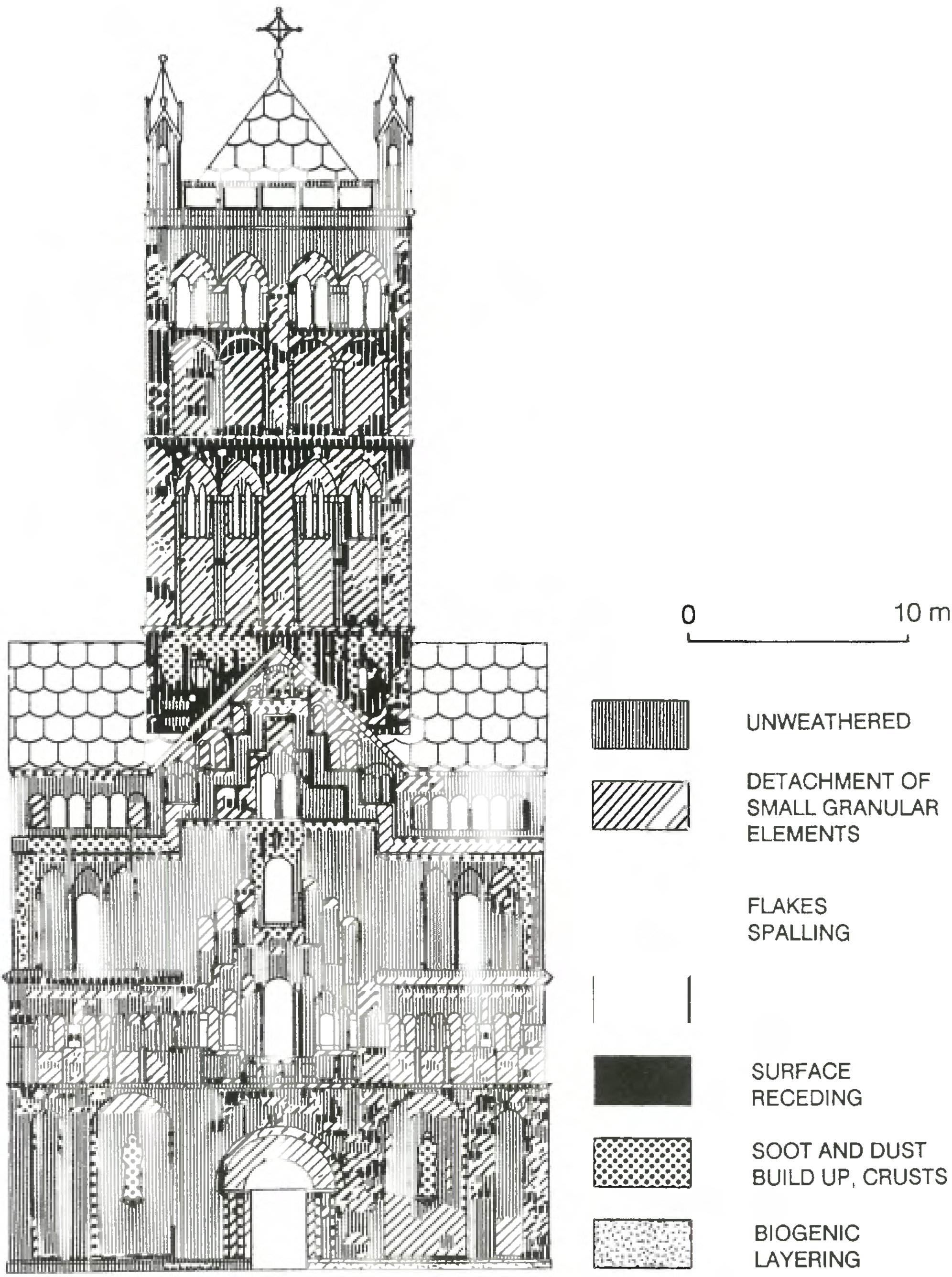

Figure 2.2 Mapping of weathering forms.
West facade of the St. Quirinus Minster, Neuss.

The influence of combined weathering factors on the texture of the Rhenish tuffs was investigated using freeze/thaw cycling and salt crystallization tests [5; 6]. SO_2-weathering experiments provided information about the ability of the tuff to form gypsum.

In order to prove the efficacy of a silicic ester-based consolidating agent, tuff samples were impregnated. The porosity modification due to deposition of silica gel in the pore space was measured using mercury porosimetry.

2.4 RESULTS AND DISCUSSION

2.4.1 Building Mapping

An important first step towards comprehending the complex process of weathering is the exact documentation and evaluation of the material condition of the historic 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; and
- measuring and sampling of 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, second, 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 thirteenth 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 2.1. According to this lithological mapping, more than 95% of the facade is of volcanic rock: 65% constructed out of the Roman and Weiberner tuffs, and some 30% 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 lithological mapping thus documents 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 and collated, and this constitutes the basis for a classification scheme, which facilitates mapping with great accuracy.

Table 2.1 Classification scheme for the weathering forms of Rhenish tuffs

MAIN WEATHERING FORMS	CATEGORY OF DAMAGE
UNWEATHERED	No damage
Stone surface completely intact	1
Some detachments of small components,	1–
DETACHMENT OF SMALL GRANULAR ELEMENTS	Slight damage
Detachment to 5 mm depth over <50% of stone surface	2+
Detachment to 5 mm depth over >50% of stone surface	2
Detachment to >5 mm depth, surface begins to recede	2–
FLAKES, SPALLING	Moderate damage
Loosening to 10 mm depth over <50% of stone surface	3+
Loosening to 10 mm depth over >50% of stone surface	3
Loosening to >10 mm depth, surface starts to recede	3–
SCALES	Severe damage
Scales >20 mm depth over <50% of stone surface	4+
Scales >20 mm depth over >50% of stone surface	4
Scales >20 mm depth, surface starts to recede	4–
SURFACE RECESSION	Very severe damage
Surface receding to 10 mm over >50% of stone surface	5+
Surface receding to >10 mm over >50% of stone surface	5
SEPARATE WEATHERING FORMS	
SOOT AND DUST BUILDUP	1–
BIOGENIC LAYERING	2
(mosses, lichens, algae and 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
DETACHMENTS	4 - 5
Small detachments	4
Large detachments	5

The classification scheme (Table 2.1) 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 deterioration. 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 can be attributed to mechanical stress. The separate weathering forms, some of which are further differentiated according to intensity of attack, 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 2.1. The distribution of weathering forms observed on the west facade of the Minster is shown in Figure 2.2. 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 that 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 any programme of continuous long-term monitoring of a building.

2.4.2 Petrographical Studies

The different tuffs from the Rhine area [1] and also the Easter Island sample [7] can be petrographically categorized into four tuff types. The analysis of one important variety of each of these four types is presented in Table 2.2. The characteristic values for the three Rhenish tuff varieties are for unweathered material. The Easter Island sample shows clear signs of weathering.

All the tuff varieties display a cryptocrystalline to vitreous and porous matrix consisting for the most part of volcanic glass, and to a lesser degree of clay minerals and chlorite. The three Rhenish tuffs also 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 characterized 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 as 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

Table 2.2 Petrographic composition and porosity values of the tuff varieties

	SELBERGITTUFF		TRACHYTIC TUFF	TACHYLITIC TUFF
Tuff type and variety	Ettringer (Coarse-grained)	Weiberner (Fine-grained)	Roman	Easter Island
Components (% by volume)				
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.
Other	—	0.1	0.1	—
Predominant zeolite type	Phillipsite	Analcite	Analcite/ Chabazite	—
Porosity analyses				
Bulk density (g/cm^3)*	1.66	1.32	1.35	1.48
Density (g/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/g)**	19.95	8.94	5.32	34.02

* mercury porosimetry ** nitrogen adsorption method

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, with an irregular distribution.

All of these tuffs show a very high total porosity – between 30% and 50% by volume – and a wide spectrum of pore radii, between 0.002 μm and 1 000 μm. When the results from mercury porosimetry (Figure 2.3) are compared with porosity measurements obtained from microscopy image analysis (Figure 2.4), 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 account for 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

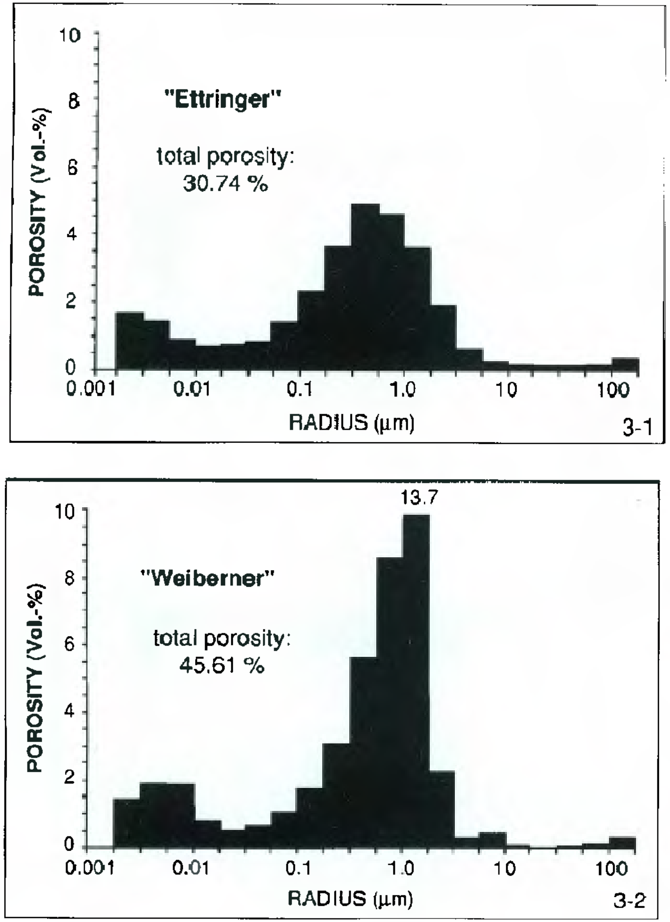

Figure 2.3 Pore radius distribution - mercury porosimetry.

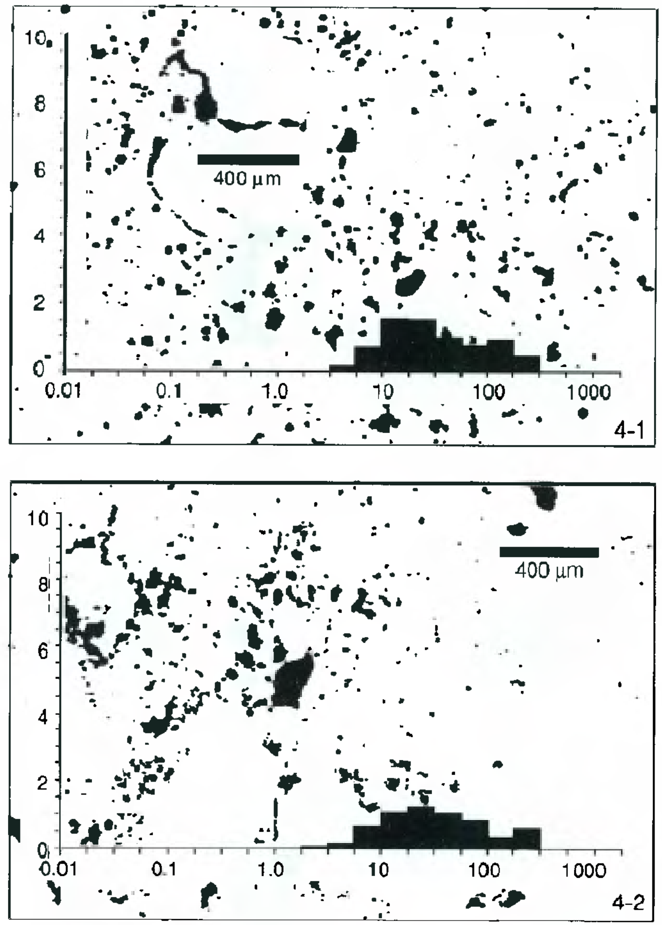

Figure 2.4 Computer enhanced images of macropores and pore radius distribution – image analysis.

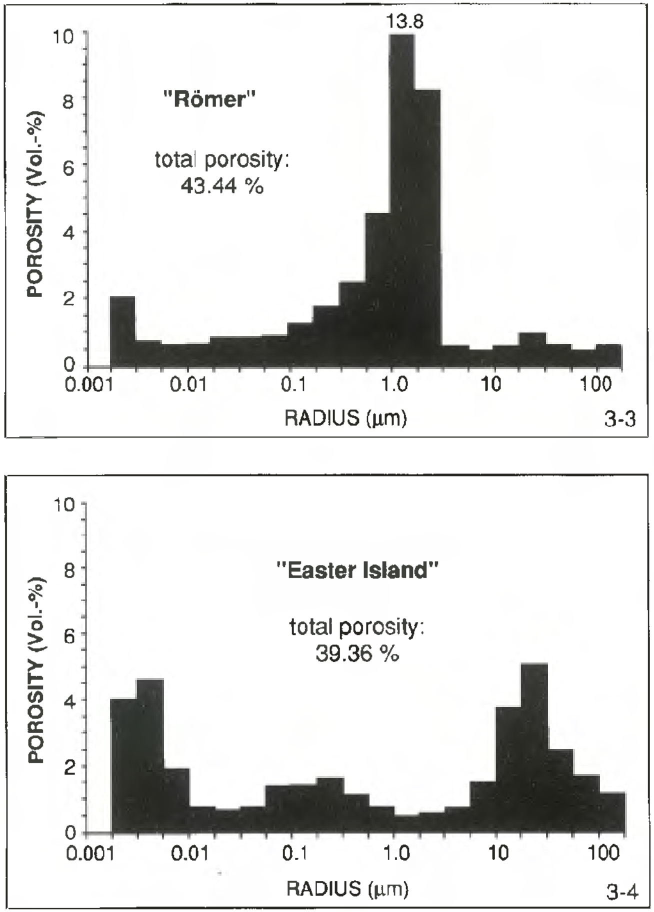

Figure 2.3 (cont.) Pore radius distribution - mercury porosimetry.

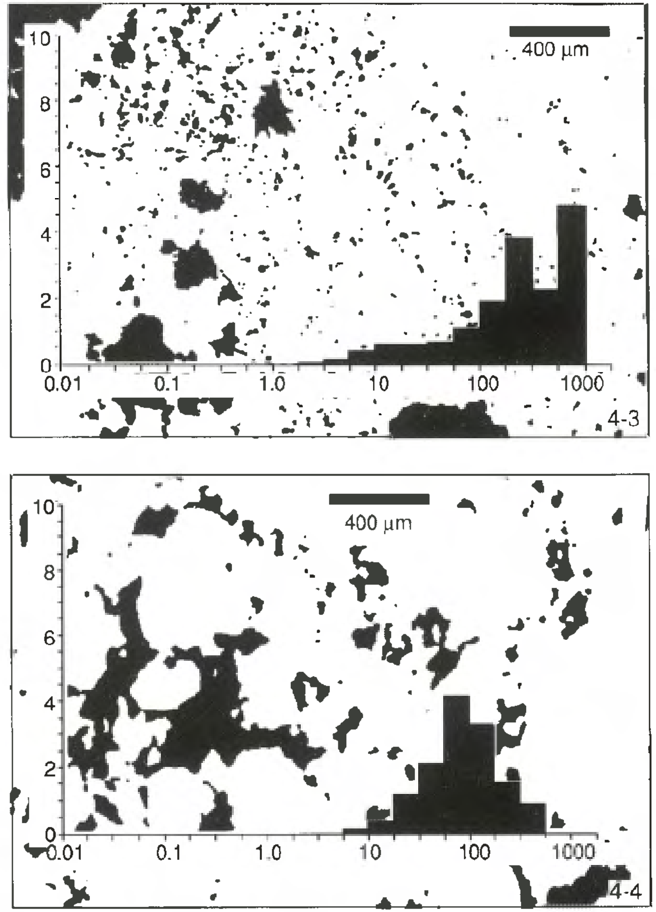

Figure 2.4 (cont.) Computer enhanced images of macropores and pore radius distribution – image analysis.

WEATHERING PROFILE - WEIBERNER TUFF

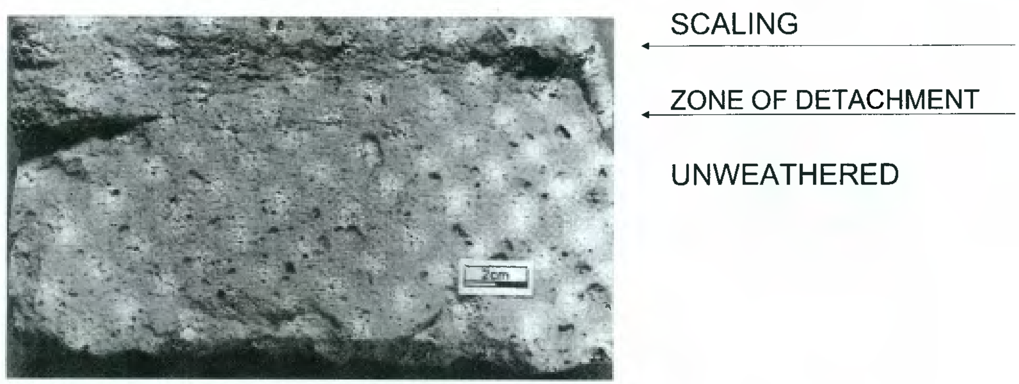

Figure 2.5 Weathering profile - Weiberner tuff.

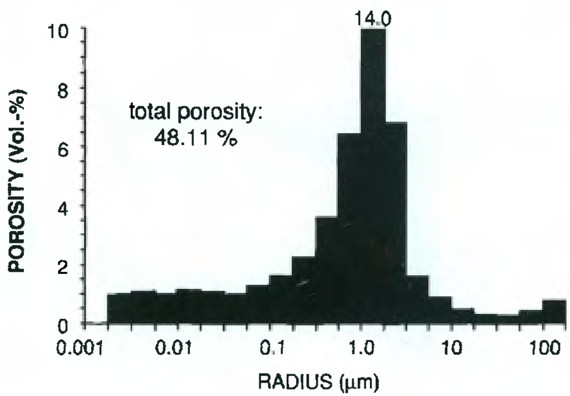

Figure 2.6 Pore radius distribution - mercury porosimetry.

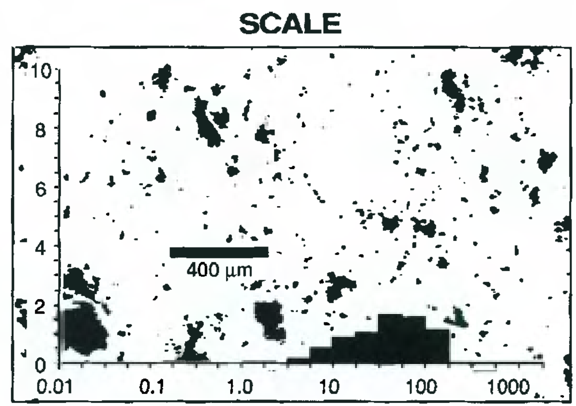

Figure 2.7 Computer enhanced images of macropores and pore radius distribution – image analysis.

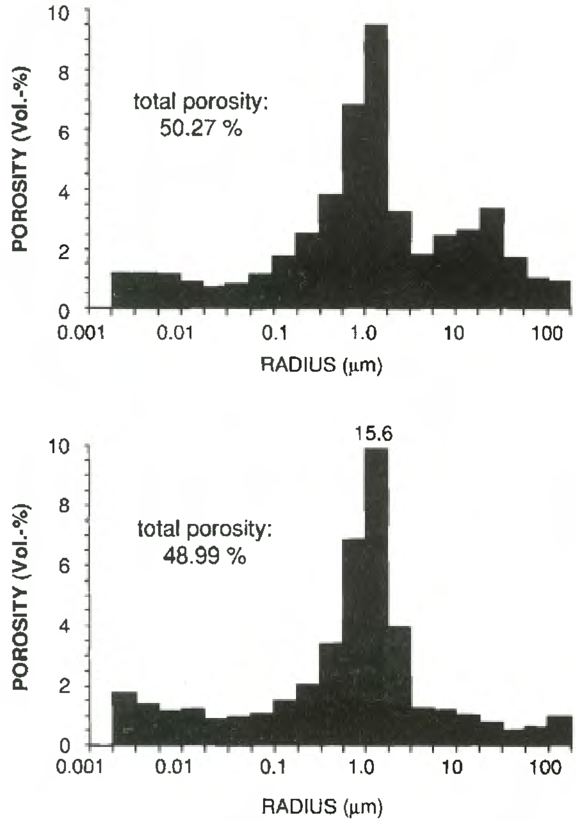

Figure 2.6 (cont.) Pore radius distribution - mercury porosimetry.

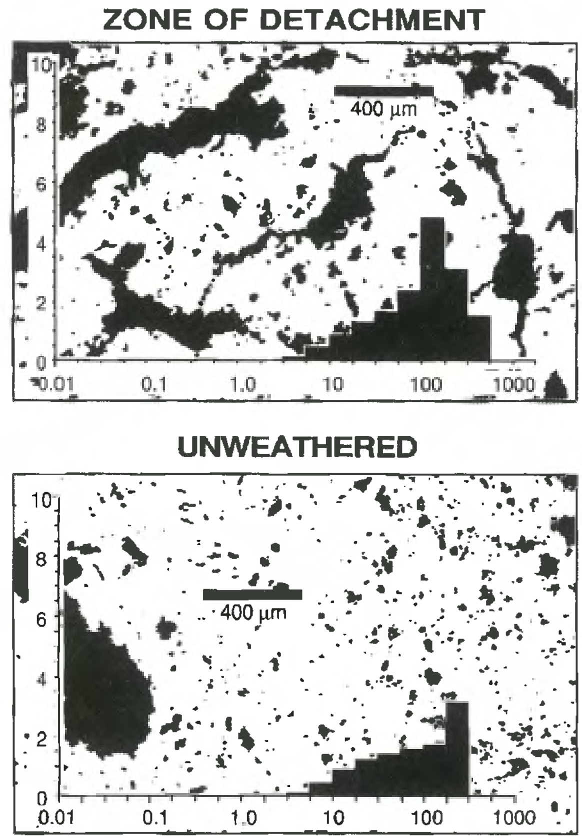

Figure 2.7 (cont.) Computer enhanced images of macropores and pore radius distribution – image analysis.

DIFFERENCE PORE RADIUS DISTRIBUTION

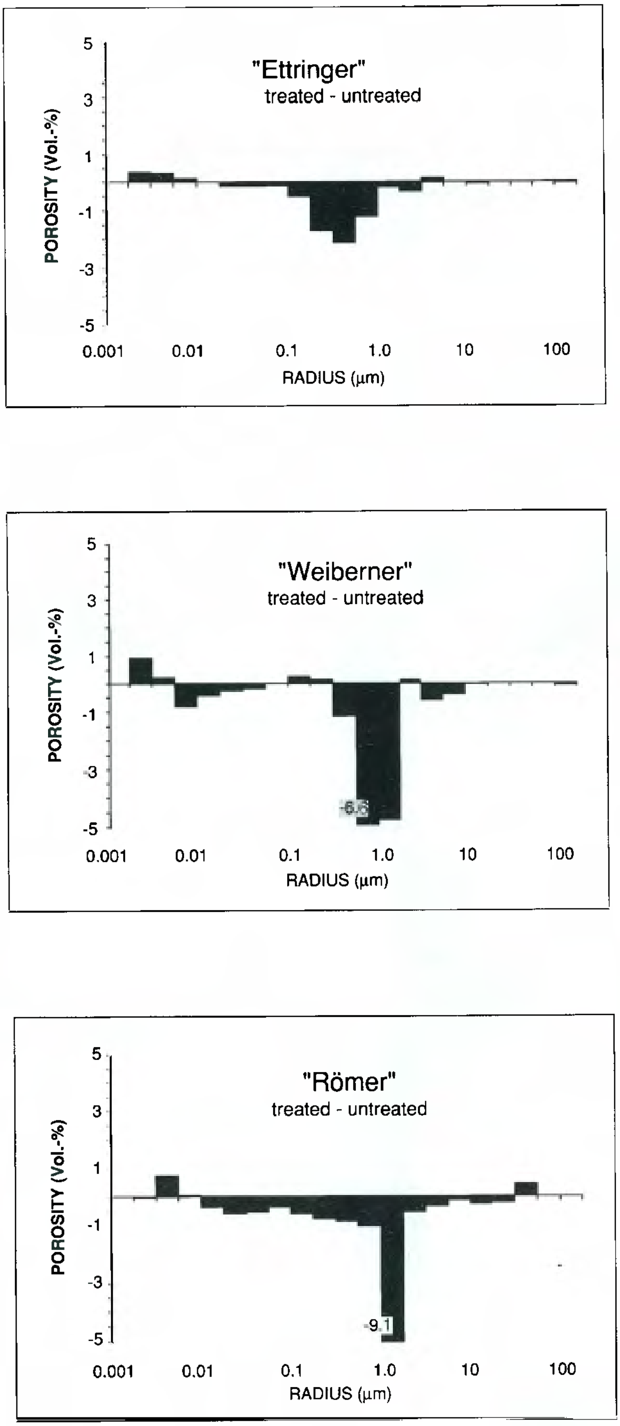

Figure 2.8 **Changes in pore radius distribution after deposition of silica gel.**

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 of this tuff type.

The weathering forms discussed in Section 2.4.1 are controlled by material and structural changes. As a result of these different changes, weathering profiles develop.

One of the main weathering forms which commonly occurs with tuffs is scaling. Scales are layers of stone, several millimetres to centimetres 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 zone of detachment – which can be a few millimetres to centimetres thick – displays severe textural destruction. A sequence of three porosity distributions – shown in Figures 2.6 and 2.7 – was determined in the weathering profile of the Weiberner tuff illustrated in Figure 2.5. The succession of unweathered rock, zone of detachment and scaling corresponds to the spatial succession from the unweathered interior to the exposed surface of a building stone from an historic building. There is a clear increase in the proportion of large pores in the zone of detachment. This displacement of the pore radius spectrum in favour of large pores is related to the formation of fractured pores running parallel and perpendicular to the rock surface in the zone of detachment. The 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.

2.4.3 Laboratory Investigations

Weathering simulation under laboratory conditions provides a further opportunity to observe and analyse the development of damage. The important natural processes of freeze/thaw cycles, salt crystallization and the influence of pollutants were reproduced on a laboratory scale. Additionally, the efficiency of a consolidating agent was studied. The test conditions applied in the four trials were as follows:

- **Frost resistance test** – following DIN 52104 standard procedure [5]
  Samples: 5 samples, each a regular cube of 5 × 5 × 5 cm.
  Preparation: samples dried at 105±5°C to constant weight, and then allowed to cool to room temperature.
  Test procedure: samples are saturated with water at 150 bar; test cycles consist of 6 hours freezing at −25±2°C and 6 hours thawing at +25±2°C in water.
  Number of cycles: maximum 100 cycles.
  Apparatus: climatic chamber (Hereus-Vötsch, model VUK 04/500).

Control measurements: visual examination and photographic documentation; loss of weight; ultrasonic velocity.

- **Salt crystallization test** – following DIN 52111 standard procedure [6]
  Samples: 5 samples, each a regular cube of 5 × 5 × 5 cm.
  Preparation: samples dried at 105±5°C to constant weight, and then allowed to cool to 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: maximum 20 cycles.
  Control measurements: visual examination and photographic documentation; loss of weight; ultrasonic velocity.
- **SO_2 test** – following DIN 50018 standard procedure [8]
  Samples: 5 samples, each 2 × 3 × 0.5 cm; 5 powder samples.
  Preparation: samples dried at 105±5°C to constant weight, and then allowed to cool to room temperature; preparation of powder samples.
  Test procedure: 8 hours in atmosphere of 100% RH at 35±2°C, with 2 000 ppm SO_2; 16 hours cooling to ambient temperature and atmosphere.
  Number of cycles: maximum 20 cycles.
  Apparatus: Kesternich chamber.
  Control measurements: visual examination and photographic documentation; X-ray diffraction; scanning electron microscopy (SEM).
- **Impregnation** with a consolidating agent
  Samples (5 × 5 × 5 cm) were impregnated three times by a single component system – a commercial product – based on a silicic acid ester. The impregnation cycles consisted of three immersions for 1 minute, followed by drying to constant weight under ambient temperature and humidity conditions. Control measurements were carried out using mercury porosimetry.

The weathering forms of the tuffs which developed as a result of the laboratory freeze/thaw experiments are similar to those observed at the building. In principle, all tuff varieties can be said to be susceptible to freeze/thaw stress. The stability of the tuff types in relation to such stress form a series: trachytic tuffs are more stable than the fine-grained Selbergittuffs, which in turn are more stable than the 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 show a very slight variation in their resistance to salt wedging forces, but they are all severely damaged in a relatively short time.

In the next test, different tuff varieties were exposed to a water-saturated atmosphere containing SO_2. After only a short time under experimental conditions, newly-formed gypsum could be detected on all tuff varieties. Gypsum formation such as this, which is also observed on the buildings, constitutes a chemical alteration within the rock, which in turn contributes to mechanical destruction of the rock texture.

In the last series of tests, a silicic-ester-based consolidating agent was introduced into the pore space, which could be quantitatively measured and studied. In all tuff varieties a considerable reduction of the entire porosity occurs on impregnation. The modification of the pore radii by the deposition of the gel-like silica is illustrated with a difference histogram (Figure 2.8) of treated sample minus untreated sample. Only the volumes are illustrated, as being either eliminated (minus porosity) or newly created (plus porosity) by the gel-like silica deposits. Plus porosity arises when only large pores are partly filled with this material. This produces additional small-dimensioned pores, which are added to the existing small pores.

An 18% reduction in pore space occurs in the Ettringer tuff. The deposition of silica occurs mainly in pores in the radius range of 0.1 μm to 1.0 μm. In the Weiberner and Roman tuffs, 32% of the pore space is filled with this material. In both of these varieties there is also a reduction of porosity within the range of the maximum pore radius distribution, i.e., those in the range of 0.1-10.0 μm. Pore spaces with radii <0.01 μm are not reduced by deposition, but the volumes remain constant or increase due to the reduction of the large pores.

2.5 CONCLUSIONS

In order to be able to quantitatively record the weathered state of a stone-built historic monument, both accurate investigations at the building and diverse laboratory work are necessary. On-site work includes registering and mapping the type of building stones and their state of weathering. As a rule, 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. The scheme covered all the weathering forms specific to tuffs. These different weathering forms were assigned to five damage categories so as 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 could also be used to ensure that sampling, taking of measurements and long-term monitoring of a building could all be carried out in the most efficient manner possible.

The heterogeneous petrographical composition of the tuffs is an important reason for the very variable weathering behaviour of these rocks. The chaotic pore structure, as shown by the extremely high total porosity and 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 investigations using microscopic image analysis 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 cycles 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, as, based on the analysis of tuffs with different porosity distributions, it could be established that most silica gel deposition always takes place within the range of maximum porosity.

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RESUMEN

Las tobas volcánicas de Alemania occidental 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 la representación gráfica de un esquema de clasificación de formas de deterioro de las tobas sobre un levantamiento del edificio fue posible realizar una descripción objetiva y reproducible de los daños. Se presenta tal representación gráfica de una catedral medieval. Tambien se dan los valores característicos relevantes al deterioro de tobas renanas y de una toba de Isla de Pascua. 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.

RESUME

Depuis des siècles, les tufs volcaniques de l'ouest de l'Allemagne ont servi à la construction d'importants édifices historiques. Gravement endommagés par les intempéries, ils nécessitent des actions de préservation immédiates. L'efficacité de ces actions dépend de la connaissance précise des causes et de l'ampleur des dégâts. En appliquant au relevé d'un bâtiment une échelle de classification des formes d'altération des tufs, on peut obtenir une description objective et reproductible des détériorations. Les résultats du relevé d'une cathédrale médiévale sont présentés. Les valeurs caractéristiques relatives à l'altération sont également décrites pour des tufs rhénans et un tuf de l'Ile de Pâques. Le comportement des tufs est examiné à l'appui de tests de laboratoire. L'analyse porosimétrique constitue une méthode utile d'évaluation de l'état d'altération.

KURZFASSUNG

Tuffe aus dem westlichen Deutschland werden seit vielen Jahrhunderten für die Errichtung bedeutender historischer Bauwerke genutzt. Starke Verwitterungsschäden an diesen Bauwerken machen Schutzmaßnahmen dringend erforderlich. Die Wirksamkeit dieser Maßnahmen ist abhängig von genauen Kenntnissen des Schadenszustands und der Ursachen.

Eine Bauwerkskartierung auf der Grundlage eines Klassifikationsschemas von Tuff-Verwitterungsformen erlaubt eine objektive und reproduzierbare Zustandsbeschreibung. Die Ergebnisse der Kartierung eines mittelalterlichen Münsters werden gezeigt. Weiterhin werden verwitterungsrelevante Kennwerte rheinischer Tuffe und eines Osterinsel-Tuffs vorgestellt und das Verhalten von Tuffen in Labortests diskutiert. Porenraumanalysen stellen dabei eine wichtige Methode zur Erfassung des Verwitterungszustandes dar.

STUDY OF THE DETERIORATION OF VOLCANIC ROCKS FROM EGYPT

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ABSTRACT

Deterioration of some volcanic rocks from Egypt was investigated by X-ray diffraction, atomic absorption and thin-section analyses and scanning electron microscopy. The mechanisms of deterioration due to the role of the 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.

3.1 INTRODUCTION

Volcanic rocks are formed by solidification of magmas on the surface of the earth's crust and they may comprise both crystalline and glassy phases.

Since Neolithic times, and continuing through the Pre-dynastic and Dynastic periods, ancient Egyptians used volcanic rocks such as basalt, andesite, obsidian, porphyrites and tuffs. Basalts were widely used in making vessels, sarcophagi and statues, and for construction in parts of temples and in the paving of the roads to them. Andesite was used for working hard stone, and remains of such andesite tools were found in old quarries of granite in Aswan and of quartzite in Gebel-El Ahmer. Obsidian was well known for the manufacture of weapons, spear-heads, amulets, beads, scarabs, eyes of statues, small vessels and sarcophagi. All these volcanic stones occur as outcrops in Egypt: in the Eastern Desert, Fayoum, Aswan and Sinai [1].

The aim of the present work is to study the deterioration mechanisms that weather volcanic rocks naturally, and to use artificial ageing techniques in order to suggest suitable materials for the conservation of such volcanic rocks.

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3.2 EXPERIMENTAL DETAILS

3.2.1 Samples

Eight different volcanic rocks from Egypt were investigated: basalt, andesite, pyroclastic tuff, pumice, green tuff, obsidian, rhyolite and greyish-black tuff. All of these samples were obtained from the Geological Museum in Cairo, and originated from six different localities: four in the Eastern desert, one from Sinai and one from Aswan.

Two weathered samples of basalt taken from the Ne-Weser-Rah Temple (5^{th} Dynasty) at Abu-Sir were also studied.

3.2.2 X-ray powder diffraction analysis (XRD)

The samples were ground in an agate mortar to a fine powder, pressed into the specimen holder, and mounted in a Philips X-ray diffractometer. They were analysed using CuK radiation (1.5418 Å) with a Ni filter, at 40 kV and 20 mA.

3.2.3 Thin section analysis

The volcanic rock samples were sectioned and mounted on microscope slides. The structure and mineralogy of each rock were identified using a Leitz polarizing microscope.

3.2.4 Atomic absorption analysis

The analysis was carried out on the leaching water obtained by immersion of obsidian cubic samples in de-ionized water for two months. The concentrations of Na, K, Fe, Mg and Ca ions were measured.

3.2.5 Artificial Weathering

The rock samples were cut into small cubes (3 × 3 × 3 cm) and dried to constant weight in an oven at 105°C. The weathering cycles consisted of a 4-hour immersion in distilled water at 65°C in a covered beaker; 4 hours drying at 65°C; a 12-hour exposure to UV radiation (254 nm); and 4 hours at room temperature.

After 420 hours the UV exposure was replaced by immersion in distilled water. The ageing lasted for 60 cycles in all.

3.2.6 Scanning electron microscopy (SEM))

SEM examination was carried out on four rock samples which showed visual alteration after artificial weathering. These were the basalt, obsidian, rhyolite and greyish-black tuff. The specimens were attached to the stubs by silver paint, and gold coated.

3.3 RESULTS

3.3.1 Basalts

The sample of sound basalt had a fine-grained texture and was black in colour. XRD showed the presence of augite, anorthite and grunerite. The presence of this last mineral was confirmed through thin section analysis.

The weathered samples from the Ne-Weser-Rah Temple at Abu-Sir were pale grey in colour and very friable, quite distinct from the underlying sound stone. These samples showed only the presence of augite and anorthite. This was confirmed through thin section analysis, which showed augite crystals in a matrix of calcic plagioclase feldspars.

After artificial ageing, the surface of the basalt cube became pitted, with reddish-brown material filling these pits. The material was identified as hematite and goethite.

SEM examination of the artificially aged sample showed the formation of cracks and pits, and alteration of the constituent minerals. This is shown in Figure 3.1.

3.3.2 Andesite

The andesite sample was black in colour, with very fine, white grains. XRD showed the presence of oligoclase, augite, grunerite and traces of kaolinite. Thin section analysis showed clarified large crystals of the plagioclase feldspar in a matrix of ferromagnetic minerals.

The artificial ageing process caused no visible surface alteration: it was still smooth, without pits or change in colour.

3.3.3 Pyroclastic Tuff

This tuff was greyish black in colour with a smooth surface. XRD showed the presence of quartz, andesine, with traces of kaolinite. Thin section analysis showed fine crystals of quartz and plagioclase feldspar, with some alterations to clay minerals.

The artificial ageing regime did not appear to affect this tuff.

3.3.4 Pumice

The pumice was grey in colour and with typical froth-like appearance. XRD showed it to be essentially amorphous, with only very small peaks for microcrystalline quartz and feldspar minerals. Thin section analysis showed the characteristic texture of this rock – vesicular in a glassy matrix.

The artificial ageing regime led to the appearance at the surface of a brownish material consisting of iron oxides.

Figure 3.1 SEM photomicrograph of basalt after artificial ageing, showing cracks, pits and the alteration of the surface minerals (× 2000).

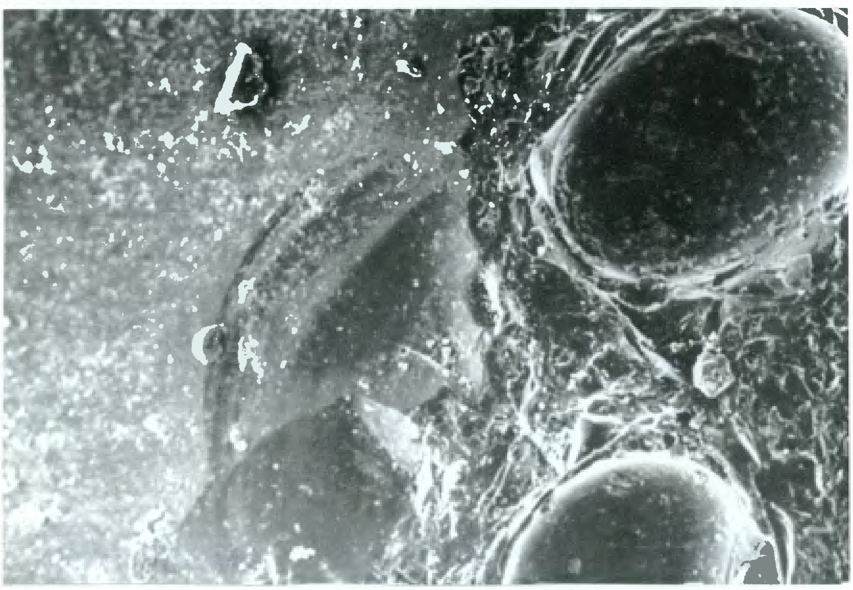

Figure 3.2 SEM photomicrograph of obsidian after artificial ageing, showing disintegration and alteration occurring around cavities and holes (× 200).

Figure 3.3 SEM photomicrograph of rhyolite after artificial ageing, showing alteration and disintegration of minerals at the surface (× 2000).

Figure 3.4 SEM photomicrograph of greyish-black tuff after artificial ageing, showing disintegration of the minerals at the surface (× 1000).

3.3.5 Green Tuff

This tuff was pale green in colour, with a banded structure. XRD showed the presence of quartz, sepiolite, kaolinite and traces of biotite and muscovite. Thin section analysis revealed fine crystals of quartz and sepiolite in a ground mass of micas, biotite and muscovite.

Artificial weathering of this tuff resulted in a slight change in colour, from green to pale grey, and the appearance of very fine fissures.

3.3.6 Obsidian

This was a black rock of glassy appearance and very smooth surface. XRD showed it to be mainly a glassy material with a few small peaks indicating the presence of minor microcrystalline phases. This was confirmed by thin section analysis, which showed a few crystals of quartz and altered feldspars.

After artificial ageing, white and brownish-red materials appeared in the cavities and pits at the surface of the sample. On analysis, the brownish material was found to be iron oxide, and the white material sodium and calcium silicates.

Atomic absorption analysis of the water in which the samples had been immersed for two months showed the presence of 0.15 ppm Na, 0.05 ppm K, 0.15 ppm Ca, 0.05 ppm Mg and 0.25 ppm Fe in the leachate.

SEM examination of the artificially aged sample showed alteration occurring around cavities and holes, as shown in Figure 3.2.

3.3.7 Rhyolite

The sample was pale red in colour and had a fine-grained texture. XRD showed the presence of quartz, sanidine and albite. Thin section analysis showed the quartz and the potash feldspar minerals to have a spherulitic texture characteristic of acidic volcanic rocks.

After artificial ageing the sample changed in colour from pale red to beige.

SEM examination of the artificially aged sample showed alteration and disintegration of the constituent minerals, as shown in Figure 3.3.

3.3.8 Greyish-black tuff

The sample had a banded structure, with the black parts having a glassy appearance. XRD of the whitish-grey parts showed the presence of α-cristobalite, α-quartz and trace amounts of β-quartz. The grey portion of this tuff showed the presence of quartz and anorthoclase, while the black parts were mostly amorphous.

After artificial ageing there was a change in colour in the greyish portion, which also developed cracks, while the black portions showed pitting.

SEM examination of the artificially aged specimen showed deterioration of the surface, the formation of pits and holes, and alteration of the surface layer. This is shown in Figure 3.4.

3.4 DISCUSSION

The weathering of volcanic rocks in Egypt is due to chemical and physical processes. The rate of these processes increases in the presence of cavities, fissures and cracks in the rocks. The volcanic tuffs have a large water content in their non-crystalline portion. The devitrification phenomenon of volcanic rocks has occurred with geological time, and led to the formation of minerals, i.e., the more stable crystalline state, and to colour changes. Devitrification of glass is very slow under normal conditions, but it may be accelerated by circulating solutions.

At the Ne-Wasar-Rah Temple at Ab-Sir, water is the dominant deterioration factor of basalt, in addition to the variation in temperature between day and night. The 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 the basalt. The chemical weathering of this stone is due to a dissolution process of the constituent silicate minerals, causing undesirable discoloration of the ferromagnesian minerals. The colour of the basalt on this temple has changed from almost black to pale brownish grey.

Exfoliation of the surface layer has occurred, due to the physical weathering process, i.e., differential thermal expansion of the constituent minerals. The exfoliation is very clear and is accompanied by the presence of brown friable material between the separating layers.

The artificial ageing of basalt carried out in the laboratory reproduced the deposition of brown material in the pits and cracks that formed on the surface of the stone.

Other deterioration mechanisms may be closely connected with the presence of microveins in the basalt's structure [2]. This is evidently compounded by the presence of soluble salts [2]. The formation of iddingsite on olivine is another deterioration process [3]. The depth of alteration has been monitored through the examination of plagioclase minerals [4].

In the case of obsidian and pumice, which are composed almost entirely of glass, devitrification plays an important role in the deterioration process. It was found that the samples were rapidly altered by artificial ageing as a result of the leaching of iron, calcium, sodium and traces of potassium and magnesium from the glass matrix. These elements re-deposited in pits and cavities on the surface of the samples.

The comparison of the rates of deterioration for basic and acidic volcanic rocks after artificial ageing showed that the basic rocks deteriorate faster than the acidic ones. This may be possibly due to the presence of large amounts of ferromagnesian minerals in the basic rocks. The mechanism of deterioration of microcrystalline acidic volcanic rocks is similar to that of granite [5]. The appearance of pits occurred more on the surface of basalt (basic) than on rhyolite (acidic). On the other hand, the discolouring of basalt was less than that of rhyolite.

The degree of crystallinity in volcanic rocks is a determinant factor in the deterioration process. Rocks with a higher amount of crystalline components will take longer to deteriorate than those with a higher glassy-phase content.

3.5 CONCLUSIONS

The present work showed that the 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 wide variations in temperature, which lead to exfoliation and cracks, especially in the glassy rocks. Devitrification of glassy rocks plays an important role in the change of colour observed at the surface.

The application of water-repellent materials to minimize the effect of water is very important for the conservation of archaeological objects made of volcanic stones.

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RESUMEN

La deterioración de algunas rocas volcánicas de Egipto fue estudiada por medio de difracción de rayos-X, absorción atómica, secciones delgadas y microscopía electrónica de barrido. Se discuten los mecanismos de deterioro debidos a los efectos del agua, cambios de temperatura y exposición a radiación ultravioleta. Se realizó un estudio comparativo de las rocas básicas y ácidas incluyendo el grado de cristalinidad como uno de los parámetros en el proceso de deterioro.

RESUME

La détérioration de quelques roches volcaniques d'Egypte a été étudiée par différentes moyens: diffraction des rayons-X, absorption atomique, analyses de lamelles et microscopie électronique à balayage. Les mécanismes de détérioration par l'action de l'eau, les changements de température et l'exposition aux rayons ultraviolets sont décrits. Une étude comparative des roches volcaniques basiques et acides est présentée en utilisant le degré de cristallinité comme un des paramètres du processus de détérioration.

KURZFASSUNG

Die Schadensbilder mehrerer ägyptischer Vulkangesteine wurden mittels Röntgenbeugung, Atomabsorption, Dünnschliff- und Rasterelektronenmikroskopie untersucht. Die Schadensmechanismen durch Einwirkung von Wasser, Temperaturwechsel und UV-Strahlung werden diskutiert. Eine Vergleichsuntersuchung basischer bzw. saurer Vulkangesteine unter besonderer Berücksichtigung des Kristallinitätsgrades als verwitterungsrelevante Kenngröße wird vorgestellt.

THE CUAUHCALLI – A MONOLITHIC AZTEC TEMPLE AT MALINALCO, MEXICO: DETERIORATION AND CONSERVATION PROBLEMS

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ABSTRACT

The Cuauhcalli is the most important monolithic Aztec temple at the archaeological site of Malinalco in Mexico state. The site is located on a partly artificial terrace built on the so-called Hill of the Idols. There are several other structures, some of which, as is the main temple, are carved directly out of the bedrock. The stone is a basaltic tuff and its deterioration is mainly caused by water infiltrations. These hydrolyse some of the minerals in the stone, increasing its general porosity. Lichens, as well as other micro-organisms, are found on the monuments. Conservation measures and the effectiveness of applied treatments are discussed.

4.1 INTRODUCTION

The archaeological site of Malinalco, as an example of monolithic construction in pre-Hispanic America, is unique both for the beauty and for the historic importance of its monuments. The investigation of the deterioration problems and the application of conservation measures to the construction materials of the monuments at this site form part of the Malinalco Archaeological Project [*Proyecto Arqueológico – Malinalco 1987-1988*]. This regional development project includes archaeological survey, restoration of the buildings and application of measures necessary to ensure the stability

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of the construction materials. These measures aim to improve the condition of the stone and other materials and to reduce their deterioration rate, thus contributing to the preservation of the monuments for the future. These activities are necessary so as to prepare the site for the reception of large numbers of visitors and to make it attractive.

The site is on a partly artificial terrace built on the hill known as "Hill of the Idols." This outcrop is located to the southwest of the town of Malinalco. It is about 10 km from the city of Tenancingo, and some 100 km to the south-west of Mexico City. It belongs to the municipality of Malinalco, in the south of the State of Mexico. The site is located at 18° 57′ N and 99° 30′ W, and is 1 750 metres above sea level.

The Hill of the Idols is in a mountain chain that crosses an L-shaped valley from east to west. These mountains present outcrops of strange forms caused by erosion and stepwise fractures. The chain belongs to the Tepoztlán formation of the Tertiary System, an older period than that of the higher mountains surrounding the valley. The valley, due to its particular location, has subtropical, sub-humid weather, with frequent rains in summer. These rains and the soil of the valley make it very fertile. The mountains of the Tepoztlán formation have poorer soil, but are covered with vegetation which is adapted to that environment and grows luxuriously during the rainy season. The surrounding, higher mountains have a cooler climate with a conifer-based flora.

The terrace where the Hill of Idols is located is in a climatic transition zone, where tropical deciduous and sub-deciduous forests mix with tropical scrub. It is about 125 m above the level of the town, with an excellent view over the town and the valley. It served thus as a vantage point to watch the activities in the valley and for astronomical observations.

4.2 DESCRIPTION OF THE SITE

The name of Malinalco derives from the word *mallinalli* of Nahuatl origin, and which means grass. It can also be interpreted as an abbreviation of *malinalxochco*, meaning "place where Malinalxochil, sister of the god Huitzilopoztli, is adored."

The archaeologist García Payón conducted the first survey and restoration of the area, between 1936 and 1939 [1]. The site is considered an outstanding example of monolithic architecture. The most important construction is the principal temple, the *Cuauhcalli,* which means variously "house of the eagles; place where the sun lives; house of the lord eagles; place where the brave men worship the sun."

The elements associated with the temple, which corresponded to the military orders of the *Cuauhtli-Ocelotl,* are warlike: sculptures of eagles, ocelots, the war serpent *Izcoatl,* standard bearers, the devouring jaws of a serpent identified as *Tlaltecutli,* a dedication to *Coatlicue,* mother of *Huitzilopochtli,* god of the sun, but also of war, for which the Mexica warriors lived.

According to García Payón, the buildings date to 1476, which was the year in which *Atzayactl* conquered this region. *Ahuizotl*, another of the Mexica lords, ordered the construction of these monuments between 1487 and 1490. That was the period when the stone quarriers, *tetlepancle,* carved these monolithic temples. In 1503, the successor to *Ahuizotl*, *Moctezuma Xocoyotzin*, continued with the construction of the buildings, though one of them was left unfinished as a consequence of the Spanish conquest.

In addition to the immediate complex of Cuauhcalli – temple Nº I according to the numeration system of García Payón – there are several other masonry structures, one of them being in part monolithic. These pyramidal bases constitute the *Cuauhtinchan* complex. In front of these temple are the very deteriorated ruins of a pyramid, Nº II, of rectangular plan with stairs and balustrades. To the east of the Cuauhcalli complex, and forming part of the slope of the hill, is a building designated Nº III. This is a masonry structure with the blocks jointed using a lime and earth mortar. It consists of two chambers, which were used for the cremation of dead warriors. Structure Nº IV comprises the ruins of the temple of the sun. This is a partly monolithic, partly masonry structure, forming a great rectangular room. Structure Nº V, a very deteriorated circular masonry structure, is located at the side of the pyramid designated Nº II. Also carved out of the hill is Nº VI, the ruins of another monolithic structure. Temple Nº VII, to the west of the Cuauhcalli, is of rectangular plan, but never finished.

The Cuauhcalli has a pyramidal base carved in bedrock, with two sloping sides and central stairs flanked by a balustrade besides which are the remains of two ocelot sculptures. In the centre, between steps 4 and 7, a standard bearer is also found. The temple has a circular plan and was carved completely out of the rock. It is sited on the higher part of the terrace. The entrance is an opening representing the mouth of a serpent, with protruding eyes and eyebrows, and curved eye-teeth, with a forked tongue on the floor. At its sides are two pedestals with remains of sculptures. The interior has a circular bench along the wall. In the deepest part, at the centre of the bench, an ocelot skin is carved. To each side of it, as well as in the centre of the room, eagles are carved. All these elements are part of the monolithic structure.

The temple has a perfect orientation towards the south. The entrance to the temple, its central sculptures, the stairs leading to it and the small platform above them, as well as the pyramidal base, were used for the observation of the sun during the day. The front wall of the temple is in line with one of the surrounding mountains to the east, in which a notch was cut to improve the view of the rising sun. Thus, dawn was divided into three different periods each year, two of 52 days each, which represent the 52-year long century of the Aztecs, and another of 260, which corresponds to the ritual calendar of the year of Venus.

The architectural and aesthetic values of the temple are thus increased by its religious connotation, so much so that from the start of the archaeological studies by García Payón, it has been called "the sanctuary." This name is probably appropriate to Aztec mythology and the practices carried out there.

In 1521, the conquistador Andrés de Tapia arrived with a group of soldiers at the site. According to historical sources he destroyed the buildings and set them on fire, but Clavijero [2] believes that Tapia fought with the natives, vanquished them and followed them to the foot of the hill, which he did not climb because it was inaccessible on horseback.

4.3 DESCRIPTION OF THE ROCK

According to Palacios [3], the Hill of the Idols is part of the Tepoztlán Formation. This formation appears as outcrops about 3 km both north and south of the town of Tepoztlán, and was extensively described by Fries [4].

This formation is mainly composed of andesitic volcanic debris deposited in layers of varying thicknesses ranging from 0.5 to 10 m. The composition of samples from this formation is that of a porphyritic andesite, containing orthopyroxenes, clinopyroxenes and amphiboles. This composition is similar to that of the Malinalco samples, whose layers have tuff-like and detritic components with textures varying from a fine clay to fragments of up to 50 to 60 mm in diameter. The alternating layers – with different-sized inclusions – never reach thicknesses of more than 2 m, nor do they contain larger fragments. In general, the layers of the rock out of which the monuments were carved have a fine to medium texture, with poorly classified fragments. Their colour varies from a light to a darker grey, not showing the reddish, greenish or yellowish hues of other parts of the formation. This could possibly be due to the fact that these colourings are superficial and were eliminated during the carving of the monuments.

4.3.1 Mineralogy

The samples correspond to a palagonized basaltic tuff of crystalline, poorly classified porphyritic texture. One of the characteristics of this rock is the presence of basaltic fragments of up to 3 mm in size. This is at variance with the andesitic composition reported for the Tepotztlán Formation [4], and provides an explanation for the darker colour of the Malinalco rock.

The matrix of the rock is vitreous, yellowish in colour and characterized by small spherical, slightly bi-refringent bodies. It has been classified as palagonite, a hydrated basaltic glass. The presence of mineral fragments suggests a pyroclastic rock, though the matrix, possibly due to hydration, does not present the real texture of a tuff.

Euhedral to subhedral olivine phenocrysts up to 1 mm long are present, constituting about 5% of the rock. The olivine is altered to iddingsite along its edges, and also to minerals of the serpentine group. The plagioclase occurs in randomly oriented microphenocrysts of about 0.1 mm in length, and shows no alteration. Clinopyroxenes and opaque minerals, possibly magnetite and pyrolusite, are also present.

Plagioclase, possibly albite, and clays of the smectite group (montmorillonite), ilmenite, clinohumite and pyroxenes (augite and enstatite) have been identified using X-ray diffraction. Other probable minerals are smythite, fayalite and rhodonite.

Samples of a weathered part of the rock, of whitish appearance due to hydration processes, show alteration of the plagioclase (albite) to clay (montmorillonite) and of clinohumite to fayalite. Ilmenite was not found in these samples, possibly because of its alteration into fayalite.

4.3.2 Physical measurements

It has been observed that the deterioration of the sculptures and the building is greater in the more porous layers, even though the mineralogical composition is similar. Stone masons differentiate two rock types of different durability, corresponding to the more or the less porous layers. Samples were taken from two different layers of the same strata from which the ocelots at the side of the temple had been carved. One is a coarser-grained, less deteriorated layer, and the other is a more deteriorated, finer-grained layer. Porosity, bulk specific gravity and apparent density were determined on these samples. The procedures used are described in Appendix 4-A, and the results of the measurements are given in Table 4.1.

Table 4.1 Physical measurements on coarse- and fine-grained samples

	Bulk Specific Gravity	Apparent Density (g/cm^3)	Porosity (%)
Coarse	2.24	1.7	35.8
Fine	1.76	1.4	47.2

The fine-grained rock, with a proportionally larger amount of clays, shows higher porosity and lower apparent density. The combination of fine pore structure and small particle size gives rise to a high specific surface area, and so the adsorption of liquids and gases is enormous. Thus chemical and physical weathering processes are speeded up and this explains the more deteriorated state of these layers.

4.3.3 Deterioration

The hydrolytic process of deterioration produces the alteration of the plagioclases into clays, and of the olivines into serpentine minerals. The laterization usual in humid climates is not observed.

The high porosity of the stone enhances the retention of humidity, and this in turn favours the propagation of micro-organisms which cause biodeterioration.

In Malinalco there is a proliferation of foliose lichens – probably *Parmelia* spp. according to the characteristics described by Hale [5] – and some crustaceous (crustose) species.

The deterioration observed could be caused by a number of factors, singly or in combination:

- lichens tend to keep the stone damp by preventing the evaporation of water from the surface;
- due to their cyclic shrinking and expansion upon humidity changes, lichens exert mechanical stresses on the surface and subsurface of the stone;
- they introduce rhizinae into the stone, thus helping to break up the structure and inducing loss of material, and
- they produce organic acids which chelate with cations of certain metallic elements, facilitating leaching and leading to chemical breakdown of the stone.

Also present on the stone are blue-green (cyanophyceae) and green (chlorophyceae) algae, mosses and other microflora.

4.4 TREATMENTS APPLIED

As mentioned above, restoration of the buildings was carried out by García Payón in the late 1930s. This also included cleaning and improving the original drainage system cut into the rock of the hill above the structures. The temple was covered with a thatch roof, following what was considered to have probably been its original design.

Due to lack of maintenance, the drainage system and the thatch roof of the temple deteriorated. This increased the humidity in the stone and favoured microfloral growth. To correct this situation action was initiated in the form of Proyecto Arqueológico – Malinalco 1987-1988.

The thatch roof was repaired and drains were adapted to divert the water running off the part that covers the entrance to the temple. The drainage system was in operation again by the end of the 1988 rainy season, and its efficiency was demonstrated during the heavy rains of 1989.

To eliminate the microflora, different treatments were carried out on the Cuauhcalli and other buildings around it. The aim was the elimination of lichens and mosses.

The first method tried was mechanical cleaning of the thick layer of microfloral growth that covered the surface of the stone. According to the reports, these were 1 to 5 cm thick, with their thickness in direct proportion to the humidity of the underlying stone. The cleaning was carried out on the main temple (N° I), structure N° VI, and the rock wall between them. The cleaning was not considered adequate and had been discontinued by the end of 1987. Appendix 4-B gives more details on this intervention.

During the second year of the project, treatment commenced with careful mechanical cleaning of Cuauhcalli, using scalpels and brass-bristled brushes. This was followed by an application of ammonia water and formalin, and then a hydrogen peroxide treatment to eliminate all remnants of microbiological organisms.

Tests with various biocides were carried out at the same time. These included cuprous oxide (Cu_2O), copper oxychloride (20 g/l) and a commercial herbicide (*Gramoxone*, 1:100 (v:v) in water). These treatments did not produce satisfactory results. Even though the micro-organisms were killed by the biocides, new organisms established themselves once the biocide was washed away by the rains. The biocides tested did not have the residual effect needed to provide long-term effectiveness.

The best results were obtained by the combination of mechanical cleaning and formalin and hydrogen peroxide treatments. Nonetheless, by 1990, two years after the intervention, biological growth was again extensive.

4.5 GENERAL RECOMMENDATIONS

The key to the preservation of these monuments is minimizing the humidity present in the structures. Hence maintenance of the roof and the drainage system is of fundamental importance.

The control of the biological growth on the Malinalco monuments needs the development of a practicable maintenance programme. On the basis of previous experience, and learning from results obtained in other archaeological areas with similar problems [6; 7], various treatments and products are suggested for testing. Among the different commercial biocides, based on copper compounds, organo-tin or quaternary ammonium amines, the simpler system recommended by Hale [7; 8] should also be considered. Hale recommends a treatment based on the use of a dilute sodium hypochlorite solution (commercial domestic bleach), followed the next day by application of a 4% aqueous solution of borax. To ensure adequate penetration of the borax solution, at least 300 ml/m^2 are needed. In areas of heavy infestation, 500 ml/m^2 are recommended. The treatment should be applied at the end of the rainy season, with re-application every six months until total elimination of the microflora is obtained. The advantage of this procedure, apart from the availability of the products and their low cost, is that it obviates the need for the slow process of mechanical removal of the micro-organisms, which fall off easily after the treatment.

These procedures should first be tested on the walls of the stairs that lead to the terrace, as they do not have any carved details.

Meanwhile, the monuments themselves should be regularly cleaned using the method successfully applied in the second year of the project (1988). When the biocidal effectiveness and the non-deleterious effect of the bleach + borax treatment on the underlying stone has been proven, the labour-intensive treatment can be replaced by the simpler one.

Such trials were currently under way at the time of writing.

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APPENDIX 4-A

Physical tests

(i) *Bulk specific gravity determination*

The sample is weighed dry in air (W_{sa}), placed into a pycnometer, covered with water, and weighed (W_{ps}). The weight of the pycnometer full of water is also determined (W_{pyc}). The bulk specific gravity (S_p) is calculated by

$$S_p = W_{sa} / ((W_{pyc} + W_{sa}) - W_{ps})$$

(ii) *Apparent density determination*

The apparent density (D_a) is measured using the bulk density method of Blake [8]. The sample is weighed after drying to constant weight at 105°C, then covered with paraffin and weighed in air and in water. The formula used is:

$$D_a = d_w \times W_{ods} / [W_{sa} - W_{spw} + W_{pa} - (W_{pa} \times d_w / d_p)]$$

where:

d_w = density of water at temperature of determination,
W_{ods} = oven-dry weight of sample,
W_{spw} = net weight of sample plus paraffin in water,
W_{pa} = weight of paraffin coating in air, and
d_p = density of paraffin

(iii) *Determination of porosity*

This was carried out according to the method described by Davies [9]. It is calculated from the apparent density using the formula:

$$\text{Porosity} = 1 - ((D_a / 2.65) \times 100)$$

APPENDIX 4-B

Biological treatment

Mechanical cleaning in the first year of the project was carried out by Esperanza Teyssier Mont, of the Zona Arqueológica de Teotihuacán. The evaluation of the treatment was done by Pablo Torres, a biologist of the Dirección de Conservación del Patrimonio Cultural. Both institutions come under INAH.

The cleaning during the second year of the project was carried out by Guadalupe Peredo R., of the Instituto Mexiquense de Cultura. The tests with the copper-based biocide and the commercial herbicide were carried out by agronomist Vicente Zacarías.

During the first restoration in the late 1930s, upon partial crumbling of an adobe wall due to heavy rains, remains of a wall painting appeared. These remains were poorly consolidated and were easily lost by mere brushing. Hence a layer of transparent varnish (*Duco cement* – a nitrocellulose-based resin) was sprayed on the painting and the remnants of mud covering it. After the rains, the surface was cleaned and a thick coat of the same varnish was applied. Later, the artist and archaeologist Miguel Angel Fernández reconstructed them [2].

The use of this commercial adhesive as a fixer for polychromy on pottery and mural paintings was common practice at the time of the restoration carried out over 50 years ago. This procedure produced disastrous results because the product yellows and shrinks with time, pulling away the painted layer.

RESUMEN

El Cuauhcalli es el templo monolítico azteca más importante en el sitio arqueológico de Malinalco, Estado de México. Este sitio se halla sobre una terraza parcialmente artificial sobre el llamado "Cerro de los Idolos." El sitio cuenta con varias otras estructuras, algunas de las cuales, como el templo principal, talladas directamente en la roca.
La piedra es una toba basáltica y su deterioración está causada principalmente por filtraciones de agua. Esta hidroliza algunos de los minerales aumentando la porosidad general de la piedra. Sobre los monumentos se encuentran líquenes y otros micro-organismos. Se discuten las medidas de tratamientos aplicadas y su efectividad.

RESUME

Le Cuauhcalli est le plus important temple monolithique aztèque du site archéologique de Malinalco au Mexique, qui est situé sur une terrasse en partie artificielle construite sur la colline dite des idoles. Il compte plusieurs autres structures, dont certaines, comme le temple principal, sont taillées directement dans la roche. La pierre est un tuf basaltique qui se détériore principalement sous l'effet d'infiltrations d'eau. Celles-ci hydrolysent certains des minéraux de la pierre, augmentant sa porosité générale. Des lichens ainsi que d'autres micro-organismes se trouvent sur les monuments. Les mesures de conservation et l'efficacité des traitements appliqués sont décrites.

KURZFASSUNG

Der Cuauhcalli ist der bedeutendste monolithische Aztekentempel im Grabungsgebiet von Malinalco im Staat Mexico. Die Grabung liegt auf einer teilweise künstlich aufgeschütteten Terrasse am sogenannten "Hügel der Idole". Neben dem Tempel befinden sich noch andere Anlagen, von denen einige, so wie dieser, unmittelbar aus dem anstehenden Fels gearbeitet sind. Das Gestein ist ein Basalttuff, für dessen Verwitterung hauptsächlich Wasserinfiltrationen verantwortlich sind. Dieses Wasser bewirkt eine Hydrolyse einzelner Minerale im Gestein, und damit eine Erhöhung der Gesamtporosität. Weiters bedecken Flechten und andere Mikroorganismen Teile der Monumente. Der Beitrag diskutiert Konservierungsmaßnahmen und die Wirksamkeit der vorgenommenen Schutzbehandlungen.

TEXTURE AND MECHANICAL DIS-AGGREGATION OF TUFFS FROM ITALY AND ECUADOR

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ABSTRACT

The pore structure of two tuffs was investigated by means of mercury porosimetry. The high percentage of absorption pores explains the disruptive effect of wet/dry cycling 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 agree with a previous laboratory study and observations in the field on one of the tuffs. The results show a clear relationship between texture and mechanical failure of these stones. The possibility of and requirements for preservation treatments are also discussed.

5.1 INTRODUCTION

The volcanic tuffs quarried in the areas of Naples (Italy) and Cochasquí (Ecuador) show various similarities [1; 2; 3]. Both tuffs have very high open porosity (almost 50%), absorb enormous amounts of water very rapidly, and the stress caused by wet/dry cycling appears to be the main cause of decay for both materials. The rate at which each deteriorates is different: the Ecuadorian tuff crumbles much more rapidly than the Italian one.

In order better to understand the deterioration processes, pore structures were investigated by measuring total porosity, pore-size distribution, and specific surface area of stone specimens, using a mercury porosimeter.

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The experimental results were used to calculate salt crystallization pressures, which are involved in the decay process of the Neapolitan tuff and, presumably, could also play a part in the deterioration of the Ecuadorian tuff.

5.2 MATERIALS

5.2.1 The Neapolitan tuff

This tuff had been studied previously [1] by examination of both decayed and well preserved stones from Castel dell'Ovo, on the Bay of Naples, as well as pristine stone from various local quarries.

It 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 abundant zeolites.

Initially, stone decay manifests itself by the crumbling away of exposed surfaces, as clearly shown on walls rebuilt only 15 years ago.

In weathered stone specimens, 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 physico-mechanical rather than a chemical decay, as the latter would be expected to cause variation with depth when occurring in a porous stone.

Observations carried out on specimens from both well preserved and highly weathered areas in monuments, as well as from quarries, seemed to confirm physico-mechanical decay. In fact, the slightly different physical characteristics observed in the various types of specimens did not appear to be related to the state of preservation of the stone. In particular, higher values of porosity were detected in quarry specimens when compared with weathered ones. This implies that the different physical characteristics can be attributed to provenance, and that the alteration process is not responsible for an increase in porosity, as would be the case for chemical decay.

The previous study [1] suggested that the tuff decay depends mainly on water imbibition and crystallization of sodium chloride absorbed indirectly from the atmosphere and, in the case of Castel dell'Ovo, also directly as sea spray.

Another mechanism that could contribute to deterioration is the strain produced in the crystal lattice of chabazite (the main zeolite) when calcium is replaced by sodium ions [4]. This ion exchange mechanism and hydrolysis of the zeolites could result in the fracture of crystal grains and consequent crumbling of the stone. However, this would mean that the porosity of the exposed surface – to a depth of many centimetres since NaCl has been detected at great depth – should be higher than the interior part of the stone not reached by sea water. Since this is not the case, it can be assumed that ion exchange and hydrolysis processes play a minor role compared with the disruptive effects of water imbibition and sodium chloride crystallization processes.

5.2.2 Cangagua tuff from Ecuador

The *Cangagua* tuff, a slightly hardened volcanic tuff, is the building material of the *tolas*, funeral tumuli constructed by the pre-Inca civilization of the Caranquis, in Cochasquí, Ecuador.

Previous investigations were carried out on specimens obtained from Cochasquí [2; 3]. They show that the material is a pheno-andesitic tuff made up of a chaotic aggregate of crystalline and lithic fragments (about 50% of the rock) in a matrix 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 is highly porous and water permeable.

The Cangagua and Neapolitan tuffs differ in their water absorption rates. The Cangagua tuff absorbs about 10 kg/m^2 water in about 4 minutes by capillarity; Neapolitan tuff absorbs water a little slower, 3-7 kg/m^2 in the same time. The Cangagua tuff crumbles on simple immersion in water; after one or two wet/dry cycles, fairly large fragments break off, and after 3-4 cycles the specimens crumble completely. Neapolitan tuff is relatively more resistant; only a few, small, surface cracks appear after 3-5 wet/dry cycles. About 15-18 cycles are necessary to increase the number and depth of cracks and for scaling to occur. This then reproduces exactly the deterioration phenomena observed *in situ*.

5.3 EXPERIMENTAL RESULTS

The specimens of Neapolitan and Cancagua tuffs used for the measurements with the mercury porosimeter were cut from the same blocks from which were taken the samples used for the previous studies reported [2]. Therefore the results obtained are directly comparable.

The results of tests on two specimens from two different blocks of Neapolitan tuff and a specimen from the single Cangagua tuff block previously investigated, are reported in Table 5.1 as representative examples of all measurements carried out.

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 the Neapolitan tuff are in agreement with those previously determined by saturation with water under vacuum, where the total porosity values for specimens comparable to those reported in Table 5.1 were 48.5% and 52.0%.

In contrast, the present value for the total porosity of the Cangagua tuff is slightly less than that previously determined by saturation with water under vacuum (47.7%) or by the Kobe method (estimation of the air volume filling 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 a higher total porosity, the Cangagua tuff also has a higher percentage of pores with radii <0.01 μm than that indicated in Table 5.1. More precise measurements using another method are planned to assess this hypothesis.

Table 5.1 Experimental results

	Neapolitan tuff				Cangagua	
Sample number	2		3		6	
Bulk density (g/cm^3)	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	9.7	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<1.0	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

where: A = percent of total porosity; B = pore volume %; and r = pore radius in μm

5.4 FAILURE AS A RESULT OF WATER ABSORPTION

The mechanism of dis-aggregation as a result of water absorption has been described as follows [5]. The water molecules align themselves in an orderly 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 (absorbed) water 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. As wet/dry cycling occurs, the stone is alternately stressed by the absorbed water and unstressed when the water evaporates. The fatigue induced by the sorption-desorption cycle can lead, more or less rapidly, to dis-aggregation.

The pores that can be totally filled with absorbed water (absorption pores) are those with radii <0.5 μm [6]. It can be seen from Table 5.1 that, in the Neapolitan tuff, 40-60% of pores are absorption pores and that they represent 20-30% of the stone volume. The high pressure that can develop due to water absorption in this structure can exceed the compressive strength of the stone and lead to disruption. In practice, this disruptive stress appears to occur mainly in a rather thin subsurface zone, although water easily penetrates to great depth in the Neapolitan tuff. The effectiveness with which water penetrates into the stone can be easily explained. The penetration depends on the amount of capillary pores (radius between 0.5 and 5 μm) and pores with radii

>5 μm, allowing the passage of free water [6]. Because the absorption pores (radius <0.5 μm) are filled with oriented water, they prevent the passage of fluid. Therefore, absorption pores are more likely to be completely filled in the zone close to the exposed surface. In addition, water is drawn to the surface during drying, and the filling of the finest pores is likely to occur at the expense of the inside water migrating through the capillary network.

The total absorption pore volume of the Cangagua tuff is similar to that of the Neapolitan tuff, but the percentage of smallest absorption pores (radii <0.01 μm) is more than three times that of the Neapolitan tuff and, as noted above, possibly even higher. Therefore complete filling of absorption pores is easier, and the pressure developed is higher because of its inverse relationship with the pore radius. The higher pressures exerted on the pore walls can easily exceed the very low compressive strength of the Cangagua tuff and lead to dis-aggregation more rapidly than occurs with the Neapolitan tuff.

The greater amount of pores filled with absorbed water, which leads to higher stresses and consequent lower stone cohesion, may also explain why the disruptive effect of water absorption develops more deeply in the Cangagua tuff, and not only close to the surface as is the case for the Neapolitan tuff. In fact, all the above factors can result in rapid surface fracturing. As the fractures provide external water with direct access to the interior absorption pores, only very few wet/dry cycles are needed to crumble the Cangagua tuff specimens completely.

5.5 FAILURE BY SALT CRYSTALLIZATION

Crystallization of sodium chloride certainly plays a part in the decay of the Neapolitan tuff. Salt crystallization could also play a role in decay of the Cangagua tuff, even if previous studies did not report the presence of soluble salts [2]. Therefore, it was considered useful to calculate the crystallization pressures which can develop in these stones, should enough soluble salts be present to produce the necessary supersaturated salt solution [7].

The thermodynamics of crystallization and the resulting crystallization pressures have been considered analogous to the thermodynamics of frost mechanisms in porous materials [8; 9]. Based on these theoretical considerations, the crystallization pressures which could build up in a number of stones have been calculated [10; 11]. The calculation is based on the pore-size distribution determinations and on a model of pore geometry that assumes 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 tuffs under consideration, crystals grow preferentially in pores with radius >1 μm. The pressure that would develop should crystallization also take place in the smaller pores, once the larger ones are filled with crystals, can be calculated.

Five classes of the smaller pores are considered, with pore radii in the ranges already considered in Table 5.1, with median radii of 0.005, 0.030, 0.075, 0.30 and

0.75 μm. The median radii of the pore classes are taken as r values. The respective crystallization pressure (p) is calculated using the equation:

$$p = 2\sigma / r$$

where σ is the surface tension between solid and liquid, taken as 80 dyne/cm.

The calculated pressures for the five classes of pores are 3200, 533, 213, 53 and 21 N/cm^2 respectively.

To calculate the effective pressure that can build up in the stone it is necessary to take into account the volume percentage of small pores of each class, V_r (the values in columns **B** in Table 5.1), which should be related to the volume percentage of large pores (radius >1 μm), V_R. 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 calculated values are reported in Table 5.2.

The total pressures which can build up in the Neapolitan tuff are rather high and presumably exceed the strength of the material which, based on the analysis of thin sections using a petrographic microscope, showed low cohesion [1]. The resulting stress can lead to mechanical failure.

Table 5.2 **Crystallization pressures**

		Neapolitan tuff				Cangagua	
	Sample number	2		3		6	
	Pore size class (μm)	C	D	C	D	C	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	0.16	3	0.01	0	0.36	8
	Total pressure (N/cm^2)		748		405		1258

where: C = V_r/V_R; D = crystallization pressure (N/cm^2). The theoretical crystallization pressures (N/cm^2) are: a=3200; b=533; c=213; d=53; e=21.

The total pressures that can be generated in the Cangagua tuff 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.

5.6 CONCLUSION AND DISCUSSION

The results obtained indicate that the particular pore structure of these two tuffs, which show a very high volume of absorption pores, may be responsible for the rapid dis-aggregation they undergo as a result of mechanical stress due to absorbed water. The more rapid failure of the Cangagua tuff compared to the Neapolitan tuff is also explained on the basis of pore-size distribution. The Cangagua tuff, besides having a lower strength, also shows a higher percentage of absorption pores in the smallest radius class and is therefore subjected to higher pressure due to water absorption.

The high crystallization pressure that can build up (depending on the pore structure) can also explain the deteriorating effect of salt crystallization in the decay processes of the Neapolitan tuff. This could also play a role in the Cangagua tuff deterioration should soluble salts be absorbed by the stone as a result of environmental conditions.

The results obtained for the Cangagua tuff can be compared with those of a recent study on the volcanic tuff from Rano Raraku: the quarry for the famous *moai* statues of Easter Island [12]. The petrographic characteristics of the two tuffs show some similarities. Frequent strong rains on Easter Island have been considered the single most significant deterioration factor, causing mechanical erosion and responsible for selective chemical dissolution processes.

Investigation of the physical characteristics of the Easter Island tuff by a complete analysis of pore structure and wet/dry weathering tests should be carried out to check whether the decay also involves stress due to water absorption, analogous to the processes operating in the Cangagua tuff.

The Cangagua tuff in the Cochasquí monuments is also subject to a local climate of heavy rains and it seems clear that rainwater is the most significant deterioration factor. The synergistic mechanical and chemical actions of water suggested for the Easter Island tuff may also operate in the Cangagua tuff decay process. However, the selective dissolution of alkali in glass is a rather slow process [13], while saturation of the stone with water has an immediate disruptive effect, as shown by wet/dry cycling. Therefore the most significant deterioration process for the Cangagua tuff is the mechanical dis-aggregation caused by the stress due to water absorption.

General experience [14; 15] shows that to prevent the deleterious action of water, and also of seawater, it is necessary to impregnate in depth with a hydrophobic product. The application of a water repellent to the surface of a porous stone cannot provide effective protection, particularly if the stone is subjected to heavy rain. This also applies to stones that have been previously consolidated, as such treatments do not substantially change the porosity of a porous stone.

In comparison, in-depth impregnation with a water repellent (even without a previous consolidation treatment) can provide very good resistance to alteration processes. This was clearly demonstrated by the results of wet/dry cycling tests carried out on treated Cangagua tuff [2; 3].

A final point should be emphasized: these tuffs have a very fine pore structure and the in-depth penetration and homogeneous distribution of the conservation products has to be carefully assessed before use in the field. Thus a commercial product containing an oligomeric alkylalkoxysiloxane and ethyl silicate (*Wacker H*), which has given good results in the preservation of various types of stone, showed very poor penetration in the Neapolitan tuff and consequently a very poor preservative effect [1].

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RESUMEN

La estructura porosimétrica de dos tipos de tobas fue investigada por porosimetría de mercurio. El alto porcentaje de poros de absorción 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.

RESUME

La structure porosimétrique de deux tufs a été examinée à l'aide du porosimètre à mercure. Le pourcentage élevé des pores d'absorption explique les perturbations entraînées par l'alternance des cycles de mouillage-séchage observées antérieurement; les différences de distribution porosimétrique présentées par les deux tufs concordent également avec celles de leur résistance à cette contrainte climatique. Les pressions de cristallisation des sels ont été calculées en se basant sur la distribution porosimétrique: les résultats confirment ceux d'une étude antérieure effectuée en laboratoire ainsi que les observations faites sur le terrain sur un des tufs. Les résultats montrent nettement le rapport entre la texture et les défauts mécaniques de ces pierres. Les possibilités et les conditions des traitements de conservation sont également évoquées.

KURZFASSUNG

Das Porengefüge von zwei Tuffgesteinen wurde mittels Quecksilber-Porosimetrie untersucht. Dabei ergibt sich ein hoher Anteil an Absorptionsporen, der die an diesen Gesteinen beobachtete Empfindlichkeit gegenüber Feuchte-Trocken-Zyklen erklärt. Die ermittelten Unterschiede der Porengrößenverteilung zwischen den beiden Steintypen stehen ebenfalls im Einklang mit deren unterschiedlich hohen Resistenz gegenüber dieser Art von Beanspruchung. Auf Grundlage der Porengrößenverteilung wurden mögliche Salzkristallisationsdrucke berechnet; die entsprechenden Werte stimmen mit den Ergebnissen aus früheren Laborstudien und mit in-situ Beobachtungen besonders an einer der Tuffarten überein. Die Resultate zeigen eine eindeutige Beziehung zwischen Struktur und mechanischer Festigkeit dieser Gesteine. Möglichkeiten und Anforderungen einer konservierenden Behandlung werden ebenfalls diskutiert.

THE VOLCANIC ROCKS OF THE MONUMENTS OF THE FORUM AND PALATINE (ROME): CHARACTERIZATION, ALTERATIONS, AND RESULTS OF CHEMICAL TREATMENTS

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ABSTRACT

A field study was carried out in the Forum and Palatine areas in Rome, and in volcanic areas of the Province of Rome, 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 and type of alteration was collected. The chemistry of the alteration and its products is described. Results of conservation treatment tests with two consolidants, both *in situ* and in the laboratory, are given for the six types of stone studied. The treatment efficacy was assessed by means of a water absorption index. Results show that the same consolidation treatment apparently provides better protection when applied once only, rather than when applied repeatedly.

6.1 INTRODUCTION

In many countries, principally in South America and in eastern Asia, volcanic rocks have been used for works of art. In Italy, examples of monuments built with volcanic stones are mainly found in Latium and Campania in central Italy, with some also in Sicily and Sardinia.

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Except for some types of lava, the volcanic rocks employed in monuments generally have a relatively large grain size and are non-homogeneous and porous. As a result, in only few instances can they be employed for finely detailed decorative elements, which are more prone to degradation. Because of the changes occurring in the environment as a result of human activities, volcanic rocks present increasing problems of conservation.

Latium is the region where Rome, the capital city, is located. Over 6 000 of its 17 000 km^2 area are covered by the products of eight large volcanic events, 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 ancient walls of Rome, whilst those of the Sabatini complex are present in the northern periphery of the city and reach their maximum development between the Tiber and the Tyrrhenian Sea. In Latium, various types of volcanic rocks may be found, including lavas, ignimbrites, phreatomagmatic products, fall tuffs, mudflows, and tuffites.

They have very diverse structural and compositional characteristics, depending on the type of originating magma, the modes of eruption and of deposition, the magma cooling path, and the influence of hydrothermal and alteration processes, which have strongly modified most of them. "Pyroclastic rocks" includes all volcanic products that are not lavas, such as tuffs, pyroclastic flows, phreatomagmatic flows, mudflows and tuffites. In volcanological-petrographical literature, "tuff" is normally used instead of "pyroclastic rocks" to describe any volcanic rock other than lavas, and the term tuff will be used in this paper.

The study reported here focused on the characterization and study of the alteration of six types of tuffs used for structural and decorative elements in monuments of the Roman Forum and the Palatine. The study also considered laboratory tests and *in situ* application of chemical products for the conservation treatment of these rocks. As these rocks represent a wide range of structural, compositional and physico-mechanical properties, the results of this investigation can be extrapolated to similar volcanic products in other areas.

6.2 METHODS AND INSTRUMENTATION

First, a detailed field study was carried out in the Roman Forum and Palatine area to identify and describe the tuffs used in each monument and their alteration processes according to NORMAL recommended methods. Then samples of the six main tuff formations were collected from the monuments in collaboration with experts from Soprintendenza ai Beni Archeologici di Roma. In order to identify the locations of the quarries used in Roman times, the field work was extended to the environs of Rome where the tuff outcrops occur.

The samples were analyzed by optical microscopy of thin sections, X-ray powder diffraction analysis (XRD), scanning electron microscopy (SEM), thermal analysis, wet chemical analysis, and atomic absorption spectrophotometry. Over 180 cubes, each 3 × 3 × 3 cm, were analyzed with a Carlo Erba mercury microporosimeter to determine their porosity, the pore size distribution, their surface area, and, with standard techniques, the absorption coefficient.

Due to space limitations, only one of the rock types is reported here as an example of how the study was carried out. The volcanic formation, the location of the outcrops and quarries, the use of this stone in monuments, its petrographic characterization, its physico-mechanical properties and the alterations it presents are reported. Upon request, similar information on the other rock types can be obtained from the senior author of this paper.

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.

Similar 3 × 3 × 3 cm cubes were treated with two consolidation products (*Wacker OH* and *Wacker H*) and their post-treatment properties measured.

The same products were applied *in situ* on areas of approximately 0.25 m^2 each on the monuments from which the original samples had been collected.

6.3 CHARACTERIZATION OF THE PYROCLASTIC ROCKS

The six tuffs 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*.

As mentioned in the previous section, the paper presents the complete data obtained for only one tuff, the Peperino, as an example of the work carried out.

Peperino dei Colli Albani

- **Volcanic formation**: Peperino from the volcanic complex of the Alban Hills
- **Current name**: Peperino
- **Historic name**: Lapis Albanus
- **Outcrops**: This volcanic formation appears as outcrops in the centre of the Alban Hills complex around Lake 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**: 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 BC.

- **Roman monuments of the Forum and Palatine where it was used**:
Tullian Prison (middle of third century BC): lower room;
Temple of Magna Mater (also known as the Temple of Cybele) (3 BC): external architectural decorations;
Floor of the Forum (100-80 BC): close to the Lacus Curtius and the Comitium;
Saint Omobono (100-80 BC): foundations and external slabs;
Forum Olitorium (90 BC): northern Ionic temple; external architecture combined with frames of travertine; median temple; columns; wall of the cella; part of the trabeation;
Tabularium (78 BC): flutes of the half-columns of the balcony;
Forum Olitorium (80-50 BC): Doric temple and foundations;
Temple of Saturn (42 BC): podium covered with travertine;
Forum of Augustus (31-2 BC): fence wall where the Peperino is mixed with Pietra Gabina (*vide infra*);
Temple of Mars Ultor (2 BC): bases of the columns which are positioned in the basement as *opus quadratum* of lithic tuff;
Temple of Jupiter Stator (Augustinian age): restoration;
Temple of Antoninus and Faustina (141 BC): external walls (see Figures 6.1 and 6.2);
Temple of so-called "Fortuna Virilis" (sixth to first centuries BC): Peperino was employed together with other tuffs and travertine. The temple underwent several re-constructions.
- **Petrographic definition**: Mudflow
- **Macroscopic and microscopic characteristics**: Peperino tuff is a compact, fine-grained, grey rock with evident inclusions of both volcanic and sedimentary rocks. There are frequent white limestone fragments from the basement rock, with dimensions up to a few decimetres, but usually not more than a few centimetres. Together with the lithic fragments there are various minerals, such as pyroxenes, biotite, analcimized leucite, magnetite, olivine and biotite, frequently with well-developed habits. The matrix is made of very fine ash; only a small fraction of the ash is zeolitized (Figures 6.3 and 6.4).
- **Physico-mechanical properties**: The Peperino tuff 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/cm^3) and scarce diffusion of outcrops, does not favour its use as building blocks.

The physical characteristics of the Peperino tuff from Marino [1] are summarized in Table 6.1.

Table 6.1 Physical characteristics of the Peperino from Marino

PARAMETER	UNIT	RANGE	MEAN ± σ
Weight per unit volume	g/cm^3	2.005 - 2.126	2.075 ± 0.012
Weight per unit volume (dry)	g/cm^3	1.798 - 1.998	1.947 ± 0.026
Absolute specific weight	g/cm^3	2.570 - 2.820	2.672 ± 0.076
Porosity (n)	%	25 - 32	27 ± 0.9
Absorption coefficient	%	13 - 18	14.3 ± 0.6
Uniaxial compression resistance	kg/cm^2	262 - 276	267 ± 1.6
Traction resistance*	kg/cm^2	26.4 - 35.9	31.6 ± 1.6
Flexing resistance	kg/cm^2		69
Abrasion coefficient (trituration meter)	mm		15.5
Abrasion upon sand blasting (weight loss)	g		0.78

* using the Brazilian method. **Source:** Berry and Sciotti [1]

- **Alterations in the Roman Forum and Palatine monuments**
  Scaling is common, and all external surfaces show marked phenomena of scaling which may reach a depth of a few centimetres. The process seems related to static problems, and is more marked in building elements which have been subjected to structural overload. Scaling may also be related to the smoothing work carried out on the surfaces during the preparation of blocks.
  Fissuring is particularly evident on the corners of frames or parts of columns. Fissures are induced both vertically and normally to the exposed surface, and appear to be related to the superficial stresses suffered during preparation of the architectural elements.
  Dis-aggregation is marked under the scales, and also very often within the scales themselves.
  Chemical processes of alteration seem to be subordinate to other processes, a situation common to all tuffs.
- **Analysed samples** (Taken from the Temple of Cybele)
  Sample 79/CIB/50 — Architectural decoration: capital. Detached scales.
  Sample 79/CIB/51 — Powdery deposit under the scales of sample 79/CIB/50.
  Sample 79/CIB/52 — Architectural decoration: fluted column. Detached scales.
  Sample 79/CIB/53 — Powdery deposit under the scales of sample 79/CIB/52.
  Sample 79/CIB/54 — Architectural decoration: architrave. Detached scales.
  Sample 79/CIB/55 — Powdery deposit under the scales of sample 79/CIB/54.

6.4 ALTERATION PROCESSES OF THE PYROCLASTIC ROCKS

6.4.1 Mechanical processes

From the field study of the alterations observed on the Forum and Palatine monuments some assumptions can be made as to modes of alteration and factors influencing them. A large part of what are currently named tuffs were brought to the surface during excavations carried out in the last century. In general, these materials were saturated

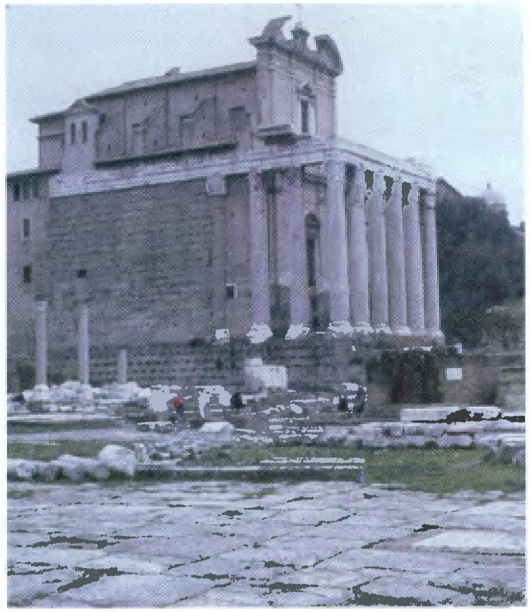
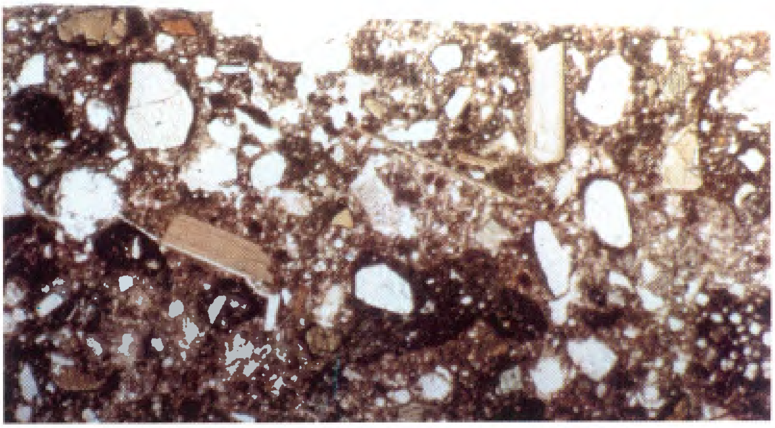


Figure 6.1

The Temple of Antoninus and Faustina.

Figure 6.2

The podium is made from blocks of Peperino.



Figures 6.3 and 6.4 Thin section of Peperino, showing the compact, relatively homogeneous structure of this mudflow, rich in crystals of pyroxene, biotite, sanidine and analcimized leucite. (Top: PPL, ×31; Bottom: XPL, ×31)

Figure 6.5 **Scaling and alteration on the surface of the Peperino blocks of the podium of the Temple of Antoninus and Faustina. They affect a thickness of only a few centimetres and are more marked at the contact surface between blocks.**

Figure 6.6 **Basement walls of the Tabularium. It is an "opus quadratum" of Pietra Gabina blocks. The texture of this material renders it susceptible to de-cohesion and differential erosion phenomena.**

Figure 6.7 The structure of the archaic sewer is made with blocks of Tufo grigio granulare. These show marked rounding of the exposed surfaces and scaling of the surface to a depth of at least 1 cm.

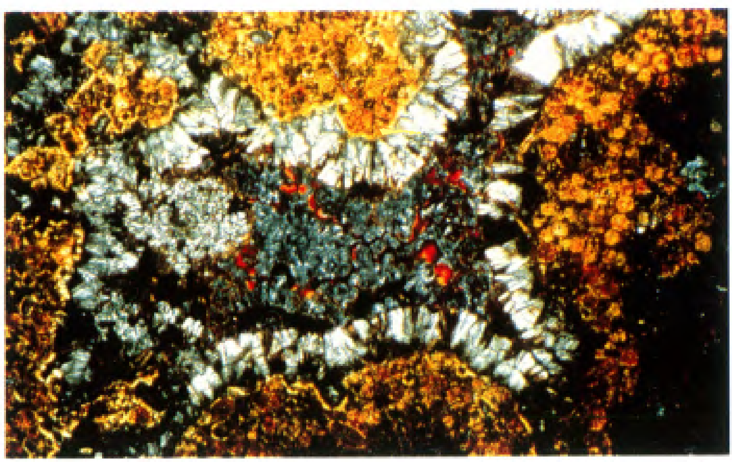


Figure 6.8 Thin section, XPL, ×31. Tufo rosso a scorie nere showing zeolite crystals lining the scoriae.

with water, as the water table in the Forum is very close to the surface. As long as environmental conditions allow the rocks to retain their humidity, they appear compact, preserve their original shape and still bear on the surface the scars of the chisels used in the quarries.

In terms of conservation, the significance of the amount of water in the stone may be seen in examples furnished by the behaviour of the Tufo grigio granulare (locally known as *Cappellaccio*) in two monuments. The first example is the Temple of Saturn, where the ancient basement has a 5 × 2 m trench made of blocks of the tuff. They are in a humid environment and since their excavation in 1985 they have showed very little sign of alteration. The Romans must have known that this material was very suitable for humid conditions or for underground structures, as it was used for the walls of wells and cisterns long after better-quality tuffs were introduced in the building industry [4]. The second example is that of blocks of the same Tufo grigio granulare used in an ancient sewer located between the Temple of Concord and the Temple of Vespasian. These blocks were exposed during excavations carried out in the early 1980s and left with no protection. After only two years, the natural drying/wetting cycles had induced major loss of cohesion, with rounding of the blocks in the upper row. Though no quantitative assessment can be made, it appears that covering of this structure in 1985 slowed down the alteration process considerably.

Similar behaviour was observed in most of the other tuffs, though with diverse evolution related to their structural variability. Exfoliation, fissuring, loss of cohesion and lifting and detachment of scales are common phenomena, which are markedly accelerated during the uncontrolled exposure of water-saturated blocks. The best state of preservation can be seen in recently excavated structures, such as the Votive Stele, or in structures that since their excavation have been well protected, such as the floor of the Opimian phase of the Temple of Concord. 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 they have very good mechanical properties; if in the open and exposed to icing and humidity, they become friable and dis-aggregate."

As regards chemical processes of alteration, their influence on degradation of the tuffs is very limited in comparison to the 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.

6.4.2 Investigations on chemical alteration products

Specific sampling was carried out on patinae, scales, whitish deposits under the scales, efflorescences and whitish surfaces of the various tuffs in order to identify secondary components derived from the alteration or modification of the primary constituents. X-ray powder diffraction analyses revealed that gypsum is practically the only common secondary mineral, and then in only limited quantities. Gypsum is much more common in the whitish, powdery material under the scales than within the compact rock, and is very abundant in the white efflorescences. The maximum content was found in some samples of the Pietra Gabina, where the sulphate ion reached 8-9% by weight.

The Pietra Gabina of the Tabularium also has minor amounts of halite (NaCl), which can be accounted for from reports in the literature which record the use of the upper part of the Tabularium as a deposit for common salt in the fifteenth and sixteenth centuries. Even the base of the structure shows some salt that leached through. No traces of NaCl were observed in any other of the tuffs analysed.

Confirmation of the very low content of secondary components in these tuffs is given by their low soluble-salts content. Applying the standard procedures of NORMAL 13/83 [10], colorimetric and spectrophotometric methods were used to determine the contents of sulphate, nitrate, nitrite, chloride, sodium, potassium, ammonium, calcium and magnesium ions. Results show that their concentration is very low in most samples. Efflorescences and powdery deposits under the scales are, on average, the richest in soluble salts. The samples analysed were collected from blocks *in situ* or from blocks excavated a few years before. Therefore it is not possible to assess the rate of transfer of soluble salts from the surface to deeper layers. As a control – no chemical alteration – sample 85/SAT/01 of Tufo grigio granulare could be used since it was collected only a few months after excavation. In this sample, sulphates, chlorides, ammonium, sodium and potassium were found, and the other ions were below detection limits. The values found are very low and comparable with others from materials exposed for a much longer time.

Among the ions analysed, only sulphate distribution shows a pattern that may be tentatively correlated with the structural-compositional characteristics of the blocks and with their exposure to atmospheric agents. Soluble salts appear to derive from interaction of the tuffs with atmospheric pollutants, where sulphate ions predominate. Migration of sulphate ions and of other ions within the rock pores is conditioned by the degree of humidity of the blocks. This movement is also dependent upon the high concentration gradients which develop between the outer surfaces and the internal net of pores within the tuffs. Frequency and intensity of the wetting/drying cycles favours the concentration of salts in discontinuities such as fissures and micro-fractures, in part induced by mechanical stresses. Such concentrations tend to accelerate phenomena of scaling and exfoliation, and this hypothesis is supported by the high sulphate concentration within the powdery deposits under the scales.

In conclusion, damage related to soluble salts originates from exposure to atmospheric agents and cannot be considered critical, due to the structure of the tuffs and their pore pattern.

6.5 CONSERVATION TREATMENTS

The treatment tests in the laboratory were carried out on 3 × 3 × 3 cm cubes; because they were taken directly from blocks of the monuments being studied, only a limited quantity of samples could be obtained. A control cube was also taken from the interior of the block being studied. This was taken from at least 15 cm in from the outside surface as macro- and microscopic observations indicated that no external process had influenced the rock's properties to that depth.

For each sample, the capillary water absorption coefficient (***CA***) [11], the porosity (***P%***) and pore size distribution [12], the bulk density (***BD***) and the specific surface area (***SSA***) were determined before and after treatment. The effectiveness of the treatment was evaluated from these measurements by calculating a variation index for each parameter.

The products tested were *Wacker OH* and *Wacker H*, both from Wacker Chemie. *Wacker OH* is an ethyl ester of orthosilicic acid and is a consolidating agent. It was used both as a single treatment and in combination with either a second application of *Wacker OH* or a subsequent application of *Wacker H*, which is a mixture of an ethyl ester of the orthosilicic acid with a polysiloxane, and which acts both as a consolidating and as a hydrophobization agent.

The *Wacker OH* was applied by capillary absorption by the simple means of totally immersing the sample in the product until it was totally saturated. Only five of the six tuffs could be tested in the laboratory as insufficient samples of the Tufo lionato were available to complete the tests.

Wacker H was applied to the Tufo giallo and to the Peperino, chosen for their difference in structural properties. The other three tuff types were retreated with *Wacker OH.*

The choice of products was based on the nature of their consolidating effect: the precipitation of amorphous silica in the pores of the tuffs. As the silica precipitated is chemically similar to the glassy matrix of the tuff, no foreign substance is introduced that might possibly be chemically active. It should be borne in mind that these tuffs contain a high percentage of zeolites, which are highly reactive minerals with a considerable ion exchange capacity. This capacity for ion exchange could easily lead to interaction with a chemical substance introduced into the system. Such interaction did not become apparent with the products tested.

In situ impregnation tests were carried out using *Wacker OH* alone. The treatments were applied to larger surfaces on the monuments under study – 0.25 m^2 compared to the 0.0009 m^2 of the cube faces – in order to verify results obtained in the laboratory. No tests could be carried out *in situ* for the Peperino tuff. The treatments were carried out on dry surfaces, but in environments of average or high humidity.

The treated samples were not analysed until at least three months after application, in order to be sure that the hydrolysation process was complete.

Because of potential osmotic effects, the products were used undiluted for both laboratory and *in situ* testing, thus avoiding any risks of uneven distribution of the active ingredient in the pore system of the tuff. This also enabled data to be obtained regarding the effect of excess consolidating agent in the pores of the stone.

Table 6.2 summarizes all the data obtained for untreated and treated samples, under both laboratory and *in situ* conditions.

Table 6.2 Physical parameters of the untreated and treated samples

Volcanic rock	Treatment	Porosity (%)	Bulk density (g/cm^3)	Specific surface (m^2/g)	Absorption coefficient (g/cm^2.s$^{0.5}$)
Tufo giallo	Untreated	37.40	1.42	6.60	0.150
	Wacker OH	32.61	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 a 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	Untreated	38.56	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

6.5.1 Physical characteristics of the untreated tuffs

Table 6.2 gives the values of ***P%***, ***DB***, ***SSA*** and ***CA*** for the untreated tuffs. It can be seen that the values range widely according to differences in structural characteristics of the various tuffs. Porosity varies from 28.9% for the Peperino to 46.0% for the Tufo giallo; the bulk density from 1.16 g/cm^3 for the Tufo rosso a scorie nere to 2.05 g/cm^3 for the Peperino; and the specific surface area from 27.7 m^2/g for the coarse-grained Tufo rosso a scorie nere to 6.6 m^2/g for the fine-grained Tufo giallo.

The wide variability in physico-mechanical characteristics of these tuffs reflects the variability of the possible conditions under which they were formed. Therefore each case requires a complete study so as to acquire the necessary knowledge of the particular material, and great caution is recommended before proceeding to any consolidation treatment.

6.5.2 Treatment with *Wacker OH*

Table 6.2 also gives data for physical characteristics measured after the first and the second treatment with consolidant. The first general observation is that in all cases the values of ***P%***, ***CA*** and ***SSA*** tend to decrease with the treatments. The impregnation of the samples with the consolidant results in a reduction in total porosity of the stone and therefore reduces the water absorption rate. The partial closing of the pores or the decrease in their diameter was shown by decreased specific surface areas. 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 the treatments as the consolidant precipitated within the pores. Variations in weight (Table 6.3) observed before and after treatment indicate the amounts of material deposited in a sample. It should be pointed out that the relative increase in weight was higher in the second treatment.

Table 6.3 Weight increase of the samples after treatment

Volcanic rock	Treatment	Bulk density (g/cm^3)	Initial weight (g)	Weight increase (g)	Weight increase (%)	Weight increase per surface unit (g/cm^2)
Tufo giallo	Wacker OH	1.71	35.15	2.30	6.54	0.04
	Wacker H	1.56	35.80	2.41	6.73	0.04
Tufo rosso scorie nere	Wacker OH	1.48	31.65	3.12	9.85	0.06
	Wacker OH (2nd treat.)	1.55	31.65	4.48	14.15	0.08
Tufo grigio granulare	Wacker OH	1.56	31.92	3.01	9.43	0.06
	Wacker OH (2nd treat.)	1.50	31.92	4.73	14.82	0.09
Pietra Gabina	Wacker OH	1.96	46.15	2.43	5.26	0.04
	Wacker OH (2nd treat.)	1.98	46.15	3.53	7.65	0.06
Peperino di Albano	Wacker OH	2.01	50.87	1.15	2.21	0.02
	Wacker H	2.00	50.87	1.55	2.95	0.03

In order to check whether an increase in the amount of consolidant improved mechanical properties and resistance to alteration, a second treatment was applied to samples of Pietra Gabina, Tufo grigio granulare and Tufo rosso a scorie nere. In all three cases (Table 6.3), the second treatment clearly brought about a decrease in mechanical properties of the material, as reflected in the increase of *CA* and the changes in pore size distribution discussed below.

In the case of the Tufo rosso a scorie nere, the capillary absorption curves showed an anomalous pattern. The first impregnation with *Wacker OH* resulted in a system with an absorption rate which was initially low, but which changed rapidly to fast absorption, with total saturation in approximately six hours. This behaviour can be attributed to the peculiar texture of this material, which is very rich in glassy scoriae and has a high porosity. The second treatment with this product increased the capillary absorption coefficient to values even higher than those of the untreated material.

From the pore size distribution it can be seen that the percentage of pores <0.4 μm decreased while the large pores (diameters >2 μm) increased. This can be attributed to rupture of the internal pore net of the rock.

The Tufo grigio granulare also showed a clear variation in its capillary water absorption coefficient upon treatment. The first impregnation reduced the initial water absorption rate to one-sixth that of the untreated sample, while the second treatment shifted the water absorption curve closer to that of the untreated one (Figure 6.9).

This can be explained as a function of the change in pore size distribution as a result of the treatments. During the first impregnation a reasonably good distribution of the consolidating agent within the pore net of the tuff was achieved, as indicated by the similar diminution of all pore sizes. During the second treatment, rupture of the internal pores occurred, indicated by the large increase in numbers of pores >10 μm (Figure 6.10).

The capillary water absorption pattern for the Pietra Gabina tuff showed that the first treatment reduced the initial water absorption rate significantly, but the curve does not reach saturation point, even after 24 hours. The second treatment produced a curve similar to that of the untreated sample, but with a slightly lower water absorption rate.

The explanation can be found by considering the change in pore size distribution in the samples following the treatments. It appears that though total porosity decreases, the percentage of larger pores (diameters >2 μm) increased markedly, especially after the second treatment, which, as noted above, can be attributed to rupture of pores as a result of the increased amount of consolidant introduced.

6.5.3 Treatments with *Wacker OH* and *Wacker H*

Application of *Wacker H* was carried out as the second treatment on the two tuffs which had the most diverse structural properties: the Tufo giallo, a pyroclastic flow, very rich in zeolites, with 46% porosity and a bulk density of 1.41 g/cm^3 [13]; and the Peperino, a cold mudflow, with only minor amounts of zeolites, 29% porosity and a bulk density of 2.05 g/cm^3.

Capillary water absorption coefficients showed significant reductions following treatment, especially for the Peperino. The pore size distribution after the treatment with *Wacker OH* changed little for the Tufo giallo, but changed significantly for the Peperino, where the percentage of smaller pores (<1 μm) changed significantly. After

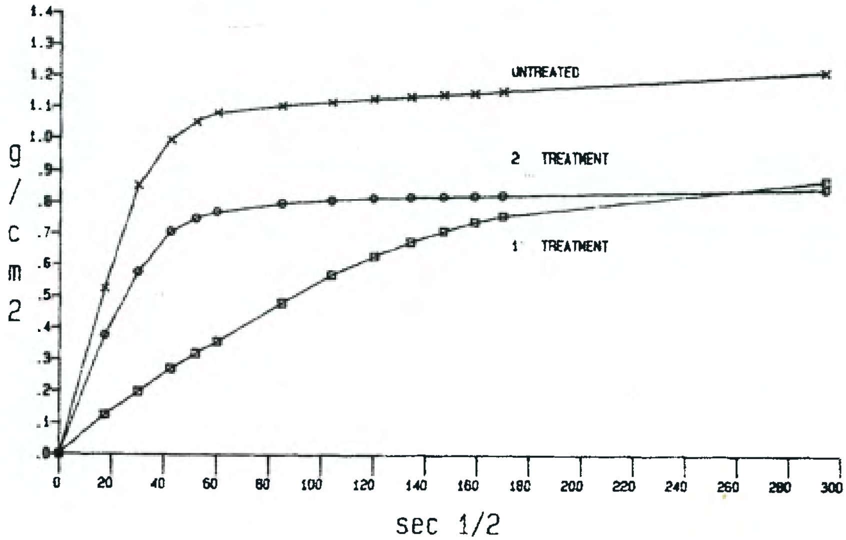


Figure 6.9 Water absorption curves for the untreated and treated samples of Tufo grigio granulare.

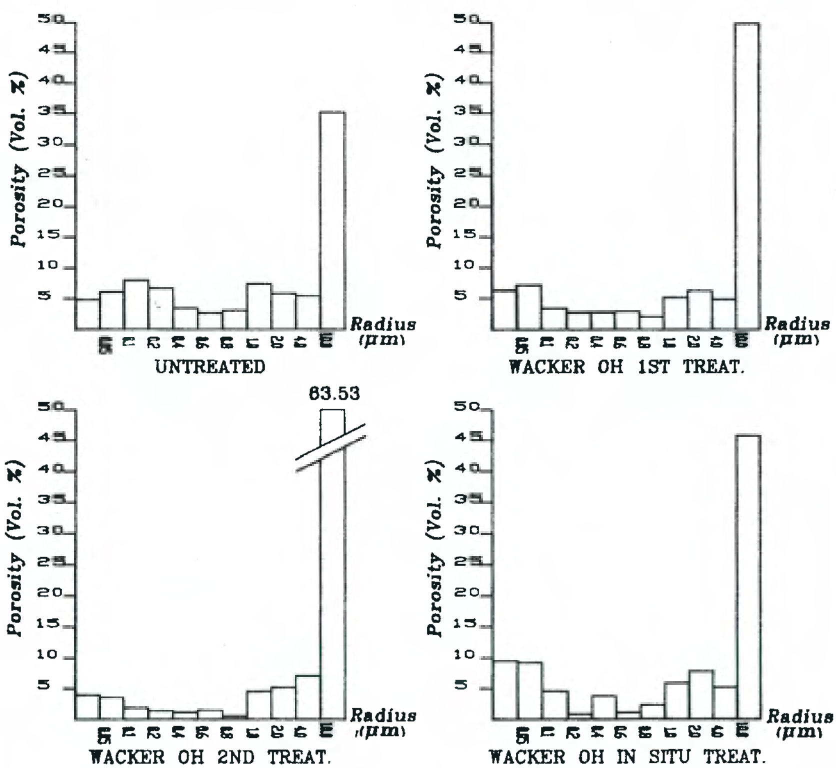


Figure 6.10 Pore size distribution histograms for the untreated and treated samples of Tufo grigio granulare.

treatment with *Wacker H*, the pore size distribution for the Tufo giallo showed an increase in smaller pores, while for the Peperino the main change occurring was an increase in the percentage of the 1-2 μm pores and a decrease in larger ones (>4 μm).

6.5.4 *In situ* consolidation tests

In order to assess the efficiency of consolidation treatments with *Wacker OH* in field situations where an advanced stage of degradation has been found, the product was applied directly to the tuff blocks of the monuments from which the original samples had been collected. The treatment was carried out on areas of 0.25 m^2, large enough so that the overall results would not be unduly influenced by minor inhomogeneity in the material or its deteriorated surface. When for particular reasons it was impossible to work directly on the monument, the treatment was applied to nearby blocks of the same material.

The product was tested on:

- **Tufo giallo**: altered blocks at the back of the Temple of Saturn.
- **Tufo rosso a scorie nere**: podium blocks of the Temple of Concord.
- **Tufo lionato**: back wall blocks of the cella of the Temple of Concord.
- **Tufo grigio granulare**: sewer system, in front of the Temple of Concord.
- **Pietra Gabina**: blocks of the Tabularium, at the back of Temple of Concord.
- **Peperino**: no *in situ* tests were carried out.

The consolidant was applied by brush, using approximately one litre of the undiluted commercial product per square metre of surface. The application was continued until the rock was saturated. The treated surfaces were protected by temporary covers to prevent both washing off by rain and heating by direct sunlight. The tests were carried out in October 1989 under favourable climatic conditions – very little rain and mild temperatures. The samples for porosimetric analysis, the only type of measurement for which sampling was possible and that could produce informative data, were collected in January 1990. A three-month period was considered long enough to guarantee complete hydrolysis and condensation of the ethyl silicate.

Field observations made with the help of a magnifying glass showed that the treated surface had increased cohesion and that there was a significant decrease in powdering and dis-aggregation. However, the treatment did not substantially reduce the tendency of the stone to scale and exfoliate. Moreover, the consolidating agent tended to accumulate in the characteristic open surface fissures of these tuffs, thus distribution within the rock was not homogeneous. Scales approximately 5 mm thick were detached from the surface of the treated tuffs, and the total porosity, pore size distribution, bulk density and specific surface area were determined.

The values obtained showed that the consolidating treatment applied to the surface of these materials gave reasonably good results, as may be seen from the decrease in total porosity and specific surface area (Table 6.2). The increase in bulk density reflects the amount of silica that was deposited in these surface layers.

6.6 DISCUSSION

Assessment of the effectiveness of the applied treatments is not easy, as the measured parameters, such as bulk density, porosity, specific surface area and capillary water absorption, already vary widely from one type of tuff to the other. Therefore the available experimental data were processed using the percentage relative change of a given parameter (***RC*%**). This is calculated for each parameter using the formula:

$$RC\% = \frac{P_o - P_i}{P_o} \times 100$$

where:

$RC\%$ = relative change of the given parameter
P_0 = value of the parameter for the untreated sample
P_i = value of the parameter for the treated sample

The various calculated ***RC*s** are reported in Table 6.4. An analysis of the values obtained shows an overall agreement with what would be expected from consolidation treatments. Nevertheless, there are various inconsistencies when reviewing individual data in detail.

The relative change in porosity, $\boldsymbol{RC_p}$, appears to indicate that a second treatment leads to better results. This contrasts with experimental data, such as the pore size distribution, which indicate rupture of the pores owing to excess deposition of the consolidating agent.

The relative change in bulk density, $\boldsymbol{RC_{bd}}$, is not always significant, as there are marked local variations in this parameter due to natural inhomogeneities in the tuffs.

The relative change in the specific surface area, $\boldsymbol{RC_{ssa}}$, and that of capillary absorption, $\boldsymbol{RC_{ca}}$, seem better to reflect the effects of the consolidation treatment. Figure 6.11 shows the histogram based on the values of the $\boldsymbol{RC_{ca}}$ parameter. In agreement with the pore size distributions obtained, the changes are well reflected in the decreased – or even negative – values obtained 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 consolidant is introduced into the tuff. The addition of a hydrophobic agent, or of a product with both elastic and binding properties, gives much better results and favours sealing of the micro-fissures. Scaling and exfoliation should be resolved by other, non-chemical, treatments.

Table 6.4 **Relative changes in the measured parameters: porosity, bulk density, specific surface area and capillary absorption coefficient**

Volcanic rock	Treatment	Porosity RC_p %	Bulk density RC_{bd} %	Specific surface RC_{ssa} %	Absorption coefficient RC_{ca} %
Tufo giallo	Wacker OH Wacker H Wacker OH *in situ*	+12.80 +28.37 +29.84	−20 −10 −11	−26.96 −10.45 −10.45	+46.00 +99.33 —
Tufo rosso a scorie nere	Wacker OH Wacker OH (2nd treat.) Wacker OH *in situ*	+19.89 +27.19 +10.91	−27 −34 −50	+65.34 +73.28 +60.76	+66.66 −16.66 —
Tufo lionato	Wacker OH *in situ*	+40.40	−14	+46.91	—
Tufo grigio granulare	Wacker OH Wacker OH (2nd treat.) Wacker OH *in situ*	+37.44 +42.72 +27.49	−20 −14 −32	+50.55 +72.55 +33.60	+83.33 +30.00 —
Pietra Gabina	Wacker OH Wacker OH (2nd treat.) Wacker OH *in situ*	+39.12 +59.07 +42.93	−2 −3 −0.5	+61.14 +71.27 +43.38	+71.43 +28.57 —
Peperino di Albano	Wacker OH Wacker H	+17.35 +28.07	+120 +6	+1.85 −1.65	+85.29 +97.06

6.7 CONCLUSIONS

From the examination of over forty Roman monuments in the Forum and on the Palatine, it appears that, in the beginning, tuffs outcropping in the local area were used for construction, and then other, better, materials were brought in from further away. Most of the main quarries were located along the valleys of the Tiber and Aniene rivers, the ancient highways for goods, which led to the centre of Rome. The exception is the Peperino di Albano, the quarries of which, although located away from the rivers, offered such a good building material that it could also be used for decorative architectural elements.

The tuffs used in the monuments are ignimbrites, mudflow, and phreatomagmatic deposits with varying structural and physico-mechanical characteristics. This diversity occurs between elements of the same material, and also between various levels of the quarry or between different quarries. The various tuffs were used in widely differing applications: from foundations, to structural elements, to architectural decorations.

Mechanical deterioration processes are by far the most important and cause the worst damage. Chemical deterioration processes are subordinate. The overall impression from a series of field studies carried out in diverse seasons and years, monitoring the changes in the tuff blocks after their excavation, permits some conclusions to be made about the degradation process. The blocks are well preserved at depth, though

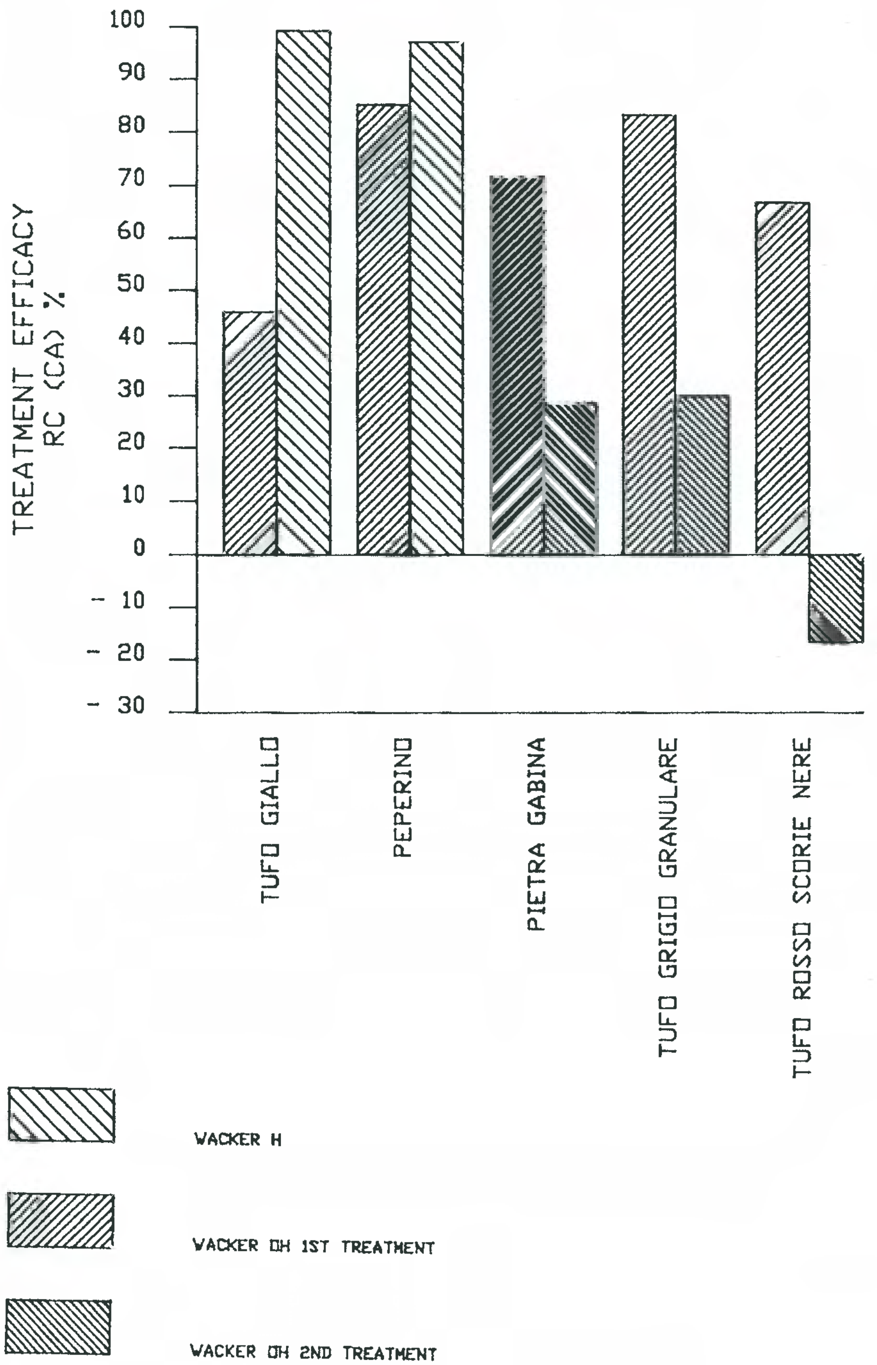


Figure 6.11 **Histogram comparing treatment efficacy, based on RC_{ca}, for the two treatments studied on different tuffs.**

water saturation decreases their mechanical strength. The exposure of these blocks is a critical point. If their loss of humidity is not controlled and regulated by protective structures – protecting them against heating/cooling or freeze/thaw cycling – their degradation is rapid. This degradation may already be obvious in the first or second year after excavation.

Fissuring, exfoliation, lifting and detachment of scales are typical forms of mechanical alteration. They appear to be due to mechanical stresses induced in the surface layers of the block by the shaping and chiselling done in the quarries. Of different tuffs studied, the Tufo grigio granulare and the Tufo giallo present the most deteriorated state, with loss of cohesion and rounding of corners. The detachment of large scales common in the Peperino di Albano can be attributed to mechanical stresses.

Most of the alterations are related to presence of fissures of varying dimensions: large ones caused by prolonged, strong seismic activity occurring in the Rome area, and development of small ones, favoured by crystallization of secondary salts (mainly gypsum), which form under the scales on the surface of the blocks and the architectural elements.

Before deciding on any conservation treatment, it is essential to build up detailed knowledge of the tuffs in question, as the variability of these materials means that a statistically significant number of analyses with appropriate techniques are required for their proper characterization.

From the experimental data, it appears that the best treatment results were obtained with only one application of *Wacker OH*. A second treatment, or a prolonged application of the consolidating agent, modifies the pore size distribution due to collapse of the internal pore walls, thereby reducing the efficacy of the treatments.

On the two tuffs with the most differing structural and physico-mechanical characteristics, a second treatment with *Wacker H* (a combined consolidant and hydrophobization agent) was tested. Very good results were obtained. These experimental results imply that the presence of a binding agent, such as the siloxane, improves the surface conditions of the blocks and aids homogeneous distribution of the product in the pores of the stone.

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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 describen 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 *in situ*. La eficacia del tratamiento fue evaluada 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.

RESUME

Une étude sur le terrain a été réalisée dans les zones du Forum et du Palatin (Rome) ainsi que dans les régions volcaniques de cette province en vue d'identifier les monuments qui ont utilisé des matériaux volcaniques comme éléments structurels ou décoratifs. Six principaux types de pierres volcaniques ont été recensés. On a recueilli des données détaillées sur la pétrographie, les utilisations, l'emplacement d'anciennes carrières et le type d'altération. Le processus chimique de l'altération et ses effets sont décrits. Les résultats des traitements expérimentaux de conservation, effectués tant *in situ* qu'en laboratoire à l'aide de deux consolidants, sont présentés pour les six types de pierres étudiées. L'efficacité des traitements a été évaluée au moyen d'un indice d'absorption hydrique. Les résultats montrent qu'une seule application d'un même produit consolidant assure apparemment une meilleure protection que des applications répétées.

KURZFASSUNG

Zum Zweck der Erfassung von Monumenten, an denen vulkanische Gesteine als Architektur- bzw. Dekorationselemente verbaut sind, wurde eine Feldstudie in den antiken Bezirken von Forum Romanum und Palatin in Rom bzw. in den Vulkangebieten seiner Provinz durchgeführt. Dabei konnten sechs Hauptgruppen vulkanischer Gesteine identifiziert werden. In der Folge wurden vollständige Datenblätter mit Angaben zur Petrographie, zur Verwendung, der Lage der antiken Brüche und den Schadensformen angelegt; eine chemische Charakterisierung der Verwitterung und ihrer Produkte wird in der vorliegenden Arbeit gegeben. Konservierende Versuchsbehandlungen mit zwei Festigungssystemen wurden an den sechs Steinsorten durchgeführt, und zwar sowohl in-situ als auch im Labor; die Resultate werden vorgestellt. Die Wirksamkeit der Behandlungen wurde mit Hilfe des Wasseraufnahmeindex bewertet. Es zeigt sich, dass eine einmalige Konsolidierung offensichtlich einen besseren Schutz gewährleistet als eine wiederholte.

CHARACTERIZATION AND STATE OF DECAY OF THE VOLCANIC TUFF OF THE TABULARIUM IN THE ROMAN FORUM, ITALY

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ABSTRACT

The Tabularium was reconstructed using a volcanic tuff named Lapis Gabinus, after the old Town Council Building of the Romans burnt down in 83 BC. The results of a detailed study of the mineralo-petrographical characteristics and the physico-mechanical properties of this tuff are reported. The use of the Tabularium as a salt store in medieval times caused marked decay in the tuff blocks and columns, with extensive occurrences of scaling, crumbling and alveolar weathering. Consolidants were applied in the early 1970s, 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.

7.1 INTRODUCTION

The Tabularium dominates the Forum Valley towards the south-west. It includes an important substructure built from a Quaternary volcanic tuff known locally as *Lapis Gabinus* or *Pietra Gabina* and which was used as a building stone up to the time of the Roman Empire. It was built in 78 BC by Q. Lutetius Catulus in order to preserve government documents and public deeds (*tabulae*) after the Capitolium burnt down in

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Figure 7.1 **The structure of the Tabularium is located at the base of the Capitolium and overlooks the Roman Forum. In the lower part, the blocks of the Lapis Gabinus tuff may be seen. The columns bordering the entrances at half height are also made of this tuff. In the last few years, excavations lowered the ground level considerably and exposed the base of the wall.**

83 BC. Its location was close to a complex that was already the most ancient archive of the Roman State, having been in use since as early as the fifth century BC [1].

During the Middle Ages, as frequently occurred with "monopoly" facilities, it was used as a warehouse for storing common salt. The masonry and the columns of the monument have suffered from the effects of the salt over time, which in some places caused considerable decay – so much so that the very stability of the monument was undermined.

The present study gives the structural, mineralogical, petrographical and mechanical characteristics of the tuff blocks used to build the Tabularium, and provides an evaluation of the restoration measures taken some 20 years previous to this study.

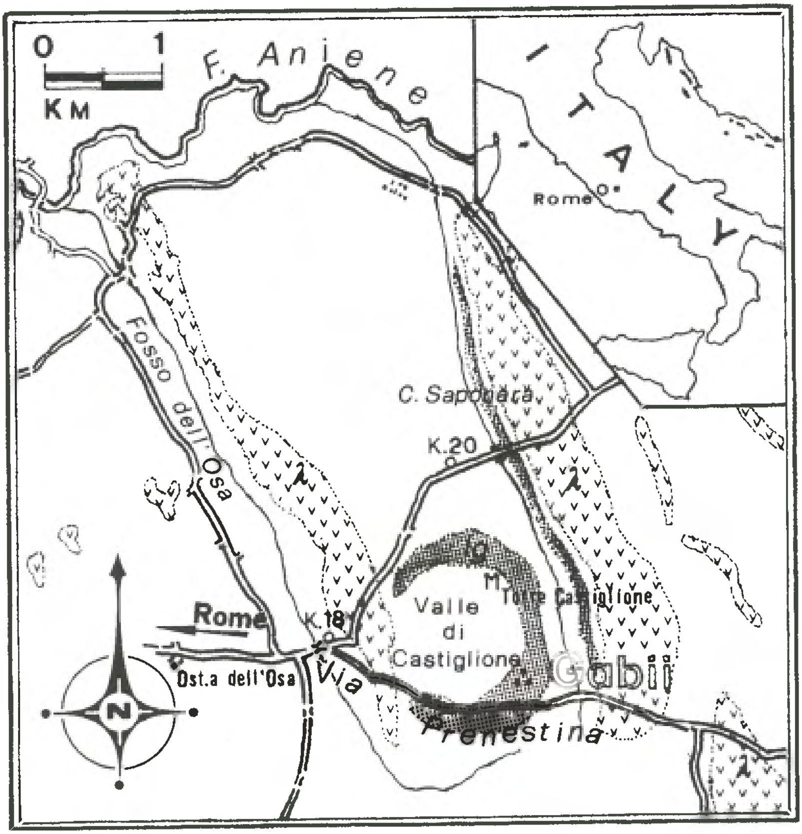


Figure 7.2 The area where the Lapis Gabinus outcrops are located, 20 km to the east of Rome. lg= Lapis Gabinus tuff; Æ = leucitic lava.

Figure 7.3 Typical surface of a Tabularium block, with exfoliation and scaling.

7.2 CHARACTERIZATION OF THE LAPIS GABINUS

7.2.1 Geological setting and petrography

The Lapis Gabinus is a type of granular tuff: a product of a late stage of the volcanic activities in the Alban Hills [2; 3]. The Lapis Gabinus outcrops occur mainly in the crater depression of Lake Castiglione, 20 km to the east of Rome, near the remains of the town of Gabii (Figure 7.2). 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 out to the west of the Saponara leucitic lava flow and along the eastern border of Lake Castiglione [4; 5], which had already been reclaimed by the fifteenth century. *In situ*, the Lapis Gabinus tuff often presents typical bedding with layers containing larger inclusions alternating with incoherent sandy layers. The thickness of the formation can reach 60 m. The structural and textural characteristics are typical of the products of phreatomagmatic activity [6; 7] with depositional characters of a base surge [8; 9].

The material used in the buildings of the Roman Forum can 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 calcareous or marly inclusions range in colour from white to pink to deep orange, and have rounded edges. In some facies, such as the one typical of the blocks used for the Tabularium, there is an abundance of zeolites (Figures 7.7 and 7.8). This mineralization may be seen in polished sections as whitish veinlets that mark the outline of darker volcanic elements.

Thin sections, both from 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 are leucite, pyroxenes, biotite and a 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 various sizes – sometimes fossiliferous – as veins and void replacement, or as substitution of leucite. Flintstone fragments are less common.

Leucite is often shrouded in icositetrahedrons having at times crystalline germs and microlithic and glassy fragments arranged according to a concentric and radial pattern (Figure 7.4), 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. They are frequently euhedral, and sometimes show a slim boundary reaction and re-absorption recess (Figure 7.6) zoned for chemical inhomogeneities, with inclusions of apatite and opaque minerals. They can be considered as members of the augite and aegirinaugite series. Pleochroic, very thin stressed laminae of biotite are also frequent. Much less common

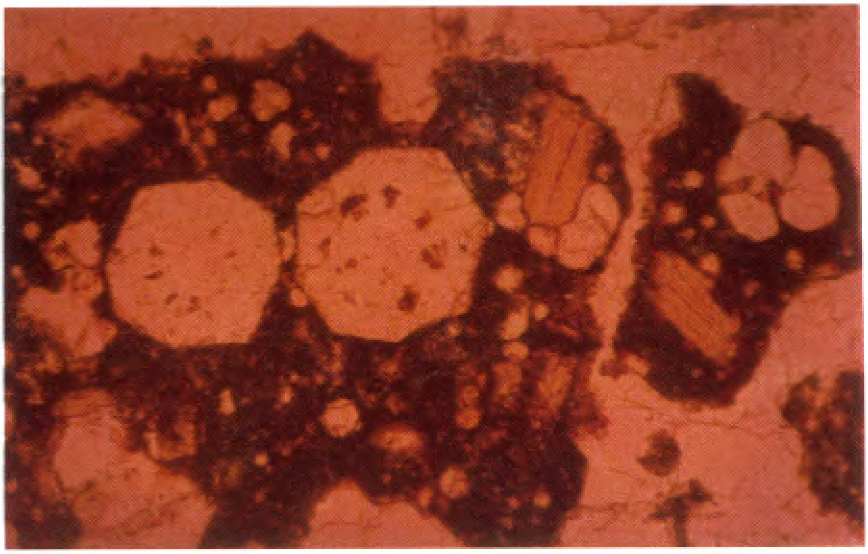


Figure 7.4 Thin section, XPL, ×50. Icositetrahedric shape of leucite, with cross-shaped ghosts and zeolite aggregates in the matrix.

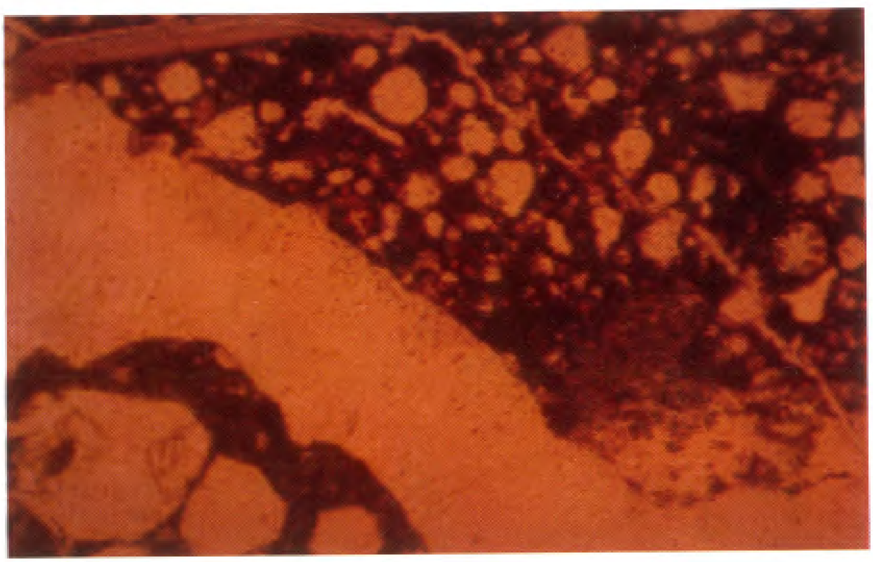


Figure 7.5 Thin section, XPL, ×12. Matrix of Lapis Gabinus tuff showing scoriae and leucite. A scoria is crossed by a fracture.

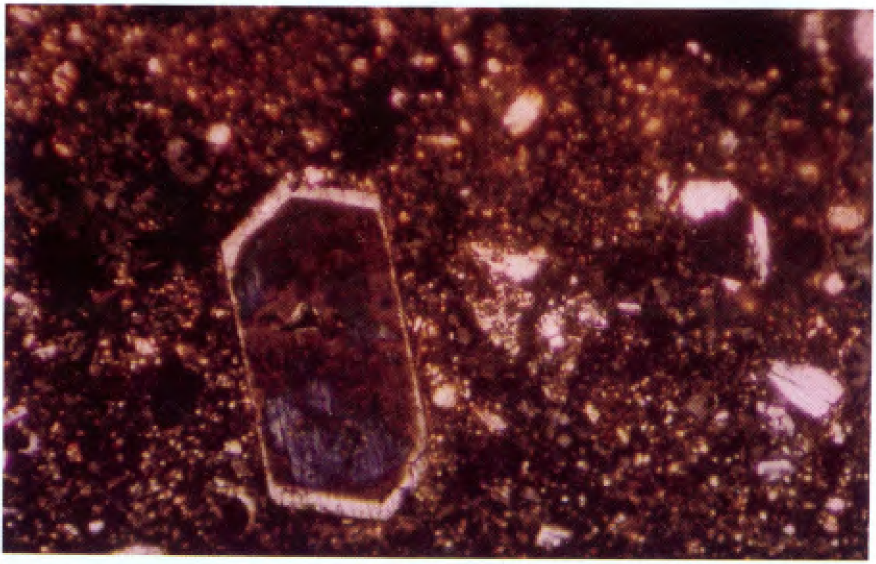


Figure 7.6 Thin section, XPL, ×95. Pyroxene crystals with zoning (left) and re-absorption embayments (right).

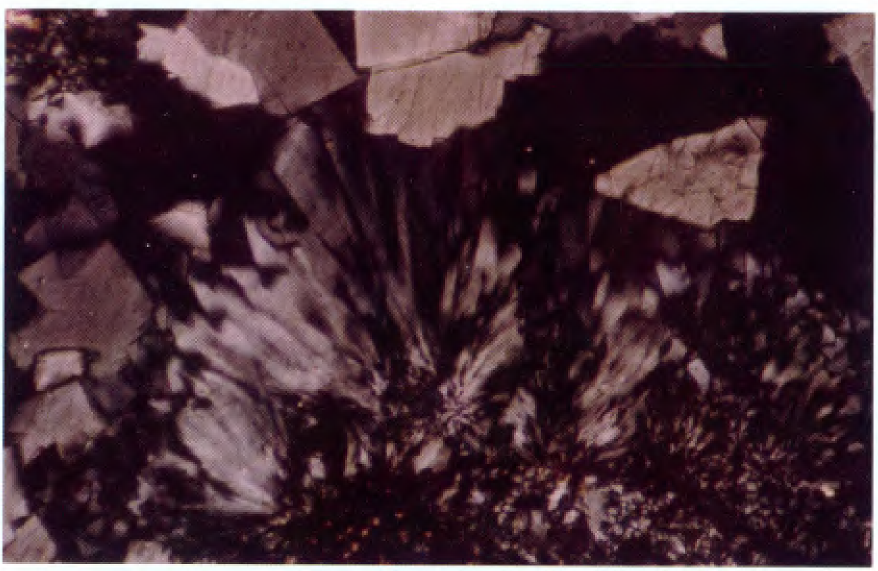


Figure 7.7 Thin section, XPL, ×50. Aggregates of fibrous phillipsite with pseudo-cubic crystals of chabazite.

Figure 7.8

SEM photomicrograph, showing twinned chabazite crystals on a fracture surface from a tuff block of the Tabularium.

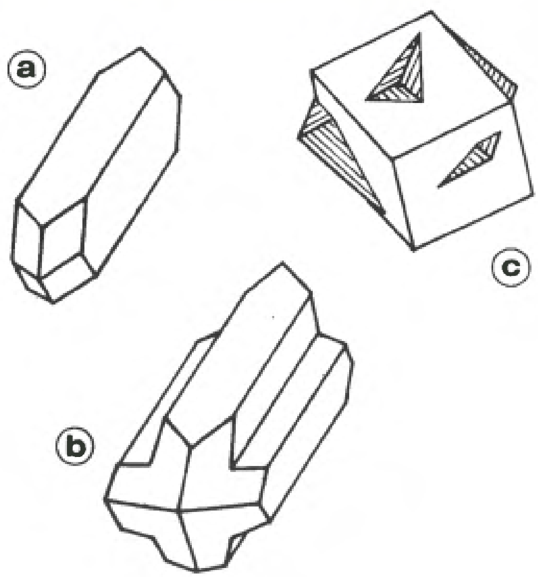


Figure 7.9

Various twinnings found in the zeolites of the Tabularium tuff:
(a) and (b) simple and complex twinning of phillipsite;
(c) pseudo-cubic interpenetrated crystals of chabazite.

among the minerals in the matrix are olivine with the typical meshwork grid, plagioclase, garnets and perowskite.

The matrix of this tuff is characterized by a mosaic of low bi-refringence 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 pseudo-cubic symmetry and interpenetration twinning. Figure 7.7 shows a photomicrograph taken with a polarizing microscope, and Figure 7.10 shows a scanning electron microscope (SEM) photomicrograph of the zeolites in the Lapis Gabinus matrix. The abundance of well-developed zeolites in the matrix suggests a derivation from "hot and wet" phreatomagmatic products [10].

X-ray powder diffraction analyses (XRD) of samples taken from blocks of the Tabularium – at the surface; at a depth of 5 cm; of the surface patina; of the extracted salts – and of the zeolitic matrix of a tuff block from the ancient quarries of Gabii, are reported in Table 7.1.

Table 7.1 **Powder X-ray diffraction of samples of the Lapis Gabinus blocks taken from the Tabularium and from the quarry.**

SAMPLE	#1	#2	#3	#4	#5
Analcime			±		±
Calcite			+	++	+
Chabazite	+++		++	+++	+++
Gypsum	++	+++			
Halite		++++	+++		
K-feldspar					±
Leucite	±		+	+	+
Mica					+
Phillipsite			+	++	+
Pyroxene	±		+++	±	++
Sylvite		++			

#1 White, soft patinae on the surface of the Tabularium blocks.
#2 Salts extracted from sample #3.
#3 Surface sample from a tuff block of the Tabularium.
#4 Sample taken at 5 cm depth in a tuff block of the Tabularium.
#5 Zeolitic matrix of a tuff block from the Gabii quarries.

7.2.2 State of decay

The Lapis Gabinus of the Tabularium was used in the form of columns and of large parallelepiped 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: exfoliation and alveolar weathering, and also damage induced by mechanical stresses. The external surface of the walls became crumbly, pulverulent, with release of the embedded clasts due to the decay of the groundmass.

Figure 7.10

Microfractures, tending to spread out towards the external surface of a block of the Tabularium tuff.

Figure 7.11

SEM photomicrograph, showing, on a fracture surface of a block from the Tabularium, pseudo-cubic twinned crystals of chabazite with (whitish) secondary gypsum granules on the surface and, centre right, a microfracture.

SEM studies of surfaces from the tuff blocks showed diffused fracturing with fissures beginning almost always in the zeolitic or glassy matrix (Figure 7.10 and Figure 7.11) along the boundaries of the various clasts, and only in some instances propagating across the debris and the phenocrysts (Figure 7.5). The same type of fracturing was also observed in blocks closest to the soil level of ancient constructions in the town of Gabii.

7.2.3 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 anions were identified: chlorides and sulphates. Nitrates were found to be present only in very small amounts (<0.001%).

Figure 7.13 gives the concentration profile of these two ions across a tuff block in the ashlar masonry. Chloride content varies widely across a block, decreasing from 0.37% at the surface to 0.12% at about one-third of the thickness of the block. It then increases abruptly to 2% at the centre of the block, decreasing finally 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 to a depth of approximately 35 cm, and then increasing to 1.0% at the interface with the mortar and to 2% in the mortar on the back surface of the block.

On the external surface of the blocks of the Tabularium, the concentration of chlorides ranged between 1.6 and 3.3%, and between 7 and 10% for sulphates. This high concentration of salts can be explained by the constant migration of saline solution from the inside towards the outside, where salts crystallize as the water evaporates.

7.2.4 Physical properties

The apparent volumetric mass and the pore volume were determined using a mercury porosimeter at 3.5 MPa, following NORMAL recommendations [12], on cylindrical and shapeless samples of the Lapis Gabinus tuff taken from the Tabularium and the Gabii area. The mean values of the apparent volumetric mass of the Tabularium material was found to be 18.24 kN/m^3, with a minimum value of 17.41 kN/m^3 and a maximum of 19.50 kN/m^3. For the quarry material, the mean value was 18.02 kN/m^3. The pore volume at a pressure of 3.5 MPa averages 28.9%, with a minimum of 19% and a maximum of 48%.

For a mean value of 27.50 kN/m^3 for the apparent volumetric mass, the pore volume varies between 29.9% and 33.9%, with a mean value of 32.7%. The difference between the two values provides an indication of the percentage of cavities completely isolated within the individual granules and that cannot be accessed at a pressure of 3.5 MPa.

Water saturation tests were carried out on the Tabularium material under various humidity conditions: ambient humidity, water-saturated atmosphere, through capillarity and through immersion (Figures 7.14 and 7.15).

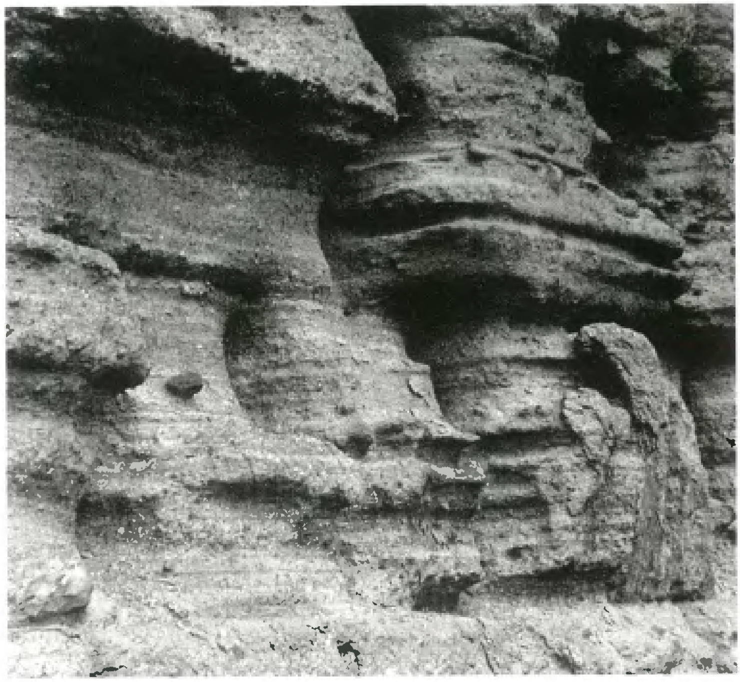


Figure 7.12

On the exposed surface of the tuff blocks of the Tabularium there is obvious decay, with alveolar weathering following the stratification of the tuff. The protruding strata are richer in zeolites.

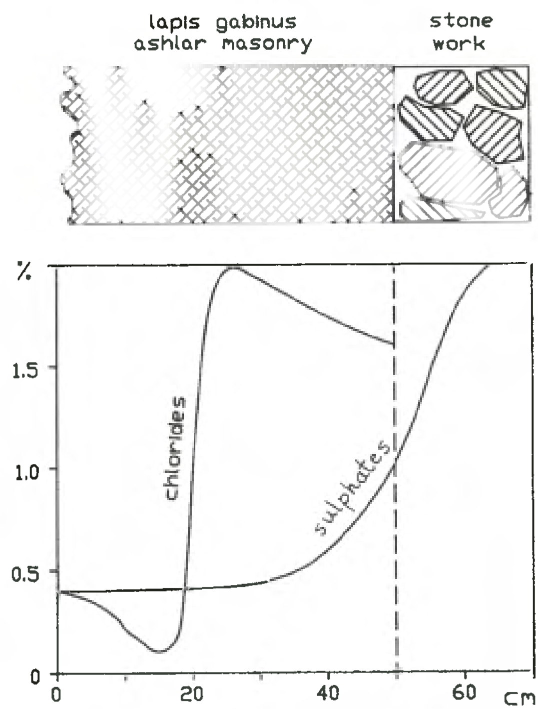
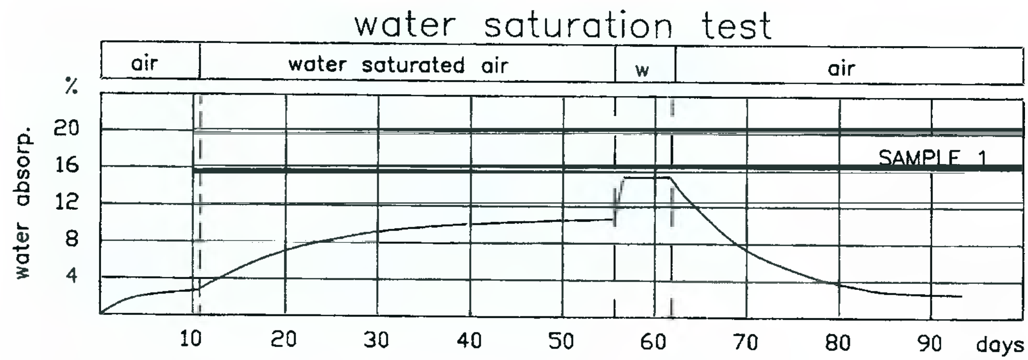
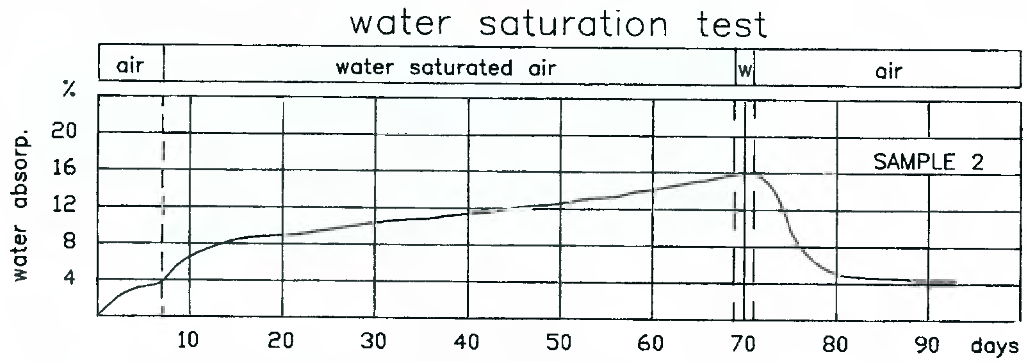


Figure 7.13

Distribution of soluble salts across a tuff block from the Tabularium. The maximum concentration of chlorides is found in the centre of the block, while for sulphates it is found in the interior.





Figures 7.14 (top) and 7.15 (bottom)

Water saturation tests on two samples of the Tabularium tuff. From the left, results of tests in air, water-saturated air, immersion in water and re-equilibration in air.

A first sample, with an initial weight of 1 300 g, was dried at 105°C for 168 hours to constant weight. The dried sample was then kept under ambient laboratory conditions for 12 days (20°C and 60% relative humidity (RH)). Under these conditions the sample absorbed 3.1% w/w of water. The sample was then placed in a water-saturated atmosphere at 22°C, where it absorbed 10.6% w/w water in 26 days. Finally the sample was immersed in a tank with the waterline at 20 cm and in 48 hours it absorbed 15.4% w/w of water. Drying under ambient laboratory conditions for 35 days, the sample stabilized at constant weight with a 3.5% w/w water content. Similar results were obtained with a second sample (Figure 7.15).

These tests show that the Tabularium Lapis Gabinus absorbs large amounts of water very easily, either through condensation from the air or through capillarity from the soil. It also shows that it as easily loses moisture as soon as the environment becomes drier. The results obtained indicate the order of magnitude of the amount of water that can be absorbed by the Tabularium tuff, which probably can vary greatly from block to block due to the heterogeneity of this material.

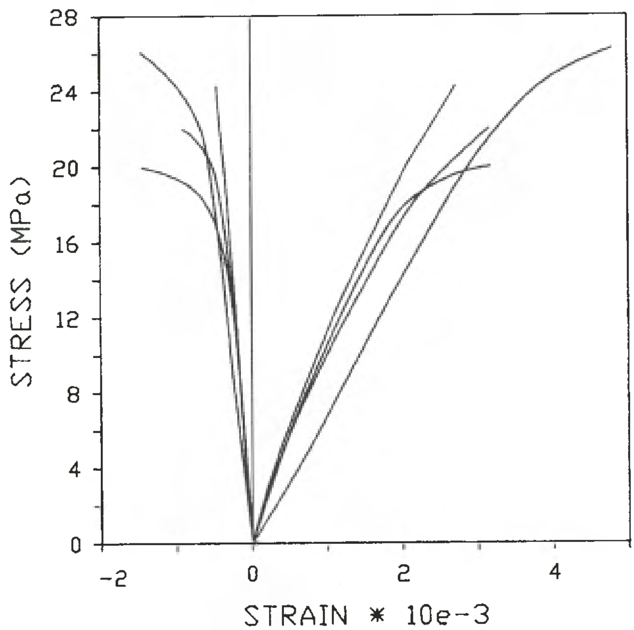


Figure 7.16 **Stress/strain diagram for three samples of tuff from the Tabularium and for one sample from one of the Gabii quarries.**

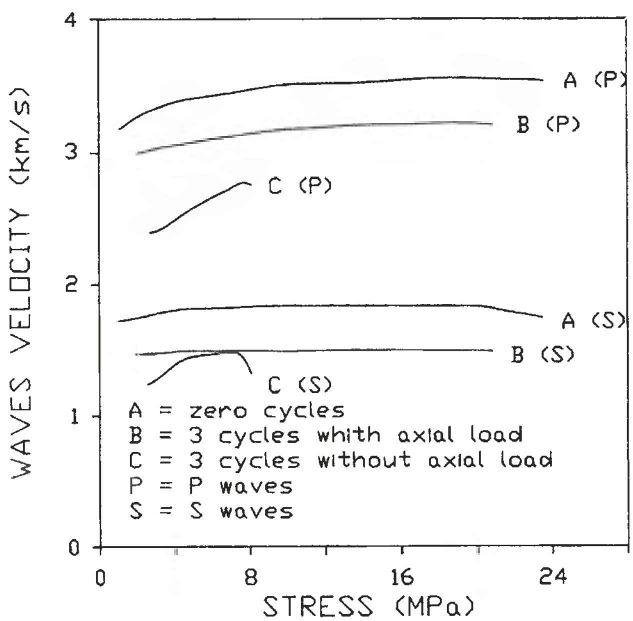


Figure 7.17 **Wave velocity for Tabularium tuff samples subjected to salt crystallization tests.**

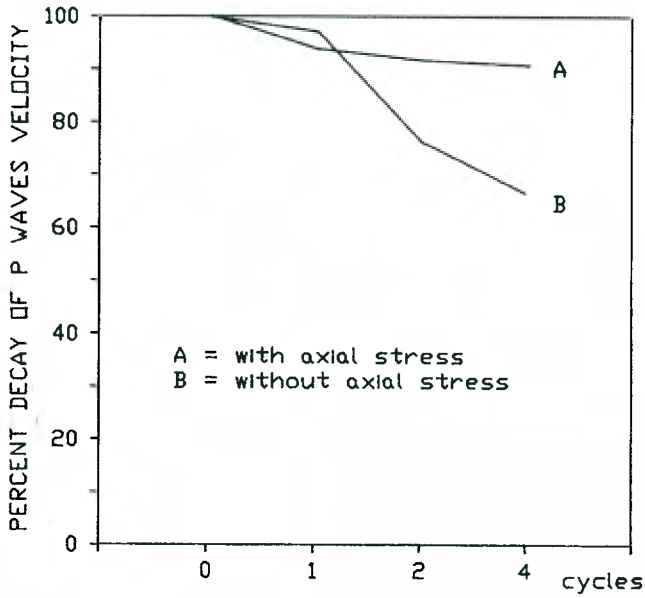


Figure 7.18 **Wave velocity decay with and without axial stress for Tabularium tuff samples.**

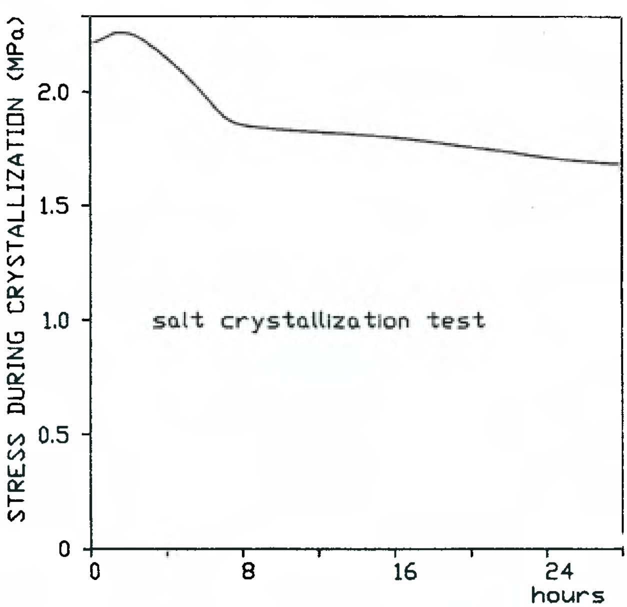


Figure 7.19 **Axial stress variation during salt crystallization in the tuff.**

Figure 7.20

Hydrophobization tests on tuff samples treated with various consolidating products.

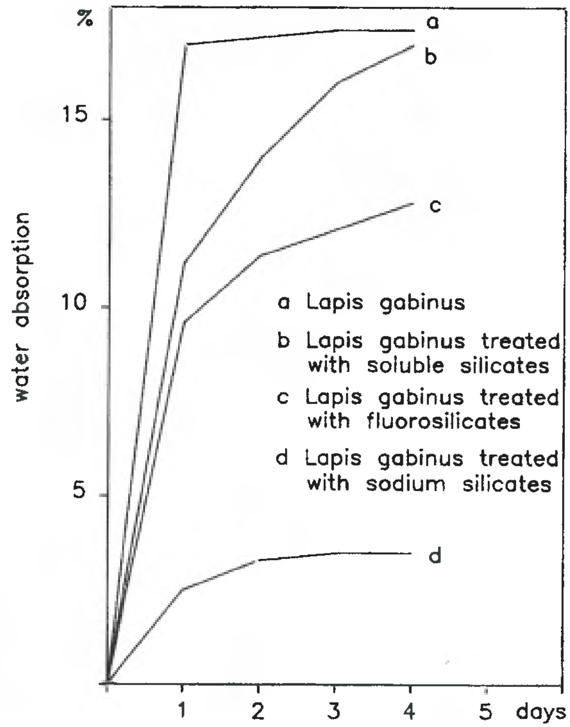
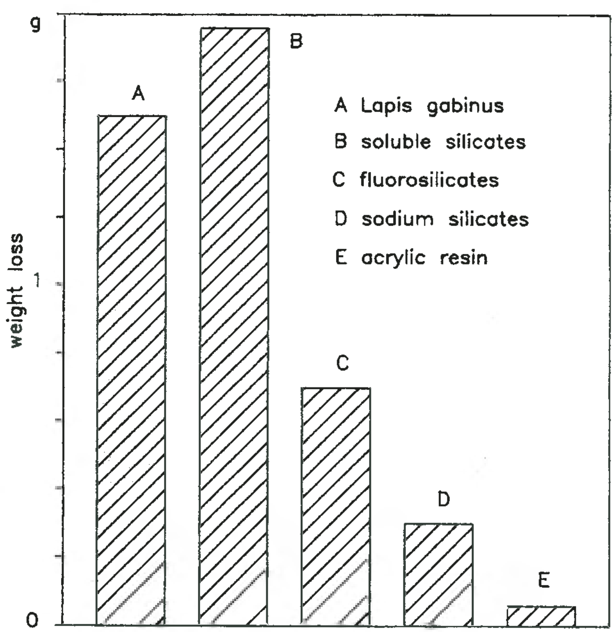


Figure 7.21

Wear test on untreated and treated tuff samples.



7.2.5 Mechanical characteristics

Tests were carried out on:
- 56 mm diameter cores from the Tabularium walls;
- fragments from the Tabularium walls; and
- 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, and 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 preserved its original mechanical properties virtually unaltered. Uniaxial failure load values reached 25.0-29.0 MPa, which are consistent with those found for cores taken from the outcrops. The stress/strain curves for the Tabularium samples and the dynamic moduli of elasticity are given in Figures 7.16 to 7.19.

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 to a depth of a few millimetres 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 ascribed to the heterogeneity of the tested materials, in part exposed to atmospheric agents for thousands of years.

In order to 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 ageing cycles, obtained by using hydrated sodium sulphate. Two test methods were used.

The first method was based on cycles of imbibition in hypersaturated 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 macrofissures, with partial loosening of the surface particles. After only three cycles the material had lost approximately 65% of its compressive mechanical strength and showed a drop of over 35% in the velocity of the transverse seismic waves.

The second method involved monitoring mechanical characteristics and transmission of seismic waves during crystallization in samples saturated with saline solution. The Lapis Gabinus specimen, previously saturated with a solution of sodium sulphate, was subjected to a static load of approximately 2.0 MPa. This value was chosen on the basis of the mean values of the vertical tensions found in the Tabularium 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 (Figure 7.17). At the end of the tests this sample was also found to be in a state of decay, but not as severe as in the first test. This is due to the fact that the vertical load restricted salt crystallization to the external surface zone of the sample. Nevertheless, after three test cycles there was already a 10% drop in the yield load of the material.

Though such tests only partly reproduce natural conditions, they show that crystallization processes inside the pores and microfissures of the Lapis Gabinus lead to a marked decay of the tuff. This occurs only if the saline solution has the possibility of evaporating on the external surface of Tabularium blocks, whereas inside, where salts remain in solution, no changes occur in the mechanical properties.

7.3 TREATMENT TESTS

In the early 1970s, 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: 1) fluorosilicates; 2) sodium silicates; 3) soluble silicates; 4) paraffined hydrorepellents; and 5) acrylic resins.

Preliminary measurements of absorption coefficients and abrasion resistance before and after treatments (Figures 7.20 and 7.21) led to a decision to use soluble silicates, which favoured a marked reduction of water absorption and an increase in mechanical properties, and acrylic resins, which induced a significant increase in the abrasion resistance of the tuff. Soluble silicates were then applied directly to blocks of the internal and external walls of the Tabularium. However, soon after application, the surfaces of the blocks were covered by a very obvious white patina, which had never appeared 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, producing an insoluble white precipitate of silicates. This effect was not observed in the laboratory samples as they were cut under abundant water, the treated surfaces were fresh and had not been exposed to 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 reduced permeability of the surfaces and improved mechanical properties. Due to difficulties today in reaching the blocks, because of extensive subsequent excavations which have lowered the field level, and lack of evident macroscopic differences, it was not possible to evaluate these twenty-year-old treatments.

7.4 CONCLUDING REMARKS

Petrographic and mineralogical data on the Lapis Gabinus tuff are scarce [4; 5], though this tuff is well known and cited in the archaeological literature for its use in important Roman monuments. Therefore this study concentrated on the characterization of the tuff's structure and composition. The blocks employed in the construction of the Tabularium are made of a pyroclastic material comprising lapilli, scoriae and lithic fragments, bound by an originally glassy matrix within which crystals such as micas, pyroxenes and leucite are dispersed. The matrix is largely substituted by zeolites (phillipsite and chabazite); analcime, another zeolite, is present as a modification product 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 zeolitized matrix.

With regard to the state of conservation of the Tabularium tuff, all the exposed surfaces present extensive scaling, similar to that found in blocks close to the foundations of structures in the ancient city of Gabii (where the Roman quarries were located). Moreover, in the Tabularium, marked alveolar weathering with significant micro- and macrofracturing is also found. 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.

The Tabularium tuff also contains high salt concentrations, mainly chlorides and gypsum. The presence of chlorides is related to the previous use of this structure as a store for common salt. The distribution 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.

Of the conservation treatments carried out in the early 1970s [11], the best results were obtained using acrylic resins, which improved mechanical properties, while soluble silicates proved inadequate, giving rise to whitish precipitates on the surface of the blocks.

These results could be linked to the peculiar exchange properties of zeolites [13; 14], minerals with large internal communicating cavities where H_2O and large cations can be accommodated to balance the positive charges missing after substitution of silica in the aluminum tetrahedra. In the ideal chabazite structure, only the site at the centre of the 8-membered ring is 100% occupied by H_2O, whilst the occupancy by H_2O of other sites varies [14; 15; 16]. Therefore zeolites have a great exchange capacity, which must be taken into account when introducing chemical agents into a zeolitized tuff. In a chabazitic tuff from Naples it was shown that the calcium of the zeolite was exchanged with sodium from seawater, inducing an anisotropic distortion of the crystalline lattice, with a 0.2% expansion along the "a" and "b" crystallographic axes [17]. Such effects are known to occur also with other cations and organic molecules.

A wide-open field exists for research 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 using methylmethacrylate [18], though *in situ* and long-term experience still have to provide conclusive evidence regarding the validity of these treatments.

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RESUMEN

El Tabulario fue reconstruído con bloques de la toba volcánica llamada Lapis Gabinus, luego del incendio del antiguo Concejo municipal de los Romanos en el 83 AC. Se presentan los resultados de un estudio detallado de las características mineral-petrográficas y de las propiedades físico-mecánicas de esta toba. El uso del Tabularion como depósito de sal en el medioevo indujo un pronunciado deterioramiento en los bloques de toba y en las columnas, observándose fenómenos de escamación, disgregación y alveolización. Se presentan los resultados de pruebas realizadas con diversos productos consolidantes aplicados hace 20 años. Se analizan las posibles interacciones de estos compuestos silícicos o acrílicos con los componentes zeolíticos.

RESUME

Après l'incendie du Conseil municipal antique des Romains en 83 av. J.C., le Tabularium fut reconstruit en utilisant un tuf volcanique appelé Lapis Gabinus. Les résultats d'une étude détaillée des caractéristiques minéralo-pétrographiques et des propriétés physico-mécaniques de ce tuf sont présentés. L'utilisation du Tabularium comme dépôt de sel au Moyen-Age a entraîné une détérioration marquée des blocs de tuf et des colonnes, caractérisée par des phénomènes importants d'incrustation, d'effritement et d'alvéolisation. Des consolidants ont été appliqués au début des années 70 et les résultats des essais effectués avec des résines acryliques et des composés siliciques sont examinés, ainsi que leur éventuelle interaction avec le composant zéolithique qui abonde dans le tuf.

KURZFASSUNG

Nach dem Brand des Stadtratsgebäudes im antiken Rom (83 v.Chr.) wurde bei der Rekonstruktion des Tabulariums ein vulkanischer Tuff mit der Bezeichnung "Lapis Gabinus" eingesetzt. An diesem Gestein wurde eine detaillierte Studie zur mineralogisch-petrographischen Beschreibung und zur Erfassung der physikalisch-mechanischen Eigenschaften durchgeführt, deren Ergebnisse vorgestellt werden. Der Umstand, daß das Tabularium im Mittelalter als Salzlager verwendet wurde, hatte starke Schäden an den Tuffquadern und Säulen zur

Folge: Schalenbildung, Absanden und Zellenverwitterung sind in grossem Maßstab zu beobachten. Vor 20 Jahren wurden Festigungstests vorgenommen. Die Testergebnisse mit Acrylharzen und Siliziumverbindungen werden diskutiert, auch was deren mögliche Wechselwirkung mit den Zeolithen betrifft, die eine wichtige Komponente des Tuffgesteins bilden.

THE SCULPTURES IN BOMARZO PARK, VITERBO, ITALY:

DETERIORATION AND CONSERVATION PROBLEMS OF THE PEPERINO

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ABSTRACT

Volcanic rocks have been used frequently in the construction of historic buildings in central Italy. At Bomarzo Park, a natural outcrop of rhyodacitic boulders inspired the carving of a large number of sculptures into this rock in the sixteenth century. These sculptures are suffering from alteration processes, mainly related to the high moisture levels of their environment. The causes of the alterations and the present conditions of the material have been studied with the aim of understanding the deterioration mechanism.

8.1 INTRODUCTION

The Park, named *Bosco Sacro* [Holy Wood], lies in a green valley at the foot of Bomarzo village, near Viterbo. It is one of the most peculiar monumental complexes of the Italian "Cinquecento" [literally "five hundred," meaning the 1500s] and is characterized by a large number of big sculptures set in meadows of luxuriant vegetation (Figure 8.1).

Compared with the usual configuration of Renaissance gardens, the Bosco Sacro does not show ordered and symmetrical perspectives. On the contrary, it provides an exciting succession of apparitions revealing themselves to the unsuspecting visitor among trees, along the paths, or behind the rocks.

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Figure 8.1 The frightful head of an ogre. It represents the entrance to the netherworld, as stated by a paraphrase of Dante's verse carved on its lips.

The sculptures have been carved into the dispersed boulders of a rhyodacitic ignimbrite locally called "Peperino."

Entering the park, the visitor first encounters a giant quartering a victim, then a big tortoise with a woman on its back. Going on, there is a fountain with the representation of Pegasus, the winged horse, and a nymphaeum which leads to an open space dominated by a leaning house. The wide terrace that stretches to the higher portion of the park shelters two big figures flanked by monsters and animals: an ogre; an elephant that clutches a warrior with its trunk; and an infernal face with open jaws. The whole park is strewn with verses engraved into the rocks; one of them mentions the name Bosco Sacro.

The author of these verses and inventor of the park was Pierfrancesco Orsini, commonly known as Vicino. He began working on this idea in 1558 when he came back to his domain after a long military campaign. Most of the sculptures were finished by 1563.

The identification of the author of sculptures and architecture is still a matter of discussion. The quality of the figures is remarkable and suggests supervision by a professional sculptor or architect [1; 2; 3].

At present these sculptures are affected by alteration processes related to the environmental thermo-hygrometric conditions. Their surfaces are often completely covered by biological growth (mosses and lichens) giving rise to a velvet layer which sometimes obscures the details of the sculptures, the anatomical details and the inscriptions. These biological patinas keep the substrate material wet for lengthy periods and therefore promote its alteration. When the rock is rich in lapilli and rock fragments it shows a special kind of degradation which puts these inclusions in relief while the surface acquires a pseudo-alveolar appearance. In the long run these processes will deteriorate the carving to such an extent that the sculptures will no longer stand out from the rocks from which they were carved.

Peperino stone shows a fairly good resistance to alteration and has good workability; therefore it has been used since ancient times as both free and dressed stone in the Viterbo area.

The present condition of this material and its degradation have been studied with the aim of contributing to the restoration of the Bomarzo artifacts.

8.2 METHODS AND MATERIALS

Both weathered and unweathered stone samples were collected for analysis. Weathered specimens were obtained from the statues (11 samples) and from a nearby quarry (1 sample). Two unweathered specimens were obtained from each of the four quarries on the outskirts of the park.

The following analyses were carried out:

- thin section petrographic observations by optical microscopy;
- determination of the mineralogical composition by X-ray powder diffraction analysis (XRD);
- determination of the major elemental composition by X-ray fluorescence (XRF);
- determination of physical characteristics: density; bulk density; open porosity; imbibition coefficient; and pore size distribution by both helium and mercury porosimetry; and
- scanning electron microscopy (SEM) observations and analyses of some patinas.

8.3 GEOLOGICAL SETTING OF THE PEPERINO

Peperino is defined petrographically as a rhyodacitic ignimbrite [4]. It belongs to the volcanic complex of Mount Cimino, in the neighbourhood of Viterbo, to the north of Rome.

Volcanic rocks from Mount Cimino are quite similar to the alkali-calcic Tuscan volcanic rocks and consolidated between 1.9 and 1.4 million years ago, based on the following succession: 1) rhyodacitic domes; 2) rhyodacitic ignimbrite (Peperino); 3) trachytic and latitic lavas; and 4) latitic and olivine-trachytic lavas. These mutual relationships are not always simple and unequivocal.

Rhyodacitic domes form particular hills and surround Mount Cimino in a circle, with the rhyodacitic ignimbrites occurring in a fan shaped plateau which spreads for 10-12 km from the volcanic vent of Mount Cimino. The thickness of the ignimbrite flow varies from a few tens to hundreds of metres, according to the geomorphology. Probably this thickness is the result of several ignimbrite flows, as shown by some ash intercalations and sharp changes in the welding degree.

8.4 EXPERIMENTAL RESULTS

8.4.1 Thin section petrographic observations

Analysis of unweathered material shows a rock characterized by a vitroclastic structure with 35% to 60% of phenoclasts. The following minerals were found, in order of decreasing abundance: plagioclases, sanidine, biotite, hypersthene, augite, and traces of olivine. Plagioclases are andesine-labradorite, often with a chipped shape. Sanidine always has a chipped shape with some rounded edges. Hypersthene and augite are mostly idiomorphic. Biotite often shows a coloured halo characterized by a lower pleochroism and sometimes partial haematization phenomena. Some biotite crystals appear strongly exfoliated as a consequence of the stresses suffered during the eruption. Lapilli are very abundant and show a characteristic fluidal glassy structure. Minor

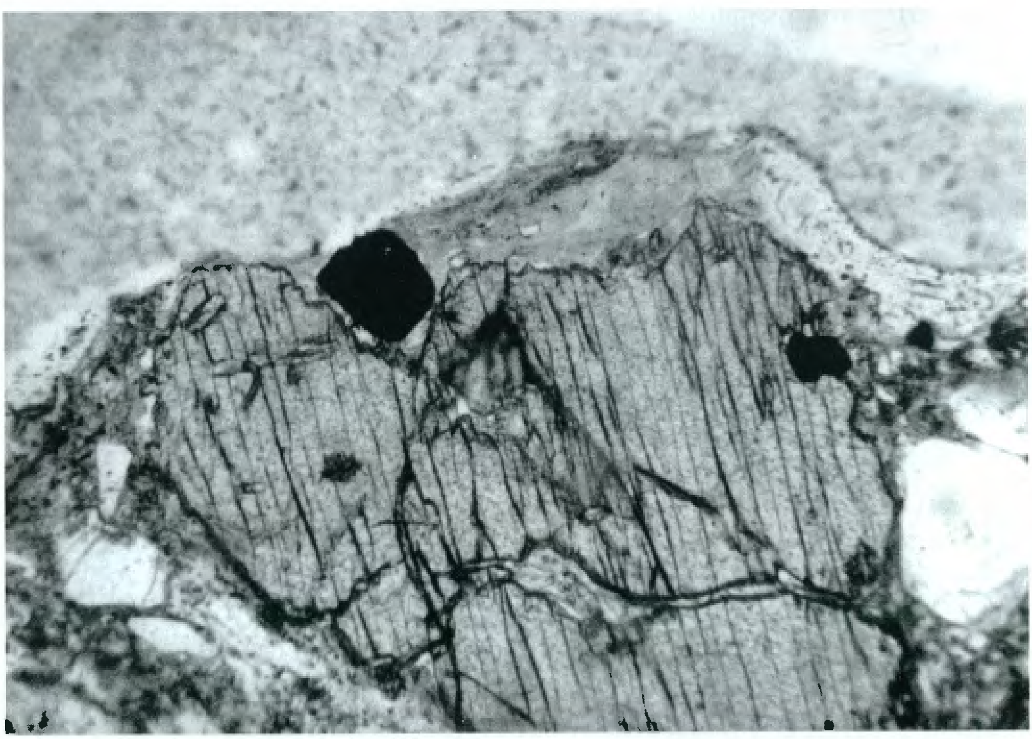

Figure 8.2 Thin section of a pyroxene located on the outer surface and affected by serpentinization phenomena.

amounts of rock fragments are present, such as metamorphic rocks rich in spinels, monzonitic rocks, limestone and siliceous rocks.

The phenoclasts in weathered rocks look quite similar to those in unweathered ones. Only some pyroxenes show serpentinization phenomena when they are on the exposed outer surface (Figure 8.2) or along some of the fractures. In contrast, the glassy groundmass shows some differences close to the surface, where there is often some de-vitrification with the glass changing into chlorite and sometimes into serpentine.

8.4.2 XRD determination of mineralogical composition

The presence of the main mineral components identified by thin-section analysis was confirmed. The weathered material has a composition identical to unweathered, which indicates that alteration products are not present in significant amounts.

The XRD analysis of the <4 μm fraction served to identify the composition of the clay portion of these samples. The unweathered samples taken from the quarries contained no clay minerals. However a diffraction band, tabular in shape, is present, and it could be due to poorly crystalline mineralogical phases. These 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 show signs of slightly stronger crystallization marked by traces of chlorite and occasional kaolinite. In one of the samples (BOM 10) these are also absent.

8.4.3 Determination of major elements

Chemical analysis of the samples taken from the quarries confirms data found in the literature classifying these rocks as rhyodacites. Data for the weathered and unweathered samples are given in Table 8.1. In spite of the high heterogeneity of the material good agreement is obtained between the data for the unweathered samples of the four quarries. The data obtained from the weathered specimens show larger dispersion.

The weathered samples show a significant decrease in Na_2O, K_2O, SiO_2 and an increase in Al_2O_3 and H_2O, as indicated by the value for loss on ignition (LOI). There is a decrease in FeO and an increase in Fe_2O_3, maintaining the same amount of total iron.

The possibility of correlating the concentration of any given oxide with the LOI, which is the parameter directly related to the degree of alteration, was considered. It was found that both Na_2O and SiO_2 gave good correlations (Figure 8.3). For the other elements, the value dispersion did not allow any significant curve to be drawn, though some correlations could be recognized.

The alteration process involves a leaching of alkali metals and SiO_2 and a relative increase in Al_2O_3. The iron, under the present alteration conditions, does not show significant mobility, even if its increasing oxidation is evident.

8.4.4 Physical characteristics

There were some difficulties in studying the physical characteristics due to the high heterogeneity of the rock. In order to minimize differences, at least three samples of each specimen were analysed. The mean values and their standard deviations are reported in Table 8.2.

A comparison between the two groups of samples (weathered and unweathered) shows, as expected, higher dispersion in the values of weathered samples and the logical variations of some parameters as a consequence of the alteration processes. While total porosity increases by 68%, the imbibition coefficient increases by 100%. From the correlation of these two parameters it can be seen that with increasing porosity the samples tend to approach the 100% saturation index (Figure 8.4).

Table 8.1 Chemical composition of the rhyodacitic ignimbrite of Bomarzo.

	Weathered samples	Unweathered samples
SiO_2	60.08 ± 1.32	61.68 ± 0.16
TiO_2	0.78 ± 0.04	0.81 ± 0.03
Al_2O_3	17.34 ± 1.04	16.48 ± 0.04
Fe_2O_3	2.93 ± 0.29	2.32 ± 0.16
FeO	3.06 ± 0.26	3.52 ± 0.25
MnO	0.09 ± 0.02	0.08 ± 0.00
MgO	2.05 ± 0.28	2.36 ± 0.16
CaO	4.14 ± 0.65	4.58 ± 0.09
Na_2O	1.79 ± 0.14	2.07 ± 0.04
K_2O	4.99 ± 0.23	5.24 ± 0.06
P_2O_5	0.31 ± 0.08	0.24 ± 0.01
LOI	2.69 ± 1.04	0.96 ± 0.16
$Fe_{(total)}$	5.56 ± 0.37	5.49 ± 0.09

Table 8.2 Physical characteristics of the rhyodacitic ignimbrite of Bomarzo.

	Weathered samples	Unweathered samples	Increase (%)
Density (g/cm^3)	2.62 ± 0.004	2.65 ± 0.02	
Bulk Density (g/cm3)	1.79 ± 0.13	2.15 ± 0.04	
Imbibition Coeff. as % volume	27.7 ± 6.1	13.7 ± 1.8	102
Saturation Index (%)	87.2 ± 7.9	73.0 ± 3.2	19
Open Porosity (%)	31.5 ± 5.1	18.7 ± 1.9	68
Micro Porosity (%) 10 - 500 000 Å	24.5	14.7	80
Macro Porosity [%] >500 000 Å	7.0	4.0	40

These data can better be understood if we take into consideration the histogram of pore size distribution in the range 10 to 500 000 Å (Figure 8.5). The change in porosity and in the pore size distribution are parameters closely related to water absorption and hence to the decay processes. Weathered samples are characterized by an 80% increase

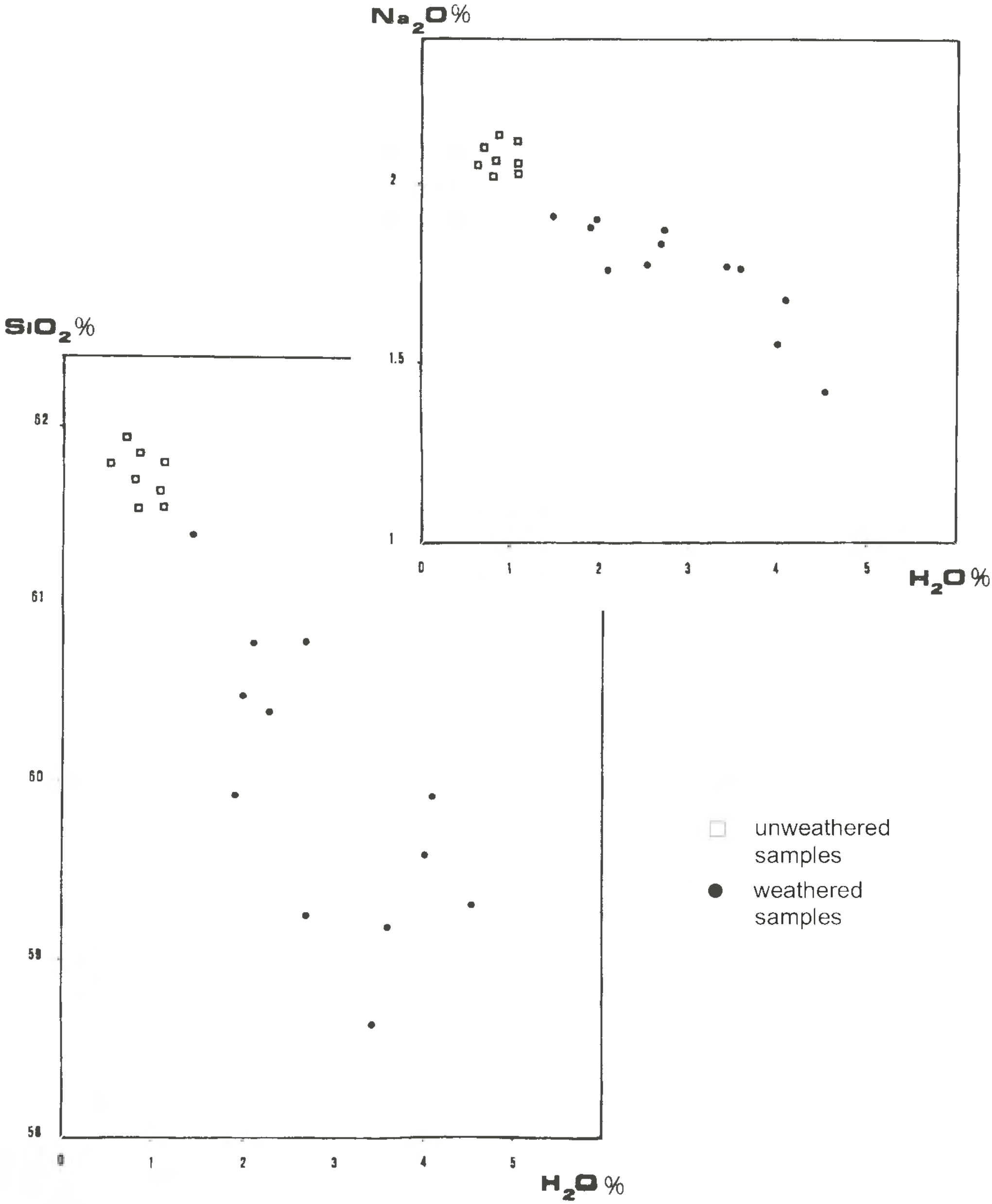

Figure 8.3 Correlation of the concentration of both Na_2O and SiO_2 with LOI (% H_2O) for weathered and unweathered specimens.

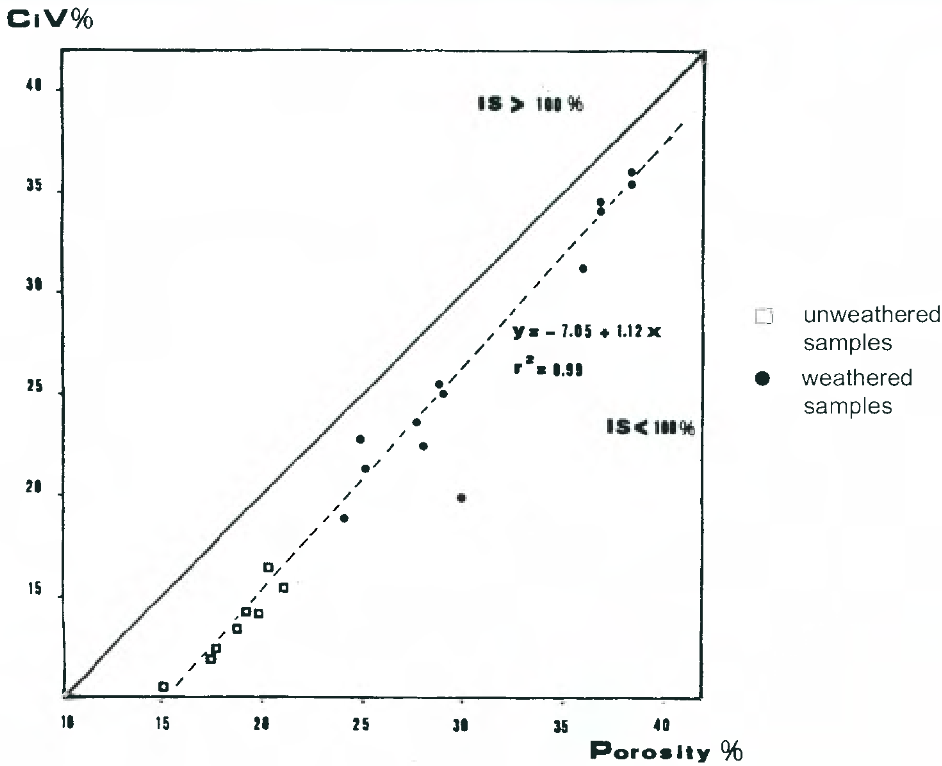

Figure 8.4 **Correlation between imbibition coefficient (CiV%) and open porosity. The solid diagonal line represents the 100% saturation index (IS).**

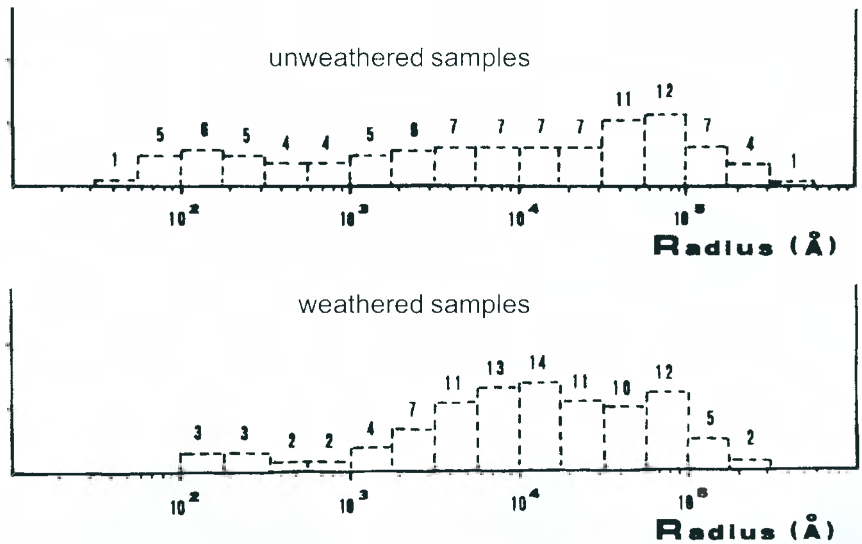

Figure 8.5 **Pore size distribution of micropores in weathered and unweathered samples.**

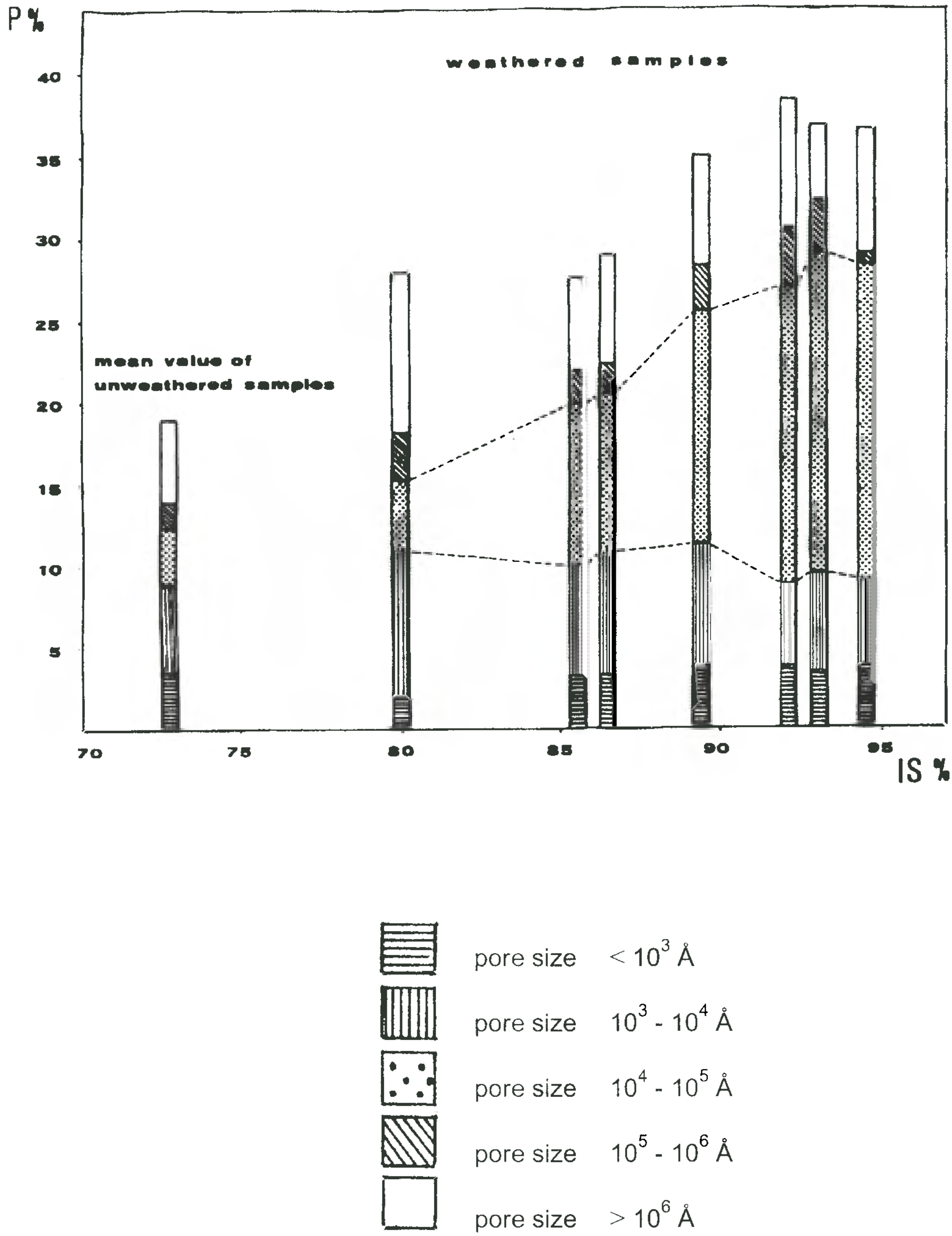

Figure 8.6 **Graph of the Porosity (P%) vs. Saturation Index (IS%). The porosity values of each sample have been divided according to the different pore size classes. For clarity, not all the weathered samples have been plotted.**

in porosity (Table 8.2) and, within these limits, by a higher increase in the 10^3 - 10^5 Å pore size range.

In order to show these changes porosity (***P***%) was plotted against the saturation index (***IS***%), with the porosity value of each sample subdivided into pore size classes (Figure 8.6). It can be seen that the increase in porosity is related to the increase in the saturation index, as already shown in Figure 8.4.

The large increase in the number of pores with radii ranging between 10^4 and 10^5 Å suggests that these pores are the ones that contribute most to water absorption and water retention within the structure.

Density and bulk density are the only parameters that show a slight decrease in weathered samples. This means that alteration compounds did not form in significant amounts and also confirms that the re-crystallization of glassy phases did not take place, as confirmed by the XRD analysis of the clay portion.

8.4.5 SEM examination

During sampling it was observed that the rock surface under compact lichen coverings had a translucent, darker appearance. This layer extended about 1.5 mm into the stone and showed greater coherence than the underlying rock. In order to identify the composition of this patina, some sections were studied by SEM and analysed using an electron microprobe.

The patina had a compact structure and a more homogeneous appearance than the underlying rock (Figure 8.7), while the microprobe analysis showed a slight increase in Fe (Figure 8.8) and P with respect to the other major elements.

All these observations support the hypothesis of involvement of the lichens in the formation of this patina. Acidic compounds produced by lichen metabolism may have caused a transformation of the primary glassy structure and a concentration of the iron, elsewhere reported in the literature as being caused by some lichens [5; 6; 7].

8.5 CONCLUSIONS

The evidence from centuries of use of the Peperino stone in monuments indicates that this material has good durability and decays only under specific conditions.

All the data collected, particularly the comparison between weathered and unweathered samples, have verified the relatively good condition of the Peperino stone and permitted an interpretation of its alteration mechanism.

The crystalline phases seldom show signs of alteration and they appear to be protected – sealed in – by the vitreous matrix. This, on the other hand, shows a few signs of alteration, such as localized de-vitrification phenomena. The result of this process is the formation of chlorite, and in some instances kaolinite, which can be detected in small quantities by means of clay mineral analysis.

The analysis of the major elements confirms that alteration mainly affects the vitreous matrix, as shown by the decrease in concentration of the alkali ions. This is

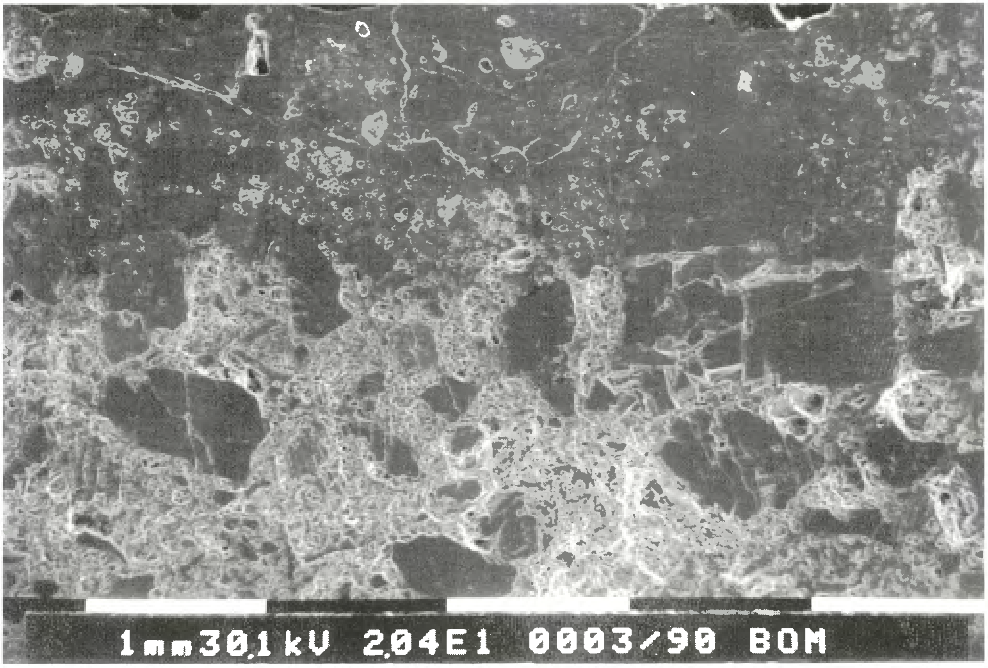

Figure 8.7 SEM photomicrograph of the patina. Note the compact structure and the more homogeneous appearance with respect to the underlying rock.

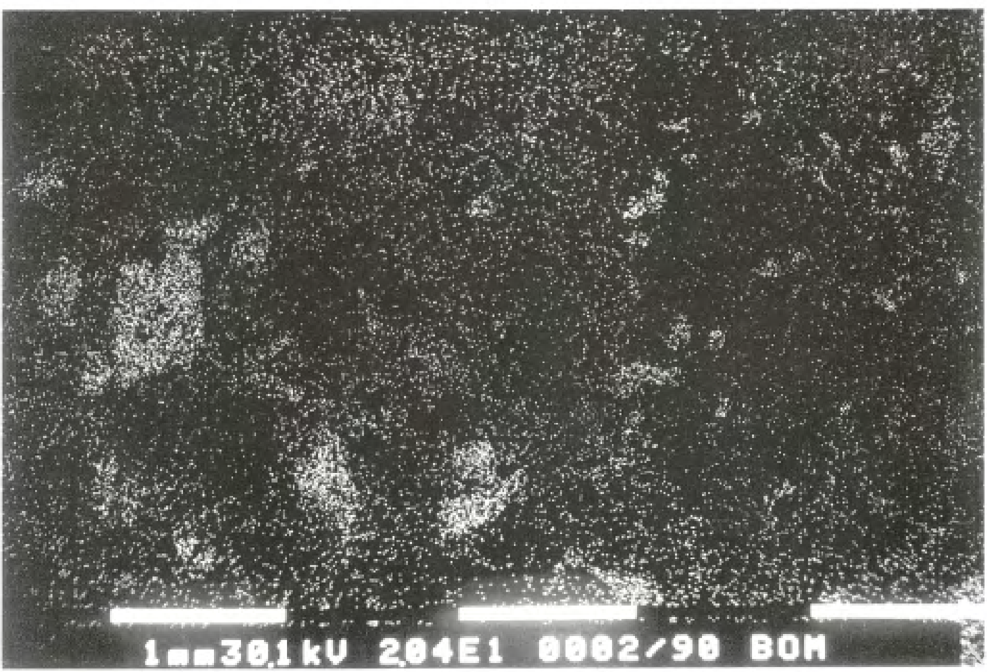

Figure 8.8 Iron distribution in the SEM photomicrograph in Figure 8.7. The surface (1.5 mm thick) shows enrichment of this element. The other spots where iron is concentrated correspond to biotite inclusions.

almost certainly due to 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 of weathered samples has revealed 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 capability of the stone to retain water inside the material can be clearly correlated with the development of this pore class.

On the whole, the stone used in the sculptures of the Bomarzo Park shows only a relatively slight degree of alteration. However, this present situation does not assure future good conservation since the material has already begun its alteration process, and this is only likely to increase in rate with time.

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RESUMEN

Rocas volcánicas han sido empleadas frecuentemente en la construcción de edificios históricos en la Italia central. En el Parque de Bomarzo, la formación natural de rocas riodacíticas inspiró la ejecución de una gran número de esculturas durante el siglo dieciséis. Estas esculturas están sufriendo procesos de alteración relacionados fundamentalmente con el alto grado de humedad del sitio. Con el fin de comprender el mecanismo de deterioro, se estudian las causas de alteración y las condiciones actuales del material.

RESUME

Des roches volcaniques ont couramment servi à la construction d'une grande partie des édifices historiques d'Italie centrale. Dans le Parc Bomarzo, un affleurement naturel de blocs rhyodacitiques ont inspiré au seizième siècle la réalisation de nombreuse sculptures. Celles-ci subissent un processus d'altération principalement dû à la forte humidité de l'environnement. Les causes de ces altérations et l'état actuel du matériau ont été étudiés dans le but de comprendre le mécanisme de détérioration.

KURZFASSUNG

Bei einem großen Teil historischer Bauten in Mittelitalien wurden Vulkangesteine verbaut. Im 16. Jahrhundert wurden im Park Bomarzo Skulpturen direkt aus verstreuten Rhyodacitblöcken herausgearbeitet. Diese Skulpturen weisen Schäden auf, die vor allem auf die feuchten Bedingungen des Aufstellungsortes zurückzuführen sind. Die genauen Schadensursachen und der Erhaltungszustand des Steins wurden untersucht, um den Mechanismus der Verwitterung zu erkennen.

LICHEN-INDUCED DETERIORATION ON AN IGNIMBRITE OF THE VULSINI COMPLEX (CENTRAL ITALY)

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ABSTRACT

This report presents the results of an investigation carried out on eight crustose and one foliose lichen species growing on volcanic tuffs from the area of Civita Bagnoregio (Central Italy). Observations on thin sections, combined with electron microprobe and XRD analysis led to the identification and localization of weathering products produced by the lichens. The most important effect of the lichen growth is the removal of calcium from the substrate to form weddellite. This accumulates in the thalli in different quantities and location depending on the species involved. Fungal hyphae penetrate deeply into the tuff; the attachment between fungal hyphae and rock often causes the detachment of some millimetres of stone under the central part of the thallus.

9.1 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]; few studies have been carried out that involve other stone types, such as volcanic tuffs [8].

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 ISBN 92-9077-115-1

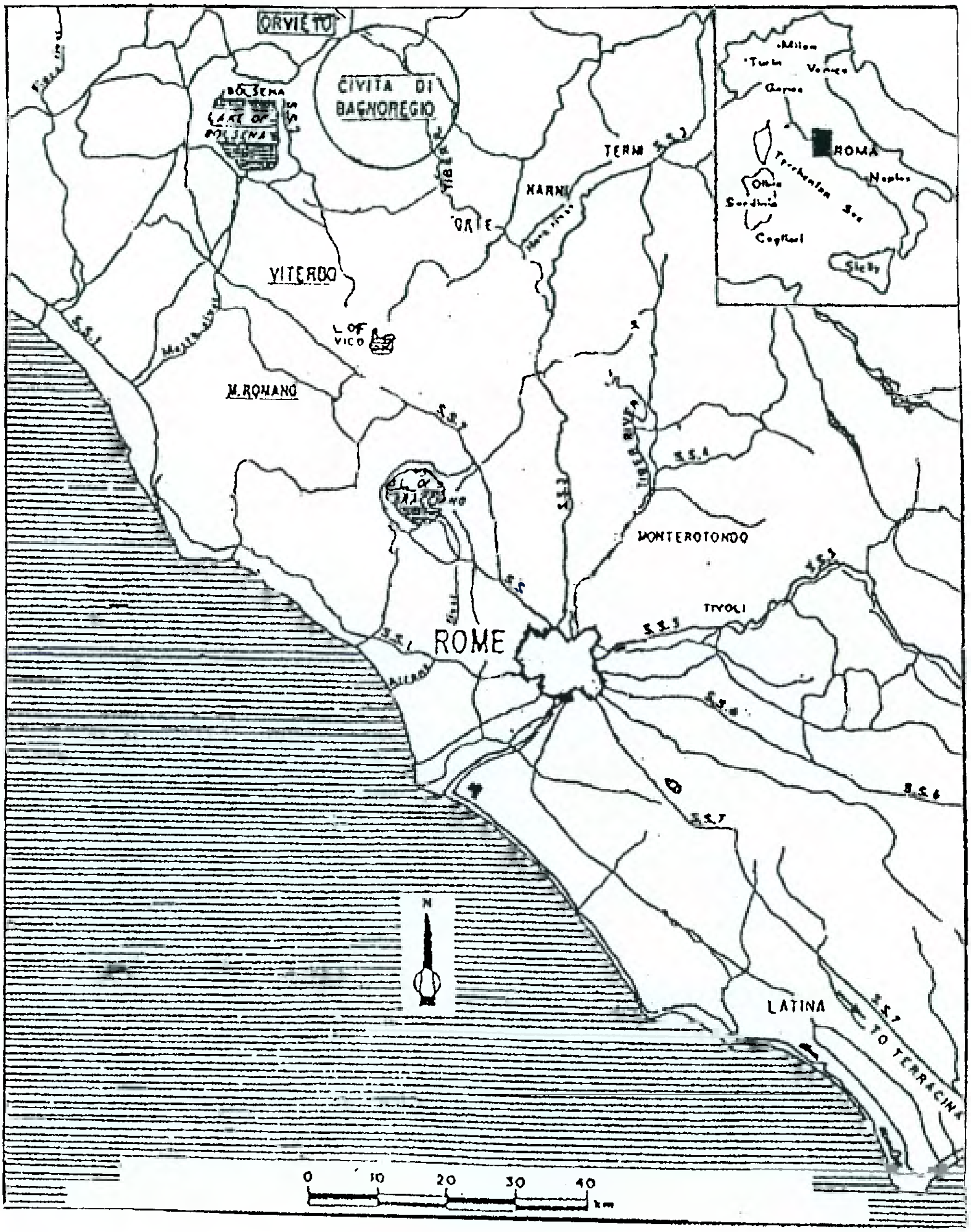

Figure 9.1 **Map of Central Italy, showing the sampling area of Civita Bagnoregio.**

Most authors consider that the deteriorative aspect connected with lichen growth is the most significant, while further investigations are required to confirm or disprove the hypothesis that in some cases the lichen can form a protective covering effective in limiting the action of other degrading agents.

This work is part of a wider study on the deleterious effects of lichens on different stones 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 volcanic rock 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 (Figure 9.1) [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 crustose and one foliose lichen species, among the most frequent in the area, were investigated in order to evaluate their weathering ability.

9.2 MATERIALS AND METHODS

The yellow, reddish or greyish volcanic rock under study is classified as a tephritic-phonolitic ignimbrite, locally called *Tufo rosso a scorie nere*, "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 million years before present" [9].

Rock specimens were taken from both an active quarry and natural outcrops.

The rock, commonly called tuff, is characterized by a vitro-clastic texture, scarcely cemented, formed of scoriae, blackish pumices, xenoliths of lava and phenoclasts embedded in a microgranular groundmass formed of glassy fragments. The phenoclasts comprise 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:

(i) portions of basaltic or andesitic lavas, or both, formed of plagioclases, pyroxenes and some olivine;

(ii) black and grey vitreous pumices with vesicular texture and high porosity;

(iii) portions of lava with pseudofluidal texture with vitreous bands which are often closed, forming flattened vitreous vesicles [11, 12, 13].

Two zeolites are also present, in varying proportions, in the glassy matrix: chabazite and, less abundantly, phillipsite. Zeolites seem to be "a very common product of autopneumatolitic and weathering processes" [10], responsible for lithification.

No clay minerals were 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: *Caloplaca flavescens* (Huds.) Laund.; *Caloplaca teicholyta* (Ach.) Steiner; *Buellia canescens* (syn. *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.

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.

Both colonized stone and stone without lichens were scraped, powdered and X-ray powder diffraction analysis (XRD) patterns obtained using CuKα radiation. The XRD analyses were carried out on both non-oriented and oriented clay samples.

Mineralogical characterization of the clay minerals was carried out on the <2 µm fraction, obtained by sedimentation.

Portions of the lichen-covered stone were fractured, coated with Au and examined by scanning electron microscopy (SEM). Polished cross-sections were analysed for Ca, Si, Fe, Al and K, using electron microprobe analysis.

9.3 RESULTS

The exposed rock showed evident effects of mechanical erosion and leaching along the surfaces of the clasts and pumices immersed in the groundmass, probably due to the action of rainwater. Sometimes this action is evident in fractures and cracks deeper inside the 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 XRD of the rocks colonized by lichens and of the lichen-free rocks were essentially the same, except for the presence in some samples of varying quantities of weddellite.

The results for the various lichen species studied are summarized below.

- *Caloplaca flavescens* (Huds.) Laund.
  The observations of thin sections showed that the thallus penetrated into the substrate and wrapped around sanidine crystals, which were rather corroded. Pyroxenes located near the thallus also were severely damaged and in intimate contact with fungal hyphae. Large quantities of weddellite were detected by XRD.
- *Caloplaca teicholyta* (Ach.) Steiner
  Fungal hyphae penetrated as much as 1.5 mm into the substrate. Abundant weddellite was present, located mainly in the medulla rather than in the upper cortex, as confirmed by electron microprobe analyses.

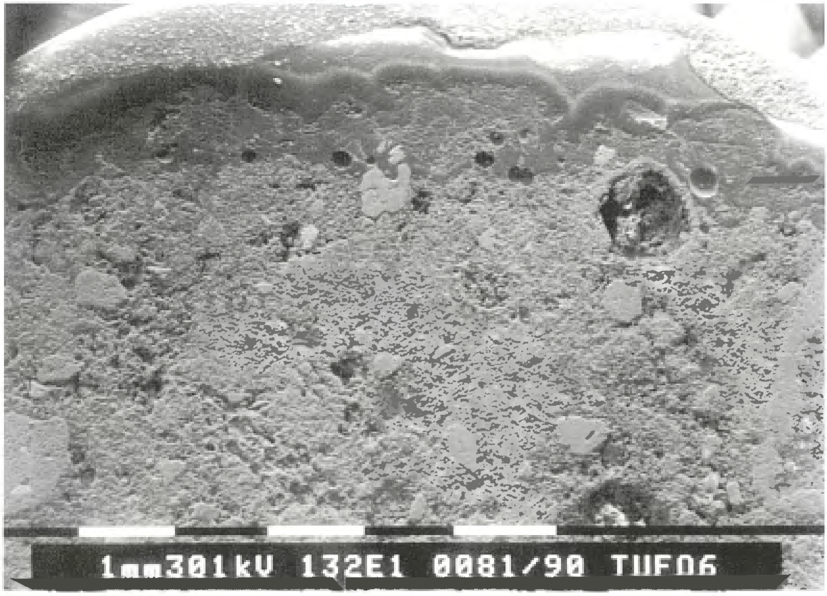

Figure 9.2 SEM photomicrograph of a polished cross-section of tuff covered by *Buellia canescens* (syn. *Diploicia canescens*).

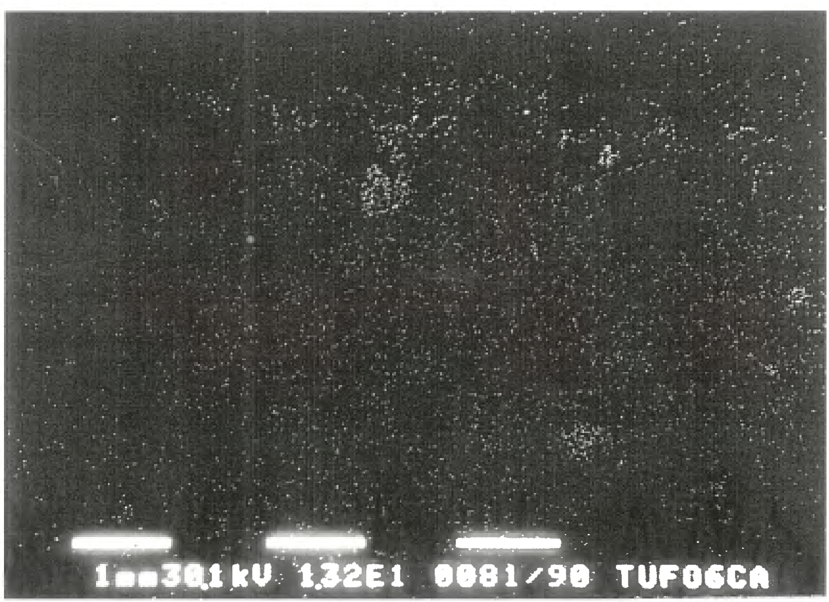

Figure 9.3 Ca-mapping of the area shown in Figure 9.2. Ca accumulated only in the surface layer of the thallus.

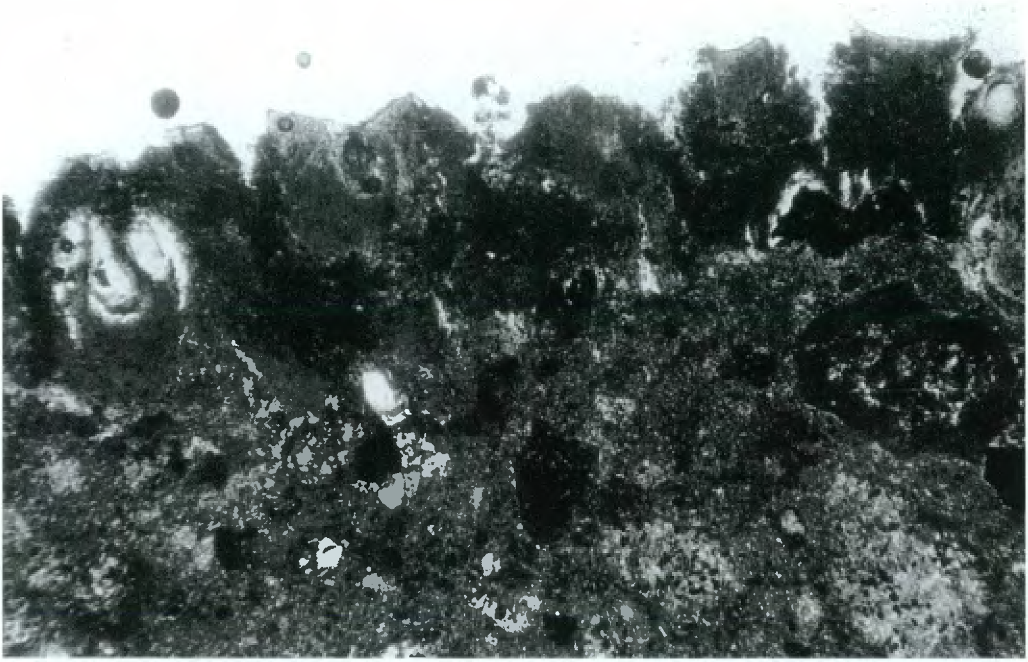

Figure 9.4 Photomicrograph of a thin section, showing the complete adhesion of *Diploschistes actinostomus* to the substrate formed of blackish pumice, glassy fragments, phenoclasts of augite and sanidine (PPL,

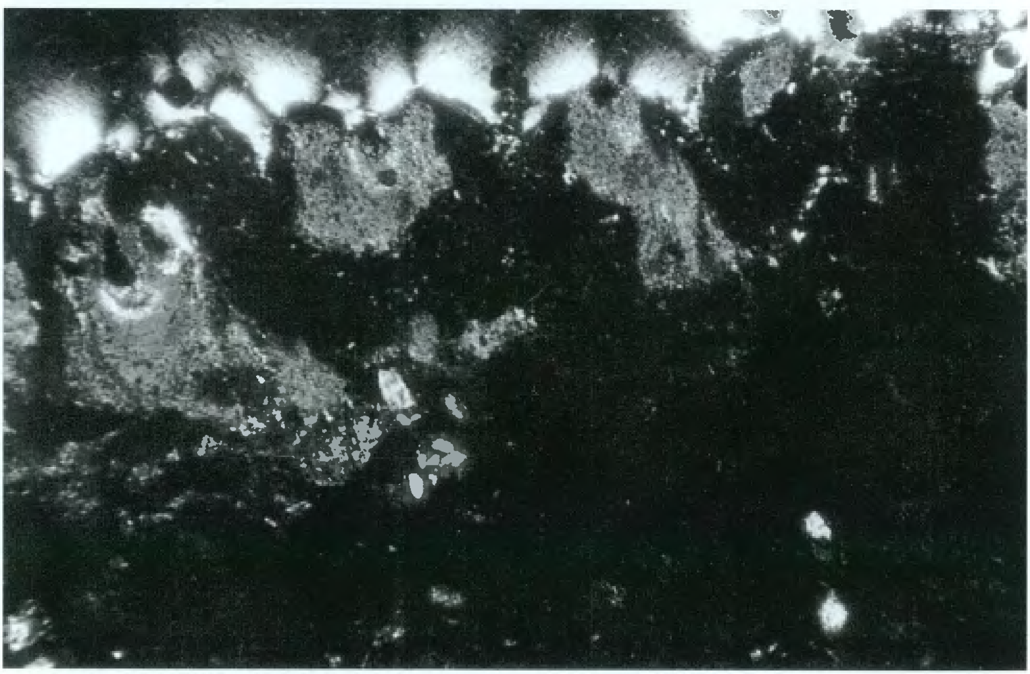

Figure 9.5 Photomicrograph of a thin section showing the large amount of calcium oxalate (weddellite) accumulated in the thallus of *Diploschistes actinostomus* (XPL, ×43).

Figure 9.6 Photomicrograph of a thin section showing *Parmelia loxodes* adhering to the substrate only by rhizines (PPL, ×108).

- *Buellia canescens* (syn. *Diploicia canescens* (Dicks.) Massal).
The thallus showed a medulla with a loose texture and did not seem to penetrate into the vulcanoclastite. Weddellite was present in small amounts and accumulated only on the thallus surface, as shown in Figures 9.2 and 9.3.
- *Diploschistes actinostomus* (Ach.) Zahlbr.
The thallus showed a distinctive growth of small bundles of hyphae which penetrated among the superficial fractures of the groundmass and in this way it was able to remove small portions of stone (Figures 9.4 and 9.5). Microprobe analysis showed a small accumulation of Si in the thallus. The accumulation of calcium oxalates (weddellite) in the lichen was abundant, but limited to the medullar zone.
- *Lecanora muralis* (Schreb.) Rabenh.
This species contained considerable weddellite distributed in the medulla and in the upper cortex. Brown hyphae, not belonging to the thallus, were present in the rock-lichen interface; the significance of these hyphae, observed also in other cases, will be the subject of a future investigation [14].
- *Lecidea fuscoatra* (L.) Ach.
Fungal hyphae penetrated the vitreous pumice and encircled some highly deteriorated augitic phenoclasts. This species had the greatest depth of penetration into the stone (4-5 mm) of all the lichens studied. No accumulation of Ca, Si, Fe, Al or K was present in the thallus.

Figure 9.7 SEM photomicrograph showing fungal hyphae of *Lecidea fuscoatra* penetrating into the substrate.

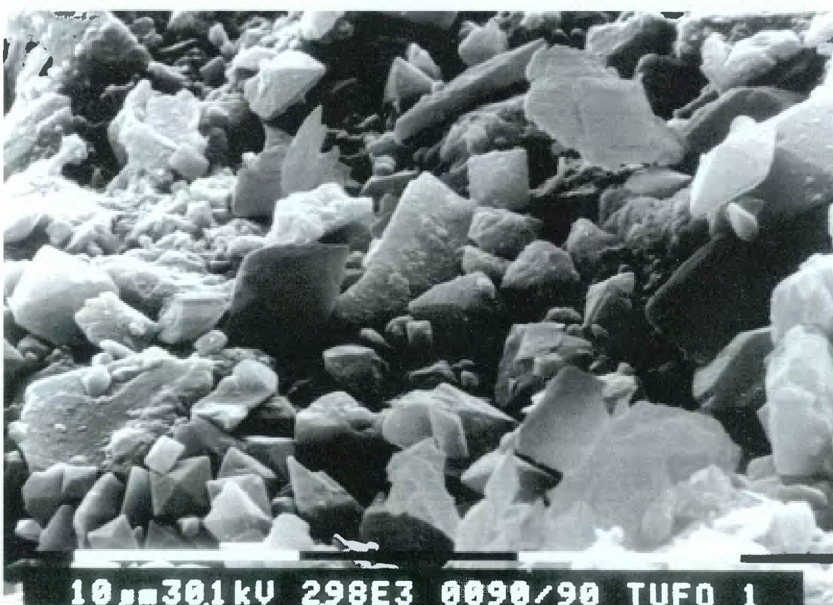

Figure 9.8 SEM photomicrograph showing crystals of weddellite in the thallus of *Diploschistes actinostomus*.

- *Ochrolechia parella* (L.) Massal.
  The thallus was rather thick, rhizoidal hyphae penetrated up to 1.5 mm into the rock, and were wrapped around highly corroded pyroxene crystals. Microprobe analysis did not show any accumulation of Ca in the lichen. This was the only lichen species to have silicon in the thallus at the same level as present in the surrounding stone. XRD showed no silicon mineral compounds in the thallus.
- *Parmelia loxodes* Nyl.
  As for all foliose lichens, adhesion to the substrate is ensured by the rhyzines, and thus penetration occurs to a lesser extent than in the crustose types. Nevertheless, some weddellite was observed in the surface layer (Figure 9.6).

9.4 DISCUSSION AND CONCLUSIONS

All the species studied showed that rhizoidal hyphae penetration of the tuff went deeper than is usual on other substrates, an average of 1.5 to 2 mm, up to a maximum of 5 mm in the case of *Lecidea fuscoatra*. The ability to penetrate tuff is facilitated by the high porosity and the heterogeneity of this stone. Hyphae are able to break into the microgranular groundmass and vitreous pumices while the phenoclasts (such as sanidine and pyroxene) and plagioclases are more often surrounded by the mycobiont but not penetrated (Figure 9.7).

By their presence, some of the species examined could initially form a protective layer against the degrading effects of water, as has already been observed on very porous substrates [14].

The deep penetration of the fungal hyphae into the rock causes the detachment of some millimetres of stone which adheres to the lower surface of the lichen. This phenomenon may be due to various causes, involving the central – oldest – part of the thallus, and may be related to the proliferation and crowding of apothecia [15] or to the fact that sometimes this central part of the thallus is the first part to die and detach [16].

The most important result of chemical deterioration induced by lichens seems to be the production of calcium oxalate. The same crystalline phase, weddellite ($CaC_2O_4.2H_2O$), was always identified.

The ability of *Caloplaca* spp. to produce calcium oxalate was confirmed. In fact, both of the species considered (*C. flavescens* and *C. teicholytha*) accumulated large quantities of weddellite.

The analytical studies showed that *Diploschistes actinostomus* and *Lecanora muralis* accumulate calcium, presumably from the stone, in their thalli (Figure 9.8). The effect of these two species and the localization of oxalates in their thalli have already been studied on other substrates, Muggia sandstone [17] and Pietra Serena [18], and the results obtained correspond with those described here.

In *Buellia canescens* and *Parmelia loxodes*, oxalate is present only in the surface layer of the thallus [19].

A involvement of lichens in the surface enrichment of iron in volcanic tuff and lavas has been demonstrated by some authors [20; 21; 22]. In the samples in this study, no preferential accumulation of iron was noted in relation to the presence of lichens. Iron oxides present at the rock surface do not seem to be derived from the action of lichens but rather are the result of natural decay.

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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 dependiendo de las especies. Las hifas de los hongos penetran profundamente en la toba, y esta acción produce muchas veces el desprendimiento de lagunos milímetros de piedra bajo la parte central del talo.

RESUME

Ce rapport présente les résultats d'une recherche portant sur huit espèces de lichens en croûte et une espèce foliacée, qui croissent sur les tufs volcaniques de la région de Civita Bagnoregio (Italie centrale). Les observations de lamelles, couplées à l'analyse par microsonde électronique et diffraction des rayons-X, ont permis d'identifier et de localiser des agents d'altération produits par les lichens. Le plus important effet de la croissance des lichens est l'élimination du calcium du substrat pour constituer de la weddellite qui s'accumule dans les thalles en quantités variables et en différents emplacements selon les espèces concernées. Les hyphes fongiques pénètrent profondément dans le tuf; leur ancrage dans la roche provoque souvent le détachement de quelques millimètres de pierre sous la partie centrale du thalle.

KURZFASSUNG

Die Arbeit präsentiert die Ergebnisse einer Untersuchung von acht krustenbildenden Flechtenarten und einer blattförmigen Flechtenart, die auf vulkanischem Tuff der Gegend von Civita Bagnoregio (Mittelitalien) auftreten. Dünnschliffbeobachtungen in Verbindung mit Mikrosonden- und Röntgenbeugungsanalysen ermöglichten die Identifizierung und Lokalisierung von Abbauprodukten aus der Aktivität der Flechten. Der in diesem Zusammenhang wichtigste Prozess ist die Herauslösung von Calcium aus dem Substrat, unter Bildung von Weddellit, der sich im Thallus anreichert, wobei die Menge und genaue Position dieser Weddellitbildungen von der beteiligten Flechtenart abhängt. Pilzhyphen dringen tief in den Tuff ein. Ihre Wirkung auf den Stein führt häufig zu einem Abheben von einigen Millimetern Steinsubstanz unterhalb des zentralen Teils des Thallus.

Part Three

TREATMENTS

ANALYSIS AND TREATMENT OF A STONE URN FROM THE IMPERIAL HOTEL, TOKYO

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ABSTRACT

The paper describes the results of analysis and the procedures of conservation for an Oya-stone urn designed by Frank Lloyd Wright for the Imperial Hotel in Tokyo. X-ray diffraction, microprobe and petrographic analyses revealed the stone to be a dacite. Attempts at cleaning the stonework were unsuccessful. Materials tried included *Orvus* detergent, sodium and potassium hydroxide-based cleaners, air abrasive, and *AB 57* poultices. Consolidation of the friable stone was achieved with a 1-10% w/v solution of *Paraloid B-72* in methyltri-methoxysilane and *Conservare OH* (= *Wacker OH*). Reconstruction employed epoxy and polyester resins and stainless steel pins; fills were carried out with sand, lime and Portland cement, or *Jahn M70* "natural" cement; in-painting of fills was executed with Prosoco's silicate emulsion paints.

10.1 INTRODUCTION

The Imperial Hotel in Tokyo was the crowning achievement of Frank Lloyd Wright's "Japanese Period." Constructed between 1916 and 1922 in a country known for its seismic activity, the complex edifice survived the otherwise catastrophic earthquake of 1923, due in part to Wright's daring and ingenious choice of site – the foundation of the building essentially floated on mud. Less ingenious but equally daring was his choice of stone for most of the hotel's structural and decorative features. Overriding the objections of the building committee, which comprised the empire's financial autocracy, Wright chose the so-called Oya stone – a workable lava quarried at Nikko. The committee objected; not on material grounds *per se*, but more on what might be

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called architectural etiquette: Oya stone was much too "common" to use in such a dignified building [1]. In addition to surviving the earthquake of 1923, the hotel escaped the spring, 1945, saturation bombing campaigns of Tokyo by Army Air Force General Curtis LeMay's newly deployed "great silver birds," the B-29s. Tokyo was also discussed as a possible third target for the atomic bomb on 10 August 1945, but was spared [2]. It was, however, the slower processes of destruction, such as environmental deterioration of the Oya stone, which resulted in crumbling and canted cornices – processes affecting almost all of the architectural and decorative elements. The poor state of preservation of the stonework, the outmoded hotel facilities and the meteoric rise of central Tokyo's real estate prices in the 1950s and 1960s ultimately led to the decision to demolish the hotel in 1967. The central lobby is now preserved in the Meiji Village architectural museum near Nagoya, from which the stone urn considered here was obtained by the Metropolitan Museum of Art in 1988 [3]. Figure 10.1 depicts one of these urns.

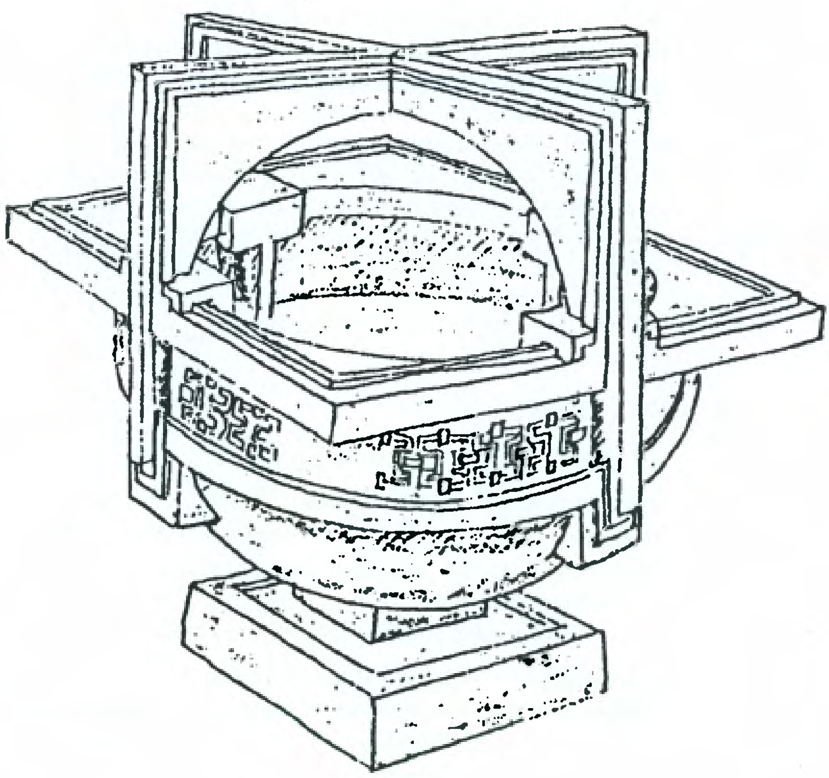

Figure 10.1 **Drawing of an urn made from lava, designed by Frank Lloyd Wright, from the Imperial Hotel, Tokyo, ca. 1922. Height 1.56 m, width 1.33 m.**

10.2 CONDITION

The stone urn exhibited a poorly consolidated surface with heavy losses. Most of the steel pins which originally held the several pieces of the urn together were badly corroded. Areas of the surface were badly discoloured by atmospheric pollutants, such as fly ash, which had tenaciously attached itself to the stone.

10.3 ANALYSIS OF THE STONE

Identification of the stone was based on examination of two thin sections, using both petrographic microscopy and electron beam microprobe techniques, as well as powdered samples subjected to X-ray powder diffraction analysis. Quantitative microprobe analyses of glass and mineral phases in the thin sections were carried out by wavelength dispersive X-ray spectrometry using a variety of natural and synthetic mineral standards, and Bence-Albee matrix corrections.

The general rock type was determined to be a porphyritic igneous rock. Phenocrysts, ranging in size from a fraction of a millimetre to about 4 mm, are of plagioclase feldspar, potassium feldspar, quartz and – rarely – pyroxene. Plagioclase feldspar, by far the predominant mineral in the phenocrysts, usually exhibits oscillatory zoning. Microprobe analysis of the plagioclase shows that for the most part it falls in the range An_{20-30} (oligoclase to sodium-rich andesine); most of the grains analysed contained cores that were somewhat more calcium-rich than the rims. Some of the feldspar phenocrysts were highly altered. A point count of about 1 cm^2 of the surface of one of the thin sections indicated that the phenocrysts made up about 40% of the volume of the rock. The remainder consisted of a predominantly glassy matrix in which were found scattered opaque minerals (ilmenite and magnetite). The average composition of the glass was 70.2% SiO_2, 11.8% Al_2O_3, 3.4% K_2O, 2.0% CaO, 1.5% Na_2O, 0.4% MgO and 0.07% FeO. The analytical totals averaged about 90%, indicative of the presence of hydrated phases. The glass present occurred as stringers which had been compressed and partially welded together; very fine-grained interstitial material seemed to contain minute quartz and potassium feldspar grains, as well as glass. The matrix overall was comparatively porous with occasional small amygdules; in none of these could the presence of other mineral phases be observed. X-ray diffraction analyses indicated the presence of zeolites in the rock. While none could be definitely confirmed by the analyses carried out on the thin sections, they could have been present in amygdules – a common alteration product of volcanic glass.

Specific classification of the rock was based on consideration of a number of parameters. The overall point count indicated that phenocrysts made up some 40% of the rock; the actual volume occupied by the phenocrysts was greater than this because of the fairly porous nature of the glassy matrix. Assuming a 50% phenocryst content, and assuming that the phenocrysts consisted mostly of plagioclase feldspar of composition An_{25}, the silica content of the rock was about 65-70% by weight. This placed the rock in the "acid" category. The observed phenocrysts as well as normative calculations indicated that over two-thirds of the feldspar in the rock was plagioclase.

Thus the rock could be classified as dacite, the fine-grained equivalent of granodiorite. The texture of the glassy matrix resembled that of extrusive acidic igneous rocks, often referred to as ignimbrites (or tuff-lavas).

10.4 CONSERVATION

10.4.1 Cleaning tests

Orvus detergent, sodium and potassium hydroxide-based cleaners, air abrasive, and *AB57* poultices were all unsuccessful in cleaning the surface of the stone without damage. The idea of cleaning the urn was therefore abandoned.

10.4.2 Consolidation

The urn was carefully dis-assembled to remove all corroded iron pins and deteriorated setting mortars. While in this state, each piece was separately consolidated with *Conservare OH*. Twenty gallons (75 l) were applied to the approximately 200 ft^2 (19 m^2) of surface. Although the surface of the stone remained dark for several weeks after treatment, the original colour returned and the surface was significantly less friable to the touch. Further local consolidation of severely weathered areas was conducted with 1-10% w/v *Paraloid B-72* in methyltrimethoxysilane (MTMOS).

10.5 PREPARATION FOR DISPLAY

10.5.1 Reconstruction

Small pieces (of the order of a few inches or several centimetres) were re-adhered with *B72*/toluene in concentrations from 20-80% w/v, or *EPO-TEK 301* epoxy resin. Larger pieces were re-adhered with *AKEMI* polyester resin. Mechanical aids such as stainless steel pins were also used at several points, notably the crossing and the springings of the arches and on the four pieces which form the rim of the bowl. These four pieces were set on the bowl with a 1:1:6 mixture (by volume) of hydrated lime:type II Portland cement:sand, and later toned with silicate emulsion paints to be less prominent with respect to the surrounding stone.

10.5.2 Replacements and fills

Small fills were executed in *M70* pozzuolanic cement. These fills were textured in a semi-dry state to match the surrounding areas. In the consolidation process care was taken not to employ the *B72*/MTMOS mixture in areas which would later be filled with *M70* because the *M70* would then fail to adhere to the hydrophobic substrate. This problem does not occur in areas treated with the non-hydrophobic *Conservare OH*.

Several areas required larger replacement pieces. Despite the known problem of possible salt formation by Portland cement, these pieces were executed in a 1:1:6 mixture of hydrated lime:type II Portland cement:sand and stone rubble. The rubble consisted of ground pieces of the lava obtained from additional pieces of the stone from the hotel. The rubble was created by passing the fractured pieces of stone through a #10 (1.68 mm mesh) geological sieve. Small, ⅛ inch (≈3.2 mm) diameter pins were set into the stone work with *AKEMI* polyester resin. These pins provided a key for the cement replacement pieces. Further texturing of these pieces was executed after the cement had cured for several weeks.

Both the *M70* infills and the cement replacement pieces are stable in ultraviolet light.

10.5.3 In-painting

All fills and replacement pieces were toned with *Prosoco*'s silicate emulsion paints, which are irreversible, but stable in ultraviolet light. Reversibility was not considered necessary when in-painting non-original materials which might themselves be removed at some later time.

In order to achieve overall tonal balance, some of the areas badly darkened with fly ash were toned with acrylic emulsion paints. Although they are less stable in ultraviolet light than the silicate emulsion paints, they are reversible in the short term, and therefore deemed more appropriate to apply to an "original" surface.

10.5.4 Installation

The urn is now installed in the American Wing at the Metropolitan Museum of Art, just outside the Frank Lloyd Wright room from the Little house which once stood in Wayzata, Minnesota.

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We would also like to thank A. Elena Charola for encouraging us to submit this small piece for her important publication on the difficult problems of the conservation of lava-type rocks.

APPENDIX

Conservation products mentioned in the text.

- *Conservare OH* (the commercial name for *Wacker OH* in the USA) and *Silicate emulsion paints* were from Prosoco, P.O. Box 171677, Kansas City, KS 66117, USA.
- *Methyltrimethoxysilane (MTMOS)* solvent was from Dow Chemical, Midland, MI 48686, USA.
- *Paraloid B-72* was from Conservation Materials, 240 Freeport Blvd., P.O. Box 2884, Sparks, NV 89431, USA.
- *M70* was from Jahn, Kloosterweg 34, 3232 LC Brielle, The Netherlands.
- *EPO-TEK 301* was from Epoxy Technology, 14 Fortune Drive, Billerica, MA 01821, USA.
- *AKEMI* was from Jaeger and Condino, 35-44 61st Street, Woodside, NY 11377, USA.
- *Wacker OH*: see *Conservare OH* above.

RESUMEN

Se describen los resultados de los análisis y del tratamiento de conservación de una urna en piedra Oya diseñada por Frank Lloyd Wright para el Hotel Imperial de Tokyo. Análisis por difracción de rayos-X, microsonda y petrográficos confirmaron que la roca utilizada para la escultura es una dacita. Los ensayos de limpieza realizados sobre esta piedra utilizando detergente (*Orvus*), limpiadores a base de soda cáustica, aire abrasivo y emplastos (*AB 57*) no dieron resultado. La consolidación de esta piedra friable se llevó a cabo con soluciones 1-10 % p/v de *B-72*/metiltrimetoxisilano y *Wacker OH*. Para la reconstrucción se utilizaron resinas epoxi y poliester y pernos de acero inoxidable. Los rellenos se realizaron con una mezcla de arena, cal y cemento portland, o un cemento "natural" *Jahn M70*. Los retoques de los rellenos fueron realizados con pinturas en emulsión de silicatos.

RESUME

L'article décrit les résultats d'analyse et les procédés de conservation d'une urne en pierre Oya créée par Frank Lloyd Wright pour l'Hôtel Impérial à Tokyo. Les analyses par diffraction des rayons-X, par microsonde et par pétrographie ont montré que la pierre est une dacite. Les essais de nettoyage de l'oeuvre en pierre ont été infructueux, notamment avec les matériaux suivants: détergent *Orvus*, nettoyeurs à base d'hydroxyde de sodium et de potassium, air abrasif et cataplasmes *AB 57*. La pierre friable a été consolidée avec une solution 1-10% p/v de *B-72*/méthyltriméthoxysilane et *Wacker OH*. Pour la reconstruction on a employé des résines époxyde et de polyester et des broches en acier inoxydable; les bouchages ont été réalisés avec du sable, de la chaux et du ciment Portland ou du ciment "naturel" *Jahn M70*; les bouchages ont été peints avec des peintures de silicates à émulsion.

KURZFASSUNG

Der Beitrag beschreibt die Analysenergebnisse und die Konservierungsmethode einer Oya-Steinurne, die von Frank Lloyd Wright für das Imperial Hotel in Tokyo entworfen worden war. Röntgenbeugung, Mikrosonde und petrographische Mikroskopie wiesen den Stein als Dazit aus. Versuche zur Reinigung der Steinoberfläche blieben ohne Erfolg, wobei folgende Mittel eingesetzt wurden: *Orvus*-Reinigungsmittel, Reiniger auf Basis von Natrium/ Kalium-Hydroxiden, Luftdruckreinigung und *AB 57*-Packungen. Eine Konsolidierung des mürben Steines konnte mit 1-10%-igen (Gew./Vol.) Lösungen von *Paraloid B-72* in Methyltrimethoxysilan und Wacker-OH erreicht werden. Ergänzungen wurden unter Verwendung von Epoxid- und Polyesterharzen und rostfreien Stahlstiften ausgeführt. Für Ausbesserungen wurde Sand, Kalk und Portlandzement oder der "Naturzement" *Jahn M70* verwendet. Das Einfärben der Ausbesserungen erfolgte mit silikatischen Emulsionsfarben.

STUDIES FOR THE CONSOLIDATION OF THE FACADE OF THE CHURCH OF SANTO DOMINGO, POPAYAN, COLOMBIA

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ABSTRACT

The portal of the Church of Santo Domingo, as well as many other important monuments in Colombia, such as the archaeological area of San Agustin, were carved out of volcanic tuff. These rocks show pronounced deterioration due to their physical condition and mineralogical nature.
The portal suffered greatly during the earthquake of 1983. It was then taken apart and the studies described in the present paper were carried out. Samples treated according to the resulting recommendations are still being field tested to evaluate the effectiveness of the proposed treatments.

11.1 INTRODUCTION

The Church of Santo Domingo in the city of Popayán is one of the monuments most beloved by the local community. The church is located close to the Cloister of the University of Cauca and is one of the sites that "must be seen" by tourists.

The portal of the church, shown in Figure 11.1, has been highly admired and commented on by critics and art historians. It is a massive structure, heavily decorated with plant motifs, plateresque columns, and a convex frieze of Palladian inspiration. The mixture of archaic and baroque elements make this portal unique. The carving, carried out in volcanic tuff, a material widely used in Popayán for the construction of facades, was finished in 1714. During the earthquake of 1983, the already weathered portal suffered significant damage.

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Figure 11.1 **View of the portal of the Church of Santo Domingo, Popayán, Colombia.**

The volcanic tuff used in the portal can be found easily within a radius of 20 to 50 km from the city. Geological studies of the area show these rocks to belong to the Popayán formation. They are composed of conglomerates of porous and permeable nature, volcanic rocks, fluvial-lagoon deposits, lava flows, volcanic mud flows and tuffs [1; 2; 3].

In previous studies [4] it was shown that the stones currently quarried around Popayán have the same petrographic composition as samples taken from the tuff of the portal.

The aim of the present study was to find an adequate consolidant to strengthen this rock by improving its mechanical resistance to deterioration. Several commercial products developed for the preservation of monuments are currently available in the USA and Europe [5; 6; 7; 8]. These products are based on synthetic resins, with various chemical compositions, ranging from epoxies, acrylics and polyurethanes to the latest developments in the area of silicones [9; 10; 11].

None of the products listed meets all the requirements considered necessary for treatment of the specific problems associated with the volcanic tuff of the facade. Nonetheless, some of the chemicals have optimal properties and the disadvantages they present are minor and can be compensated for in each particular instance. In view of this, some products were chosen for testing using various concentrations and immersion times. Physical properties of the tuff, such as bulk density, resistance to compression, porosity and water absorption, were measured before and after the applied treatments.

It should be remembered that a stone can deteriorate to such an extent that it reaches a point beyond which no treatment will save it from total disintegration.

11.2 NATURE OF THE STONE AND DETERIORATION CAUSES

Macroscopic examination of the weathered stone from the portal of Santo Domingo shows it to be in an extremely powdery and friable state. Its secondary porosity is high, due to leaching out of some minerals, such as iron oxides and biotite. Pores and larger cracks account for about 20% of the sample, and are filled with a black material resembling bitumen in appearance. The weathering is homogenous and usually begins with a de-vitrification of the volcanic glass to produce a brownish cloudy material, weakly bi-refringent. It then continues with a total replacement of the volcanic glass by a greenish material that oxidizes to a brown colour and which finally turns into a resinous material [3; 12].

The mineral portion by volume of the weathered tuff was typically olivines 23%, biotite 2%, pyroxenes 5%, and plagioclases 55%. The typical compositions were determined from microscopic analysis of thin sections of highly weathered samples [A. Pradilla, *pers. comm.*]. The primary porosity of these samples was found to be 10% and the secondary porosity 5%. In polished sections, the dis-aggregation of the minerals, as well as their alteration, can be observed.

11.3 EXPERIMENTAL CONDITIONS

11.3.1 Physical tests

The physical characteristics of the stone were determined, namely bulk density, porosity, water absorption and resistance to compression.

The first three tests were carried out according to ASTM standard C97-47 (1970) modified according to the recommendations of the Commission 25-PEM [13]. Resistance to compression was determined according to ASTM standard C674-77 and given in kg/cm^2.

These tests were repeated on samples after treatment with the various products.

11.3.2 Products tested

Preliminary tests were run on samples treated with the following products: *Paraloid B-72; Mowilith; Primal AC-33; Limes-tone; Wacker OH; Wacker H;* and *Toch 8004*, an epoxy resin. The relevant data on these products is given as an Appendix to this paper.

Based on the results of these preliminary tests, some products, such as *Mowilith* and *Limes-tone*, were not considered for further testing.

The products selected for further testing were applied to specimens of prismatic shape (approx. 2.2 × 2.2 × 3.4 cm) cut from weathered rock. These were not perfectly regular due to their highly deteriorated state. They were treated by total immersion in varying concentrations and with various immersion times, as given in Table 11.1.

Table 11.1 Treatment by total immersion of test specimens

Treatment		Product	Concentration	Immersion time
1	Acrylic resin	Paraloid B-72	5% in thinner	10 days
2	Acrylic resin	Paraloid B-72	10% in thinner	10 days
3	Acrylic resin	Primal AC-33	30% in water	10 days
4	Acrylic resin	Primal AC-33	30% in water	3 days
5	Silicate esters	Wacker OH	undiluted	2 days
6	Silicate esters	Wacker H	undiluted	1 day
7	Silicate esters	Wacker H	undiluted	5 days
8	Silicate esters	Wacker OH, then Wacker H	undiluted undiluted	1 day 2 days
9	Epoxy	Toch 8004	1:2 in acetone	3 hours

11.4 RESULTS

Visual examination of the treated specimens showed some darkening of the surface compared to the untreated stone. This was most noticeable for the epoxy resin treatment. *Wacker H* darkened it somewhat, while *Wacker OH* was less obvious.

Primal AC-33 treatment left a slightly pinkish film on the surface. This could probably be obviated by reducing the concentration of the applied treatment.

The percentage by weight of resin left in the stone after treatment is given in Table 11.2. This table also gives the results (average of three measurements) of the physical tests performed on both untreated and treated samples.

Table 11.2 Results of physical tests

Treatment	Weight increase (%)	Porosity (%)	Compression resistance (kg/cm^2)	Water absorption (%)	Bulk density (g/cm^2)
0 *	—	47.4	12.87	36.4	1.301
1	1.40	42.5	8.09	32.9	1.292
2	3.61	42.4	12.41	31.0	1.368
3	1.62	44.4	48.64	31.5	1.410
4	6.83	46.1	14.24	35.9	1.283
5	10.80	36.5	21.32	25.7	1.421
6	8.30	21.0	32.80	8.2	1.450
7	10.20	10.7	22.88	6.8	1.579
8	9.72	14.2	51.00	9.7	1.459
9	14.10	22.6	83.67	14.3	1.583

* Treatment 0 gives data for the untreated stone

11.5 CONCLUSIONS

From the results of the laboratory tests the following conclusions can be drawn:

- *Paraloid B-72* does not consolidate the stone at the concentrations tested.
- *Primal AC-33* consolidates the stone, but does not diminish water absorption. Furthermore, it was found that the amount of resin deposited within the stone was erratic and could not be related directly to the concentration of the emulsion or to the immersion time.
- The silicate ester treatments (*Wacker H* and *Wacker OH*), with or without silicones, gave the best results.
- The epoxy treatment (*Toch 8004*) resulted in a good consolidation, but the visual change to the treated stone precluded the use of this product.

The silicate ester-based treatments – N° 5 to N° 8 – gave the best results. These findings are in agreement with those obtained in a study on similar volcanic tuff stones from Ecuador [9].

It was shown that the amount of resin deposited in the stone was proportional to the application time. The most efficient treatment resulted from the combination of both products in successive applications, as shown by the result of treatment N° 8. Even though consolidation was obtained with these products, surface powdering was not eliminated. Samples treated with these products are now being weathered *in situ* for a final evaluation of the treatment.

Some final conclusions can be drawn regarding treatment of the portal to be carried out for its preservation.

- It is important that a consolidation treatment be applied as soon as possible.
- If, due to cost reasons, the treatment has to be limited to the use of only one product, then *Wacker H* would be the treatment of choice.
- For practical reasons, the application procedure can be changed to saturation by percolation.
- Care must be taken to repoint the blocks before the treatment.
- Eventual maintenance by the surface application of a water repellent should be considered.

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APPENDIX

Products tested

- *Limes-tone* (Toxement). Silicone resin. Leaves a residue of clear film. Water repellent. Not recommended as a consolidant.
- *Mowilith 30* (Hoechst). Polyvinyl acetate dissolved in a mixture of acetone and amyl acetate. Viscosity 110-150 cp. Leaves a residue of clear film. Used as adhesive. Not recommended as a consolidant.
- *Paraloid B-72* (Rohm & Haas). Co-polymer of acrylic and methacrylic esters, dissolved in a mixture of xylol, thinner and toluol. Concentration about 40% solids. Viscosity 470-770 cp. Leaves a residue of clear film. Used as adhesive and consolidant.
- *Primal AC-33* (Rohm & Haas). Acrylic emulsion in water. Leaves a residue of milky film.
- *Toch 8004* Epoxy Resin (Toxement). Epoxy resin in a mixture of acetone and other ketones. Leaves residue of yellowish film. Used as an adhesive and a consolidant.
- *Wacker H* [W-5937-H] (Hoechst). Mixture of prepolymerized ethyl silicate and alkyl triethyl silicate in ethyl alcohol. Viscosity: 42 sec. for 2-mm DIN cup. Leaves a vitreous, translucid residue. Used as a consolidant and water repellent.
- *Wacker OH* [W-6789-OH] (Hoechst). Prepolymerized ethyl silicate in ethyl alcohol. Viscosity: 42 sec. for 2-mm DIN cup. Leaves a vitreous, translucid residue. Used as a consolidant.

RESUMEN

El portal 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 portal sufrió daños importantes en el terremoto de 1983. Se desmontó y se realizaron los estudios presentados en el siguiente trabajo. Muestras tratadas de acuerdo a los resultados obtenidos se encuentran en evaluación a la intemperie para determinar la efectividad de los tratamientos propuestos.

RESUME

Le portail de l'église de Santo Domingo ainsi que nombre d'autres monuments importants de Colombie, tels la zone archéologique de San Agustin, ont été taillés dans des tufs volcaniques. Ces roches accusent une détérioration prononcée due à leur constitution physique et leur nature minéralogique.
Le portail a beaucoup souffert du tremblement de terre de 1983. Il a été démonté pour réaliser les études qui figurent dans le présent document. Des échantillons, traités selon les recommandations issues des études, sont encore actuellement testées aux intempéries pour évaluer l'efficacité des traitements proposés.

KURZFASSUNG

Das Portal der Kirche Santo Domingo ist aus vulkanischen Tuffen gearbeitet. Das gilt auch für viele andere bedeutende kolumbianische Monumente, eingeschlossen der archäologische Bereich von San Agustin. Diese Gesteine weisen aufgrund ihrer physikalischen und mineralogischen Eigenschaften besonders grosse Schäden auf.
Das angesprochene Portal wurde durch das Erdbeben von 1983 schwer beschädigt. In der Folge wurde es abgebaut und untersucht. Diese Studien werden in der vorliegenden Arbeit vorgestellt. Einige Proben, die im Einklang mit den Untersuchungsergebnissen behandelt wurden, befinden sich noch im Freien, um die Wirksamkeit der empfohlenen Konservierungsbehandlungen bewerten zu können.

INTERACTION BETWEEN VOLCANIC TUFF AND PRODUCTS USED FOR CONSOLIDATION AND WATERPROOFING TREATMENTS

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ABSTRACT

Volcanic tuffs were commonly used in many Italian regions because of their availability and workability. Their durability, however, is rather poor, and as a consequence they frequently need conservation treatments. Research on interactions between tuffs and products used for consolidation and waterproofing is therefore necessary. The present paper gives the results obtained with four different systems, all having a consolidating and a water repelling effect, applied to blocks of a volcanic tuff coming 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 ethyl silicate and methylsilane.

12.1 INTRODUCTION

Volcanic tuff is commonly found in many parts of the world and is often used for building because of its low quarrying cost and its workability.

In the Lazio region of central Italy, a considerable amount of ignimbrite is found, and this 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 in general has not survived to the present.

The archaeological remains that have survived generally owe their conservation to the fact that they were buried up to the time of discovery. Once uncovered, however, they are susceptible to environmental factors and deteriorate rapidly.

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The conservation problems associated with this material are complex, due to the presence of reactive minerals, such as zeolites, and to the high porosity. Moreover, large structures are often involved, such as city walls or remains of buildings, situated at ground level and hence difficult to protect from rising damp or from the environment.

Under these circumstances, the need for 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 ageing.

12.2 EXPERIMENTAL PROCEDURES

12.2.1 Petrographic features of the tuff

The blocks of tuff used in this study came from the Cerveteri archaeological 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 scoriae], is actually a reddish-yellow lithoid tuff with black scoriae of irregular size and shape dispersed in micropumice. The stone is an ignimbrite from the volcanic regions of Sabazia and Vico, to the north of Rome.

The matrix is deep yellow-brown, because of iron oxides and other iron compounds; there are extensive fractures and holes. The phenocrysts include sanidine, analcime derived from alteration of leucite, occasional plagioclase, pyroxene (diopsidic), occasional biotite, and olivine with signs of weathering.

X-ray powder diffraction analysis (XRD) shows the presence of chabazite (and phillipsite), and indications of extensive zeolitization, which took place during diagenesis.

The vitreous mass of the ash 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.

12.2.2 Products and application methods

Two systems based on silicon products and two based on methacrylate polymers were tested. The first two were an ethyl-silicate and silane mixture, and a polysiloxane. The second two were a methacrylate polymer applied as a monomer and polymerized *in situ*, and a solution of the same polymer. Most of the products used in recent decades for treating stone belong to these groups.

The products tested and the codes used to identify them in the table below were:

- **MMA** Methylmethacrylate monomer in a 10% solution with *Sniatron 1629* polyester resin (SNIA BPD).

- **PMMA** *Paraloid A21 LV* (Rohm & Haas). A low viscosity polymethylmethacrylate in 1,2 dichloroethane (10% w/v).
- **S** *Rhodorsil 11309* (Rhône Poulenc). A methyl-phenyl-polysiloxane dissolved in 1,1,1 trichloroethane (10% w/v).
- **T** *Tegovakon V* (Goldschmidt A.G.). An ethyl silicate dissolved in organic solvents (dry residue about 34% w/w) used for consolidation, and used in combination with *Tegosivin HL 100* (Goldschmidt A.G.), defined by the manufacturer as a low-molecular-weight modified siloxane, solvent-free, and applied for waterproofing.

The various treatments were applied to 27 × 27 × 27 cm cubes of the tuff samples. One such cube was kept untreated as a control sample. These sizes, rather unusual for laboratory testing, were adopted in order to reproduce, as far as possible, the conditions encountered when treating monuments. They also allowed for a good assessment of the penetration depth and the distribution of the treatment products. The samples were dry weighed before and after treatment, and the ultrasonic transmission velocity was measured as well.

The PMMA, S and T treatments were applied as follows. Each sample, completely enclosed in a tightly wrapped, gauze + cotton wool + gauze covering, was placed inside a polyethylene tank. The sample cubes were on supports to keep the sample off the bottom of the tank. The wrapping was then soaked with the solution under test, applied by slow dripping from infusion needles imbedded in the cotton wool. The excess solution collected in the bottom of the tank and could rise up by capillarity through the portions of the covering touching the tank bottom (Figure 12.1).

For PMMA and S, the treatment lasted 4 days. For treatment T, ethyl silicate was applied for 7 days, and then, after a further 21 days to allow for the hydrolysis and the precipitation of silica to occur, the methyl silane was applied, in the same way, for 5 days.

The MMA 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 SpA in Colleferro, under the direction of Professor A. Rio [1].

The 27 × 27 × 27 cm cubes were then cut into smaller cubes of 5 × 5 × 5 cm, with the position of each within the original block being recorded. The measurements performed on these samples were as described in Section 12.2.3 below. They were then aged with the procedures described in Section 12.2.4, and the same measurements were repeated.

12.2.3 Measurements

The parameters measured were intended to indicate the interaction between the stone and the products used, especially with regard to structural and mechanical properties, behaviour in relation to water both as liquid and vapour, and colour. All the measurements were performed on both treated and untreated (UT) samples, before and

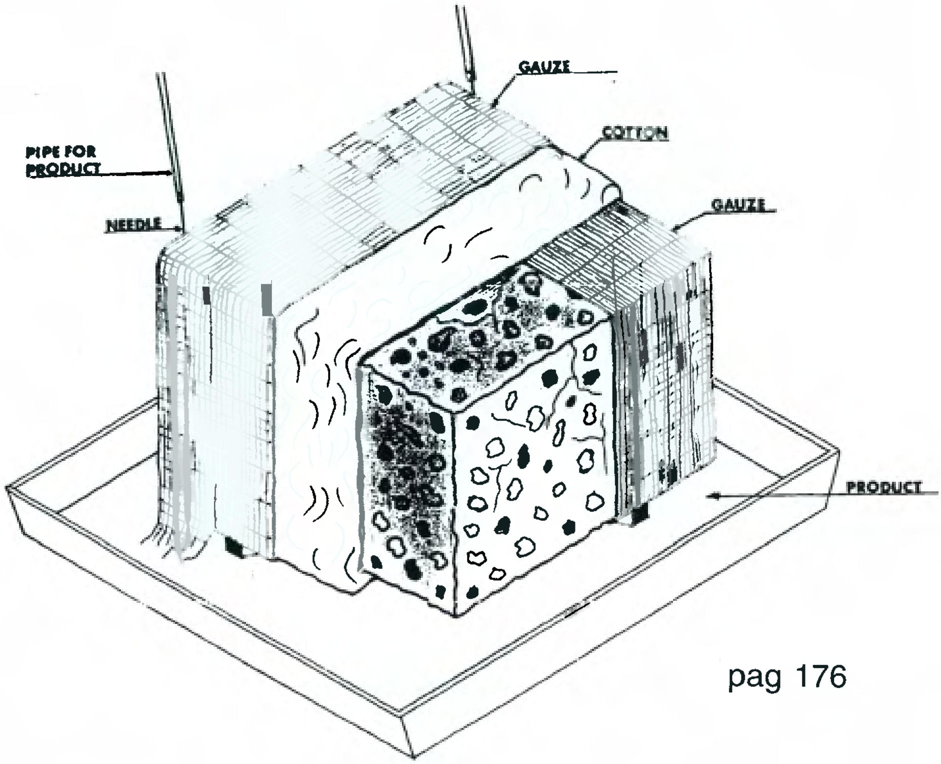

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Figure 12.1 Method of treatment for PMMA, S and T.

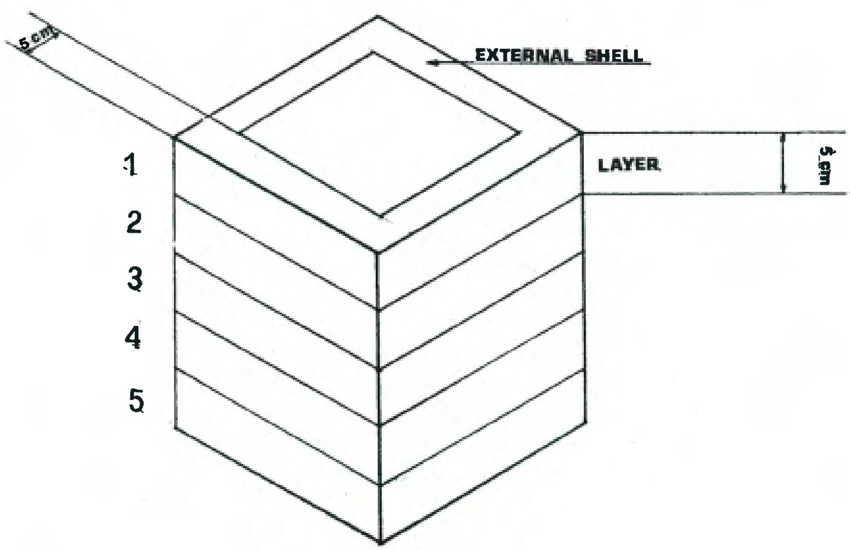

Figure 12.2 The different layers in the original blocks.

Table 12.1 **Results of measurements on the untreated samples, and on the treated samples before and after weathering.**

TREATMENT	BEFORE WEATHERING			AFTER WEATHERING (External layer)
	External layer	Internal layer	Core	
Water absorption by capilliarity, $M\infty$ (g/cm^2)				
UT	1.8	–	–	–
MMA	0.4	0.3	–	0.6
PMMA	0.2	1.0; 0.7; 0.2 [1]	–	0.25
S	0.2	0.6; 0.1 [2]	–	0.1
T	0.5	1.5	–	1.2
Water absorption by capilliarity, $CA \times 10^{-3}$ ($g/cm^2.sec^{0.5}$)				
UT	47	–	–	–
MMA	2.0	0.9	–	3.6
PMMA	0.6	5.6; 0.3; 0.3 [1]	–	2.1
S	0.5	2.9; 0.5 [2]	–	0.4
T	1.0	5.4	–	4.0
Water absorption by full immersion, *CI* – Imbibition Coefficient (ΔM / M %)				
UT	34.2	–	–	–
MMA	11.2	9.5	–	11.7
PMMA	12.7	18.0; 21.6; 7.0 [1]	–	9.0
S	8.4	15.9; 7.5; 6.3 [1]	–	9.2
T	28.6	31.2	–	28.0
Compressive strength (kN/cm^2)				
UT	0.16	–	–	–
MMA	1.87	1.78	–	1.33
PMMA	0.37	0.37	–	0.36
S	0.31	0.17	–	0.17
T	0.36	0.40	–	0.26; 0.40 [3]
Integral open porosity (*P*%) [4]				
UT	22 - 39	–	–	
MMA	16	19 - 10	16	
PMMA	21	19 - 26	19	
S	20	23.5	18	
T	30 - 41	32 - 36	28	

Note [1]: The values relate to the 2nd, 3rd & 4th layers respectively.
Note [2]: The values relate to the 2nd & 4th layers respectively.
Note [3]: Minimum and maximum values.
Note [4]: Minimum and maximum values. Core is the centre of the 27 cm cube.

Table 12.1 (cont.) **Results of measurements on the untreated samples, and on the treated samples before and after weathering.**

TREAT-MENT	BEFORE WEATHERING	AFTER WEATHERING	WEIGHT INCREASE WITH TREATMENT	ULTRASONIC VELOCITY (m/sec) [1]	
	Drying Index			Before treatment	After treatment
UT	0.26	—			
MMA	0.21	0.20	15.0%	1172	2410
PMMA	0.23	0.12	13.6%	1037	1425
S	0.19	0.13	12.0%	1141	1201
T	0.27	0.24	15.0%	1692	1837
	Water vapour permeability ($g/m^2.24h$)				
UT	370	—			
MMA	130	150 [2]			
PMMA	260	240 [2]			
S	360	320 [2]			
T	260	340 [2]			
	Colour measurements				
UT	10YR 6/6-6/5	—			
MMA	7.5YR 4/3-4/3	7.5YR 4/2			
PMMA	7.5YR 5/4	10YR 5/2-4/2			
S	10YR 4/2-4/4	10YR 4/2			
T	10YR 5/3-5/4	10YR 5/2			

Note [1]: Average values of the three directions parallel to the surfaces of the 27 cm cube.

Note [2]: Measured on only one sample.

after artificial ageing. 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 depth) and the internal core (5-10 cm). The former was conventionally indicated as layer #1.

Internal samples were registered according to the horizontal layer of origin: the layer labelled #2 is between 5 and 10 cm from the upper surface; #3 is between 10 and 15 cm; and #4 is between 15 and 20 cm (Figure 12.2). Layer #5 is considered equivalent to #1.

(i) *Porosity*

A mercury porosimeter was used, using the standard procedures of 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 radii r <1000 Å; 1000 Å < r < 10 000 Å; 10 000 Å < r < 100 000 Å; and r > 100 000 Å.

(ii) *Ultrasonic velocity*

This was measured according to the standard procedures of NORMAL 22/86 [3], using equipment supplied by the C.E.B.T.P. at Saint-Rémy-les-Chevreuse (France) and carried out by the CND Society (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.

(iii) *Compressive strength*

A dynamometer with a load increase velocity of 8.3×10^{-3} mm/sec was used for measuring. The results are given as ultimate compressive strength (kN/cm). The measurement was carried out on a minimum of 3 samples for each set of samples.

(iv) *Capillary water absorption*

This was measured using the standard procedures of NORMAL 11/85 [4] on homogeneous groups of 5 samples. The results are given as capillarity coefficient (***CA*** $g/cm^2/s^{0.5}$) and maximum absorption (***M***∞) asymptotic value of the quantity of water absorbed (g/cm^2).

(v) Water absorption by total immersion

This was measured using the standard procedures of NORMAL 7/81 [5] on homogeneous groups of 5 samples. The results are given as percent imbibition coefficient (CI%).

(vi) *Drying index*

The drying index (***DI***) was measured using the standard procedures of NORMAL 29/88 on Drying Index [6]. Homogenous groups of 5 samples were used, with a drying period of 120 hours.

(vii) *Permeability to water vapour*

This was measured using the standard procedures of NORMAL 21/85 [7] on homogenous groups of 3 samples, all from the external layer (#1).

After artificial ageing, the same number of samples could not always be prepared due to the development of fragility in the tuff. In these cases, measurements were carried out on fewer samples, as indicated in the results section.

(viii) *Colour*

The colour of the external surface of layer #1 was assessed using Munsell Soil Charts. Measurement refers only to the matrix, ignoring the large particles and black scoriae. The results are expressed as H (hue), V (value) and C (chroma).

12.2.4 Artificial ageing

Artificial ageing was carried out in two steps: first with freeze/thaw cycles, and then by exposure to salt fog.

In the first stage, the samples were immersed in de-ionized water until saturated, then sealed in polyethylene bags with 20 ml of de-ionized water. These samples were then submitted to 50 freeze/thaw cycles in a climatic chamber. The cycle was 2 h at +15°C; from +15°C to −15°C in 0.5 hour; 2 h at −15°C; from −15°C to +15°C in 0.5 h.

In the second stage, the samples were dried at 60°C, and then immersed into a solution containing 30 g/l Na_2SO_4 + 15 g/l NaCl + 5 g/l $NaNO_3$ + sufficient H_2SO_4 to bring the solution to ≈pH 4.5.

The saturated samples were then subjected to 6 dry/wet cycles comprising 4 h in a salt fog chamber at 25°±2°C, with a spray solution of the above composition, followed by 20 h in a climatic chamber under four UV germicide lamps (Philips TUV 15 WG15TO), with a total intensity of 300 lux, at 50±2°C.

After these six cycles the samples were washed with tap water and finally with de-ionized water to wash away the soluble salts.

For each of the products tested, 10 samples from the outer layer were aged.

12.3 RESULTS

All the results reported in the table are average values. As the standard deviation is not significant due to the limited number of samples, the semi-dispersion was calculated ((value$_{max}$ − value$_{min}$) / 2). Even though it is not reported in the table, this semi-dispersion was taken into account when evaluating the experimental results.

12.3.1 Methylmethacrylate (MMA) monomer

Table 12.1 gives the results obtained with samples receiving treatment MMA, and some comments on them are given below.

(i) *Amount of product absorbed and depth of penetration*

The increase in sample weight after treatment was 15%. All the measurements indicated that a satisfactory amount of the product also reached the internal part of the sample, as the penetration depth was at least 13.5 cm.

(ii) *Homogeneity of distribution*

Comparison of the amount of water absorbed by capillarity and by total immersion of the samples, both for the shell and for the core, 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 high vapour pressure. This leads to a reduction in the quantity of consolidating material in the outermost layers, which consequently tend to be less hydrophobic than the inner layers.

(iii) *Structural properties*

The porosity decreased considerably in both inner and outer layers, to an average level of around 16%. Lack of homogeneity in the external layers is due to inherent irregularities in the tuff rather than to non-homogeneous distribution within the pores of the stone.

From the porosimetric distribution evaluation it was apparent that the polymer material preferentially tended to fill pores with a radius of 1000 - 10 000 Å. Once the cavities having a radius >100 μm (not detectable before treatment with the technique used) were filled, the formation of pores in the 100 000 - 300 000 Å range was triggered. These results are in good agreement with those published by other authors, working on a Neapolitan yellow tuff [8].

Matching the porosimetric data, ultrasonic measurements also indicated a considerable reduction in internal porosity: the velocity of sound more than doubled after treatment.

(iv) *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 to the uncertainties of the measurement method rather than to any irregular distribution of the product or the characteristics of the tuff. These results also agree with those of the Neapolitan study [8].

Artificial ageing of the samples led to a reduction of about 30% in compressive strength, but the compressive strength remains much higher than in untreated tuff. It should be mentioned that no samples treated with MMA broke as a result of the artificial ageing treatment.

(v) *Behaviour of the samples toward water*

As noted above, samples from the internal layers absorb less water than the outer layers. This is especially obvious after an assessment of the ***CA*** value (affected by the first minutes of contact of the sample surface with water) and the ***CI*** value (which represents the maximum quantity of water absorbed by full immersion at atmospheric pressure).

After ageing, the parameter most affected is ***CA***, although it is still less than a tenth 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 sensitive to the ageing process.

The inflection in the capillary absorption curve before ageing 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 it should be noted that although the treated tuff is much less permeable to vapour, having absorbed less water it dries in less time than the untreated stone. Weathering increases the drying rate of the treated samples.

(vi) *Colour*

Treatment causes a colour change in the tuff, apparent to the naked eye: the colour becomes redder, darker and less saturated.

12.3.2 Polymethyl-methacrylate (PMMA)

Table 12.1 gives the results obtained with *Paraloid A21 LV* – the PMMA treatment, and some comments are in order.

(i) *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 MMA. A comparison of the results for untreated samples and those of samples in layer #2 (5 - 10 cm) shows that the product penetrated to a depth of 10 cm. The porosity value 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.

(ii) *Homogeneity of distribution*

Assuming that for a given waterproofing product the reduction in the amount of water absorbed by the sample depends directly on the amount of product present in it, then the absorption data provide an excellent assessment of the distribution of the product in the sample. 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 from different layers are compared, the results depend on their position in the original block, as shown in Figure 12.3.

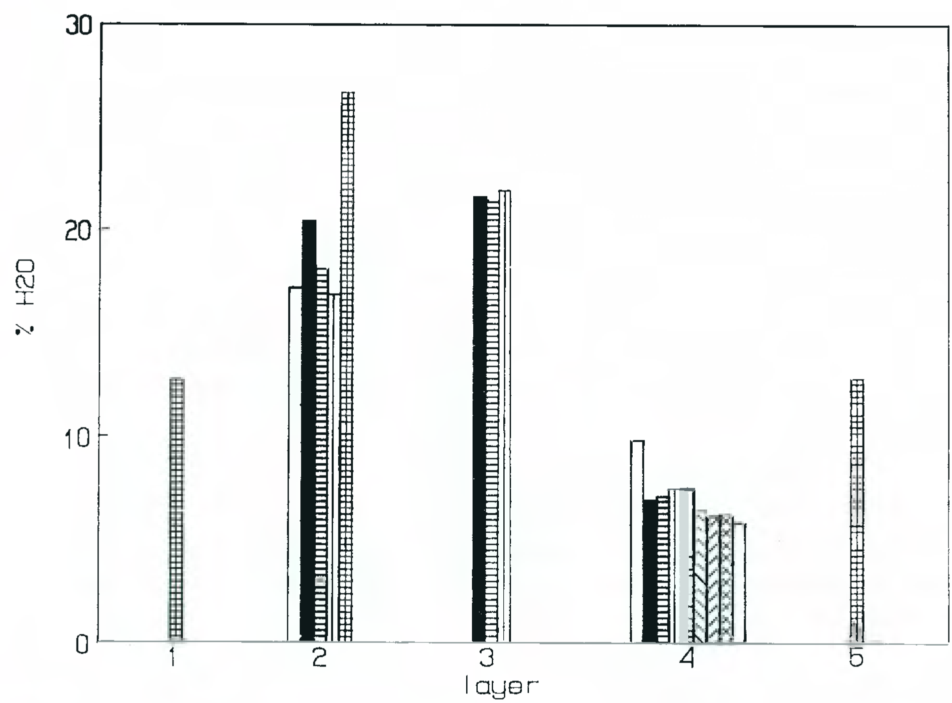

Figure 12.3 Treatment PMMA: *CI* value distribution in the different layers.

Thus layer #2 absorbs more than layer #4, and also has a higher ***CA***. Layer #3 has a ***CI*** value twice that of layer #4. This can be explained by supposing that the capillary penetration of the product does not go beyond 10 cm. The high level of solution viscosity ($\eta = 8.0$ cSt) may be the reason both for the low rate of capillary rise and for the difficulties in migrating from the first layer by gravity, or by horizontal transport. On the basis of these data it can be concluded that the 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 at the bottom of the block, some capillary absorption takes place through the wrapping.

(iii) *Structural properties*

The values of ***P***% measured on samples from different positions in the original cube reflect the variations observed in the internal layers and confirm the same poor distribution already mentioned. The results show ***P***% values near the lower limit for untreated tuff, or even slightly higher. Despite the inhomogeneity of these values, the histograms of the pore distribution show that the PMMA tends to fill pores with a radius between 10 000 and 100 000 Å.

Together with the relatively slight decrease in porosity, the increase in ultrasonic velocity is also slight, though still faster than in untreated tuff.

(iv) *Mechanical properties*

The ultimate compressive strength is doubled by treatment, both in the outer shell and in the 5-10 cm-depth samples.

Unlike the water absorption data, there are no significant differences in compressive strength relative to the position of the sample 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 the compressive strength of the treated stone.

A possible interpretation of this phenomenon could be based on the excellent adhesive properties of PMMA, implying that a small amount is sufficient to bring about a considerable improvement in mechanical resistance. However, since the product has comparatively weak waterproofing capacity, when the percentage of the product in the sample falls below a certain value its hydrophobicity is strongly reduced.

(v) *Behaviour of samples to water*

Water absorption is considerably lower than in untreated tuff. As noted in (ii) above, the maximum reduction in water absorption is shown in samples from the outer layer, especially those from the lower area.

The greatest change from untreated samples is found in the capillary absorption, where ***CA*** is reduced to about one-hundredth of the untreated value, while reduction of absorption by complete immersion is much less obvious, with ***CI*** reduced at most to one-sixth of the untreated value. After ageing, there is no change in the samples, except for the ***CA*** value, which nevertheless remains considerably lower than that for the untreated tuff.

The permeability to water vapour is markedly reduced, as shown by comparing the ***DI*** values of treated and untreated samples, but because the treated samples take up less water they also take less time to dry.

(vi) *Colour*

Treatment with PMMA produces little change in colour, turning it slightly redder, darker and less saturated. With ageing, the tone reverts to the yellow of the untreated tuff.

12.3.3 Methyl-phenyl-polysiloxane

Table 12.1 shows the results obtained with *Rhodorsil 11309* (treatment S). The following observations can be made.

(i) *Amount of product absorbed and depth of penetration*

The increase in weight with treatment was only 12% – the smallest of all four treatments. A comparison of the porosity and water absorption values for samples taken from the shell and the core shows that the product definitely reaches the core of the original stone block, although, as in the case of the PMMA, most of it is found in the outer 5 cm layer.

(ii) *Homogeneity of distribution*

The homogeneity of distribution of the product can be assessed by the degree of waterproofing of the tuff. A comparison of ***CA***, ***M∞*** and CI values for the different layers shows that the concentration of the product lessens from the upper surface – and from the lateral surfaces in general – inward. The highest concentrations of product are found in the lower layers (#5 and #4), as shown in Figure 12.4.

Irregularity in distribution seems less than for PMMA, and this may be due to the much lower viscosity ($\eta = 1.08$ cSt) of the polysiloxane solution compared to that of the methacrylate resin.

(iii) *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 value 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.

Reflecting these results, the very slight increase in ultrasonic velocity confirms that this treatment has not filled the cavities in the tuff.

(vi) *Mechanical properties*

The treatment only affects the ultimate compressive strength of the outer layer, where most of the product accumulates. Values for the internal areas are comparable to untreated tuff. After artificial ageing, values of the same order as before treatment are

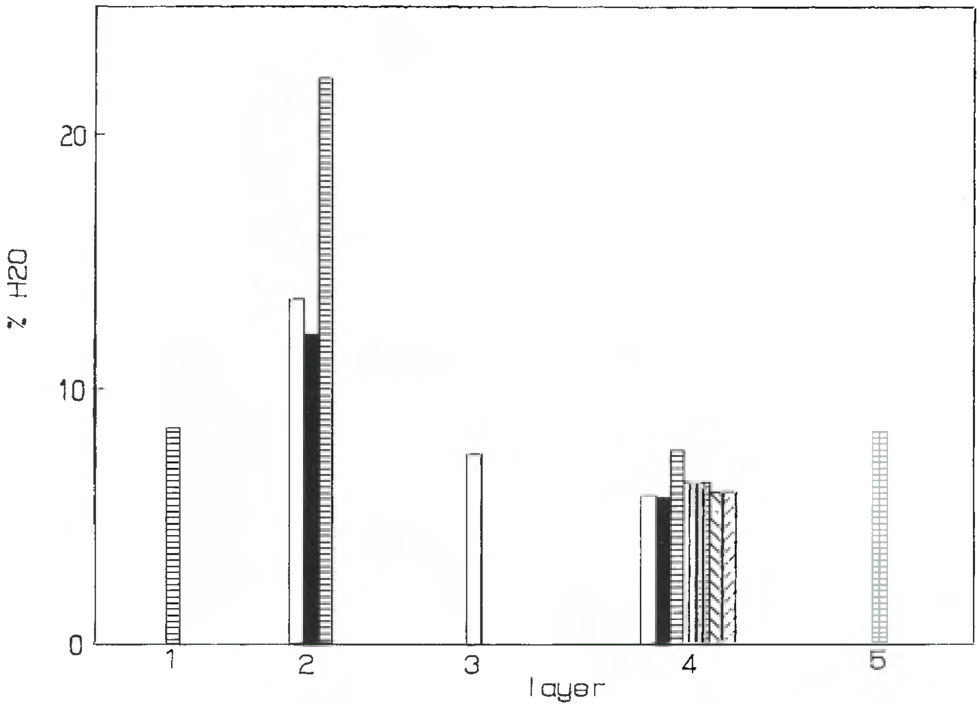

Figure 12.4 **Treatment S: *CI* value distribution in the different layers.**

obtained. Considering that compressive strength is related to the adhesive properties of the consolidating product, the results seem to indicate that this polysiloxane has no adhesive property in this type of stone. A detectable improvement of the compressive strength is only found when the product concentration exceeds 12%, which was the 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 results reported for other types of highly porous stone [9; 10].

(v) *Behaviour of samples to water*

All the water absorption figures (*CA*, $M\infty$, CI) are sharply reduced after treatment. The hydrophobicity of this polysiloxane is very high, even for internal samples. This means that even low quantities of the product are enough to produce a considerable effect.

It should also be pointed out that the treated samples remain permeable to vapour, but, taking up less water, dry in less time than the untreated samples.

(vi) *Colour*

The only effect of the treatment is a slight darkening and lower saturation level. These features persist after the ageing treatment.

12.3.4 Ethyl-silicate + Siloxane

Table 12.1 shows the results of the treatment with the mixture of *Tegovakon V* and *Tegosivin HL 100* – treatment T. The following observations can be made.

(i) *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. There is a considerable increase in the compressive strength in both the inner and outer layers, implying that ethyl silicate reached the core of the original block.

As regards penetration of the waterproofing product, the outer shell is mainly involved; samples to a depth of between 5 and 10 cm show $M\infty$, and CI values very near to those of untreated stone. Nonetheless, the ***CA*** values for the internal layers remain considerably lower, as these only reflect the initial penetration rate.

(ii) *Homogeneity of distribution*

The measurements taken do not allow an assessment of the distribution of the ethyl-silicate. As for the silane, the water absorption measurements do not show differences between the various inner layers which, as has already been stated, are only slightly affected by the product.

(iii) *Structural properties*

The porosity of the samples from different parts of the original stone block are very near to the levels for untreated tuff. This result is in obvious contrast to all the other results, especially with the increase in weight and the improvement of compressive strength and ultrasonic velocity.

Since the number of porosity measurements is sufficient to eliminate both dis-homogeneity in the stone and experimental errors, two hypotheses can be made. Either the treatment has affected the very small pores (r <50 -100 Å) that are outside of the measuring range of the technique used, or there has been a partial coating of larger cavities (r >100 µm). These cavities were not measurable before the treatment and therefore did not affect the value of ***P***. Due to the treatment, their radius could have been reduced so that they became measurable and thus increase the porosity value. 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 possible interactions between monomeric structures, such as the orthosilicic acid produced by the hydrolysis of the ethyl silicate, and minerals such as chabazite contained in the tuff. This would establish whether the resulting silica can penetrate the zeolite crystalline lattice.

If some such interactions occur, it would imply a reduction in the cationic exchange capacity of the minerals, thus diminishing the deterioration process that normally occurs in these minerals and in the stone containing them [11].

(iv) *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 to the high affinity between the product of the silicate hydrolysis and the silicates contained in the tuff.

It is significant that the ultimate compressive strength after ageing is still higher than in untreated tuff, although the values are rather scattered. It should be noted that the artificial ageing process resulted in breakage of 20% of the samples, which therefore could not be used for other measurements.

(v) *Behaviour of samples to water*

Waterproofing properties increase significantly only in the external layers, especially with regard to capillary absorption, which is measured through the outermost layer of the samples.

Drying rates of the samples are similar to the untreated tuff, although water vapour permeability is considerably lower.

(vi) *Colour*

Treatment had very little influence on the tuff colour; it was slightly darker and less saturated.

12.4 CONCLUSION

Considering the overall results, the use of samples that are much larger than those generally used for laboratory tests has proved especially effective. The influence of the inherently heterogenous nature of the tuff on the results is reduced, or even eliminated where some of the measurements were taken before the tuff was cut into smaller cubes.

The treatment of blocks of stones of the size used in ancient buildings has also ensured a good assessment of the homogeneity of penetration and distribution of the different products. The results obtained are all the more significant if one considers that, except for the methacrylic monomer, the application technique used in the study can be applied *in situ* for architectural features on buildings.

The comparison of the results of the 5 cm cubes from different locations within the original blocks gave a clearer understanding of the 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 its initially poor state of preservation resulting from long exposure to weathering. In that context, it should be noted that the untreated samples were so damaged after artificial ageing as to make some of the measurements impossible.

Of the four treatments tested, methylmethacrylate monomer (MMA) gave the most interesting results – all the measured properties improved after treatment, and the improvement remained after ageing. Considering that the ageing process involved considerable temperature fluctuations, it may be said that the differences in linear thermal expansion coefficients between the polymer and the stone, though high, are not large enough to trigger a breakdown of the compound. This is probably due to the fact that consolidation was obtained with sufficient product (comparable to the other treatments) to increase the mechanical strength but still leaving empty spaces to allow for thermal expansion. Moreover, the product had no tendency to form a surface layer, and penetrated deeply into the sample.

If treatment with methacrylic monomers has many advantages, the application technique needs improvement. Systems should be found that are suited to the needs of architectural restoration sites, while trying to reduce the chromatic effects on this type of stone.

A comparison between PMMA and the methyl-phenyl polysiloxane is also interesting. 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. Mixtures of methacrylic and vinylic monomers with silanic functions to anchor the co-polymer inside the stone [12] should also be considered for study.

Another aspect that the present authors consider should be studied is the interaction between tuff and ethyl silicate. The hypothesis postulated regarding the interaction of orthosilicic acid with zeolitic 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 mechanical properties and for slowing down the weathering process in the stones containing these minerals.

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RESUMEN

Las tobas volcánicas fueron frecuentemente utilizadas en muchas regiones italianas debido a su disponibilidad y 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 área de Cerveteri, al norte de Roma. Los siguientes productos fueron estudiados: un monómero de metilmetacrilato, un polimetilmetacrilato, un metilfenilpolisiloxano y una mezcla de silicato de etilo y metilsilano.

RESUME

Les tufs volcaniques ont été couramment utilisés dans de nombreuses régions d'Italie du fait qu'ils se trouvent en abondance et sont faciles à travailler. En revanche, il sont peu résistants et de ce fait nécessitent fréquemment des traitements de conservation. Des recherches sur les interactions entre les tufs et les produits utilisés pour la consolidation et l'imperméabilisation sont donc indispensables.
Le présent article expose les résultats obtenus avec quatre procédés différents, qui ont tous une action consolidante et hydrofuge, appliqués à des blocs d'un tuf volcanique provenant des vestiges d'un mur étrusque dans la région de Cerveteri, au nord de Rome. Les produits suivants ont été étudiés: un monomère de méthylméthacrylate, un polyméthylméthacrylate, un méthylphénylpolysiloxane et un mélange de silicate d'éthyle et de méthylsilane.

KURZFASSUNG

Wegen ihrer Verfügbarkeit und leichten Bearbeitungsmöglichkeit sind vulkanische Tuffe in vielen Gegenden Italiens als Werksteine weit verbreitet. Ihre Haltbarkeit ist jedoch recht gering, weswegen Konservierungsbehandlungen unerläßlich sind. Aus diesem Grund sind Untersuchungen über die Wechselwirkung zwischen Tuff und den Konsolidierungs- und Hydrophobierungssubstanzen nötig.
Mit vier verschiedenen Systemen – alle von verfestigender und wasserabstoßender Wirkung – wurden Testbehandlungen an Quadern eines Vulkantuffs, die aus Resten einer etruskischen Mauer im Gebiet von Cerveteri (nördlich von Rom) stammen, vorgenommen; die Ergebnisse werden hier präsentiert. Die in der Studie verwendeten Produkte sind: ein monomeres Methylmethacrylat, ein Polymethylmethacrylat, ein Methylphenylpolysiloxan und eine Mischung aus Ethylkieselsäureester und Methylsilan.

THE APPLICATION OF SILICONE PRODUCTS IN THE CONSERVATION OF VOLCANIC TUFFS

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ABSTRACT

The effect of various silicone-based products was studied on three different volcanic tuffs: two from Germany (Ettringer and Weiberner) and one from Poland (Filipowice). 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 interaction of tuff and product applied. Artificial weathering cycles were also carried out and the results obtained are discussed.

13.1 INTRODUCTION

The giant stone figures on Easter Island were executed in andesitic volcanic tuff. On the basis of the investigations carried out by Domaslowski [1], the main destructive factors have been found to be rainwater, high relative humidity, temperature variations and micro-organisms.

The action of these agents is promoted by the mineralogical composition, texture and structure of the volcanic tuffs. Clay minerals present in the rock matrix swell under the action of water and can leach out, leading to a decrease in compactness of the surface layers of the rock and finally to powdering of the same.

Unequal heating of tuffs results in shearing stress. It has been found that the giant statues on Easter Island are unequally heated during sunny days [1]. The temperature of sun-exposed fragments rises significantly, while that of the shaded parts remains close to ambient. Thus, at an ambient temperature of 28°C, the temperature

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of the stone in direct sunlight can reach 70°C, while the temperature of the stone in the shade does not exceed 36° to 38°C. Even more important temperature gradients develop between the surface and the deeper layers of the stone. This is confirmed by the high residual moisture content of the stone. Despite long dry periods, humidity at depths of 1 to 3 cm was found to be very high. This is also due in part to the high water absorption capacity of the clay minerals.

Fissuring of the stone results from differential thermal expansion of each component in the volcanic tuff: the vitreous cement matrix and the various debris of volcanic and sedimentary rocks. This results in loss of cohesion, disintegration and crumbling away of volcanic and sedimentary rock fragments, as well as powdering of cement-rock paste.

The contribution of micro-organisms cannot be neglected in the formation of deposits as a result of biochemical decomposition of aluminosilicates. The deposits, usually grey-black in colour, strongly absorb solar radiation, and consequently the stone surface heats preferentially.

Though the island is surrounded by seawater with a salt content of approximately 3.5%, no harmful effects of water-soluble salts have been found contributing to the deterioration of the tuffs [1].

Similar deterioration, not attributable to chemical agents, was found by Bianchetti and co-workers on the tuff blocks used in the Roman Temple of Cybele [2].

Previous investigations on the tuff from Easter Island [1] showed decreased cohesion of certain areas at the surface, requiring consolidation, while in depth the stone showed higher hardness and mechanical strength. Thus the main problem that needs to be addressed in tuff conservation appears to be limited to the consolidation of superficial layers which have lost their cohesion through the loss of the cementing material.

Any consolidation treatment should be followed by an efficient hydrophobization to protect the stone against the action of liquid water and water vapour. The present work has concentrated on evaluation of the efficacy of treatments with orthosilicic acid esters as protection against water in both liquid and gaseous states.

The consolidant chosen was an alkoxysiloxane, *Wacker OH*. This product is characterized by its good penetration, even in fine-pored stones. According to Lewin and Schwartzbaum, these compounds may cross link aluminosilicate layers due to the reaction of their hydroxyl groups with those of partly hydrolysed alkoxysiloxanes [3], but the formation of typical chemical bonds between hydroxyl groups of the polyalkoxysiloxanes and clay minerals is not always possible, due to the differing distance between the bonding sites on each compound [4]. However, hydrogen bonding may be expected between the minerals and the consolidant, thus resulting in improved mechanical strength.

The hydrophobization treatment was also based on silicone products, these being chosen because of their chemical affinity with the stone consolidant applied, in addition to their satisfactory water repelling properties and commercial availability.

13.2 MATERIALS

13.2.1 Tuffs

Investigations were carried out on three types of tuffs, having differing mineralogical compositions and properties. They were taken from quarries at Ettringen and Weibern, Germany, and Filipowice, Poland.

The Ettringer tuff is a fine-grained, porous rock; yellow-beige in colour. The basic component of the rock matrix is volcanic glass, associated with subordinate clay minerals (probably illites from X-ray diffraction data) as well as silica minerals. Feldspars, micas and olivines are also present together with some volcanic inclusions [M. Ziółkowska, *pers. comm.*].

The Weiberner tuff is a coarse-grained, porous rock; grey-brown in colour. Coarse debris of sedimentary and volcanic rocks are present (1-2 cm in diameter). The rock matrix consists mainly of volcanic glass of ball structure, and clay minerals, probably illites. Debris of sedimentary rocks consist mainly of mudstones and fine-pored sandstones, while among the volcanic rocks, feldspars, olivines, quartz and amphiboles were recognized.

The Filipowice tuff is a fine-grained, porous rock; violet-pink in colour, with irregularly distributed white spots. Its composition consists mainly of feldspars, quartz, biotite, calcite and rock debris. Some physical properties of these tuffs are given in Table 13.1.

Table 13.1 Physical properties of the three tuffs examined

	Ettringer	Weibener	Filipowice
Bulk density (g/cm^3)	1.85 – 1.91	1.48 – 1.59	1.95 – 2.12
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
Open porosity (%)	25.9-30.5	33.6 – 36.8	16.8 – 18.0
Volume of open pores (cm^3/g) 50 < r < 75 000 Å	0.1723	0.2986	0.1168
Pore size distribution (%)			
50 < r < 100 Å	1.5	—	—
100 < r < 1000 Å	11.0	7.5	51.5
1000 < r < 10 000 Å	46.5	19.0	32.0
10 000 < r < 75 000 Å	41.0	73.5	16.5

13.2.2 Consolidants

The tuffs were consolidated with *Wacker OH*, an alkoxysiloxane product of Wacker-Chemie. It was used both undiluted as commercially available, and in a 1:1 solution with ethanol for the finer-grained tuffs, Ettringer and Filipowice. The density and viscosity of the solutions used for the treatment are given in Table 13.2.

The commercial product is a solution of about 75% tetra-ethoxysilane oligomers in methylethylketone (MEK). In the presence of water a hydrolytic polycondensation occurs, resulting in the formation of a polysiloxane gel. This acts as a binder in the deteriorated stone, thus improving its mechanical strength. The increase in mechanical strength is directly related to the structure of the stone being consolidated [5].

13.2.3 Water repellents

Both untreated and consolidated tuffs were subjected to hydrophobization treatment. Two different products were tested: *Silak M11* and *Elastosil E 41*. A third product, *Ahydrosil Z*, was applied only to untreated samples. Details of the manufacturers of these products are listed at the end of this paper.

Silak M11 is a methylphenylsilicone resin that was applied in a 5% solution in xylene and white spirit.

Elastosil E 41 is a 90% solution of methylpolysiloxanes with silanol groups in toluene. These groups are blocked by acetic acid in unstable esters. In the presence of humidity a rapid polycondensation takes place, leading to the formation of a cross-linked polymer with water-repellent properties. This product was applied as a 5% solution in white spirit.

Ahydrosil Z is a two-component product. Component A is a 10% solution of methylpolysiloxane resin in xylene and white spirit, while component B is a cross-linking factor, added in a quantity equal to 1% of component A on a volumetric basis. This product acts as both a consolidant and a water repellent.

The density and viscosity of the solutions used in the treatment of the tuffs are given in Table 13.2.

Table 13.2 Density and viscosity of the solutions of consolidants and water repellents used in the treatments

Product	Conc. (%)	Solvent	Density (g/cm^3)	Viscosity (mPa.s)
Wacker OH (undiluted commercial)	75	MEK	**0.9575**	1.25
Wacker OH (1:1 in ethanol)	37	ethanol		–
Wacker-OH + MEK (1:1)		MEK +ethanol		
Elastosil E 41	5	white spirit	0.7824	4.80
Silak M11	5	white spirit + xylene	0.8014	1.89
Ahydrosil Z	5	mixed organic solvents	0.8164	2.64

13.3 EXPERIMENTAL DETAILS

13.3.1 Capillary rise

The capillary rise of water and *Wacker OH* both as undiluted commercial product and as a 1:1 solution was measured on prismatic samples (4 × 1 × 8 cm) of the three types of stone. The samples were dried to constant weight and then stood up on the 4 × 1 cm base, submerged 1 cm in the liquid, and the rate of absorption measured by timing the rate of progress up the exposed 7 cm of stone. The consolidant, both as commercial strength solution and diluted, showed a slower absorption rate than water. The stone structure is a decisive factor in determining the rate of penetration. The Weiberner tuff was totally wetted by water in less than 1 h, while the Ettringer tuff needed over 5 h, and the Filipowice tuff took over 24 h.

The diluted product wetted the Weiberner tuff in 2 h, the Ettringer tuff within 24 h, while the Filipowice was only wetted to the 4 cm mark in 24 h.

The commercial (undiluted) product took 2.5 h to wet the Weiberner tuff, while the Ettringer tuff was still not totally wetted after 24 h. The Filipowice stone reached only the 4 cm mark in 24 h.

13.3.2 Consolidation

The samples that were to be consolidated were impregnated by capillary rise, both in the commercial product and in the diluted solution, by immersion of 1 cm of the sample, but using the 1 × 8 cm side. The samples were turned over after 3 h and left in that position for 21 h. This assured a high degree of absorption of the consolidating compound. The samples were then taken out and cured in a climatic chamber at room temperature and at 75% RH [6] for 6 weeks. This assured the hydrolytic polycondensation of the consolidant. The samples were then taken out and allowed to dry in the laboratory (20°-22°C and 40-50% RH). The amount of product absorbed and the amount of polysiloxane gel left after curing and during drying is given in Table 13.3. The data reflect the different structure of these stones.

Table 13.3 **Amount of consolidant absorbed and remaining in the stone after curing and drying (% sample weight)**

Tuff	Solution	% Absorbed	% Gel (cured)	% Gel (dried)		
				24 h	4 days	21 days
Ettringer	W-OH 1:1	12.5 11.5	8.1 4.1	4.9 2.3	4.4 2.2	4.5 2.4
Weiberner	W-OH 1:1	24.1 20.6	14.7 7.0	9.8 4.6	9.2 4.4	9.2 4.5
Filipowice	W-OH 1:1	6.9 6.9	4.7 2.9	3.0 1.9	2.8 1.7	2.7 1.8

The rate of evaporation of solvent and by-products of the hydrolytic polycondensation (ethanol and water) was highest from the coarse-pored tuff, Weiberner, and lowest from the finer-pored ones. It is interesting to note that the amount of consolidant left within the stone remained fairly constant after the first four days in the laboratory. This implies that the gel still contained a significant amount of solvents.

Samples were not dried at a higher temperature as this is not likely to be a feasible procedure *in situ* on statues. Furthermore, the gel remaining in the stone would have a sufficient number of free hydroxyl groups left to react with a water repellent when applied. Consequently, the resistance to the action of water would improve considerably for stone treated this way.

13.3.3 Water repellents

Both untreated and consolidated samples were impregnated with water repellents by capillary absorption for 24 h. *Ahydrosil Z* was only applied to untreated samples as this cross-linking product consolidates while making the stone hydrophobic.

Table 13.4 gives the amount of water repellent absorbed for each product and each type of stone. The amount absorbed is in inverse proportion to the amount of consolidant gel present in the stone and is directly dependent on the viscosity of the water repellent.

The most porous stone, the Weiberner tuff, was the easiest to impregnate and the amount of water repellent introduced into its pores was higher and less influenced by the presence of the consolidant gel.

The impregnated samples were dried under ambient laboratory conditions (20°-22°C and 40-55% RH) for two weeks, followed by drying under vacuum at 50°C for three days.

13.4 RESULTS

13.4.1 Open porosity

Impregnation with the consolidant, with or without water repellents, reduced the open porosity of all samples. This is reflected in the decrease of open porosity with respect to the untreated specimen (see Table 13.4). The largest decrease was found for the tuff with the smallest value for open porosity, that from Filipowice. This can be explained if one considers that the introduced resins occluded the smaller pores (***r*** <1000 Å) which amount to more than 50% of the open porosity, thus effectively reducing the total porosity of the stone. The more porous Weiberner tuff showed the least decrease in open porosity.

The change in open porosity also depended on the type of product applied and its concentration. The consolidant, in the commercial concentration, reduced the open porosity more than the diluted product, though the diluted solution penetrated faster into the stone matrix. All the products applied left some open porosity in the stone, leaving the possibility open for future treatments.

13.4.2 Hygroscopicity

The evaluation of hygroscopicity, measured at room temperature and approximately 100% RH, allows the determination of the efficiency of protective treatments of the tuffs against water vapour. The data are given in Table 13.5.

Table 13.4 Amount of water repellent absorbed in the treated and untreated tuffs (% w/w), open porosity (%) after impregnation and % decrease in open porosity

Consolidant in sample (%)	Product used	Water repellent absorbed (%)	Residual open porosity (%)	Decrease in open porosity (%)
		Ettringer tuff		
0	E 41	10.2	25.8	15.6
2.38		8.1	21.5	29.7
5.17		5.7	19.3	36.9
0	Silak M11	11.1	24.1	21.2
2.30		9.0	23.4	23.5
4.46		7.9	20.8	32.0
0	Anhydrosil Z	12.9	22.0	28.1
		Weiberner tuff		
0	E 41	19.9	33.0	10.3
4.70		15.5	27.6	25.0
8.89		13.4	27.7	24.7
0	Silak M11	19.9	33.0	10.3
4.4		15.1	29.8	19.0
9.6		14.4	29.5	19.8
0	Anhydrosil Z	19.2	31.2	15.2
		Filipowice tuff		
0	E 41	5.7	–	–
1.9		3.6	13.2	26.3
2.7		2.9	10.5	41.3
0	Silak M11	7.1	–	–
1.8		4.2	10.8	39.7
2.9		3.7	9.5	46.9
0	Anhydrosil Z	6.1	–	–

The best protection against water vapour was provided by the *Ahydrosil Z* resin, followed by the *Silak M11* water repellent when applied directly to the tuff without previous consolidation.

The highest hygroscopicity, higher even than that of untreated samples, was obtained for those specimens consolidated with the undiluted commercial product. This can be explained by the amount of polysiloxane gel, which shows a high water vapour sorption capacity in the pores of the stones [5]. Subsequent treatment with the water repellents did not significantly reduce the hygroscopicity, presumably due to the low amount of these compounds left in the stone.

Table 13.5 Hygroscopicity of treated and untreated tuffs (% w/w)

Tuff	Consolidant	Water repellent	Hygroscopicity (%)	
			after 48 h	after 7 days
Ettringer	–	–	2.23	2.83
	–	**E 41**	**1.51**	1.07
	1:1		**1.78**	2.39
	W-OH		2.50	4.07
	–	Silak M11	1.01	1.26
	1:1		1.44	1.76
	W-OH		1.97	2.76
	–	Anhydrosil Z	0.94	1.20
Weiberner	–	–	**1.62**	2.23
	–	**E 41**	**0.85**	1.11
	1:1		**2.23**	2.72
	W-OH		**2.59**	3.85
	–	**Silak M11**	**0.53**	0.80
	1:1		**0.92**	1.33
	W-OH		**1.01**	1.75
	–	**Anhydrosil Z**	**0.54**	0.97
Filipowice	–	–	1.15	**1.77**
	–	**E 41**	0.97	1.42
	1:1		1.08	1.53
	W-OH		1.34	1.79
	–	Silak M11	0.46	0.82
	1:1		0.44	0.77
	W-OH		0.72	1.29
	–	Anhydrosil Z	0.32	0.72

13.4.3 Water absorption

The water repellents provided a satisfactory protection of the tuffs against the action of liquid water. The data on water absorption, obtained from samples first saturated with water through capillary rise and then totally immersed in water for 48 h, are given in Table 13.6.

All samples treated, both with and without pre-consolidation, showed a much lower water absorption than that of the untreated stone. The decrease in water absorption ranged from 58 to 88%.

The best results were obtained with the *Ahydrosil Z* resin, and the least reduction in water absorption was again obtained in those specimens that had been consolidated with the undiluted product.

13.5 ARTIFICIAL WEATHERING

The weather conditions on Easter Island correspond to a subtropical climate. Due to the frequent rains, the humidity in the air remains high, about 80% RH for most of the year. The temperature is fairly constant and exceeds 25°C for about 300 days in the year [7], which results in the development of temperature gradients within the stone, as was mentioned previously.

The ageing cycles that were developed to test the applied products tried to reflect these local climatic conditions. The samples were submerged in water at 25°C for 6 h, taken out of the water and heated at 105°C for 18 h.

After each ageing cycle any visual changes in the stone surface were noted and the water absorption capacity was re-measured.

13.5.1 Visual changes in the stone surface

The Ettringer tuff was the least resistant stone: both the untreated specimens and those consolidated and hydrophobized with the *Elastosil E 41* water repellent started powdering by the second cycle, cracking by the fourth cycle, and deteriorated completely by the sixth cycle. The samples treated only with *Elastosil E 41* resisted one more cycle before cracks appeared and resisted through nine complete cycles before completely deteriorating. Similar behaviour was observed in samples treated only with *Silak M11*. When this water repellent was applied to pre-consolidated samples these resisted through eight complete cycles.

Samples treated only with the *Ahydrosil Z* showed cracks after the sixth cycle and deteriorated after the tenth cycle.

The surface of the other two tuffs – Weiberner and Filipowice – did not show any change after twenty of these cycles.

13.5.2 Water absorption

Water absorption values after various ageing cycles are given in Table 13.6.

As the visual observations indicated, after only two ageing cycles the Ettringer tuff had deteriorated sufficiently to show a marked increase in water absorption. Consolidation and hydrophobization improved the water resistance of this stone, the most protection being provided by the *Ahydrosil Z* resin and the least by the combination of the *Wacker OH* consolidant applied at commercial strength and the *Elastosil E 41* water repellent.

The water absorption of the untreated Weiberner and the Filipowice tuffs was not affected by the ageing cycles to which they were subjected. The treated samples of these stones showed an increase in water absorption after ageing.

Table 13.6 **Water absorption data for treated, untreated and aged samples of the three tuffs.**

	Consolidant	Water repellent	Water absorption (%)			
			Unaged	After 2 cycles	After 6 cycles	After 10 cycles
Ettringer	–	–	15.4	23.1	*	*
	–	E 41	5.2	10.4	14.9	16.2
	1:1		5.9	13.5	*	*
	W-OH		6.5	15.0	*	*
	–	Silak M11	5.2	5.1	*	*
	1:1		2.7	5.2	5.8	6.1
	W-OH		3.9	8.3	10.7	10.6
	–	Anhydrosil Z	2.4	4.7	4.9	*
Weiberner	–	–	21.8	21.4	22.1	21.7
	–	E 41	4.2	4.0	4.1	3.8
	1:1		4.0	5.0	5.0	4.8
	W-OH		5.2	6.6	6.6	6.5
	–	Silak M11	3.4	5.1	4.5	3.2
	1:1		3.4	5.5	5.1	3.9
	W-OH		4.5	5.3	5.5	5.8
	–	Anhydrosil Z	2.9	3.7	3.3	3.4
Filipowice	–	–	8.5	8.4	8.2	7.9
	–	E 41	4.5	4.7	4.5	4.2
	1:1		2.4	2.8	2.9	3.0
	W-OH		2.2	3.1	3.2	3.3
	–	Silak M11	3.6	1.5	1.4	1.3
	1:1		1.3	1.8	1.7	1.7
	W-OH		1.8	2.3	2.2	2.2
	–	Anhydrosil Z	0.97	1.03	0.91	0.97

* indicates that the sample had deteriorated

The samples that had been consolidated showed a slight increase in water absorption after the first two ageing cycles, but this decreased upon further ageing. This is probably due to the dehydration of the polysiloxane gel during the drying at 105°C.

13.6 CONCLUSIONS

The results of the investigations carried out allow some assertions to be made.

- The efficacy of water protective treatments is conditioned mainly by the texture of the tuff.
  Tuffs that have a texture similar to that of the Weiberner stone are easily treated. The solutions of consolidant, with or without water repellent, are absorbed through capillary action without difficulty into the pore structure of the stone, and penetration depths of over 10 cm are obtained. Stones that have a fine-pored system are much slower in taking up the solution of consolidant, with or without water repellent, and penetration does not exceed a few centimetres in depth.
- All water repellents tested reduced considerably water absorption capacity and hygroscopicity of the tuffs, and can be used successfully in conservation efforts.
- Pre-consolidation with alkoxy-polysiloxanes followed by a water-repellent treatment provides less protection of the tuffs against water and water vapour than the water repellents applied alone.
- If the state of the object requires a consolidation, it is recommended that this be carried out through the use of a solution of methylsiloxane resin, such as *Ahydrosil Z*, which provides structural hardening as well as the best protection against water, both as liquid and as vapour, of the treatments evaluated.

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APPENDIX

Products tested and their manufacturers

- *Ahydrosil Z* from Instytut Chemii Organicznej, Poland.
- *Elastosil E 41* from Wacker Chemie, Germany.
- *Silak M11* from Zaklady Chemicze, of Nowa Sarzyna, Poland.
- *Wacker OH* from Wacker Chemie, Germany.

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 (Filipowice). Los productos ensayados fueron un consolidante (*Wacker OH*), aplicado en distintas concentractiones, y tres productos hidrorepelentes (*Elastosil, Silak* y *Ahydrosil Z*).
Las variaciones en porosidad, absorción de agua y otras características físicas fueron determinadas 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.

RESUME

L'effet de divers produits à base de silicone a été étudié sur trois tufs volcaniques différents, deux provenant d'Allemagne (Ettringer et Weiberner) et un de Pologne (Filipowice). Les produits testés étaient un consolidant (*Wacker OH*), appliqué à différentes concentrations, et trois hydrofuges (*Elastosil, Silak* et *Ahydrosil Z*).
Les modifications de la porosité, de l'absorption d'eau et d'autres caractéristiques physiques ont été mesurées et interprétées du point de vue de l'interaction du tuf avec le produit appliqué. On a également soumis le tufs à des cycles de vieillissement artificiel, dont résultats sont présentés.

KURZFASSUNG

Es wurde die Wirkung verschiedener Produkte auf Silikonbasis auf drei verschiedene Vulkantuffsorten untersucht, von denen zwei aus Deutschland (Ettringer und Weiberner Tuff) und einer aus Polen (Filipowice) stammt. Die in der Studie eingesetzten Mittel waren ein Konsolidierungsprodukt (*Wacker-OH*, in verschiedener Konzentration) und drei Hydrophobierungsmittel (*Elastosil, Silak* und *Ahydrosil Z*).
Veränderungen der Porosität, der Wasseraufnahme und anderer physikalischer Kenngrößen wurden gemessen und auf Basis der Wechselwirkungskräfte zwischen Tuff und jeweiligem Produkt interpretiert. Zusätzlich werden die Ergebnisse aus Laborwitterungszyklen diskutiert.

Part Four

TREATMENT EVALUATION

ASSESSMENT, BY RADIOACTIVE LABELLING, OF THE EFFICIENCY OF CONSERVATION TREATMENTS APPLIED TO VOLCANIC TUFFS

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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 in radioactivity is related to the rate of corrosion, and is a measurement of the durability of the stone in that atmosphere. It can be used to evaluate differences between treated and untreated samples and between diverse treatments. The corrosion resistance of three types of Japanese tuffs in an atmosphere with a high content of sulphur and nitrogen oxides was studied. The results show clearly that the tuffs examined corrode easily and that the speed of corrosion depends on pollutant concentration, relative humidity and pore structure. It was found that treatments with acrylic co-polymers were more efficient in preserving the tuffs than treatments with siloxanes.

14.1 INTRODUCTION

It is known that the radioactive labelling of crystalline substances can be carried out with accelerated ions, which impact on the surface and produce changes within the lattices due to atomic interactions and trapping of these ions [1; 2]. When ions of inert gases are used with relatively small beam energy (hundreds of eV), no mechanical damage to the surface layers occurs. Usually, there are no chemical reactions under these conditions because these would need much higher impact energy levels. The trapped ions are located in interstitial spaces. Depth of distribution depends on the original energy of the incident ions, and on the physical and chemical conditions of the surface. Non-crystalline, amorphous substances do not capture impacting ions.

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It has been found that stones can be labelled in the same way as metals and glasses, and that radioactive isotopes of inert gases are convenient for this purpose [3]. The labelling process can be followed simply through the monitoring of radioactivity. Krypton gas was used in these experiments, in the form of its radioactive isotope ^{85}Kr, which has a half-life of 10.3 years. The half-life makes it convenient to use and no special precautions are necessary. It is possible thus to continuously, and with great precision, follow all the processes leading to the release of the trapped ions resulting, for example, from the corrosion interactions of the stone sample with an atmosphere containing increased amounts of pollutants.

Samples of three types of Japanese tuffs were labelled with ^{85}Kr. As the samples aged, the changes in radioactivity were followed in a continuous flow chamber where the air was enriched with sulphur dioxide or nitrogen oxide, or both. The relative humidity (RH) was also monitored since in previous experiments it had been found to play an important role [3; 4].

The decrease in radioactivity during gas-solid interactions of labelled stone samples can result from many specific processes, including diffusion, sorption, chemical reactions, re-diffusion of the krypton atoms back to the gas phase, etc. This makes it very important that only relatively similar substances are compared in the investigations. The tuffs in this study were partly similar in their chemical composition and pore structure, and so it was assumed that the measured differences could be related to individual characteristics of the tuffs. The data obtained presumably could be extrapolated for other tuff types, always taking into account the immense variation between the various types with regard to their mineralogical composition and pore structure.

Nonetheless, the method is useful for assessing changes in behaviour when comparing samples of untreated stone with samples treated with either siloxanes or acrylic copolymers following the original irradiation. The application of polymers appears not to change the radioactivity substantially, and thus permits investigation of the relative changes that occur between untreated and treated samples. The results may aid in evaluating the efficiency for conservation of the applied materials.

14.2 EXPERIMENTAL DETAILS

The apparatus for ^{85}Kr labelling and its operation has been described elsewhere [3; 4].

The changes in radioactivity were followed with a Geiger-Müller counter and expressed as radioactive decays per unit time. After the initial labelling, the tuff samples lose around 30% of their gained radioactivity. This is followed by a steady decrease of about 5% per week. From indirect measurements and calculations [5] it was estimated that approximately the top ten atomic layers are reached under the experimental conditions used here. This shallow penetration is one of the disadvantages of the method because these top layers can be lost very quickly during corrosion processes. However, if higher impact energies are used, deeper layers would be reached, and changes within the crystals, such as dehydration or losses of crystallization water, could be induced.

It was found that the radioactive labelling of tuffs was a more complicated mechanism than for homogeneous stones, such as marbles. It was also found that the initial gain of radioactivity was larger than for calcareous stones.

The first part of the experiment was to follow the behaviour of tuff samples in corrosive atmospheres containing sulphur dioxide and nitrogen oxide. These gases were circulated in a continuous flow of 40 ml/min at concentrations between 125 and 300 ppm. The lower concentration allowed measurements to be taken within the first two hours and proved to be highly reproducible. Concentrations below that level did not yield reproducible results, possibly because of the difficulty of maintaining a constant flow at that concentration and also possibly because of interaction at the stone surface, including such phenomena as sorption, desorption and diffusion. The experiments were carried out at three RH levels. The humidity was measured by freezing the air at dry ice temperature. The exact amount of sulphur dioxide was determined by titration after absorption in an alkaline solution [3].

The second part of the experiment was to evaluate the protective efficiency of eventual conservation materials that could be used to treat the Buddha sculptures carved in rock *in situ*. There are serious problems encountered in maintaining these monuments in the face of recent changes in climatic conditions and increasing air pollution. Large-scale research and practical work have already been carried out [6; 7; 8]. Besides constructing shelters to protect these sculptures, it is often necessary to consolidate their surface and to prevent further ingress of water [9].

14.2.1 Tuff samples

Three Japanese tuffs were examined: Oya, Nara and Echizen. The Oya samples were taken from quarries at the Tochigi Prefecture, near Nikko. This stone is commonly used in facades in Tokyo and Kanto. It is a welded tuff composed of quartz and plagioclase, rarely amphiboles, and containing opaque minerals, pumice, altered volcanic glass and clay minerals. The Nara samples were taken from the vicinity of the Buddha reliefs carved into the rocks in the Nara Prefecture. The Echizen samples were taken from quarries in the Fukui Prefecture. This stone is used in facades and is commonly called Janstony tuff.

For labelling purposes, five samples, each 7 × 10 × 20 mm, were cut, polished and washed with distilled water. Table 14.1 summarizes the typical energy dispersive X-ray analysis (EDAX) of the five different areas selected and later labelled with ^{85}Kr.

Even considering that the data in Table 14.1 correspond to very localized analyses, it can be seen that the three tuffs differ considerably in their chemical composition. From the data, it has been calculated that 50% of the calcium minerals of the Oya tuff is found as gypsum. The Nara tuff contains larger amounts of calcite than the Echizen tuff, as confirmed by thermogravimetric analysis and differential thermogravimetry.

Table 14.1 **Energy dispersive X-ray analysis of five areas each of the three Japanese tuffs.**

Na_2O	MgO	Al_2O_3	SiO_2	SO_3	K_2O	CaO	TiO_2	FeO
Oya								
0.26	0.11	8.93	59.38	12.40	3.08	13.05	0.37	2.42
0.08	–	5.26	37.37	27.83	2.61	24.48	0.32	2.06
–	0.14	4.96	34.21	30.99	1.93	25.56	–	0.22
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	–	5.44	10.15	0.26	14.80
0.17	1.26	12.73	51.69	–	3.76	14.35	0.43	15.61
–	0.56	12.27	48.18	–	5.09	14.73	–	19.17
0.09	1.80	15.45	57.71	–	6.57	12.62	0.47	5.29
–	1.33	13.50	32.95	–	3.88	15.05	0.33	32.96
Echizen								
–	1.76	19.30	61.02	–	6.68	0.44	–	10.88
1.30	–	19.37	70.76	–	6.34	0.26	0.27	1.84
–	1.52	17.27	61.06	–	5.67	0.51	3.82	10.15
–	7.56	19.76	38.04	–	1.31	1.92	0.31	31.11
–	3.09	23.34	50.52	–	7.51	0.20	–	15.34

14.2.2 Porosimetry

The porosity of the stone influences both the interaction with the gas phase and the release of trapped krypton atoms as they diffuse back out of the stone.

The pore size distribution, specific surface area and other porosimetric data were measured for the three tuffs studied by means of a Micromeritics Auto-pore instrument (Model 9200 V2.03). The data are given in Table 14.2 and the pore size distribution in Figure 14.1.

Table 14.2 **Porosimetry data for the three Japanese tuffs**

Tuff	Specific Surface area (m^2/g)	Bulk Density (g/cm^3)	Skeletal Density (g/cm^3)	Porosity (%)
Oya	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

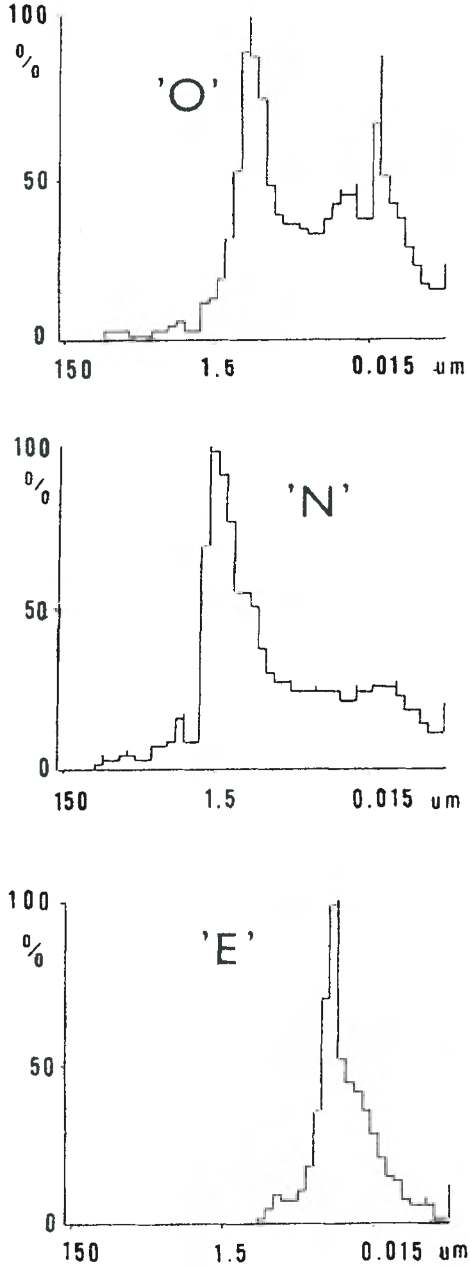

Figure 14.1 **Pore size distribution for the three Japanese tuffs.**
"O"= Oya tuff – average pore radius 0.0174 μm
"N" = Nara tuff – average pore radius 0.022 μm
"E" = Echizen tuff – average pore radius 0.0195 μm

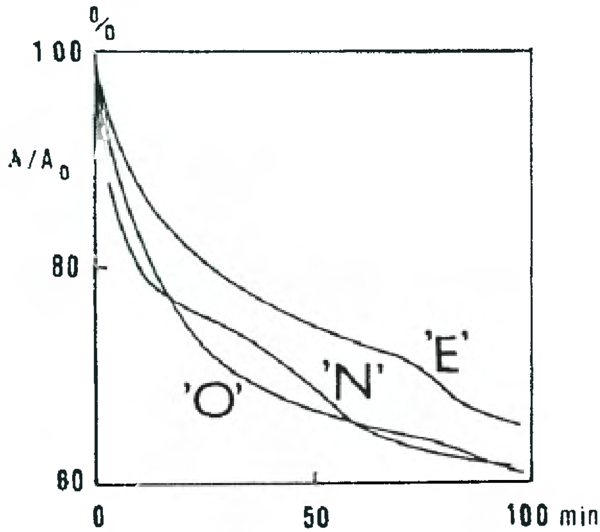

Figure 14.2 **Relative decrease in radioactivity for the three tuffs in a corrosive atmosphere of 125 ppm SO_2 at 85% RH.**
O = Oya; N = Nara; and E = Echizen tuff.

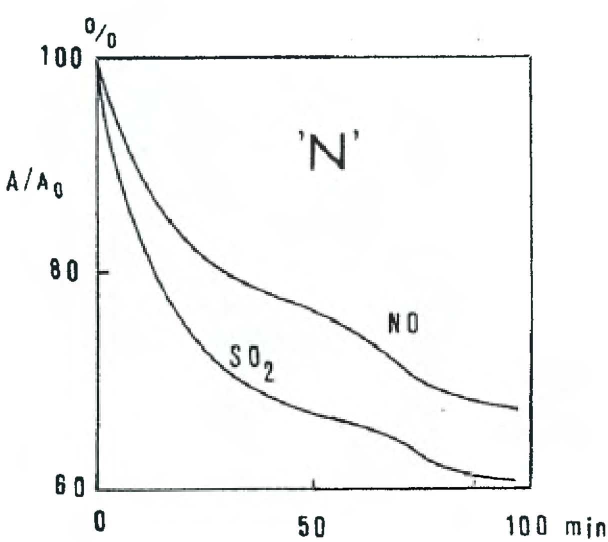

Figure 14.3 **Relative decrease in radioactivity for the Nara tuff in an atmosphere of 125 ppm SO_2 or of 125 ppm NO, both at 85% RH.**

14.3 RESULTS

14.3.1 Corrosion of tuffs

The experimental data show clearly that the three tuffs are easily corroded with either of the corrosive gases used in the tests. The radioactivity declines immediately after the sulphur dioxide or nitrogen oxide comes into contact with the surface of the stone. The differences observed between the different stones can be attributed to differences in pore structure and chemical composition. Figure 14.2 shows the behaviour of the three tuffs during corrosion with sulphur dioxide. Figure 14.3 compares behaviour of the Nara tuff with sulphur dioxide and with nitrogen oxide. The curves shown in these figures are representative of all the measurements carried out. As experiments were repeated on the same specimens after re-polishing of the surface, the heterogeneity factor of particular areas in the samples could be rejected.

The Oya and Nara tuffs reacted faster to sulphur dioxide than did the Echizen tuff, probably because of their high specific surface area and their calcite content. The speed of gas-solid reactions is generally of first order to the total surface reacting.

In the case of the Nara and Echizen tuffs, the decline in radioactivity can be linked to the high contents of iron compounds. These, due to their catalytic properties for heterogeneous oxidation reactions, enhance the oxidation occurring within the stone. Amorphous iron oxides are also known for their adsorption properties.

Figure 14.3 shows that nitrogen oxide is also reactive with tuffs. It should be noted that these reactions occurred only at high relative humidity, >80% RH.

14.3.2 Influence of RH

The influence of relative humidity on the corrosive action of the gaseous oxides was known from previous experiments [3]. It had been shown that the reaction does not proceed if the RH is below 50%.

Maintaining constant RH in the flow system was not easy, and the preparation of the samples for labelling (polishing and washing) affected the amount of adsorbed water they held. The samples were therefore prepared according to a strict routine so that at least the results were reproducible.

As expected, higher RH levels increased the reaction rate, as shown by the faster decrease in relative radioactivity. Figure 14.4 shows the differences in reaction rate for the Echizen tuff at the same concentration of sulphur dioxide at 75% and 90% RH.

14.3.3 Evaluation of treatments

It was found that the out-diffusion of krypton atoms was not hindered by the presence of the polymeric compounds tested for the conservation treatment of these stones. Three products were used in the study: *Wacker H* (**W-H**); *Wacker OH* (**W-OH**) and *Paraloid B-72* (**P**). This last product was applied in a toluene-xylene solution at 5% w/w concentration. The products were applied to the samples after labelling with ^{85}Kr.

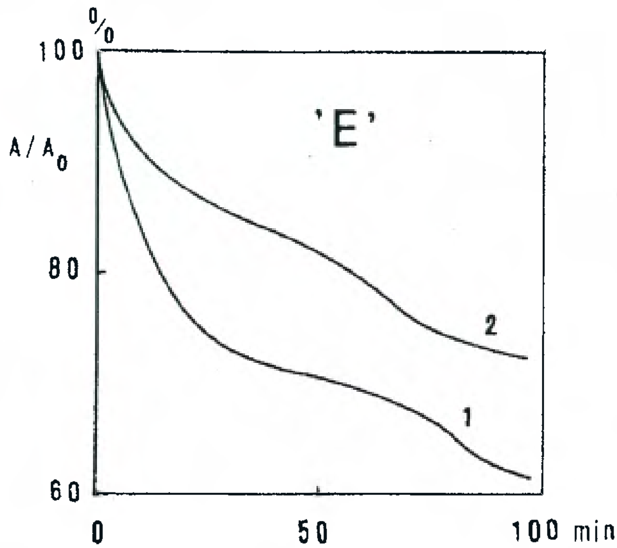

Figure 14.4 **Influence of RH on the corrosive action of 150 ppm SO_2 on Echizen tuff.** Curve 1 = 90% RH; Curve 2 = 75% RH.

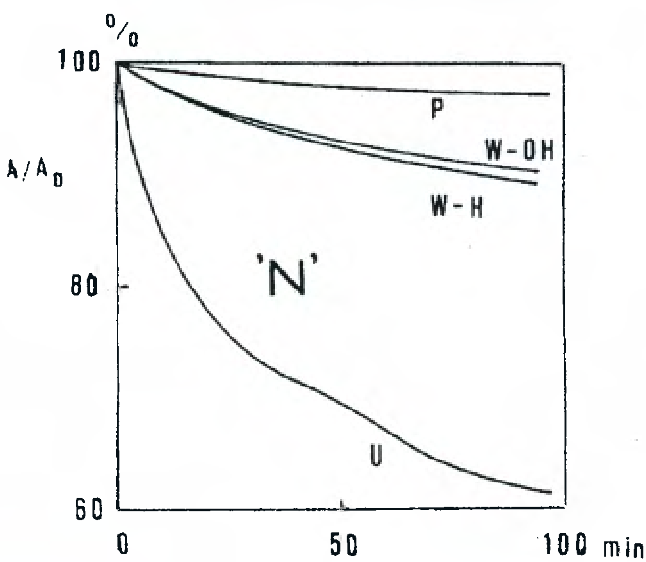

Figure 14.5 **Differences in reaction rates with 130 ppm SO_2, at 90 %RH, for Nara tuff treated with various products.**
U = untreated; W-H and W-OH = *Wacker H* and *Wacker OH* respectively; P = *Paraloid B-72.*

With the treatments at the concentrations tested, the tuffs were not protected completely from the corrosive action of the gaseous oxides. This was apparent from scanning electron microscopic observations, which showed incomplete coverage of the surfaces of the treated stones.

The decrease in relative radioactivity cannot be ascribed to the increase in mechanical strength of the material, which would prevent the breaking up of the lattice and hence block the release of the trapped krypton atoms [2]. Rather it shows that the interaction with the gaseous oxides was diminished by the presence of the polymer.

The results obtained are illustrated by the Nara tuff, which is representative for the three tuffs tested. Figure 14.5 shows the decrease in reaction rate of the treated stone when exposed to a corrosive atmosphere of 130 ppm SO_2 at 90% RH.

No large differences were observed between the two treatments based on siloxanes, even though one product is hydrophobic (**W-H**) and the other hydrophilic (**W-OH**). Thus the selection of a hydrophobic consolidation treatment is justified only when it is necessary to prevent the penetration of liquid water.

The differences in reaction rate decrease obtained between the Paraloid and the Wacker products are not significant enough to indicate better protection of the stone.

14.4 DISCUSSION

The labelling technique gives a picture of the overall processes that occur within the stone surface as it interacts with its environment. The technique complements other studies of stone corrosion and conservation as it provides comparative data on the same stone samples subjected to differing conditions.

The three Japanese tuffs studied appeared to be easily corroded by sulphur dioxide or nitrogen oxide. Their high porosity and the presence of calcite and other minerals which can react, or catalyse reactions, with these gases make them especially vulnerable to polluted atmospheres. The study showed that these stones can be compared with porous limestones with regards to their behaviour to corrosive gases. The importance of the relative humidity of the polluted atmosphere has been shown. The products tested have been shown to reduce the corrosion reaction rate. The protective treatments achieve good penetration due to the favourable pore structure and pore size distribution of these stones.

In Japan, tuffs are one of the most common stone materials – used since historical times for the carving of sculptures. Finding appropriate conservation methods for these stones is the aim of scientists and conservators in view of the need for preservation of such cultural heritage as the carved Buddhas in the Nara and Kiushu areas. Decreasing the absorption of water by the stone from which the Buddhas are carved is a primary requirement in order to reduce the reactivity of the stone surface to the polluted atmosphere.

14.5 CONCLUSIONS

The three types of Japanese tuffs studied – Oya, Nara and Echizen – were found to be easily corroded by a polluted atmosphere containing sulphur dioxide or nitrogen oxide. This reaction was monitored by following the changes in relative radioactivity of samples labelled with ^{85}Kr and exposed to different concentrations of these gases under various RH conditions. The results prove that these tuffs, due to their porosity and mineral content, react with these gases, thus making the tuffs susceptible to deterioration in polluted atmospheres. The conservation products tested – siloxane- and acrylic-based polymers – proved to reduce the rate of deterioration attributable to these corrosive gases.

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RESUMEN

Las interacciones entre superficie de piedra y atmósfera corrosiva se pueden seguir por marcado de las muestras de 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 esta 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 probaron ser más eficaces como protectores de la toba que los tratamientos con siloxanos.

RESUME

Il est possible de suivre les interactions entre les surfaces des pierres et une atmosphère corrosive en marquant des échantillons de pierre au krypton 85 radioactif dans un faisceau plasma à basse énergie. La baisse de radioactivité est liée au taux de corrosion, ce qui permet de mesurer la résistance de la pierre dans cette atmosphère. Ce procédé peut servir à évaluer les différences entre échantillons traités et non traités et entre divers traitements. On a étudié la résistance à la corrosion de trois types de tufs japonais dans une atmosphère à haute teneur en oxydes de soufre et d'azote. Les résultats montrent clairement que les tufs examinés se corrodent facilement et que le rythme de détérioration dépend de la concentration en polluants, de l'humidité relative et de la structure des pores. Il apparaît que les traitements aux copolymères acryliques préservent plus efficacement le tuf que les traitements aux siloxanes.

KURZFASSUNG

Die Einwirkung einer korrosiven Atmosphäre auf Steinoberflächen kann verfolgt werden, indem die Steinproben mit radioaktivem Krypton 85 in einem niedrig energetischen Plasmastrahl markiert werden. Die Abnahme der Radioaktivität ist dann ein Maß für die Korrosionsrate bzw. für die Haltbarkeit des Steins in der jeweiligen Atmosphäre. Eine weitere Anwendungsmöglichkeit ist die Bewertung der Unterschiede zwischen behandelten und unbehandelten Proben und zwischen verschiedenen Behandlungen untereinander.
Die Korrosionsbeständigkeit dreier Tuffsorten aus Japan in einer mit Schwefel- und Stickstoffoxyden angereicherten Atmosphäre ist Inhalt der hier vorgestellten Untersuchungen. Die Ergebnisse lassen klar erkennen, daß die untersuchten Tuffgesteine korrosionsanfällig sind und daß die Korrosionsrate eine Funktion des Schadstoffgehaltes, der relativen Luftfeuchte und der Porenstruktur ist. Es zeigte sich, daß die Tuffe mit acrylischen Kopolymeren wirksamer geschützt werden können als mit Siloxanen.

A NEW CONCEPT FOR PRESERVATION OF POROUS NATURAL STONE

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ABSTRACT

This study deals with the development of criteria for the performance of stone treatment systems and for the assessment of the effectiveness of stone protecting materials. This assessment of new materials was based on comparison of results from physical tests carried out on treated and untreated samples. A number of important criteria, which need to be optimized, have been evaluated both qualitatively and quantitatively. The laboratory tests cover measurements of properties of the polymers, the porous materials and the impregnated porous materials. The aim of this project is to develop new and highly effective stone protecting and strengthening materials through collaboration between different scientific institutes and the chemical industry.

15.1 INTRODUCTION

Deterioration damage in the form of crusts, surface scaling, exfoliation and granular dis-aggregations in structural stone members and sculptures is usually a result of environmental causes. In addition to naturally caused weathering processes, anthropogenic detrimental influences have increased. Sandstones, as well as volcanic tuffs, are particularly susceptible to these weathering processes. Conservation of these types of rock, which are characteristic of very many old buildings and monuments in Germany and other countries, involves serious difficulties.

Despite the intense efforts of curators, restorers and architects, losses of cultural and historic material cannot be prevented by applying the available procedures and substances. At best, the deterioration process can only be slowed down.

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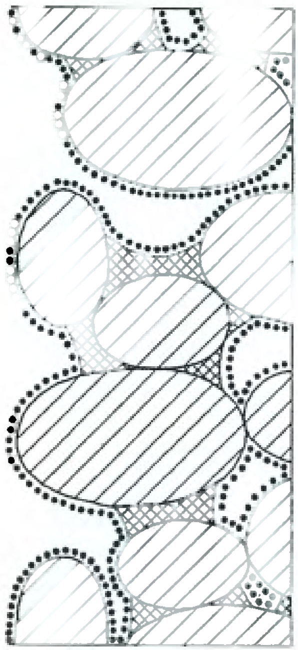
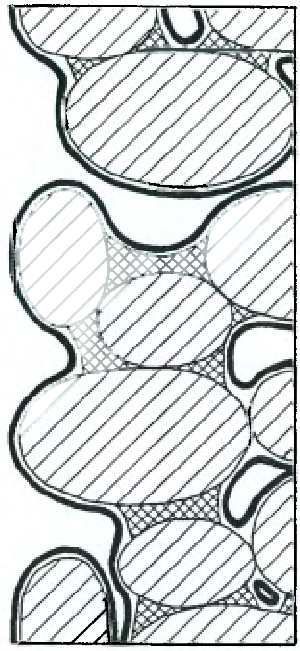
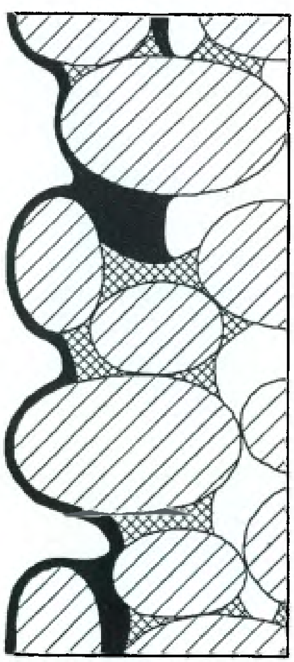


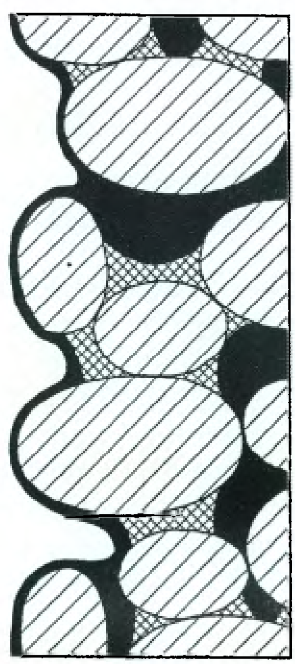
Hydrophobic impregnation



Film-forming impregnation



Surface-sealing impregnation



Bulk-sealing impregnation

Figure 15.1 Schematic presentation of the terminology for stone impregnation.

The present paper is intended as an example of the use of techniques for assessing the effectiveness of existing consolidating and protective treatments in order to optimize these treatments and the eventual development of new types of polymeric materials.

15.2 TERMINOLOGY OF STONE CONSERVATION

Stone treatments can be differentiated according to their functional nature and fall between the extremes of hydrophobic impregnation and of bulk sealing, as illustrated in Figure 15.1.

Hydrophobization treatment indicates a particular technique of impregnation that reduces the capillary water absorption properties of the material [1, 2].

Film-forming impregnation coats the internal pore surfaces – and therefore presumably protects against chemical or biological attacks – without any considerable change in the pore structure.

Sealing means the filling of pore channels in the border area of the structural member or sculpture. The external surfaces get covered by a surface layer which will reduce the water vapour permeability.

Sealing of the complete bulk volume by acrylic resin is a special technology. It needs stationary equipment and is therefore limited to relatively small sculptures and elements that can be transported to the laboratory.

A special kind of impregnation, permitting protection in addition to structural consolidation, was first described in 1988 [3]. This combination is the basis for the "supporting corset" model (see Figure 15.2). The polymer and the stone should interact to form an "integral compound" which would serve as a barrier to protect the mineral substrate from harmful environmental factors, but should not produce negative changes in the stone's properties as a building material.

15.3 TECHNICAL REQUIREMENTS

As a basis for research activities, a catalogue of requirements for protective agents has been developed through interdisciplinary collaboration [4]. The technical demands can be divided according to four primary criteria:

- aesthetic preservation of the natural stone surface;
- effectiveness and durability of protective methods;
- usability *in situ*; and
- compatibility with ecological demands.

These main criteria are in turn subdivided into several subcriteria, which are discussed in detail elsewhere [4].

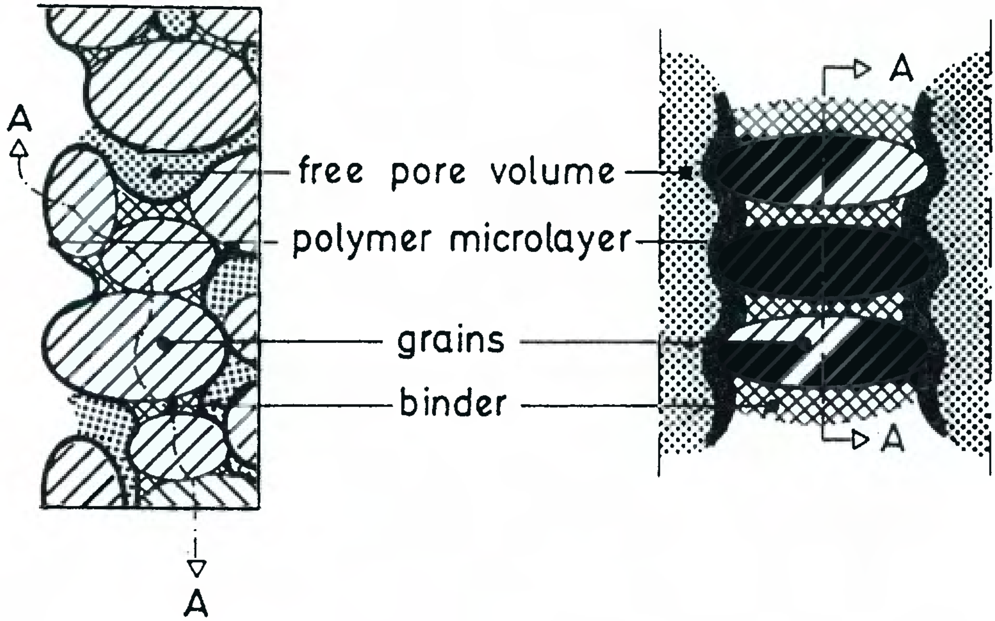


Figure 15.2 **The "supporting corset" protective polymer microlayer coating the pore walls.**

The so-called supporting corset model for protective stone treatment is understood to mean 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;
- be impermeable to liquid water;
- control water vapour diffusion;
- resist chemical and biological attack; and
- be capable of elastic deformation through a wide range of temperatures (–30°C to +80°C)

Detrital soil microcomponents are expected to be evenly coated by a microlayer of the polymer and linked to each other by polymeric bridges. As a result of the mechanical properties of the "ideal" polymer microlayer, a supporting corset is formed.

Water vapour diffusion within the bulk volume of the stone is not significantly changed because large capillary pore channels remain open. In simplified form, this concept is explained in Figure 15.2 [5]. It differs from the well-known hydrophobic treatment in that there is the distinctive formation of a protective and impermeable microlayer coating the inner surfaces of the stone. It does not have the disadvantages of silica ester treatments, such as the drastic increase in strength, the formation of a secondary pore network, or both.

15.4 EXPERIMENTAL INVESTIGATIONS

15.4.1 Aims

On the basis of the technological requirements, effectiveness tests for existing products have been carried out. These tests rely on the measurement of physical and mechanical properties, including water absorption, water vapour transmission and elastic modulus. In an iterative process, specifications were elaborated as a basis for developments of new polymer-based stone-treatment systems able to protect natural stone monuments against harmful environmental agents and to strengthen the microstructure of the stone.

15.4.2 Products tested and stones

Resins dissolved in a mixture of organic solvents may have very low viscosities and can be used successfully for deep impregnation of materials with a wide range of porosities. A suitable stone treatment must have:

- a viscosity coefficient less than about 10 mPa.s;
- moderate surface tension (between 20 and 30 mN/m);
- moderate interaction between polar and non-polar groups inside the resin molecule (in relation to the polarity of the stone);
- low average molecular weight;
- low reactivity, with a very slow increase in viscosity; and
- a low solvent content.

About 150 resin products proposed for stone treatments were studied during preliminary tests. Most of the products tested were based on an active ingredient in an organic solvent. There were seven primary categories of active ingredients, namely

- polyurethane, hardening both from ambient humidity and from special chemical components (**PUR**);
- 2-component epoxy resin systems (**EP**);
- modified acrylic resins (**AY**);
- silicon organic compounds, such as silanes and polysiloxanes (**SIL**);
- modified silica ester (**SE**);
- fluoro-ethylene (**FE**); and
- unsaturated polyesters (**UP**).

In addition, some preliminary tests were carried out using aqueous dispersions of polyurethane, polyesters and acrylic resins.

Sandstones and tuff representative of those commonly found in German stone monuments were used in the tests. Three different quarry sandstones and one quarry tuff were selected on the basis of typical characteristics such as mineral content, pore structure and colour. The stones were:

- Ebenheider sandstone (**EH**);
- Obernkirchener sandstone (**OK**);

- Sander Schilf sandstone (**SS**); and
- Weiberner tuff (**WB**).

The samples were cut into prisms of 5 × 5 × 10 cm. In order to simulate the situation of a large element, treated and weathered from the surface, the lateral (10 cm-long) faces of the samples were sealed by the application of a 1.0 mm-thick layer of **EP**, while the square (5 × 5 cm) faces remained free. The samples were exposed to different climatic conditions (8°C + 60% RH; 23°C + 50% RH; 28°C + 95% RH) until they reached a constant humidity content.

The products were applied by capillary absorption. The 5 × 5 cm face of each sample was immersed to 0.5 cm depth in the impregnating liquid at atmospheric pressure for four hours, and the samples then divided into three subsamples, each of which was cured in one of the three climatic regimes above for one month. The samples were weighed at the end of this time and the residual amount of impregnated material in the stone was determined.

Table 15.1 Properties of the untreated stones

Stone	EH	OK	SS	WB
Density (g/cm^3)	**2.59 - 2.73**	2.66 - 2.69	2.64 - 2.71	2.26 - 2.40
Maximum capillary water content (W %)	**7.99**	6.75	7.99	27.59
Water absorption coefficient ($kg/m^2h^{0.5}$)	**2.439**	1.670	1.001	6.904
Porosity (V %)	**17.3 - 20.9**	16.4 - 19.0	19.6 - 19.9	41.6 - 44.0
Average pore radius (μm)	**3.5**	2.0	1.9	0.7
Specific surface (m^2/g)	**2.44 - 4.10**	1.29 - 1.32	4.49 - 7.30	10.04 - 10.10
Water vapour diffusion factor ($g/m^2.day^{-1}$)	**82**	71	91	178

15.5 SELECTED TEST RESULTS

To illustrate the procedure followed in the evaluation of the effectiveness of a given treatment, representative data are reported for the products tested based on **SE**, **EP** and **PUR**.

15.5.1 Penetration depth tests

The penetration depth tests were carried out using various methods [5]. Depending on the stone variety, weathering grade, and physical properties of the liquid impregnating agents, penetration depths from a few millimetres up to 70 mm have been obtained. The correlations between penetration depth and physical properties of the liquid, such as viscosity or surface tension, have been reported elsewhere [6].

The different curing climates did not have a significant influence on the penetration depths of the impregnating agents.

The influence of polarity has not yet been clarified.

15.5.2 Water absorption and drying behaviour

The polymer-treated surface was immersed in water to allow water absorption to occur. Weight increase was monitored by periodic measurement until the sample reached constant weight. The data are reported as percentages of the maximum capillary water content of the untreated samples.

The drying behaviour at 23°C + 50% RH was followed gravimetrically. This behaviour is important since liquid water sometimes accumulates behind a treated zone due to condensation or rising damp.

Figure 15.3 shows the water absorption and drying curves for Ebenheider sandstone (**EH**), both untreated and treated with different polymeric substances. In comparison with the untreated sample, the treated ones have a reduced drying rate, but, as they absorb less water, they dry out in approximately the same amount of time. The samples treated with modified silica ester show a significantly hydrophobic character throughout the whole observation period. Samples treated with polyurethane show a moderate rise in water absorption after about one week, indicating that after that time the water-repellent character of the polymer is lost.

In principle it is advantageous to have shorter desorption (drying) times than absorption times. This condition was not met by the polymer systems selected for assessment.

Figure 15.4 shows the absorption of water and drying behaviour for the Weiberner tuff (**WB**). All treated samples maintain their hydrophobic character.

15.5.3 Contact angle and artificial weathering

The contact angle is determined using a drop of water of defined volume deposited on the horizontally adjusted sample surface. By means of a goniometer microscope the contact angle can be determined directly. The surface can be defined as hydrophobic if the angle is greater than 90°.

Artificial weathering allows for a comparative evaluation of the durability of different products. As a result of exposure, the polymer microlayers at the sample surface are partly destroyed, leading to changes in the surface energy, and thus to smaller contact angles. The surfaces can be wetted, but no water absorption into the capillary system takes place [5].

15.5.4 Water vapour diffusion

The polymer-treated stone volume should not act as a barrier to 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 the German standard, DIN 52615 [7]. The treated samples had a cross section of 50 × 50 mm and a thickness of 10 mm. The test was carried out according to the so-called "wet cup method." The results obtained are shown in Figure 15.5.

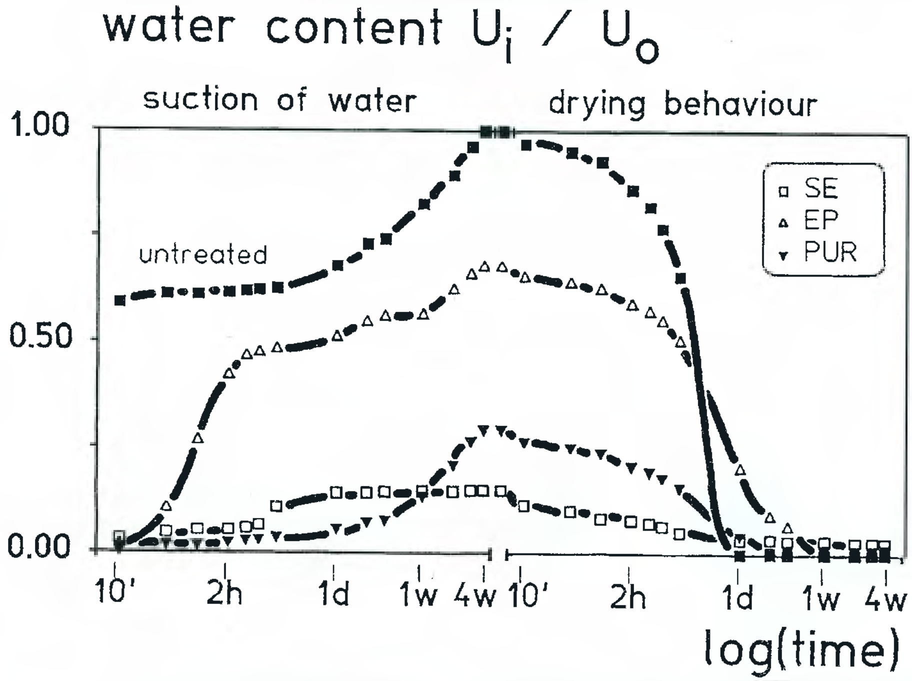


Figure 15.3 Water absorption and drying behaviour of treated and untreated sandstone (EH). The results are given as the water content relative to the maximum water absorbed by the untreated sample.

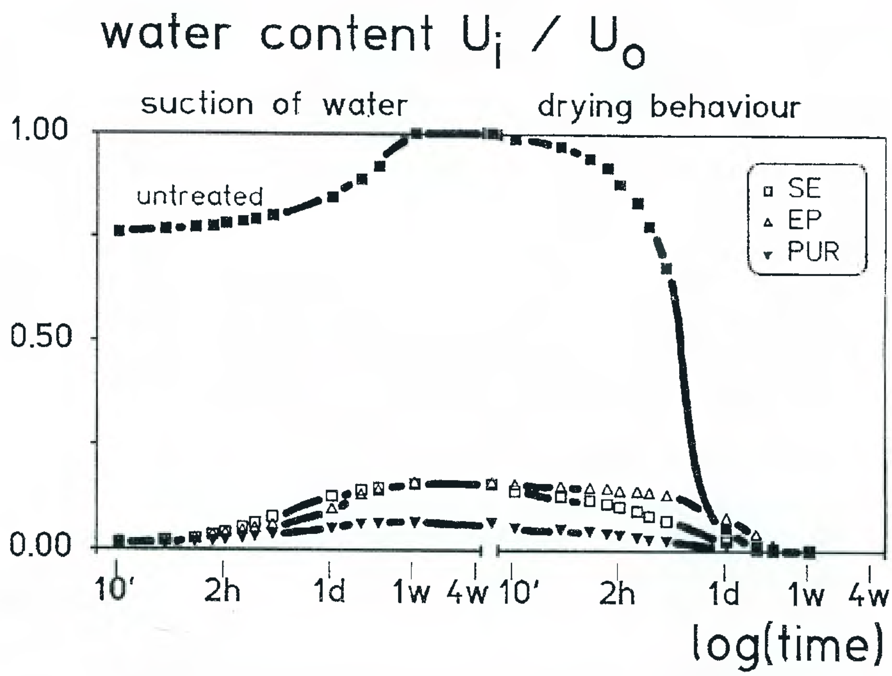


Figure 15.4 Water absorption and drying behaviour of treated and untreated tuff (WB). The results are given as the water content relative to the maximum water absorbed by the untreated sample.

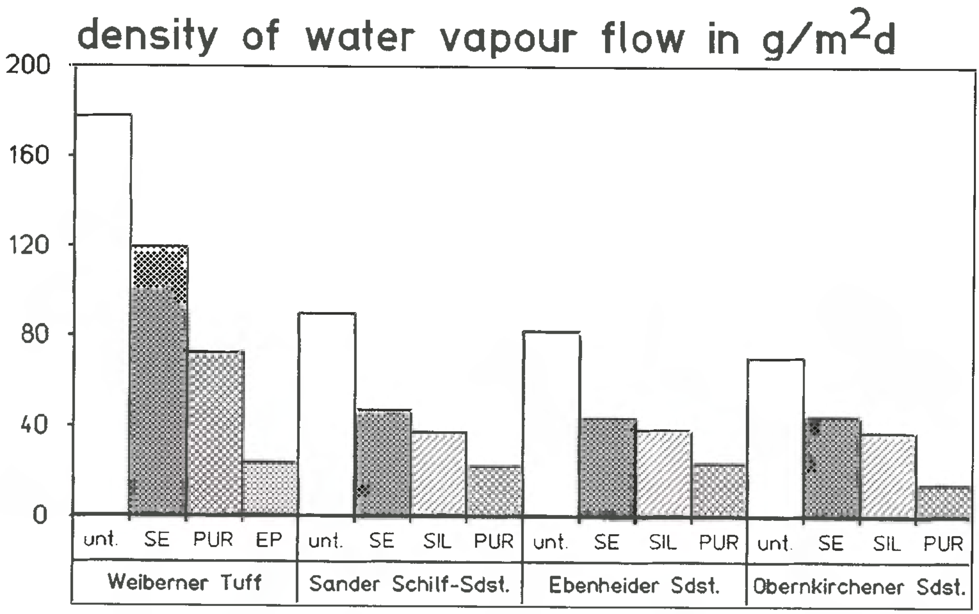


Figure 15.5 **Water vapour permeability for treated and untreated stones.**

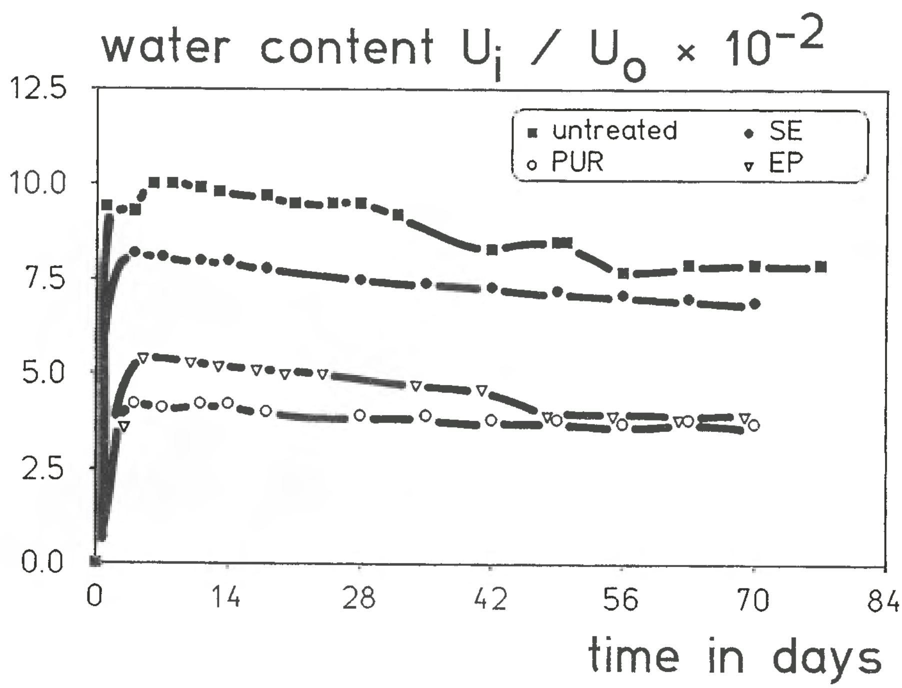


Figure 15.6 **Water vapour absorption of treated and untreated tuff (WB) samples exposed to 92% RH at 28°C. The data are given as water content relative to the maximum water absorbed by the untreated sample.**

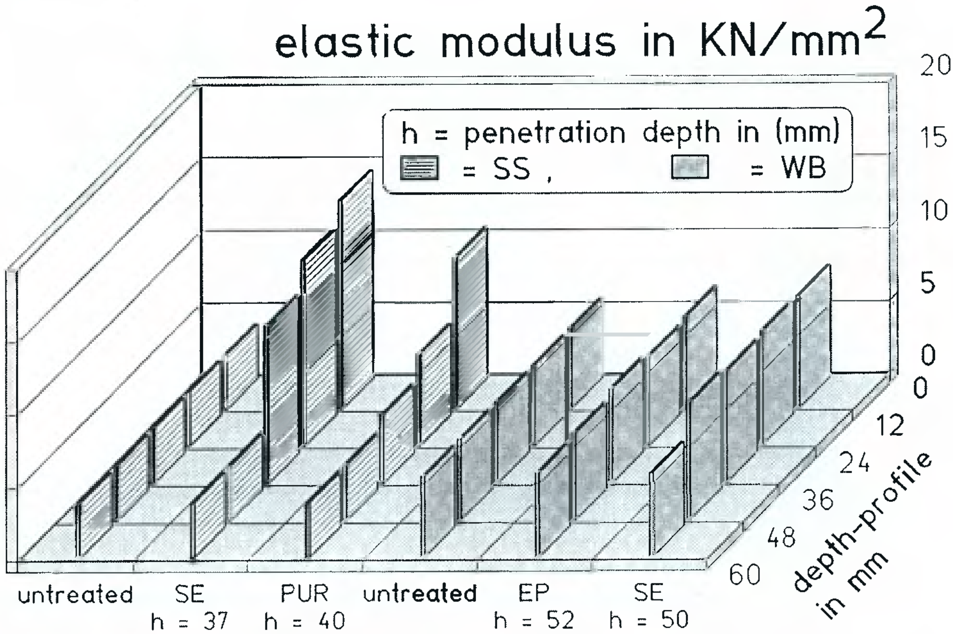


Figure 15.7 Relative elastic modulus depth profiles before and after treatment of sandstone (SS) and tuff (WB) samples.

The applied products reduce WDD by a factor of 3 to 4, although the microlayers on the inner pore walls only affect porosity in the desired way. This reduction can be attributed to the moderate hydrophobic effects of the products, leading to a reduction in the adsorbed moisture. In consequence, transportation of water molecules within the pore system is reduced. In this case surface diffusion and capillarity contribute only moderately to the diffusion of water vapour. The results of WDD tests indicate a tolerable level of change, but the product's hydrophobic features should nevertheless be optimized.

15.5.5 Water vapour adsorption

The isotherm of sorption characterizes the amount of moisture being adsorbed on the internal surfaces. Hydrophobization treatments reduce the water-adsorption capacity of the stone. This should be achieved by sealing pores which do not contribute to the bulk of moisture transport mechanisms within the stone.

Water vapour sorption was tested using 50 × 50 × 10 mm samples cut from the original prisms (5 × 5 × 10 cm). Several RH levels were used – 22%; 43%; 56%; 85%; & 92% RH – all at 28°C. The amount of adsorbed moisture is lower for the treated specimens at all RH levels tested. The larger amount of adsorbed moisture in the untreated stones can be explained through capillary condensation within pores smaller than 0.1 µm in diameter. The significantly reduced water content of the **PUR**- and **EP**-impregnated samples can be explained as a function of a reduced inner surface resulting from the sealing of intercrystalline gaps by the polymer. This has been confirmed through scanning electron microscopy (SEM) examination of the samples. In addition, the hydrophobic character of these polymers would be a contributing factor [8]. It was also observed that the length of exposure to a given atmosphere does not influence the water vapour adsorption. Figure 15.6 plots the data obtained for treated and untreated Weiberner tuff samples exposed to an atmosphere of 92% RH at 28°C.

15.5.6 Bi-axial flexural strength and elastic modulus

The strength of decayed border areas has to be increased, if necessary, so that the internal stresses can be borne safely. A large increase in the elastic modulus is not desirable as thermic and hygric internal stresses are to be avoided. The measurement of strength and elastic modulus, before and after treatment, is therefore a key factor to the assessment of any consolidant.

Obtaining significant values from these measurements is difficult due to the properties of the stone changing with distance from the surface. Therefore the technique proposed by Wittmann and Prim [9] was tried. This test procedure provides a means to determine the relative strength and the relative elastic modulus in depth profiles. From the original prismatic samples (5 × 5 × 10 cm), cylinders of 4 cm diameter were drilled and these were cut into slices of 4 mm thickness. The data obtained for the relative elastic modulus for the Sander Schilf sandstone (**SS**) and for the Weiberner tuff (**WB**) are plotted in Figure 15.7.

15.5.7 Investigations of 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 fractured sections, on which the main interest is focused, is to recognize structural features in sufficiently small areas, using SEM [11]. In addition, an energy dispersive X-ray spectrometer (EDS) equipped with an ultrathin beryllium window was used for the detection of the carbon content within the coating films. The recognized thicknesses of the polymer microlayer ranged between nanometres (nm) and microns (μm) depending upon local geometry and the type of stone [12]. Using specially developed sample preparation methods, the topography of the inner surface features can be studied down to nanometre-sized structures [13].

The visual shape of 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" which strengthens grain-to-grain contacts. Figure 15.8 shows the good adhesion between the substratum and the polymer microlayer, indicating the ability of the liquid product to penetrate and completely fill micropores.

Figure 15.9 shows that the polymer is also able to form a continuous film covering booklets of clay particles. The thickness of the polymer films is in general <1 μm. The polymer microfilm does not show fracturing or blistering, indicating that

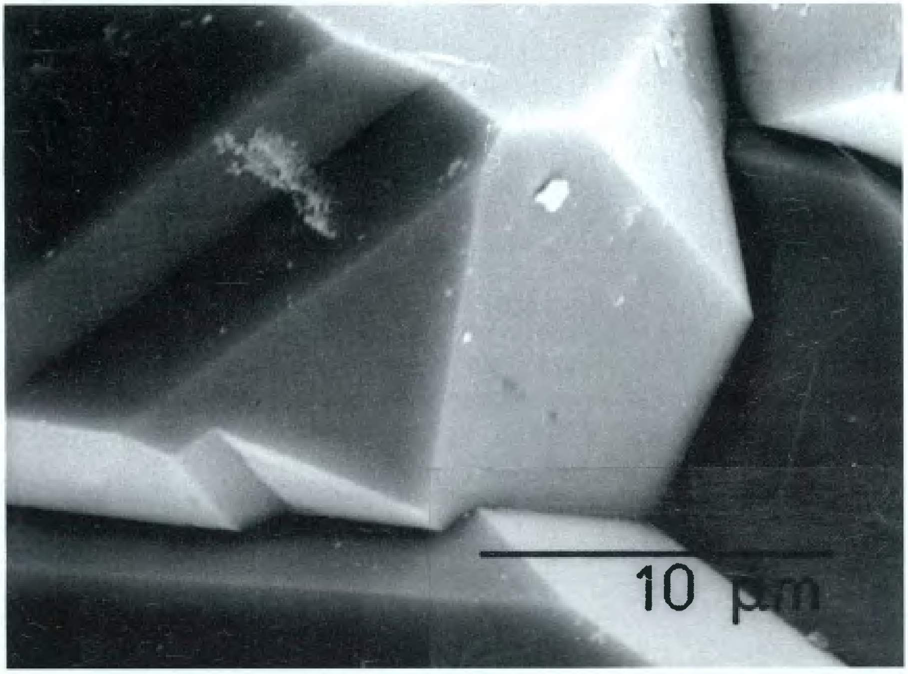


Figure 15.8 - A Quartz crystals in a sandstone (EH) (internal fracture surface) before treatment with an EP-based polymer.

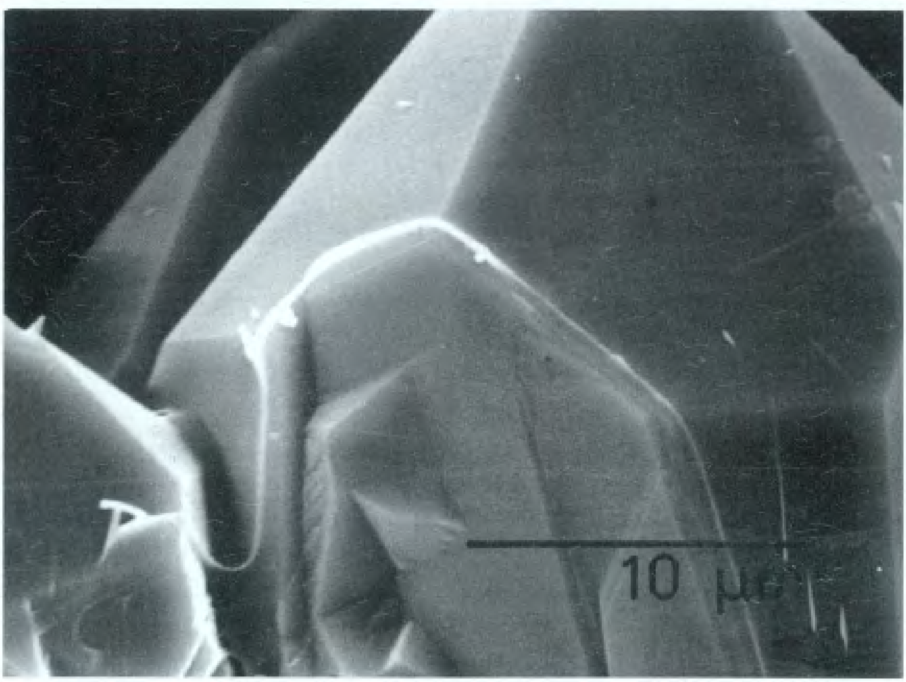


Figure 15.8 - B Quartz crystals in a sandstone (EH) (internal fracture surface) after treatment with an EP-based polymer.

Figure 15.9 - A Characteristic stacks of clays (kaolinite) in a sandstone (OK) before treatment with a PUR-based polymer.

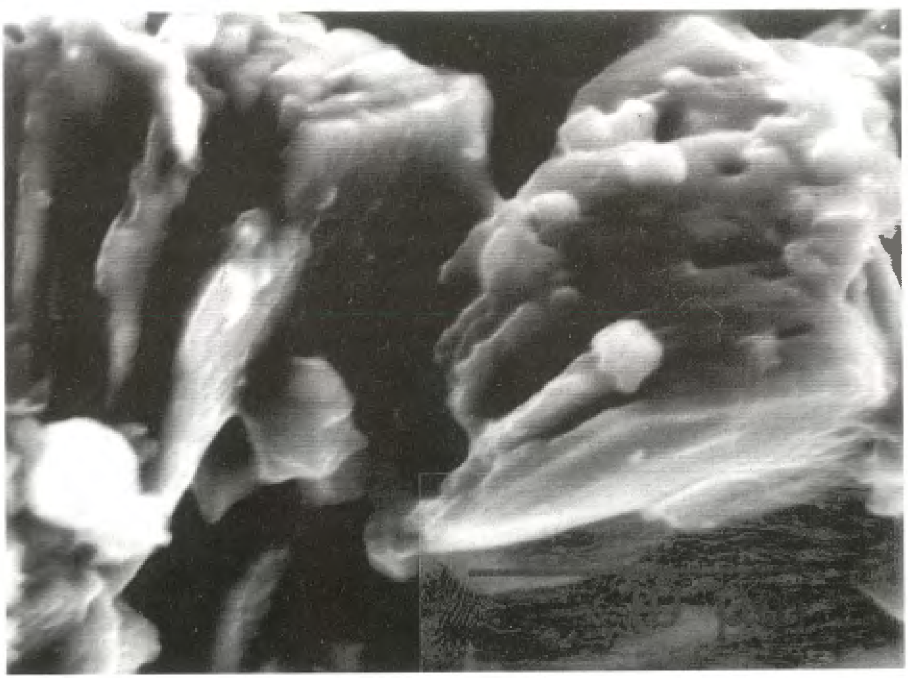


Figure 15.9 - B Characteristic stacks of clays (kaolinite) in a sandstone (OK) after treatment with a PUR-based polymer.

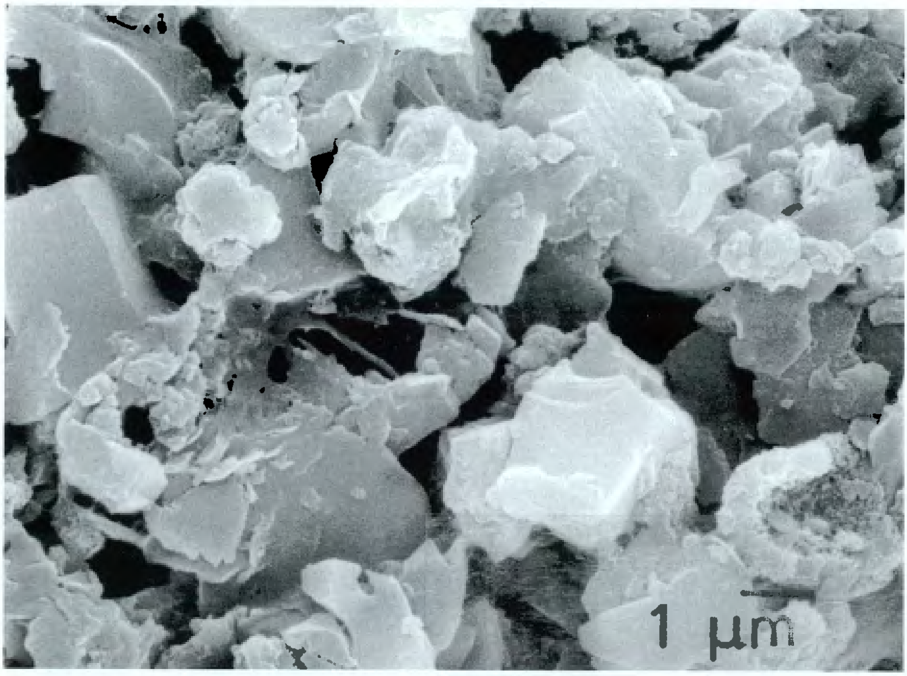


Figure 15.10 - A Internal fracture surface of a tuff sample (WB) before treatment with a PUR-based polymer.

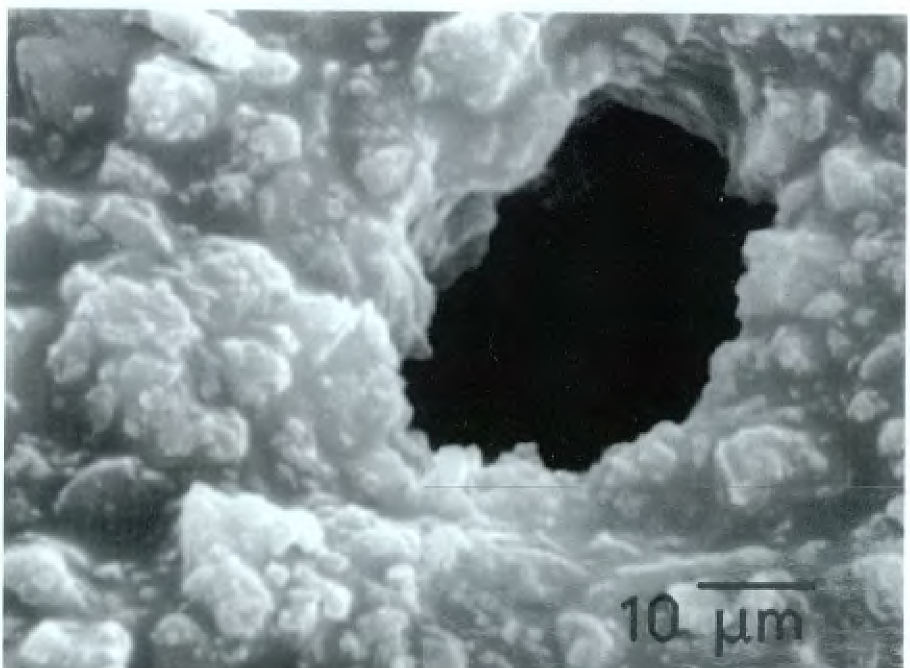


Figure 15.10 - B Internal fracture surface of a tuff sample (WB) after treatment with a PUR-based polymer.

the micromechanical stresses due to short-term, periodical wet/dry cycles of swelling clay minerals are reduced to a great extent.

The resin forms a microlayer over particles, connecting them by bridging of micropores. This can be observed in Figure 15.10 for the Weiberner tuff sample.

The SEM examination is complemented by mercury porosimetry, which can measure even slight changes in the pore radii distribution resulting from an applied treatment. In the case of sandstones, the number of pores with radii <5 μm are clearly reduced, while there is no significant change in the distribution of the larger pores. Thus these are still available for transport of water vapour through the treated volume of the stone [14].

15.6 EFFECTIVENESS EVALUATION

The evaluation of a stone treatment requires characterization through measurements of multiple-effectiveness criteria based on physico-mechanical tests. In order to carry out a computer-supported, quantitative evaluation, the effectiveness criteria are differentiated into ranks. For the exercise reported here only seven of about twenty possible effectiveness criteria were taken into account for optimizing the stone treatment systems. The seven criteria used are penetration depth, pore structure, pore radius distribution, adhesion between polymer and stone substrate ("integral compound"), homogeneity of polymer microlayers, water absorption and drying behaviour, and water vapour transmission. The quantification of these parameters allows the determination of an effectiveness coefficient.

15.7 CONCLUSIONS

The results obtained show that several polymer systems meet the technical requirements considered in this study. These types of polymers have not, as of yet, been in use for strengthening and protecting natural stone.

Some epoxies and polyurethanes show good penetration into the stone and form nearly continuous microlayers covering the mineral's 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 change the elastic modulus significantly, nor vary the colour. They do increase the mechanical strength of the stone while reducing its water absorption capability.

On the basis of these results, a selection of the most effective products was made and several test products appear to have sufficient potential to justify the investment involved in their further development. In cooperation with the chemical industry, these products could be improved and tested in a more sophisticated way. In this context, both the natural weathering and the artificial ageing of the polymer-treated stone will probably be the most important parameters for study.

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RESUMEN

El trabajo describe el desarrollo de criterios para la calidad de sistemas de tratamientos de piedra y para la evaluación de la eficiencia de materiales de protección. La evaluación de nuevos materiales 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 cualitativa y cuantitativamente. Los ensayos de laboratorio abarcan medidas de las propiedades de los polímeros, de los materials porosos y de los materiales porosos tratados. El objetivo de este proyecto es el de desarrollar materiales efectivos de consolidación y protección para la piedra mediante la colaboración de varios institutos científicos y de la industria química.

RESUME

Cette étude traite de l'élaboration de critères pour établir les résultats des systèmes de traitement de la pierre et pour évaluer l'efficacité des matériaux de protection. Cette évaluation de nouveaux matériaux s'est fondée sur la comparaison des résultats de tests physiques portant sur des échantillons traités et non traités. Plusieurs critères importants, qu'il faut encore affiner, ont été analysés qualitativement et quantitativement. Les essais de laboratoire concernent les mesures des propriétés des polymères, des matériaux poreux et des matériaux poreux traités. Ce projet vise à mettre au point des matériaux de protection et de consolidation des pierres, qui soient nouveaux et hautement efficaces, dans le cadre d'une collaboration entre divers instituts scientifiques et l'industrie chimique.

KURZFASSUNG

Die Studie beschäftigt sich mit der Entwicklung von Kriterien für Steinbehandlungssysteme und für die Bewertung der Wirksamkeit von Schutzsubstanzen. Die Abschätzung der Wirksamkeit neuer Imprägnierungssubstanzen basiert auf dem Vergleich der Ergebnisse aus physikalischen Messungen an behandelten und unbehandelten Proben. Eine Anzahl wichtiger Kriterien, die zu optimieren sind, ist in quali- und quantitativer Weise bewertet worden. Die Laboruntersuchungen beinhalten Messungen der Polymereigenschaften, der Kennwerte poröser Materialien und derjenigen von imprägnierten porösen Materialien. Das Ziel dieses Projekts ist die Entwicklung neuer, hochwirksamer Schutz- und Festigungssysteme für Stein in Zusammenarbeit mit verschiedenen wissenschaftlichen Instituten und der chemischen Industrie.

Part Five

EASTER ISLAND

Parque Nacional

RAPA - NUI

National Park

Isla de Pascua
Easter Island
CHILE

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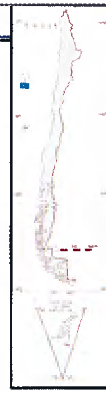
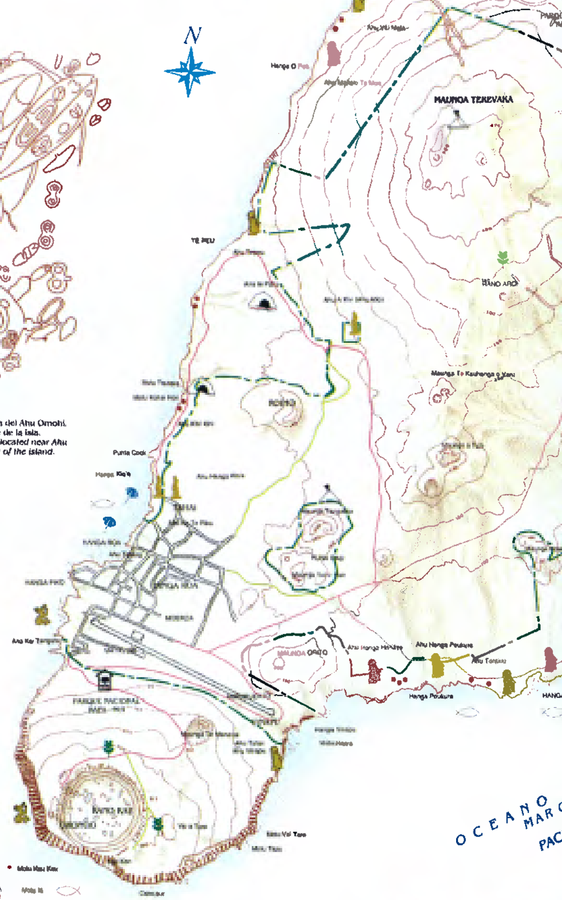


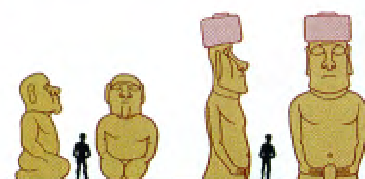
Tatuaje facial de un Rapa Nui llamado Tepano. (1890).
Face tatoos of Tepano, a Rapa Nui islander (circa 1890).

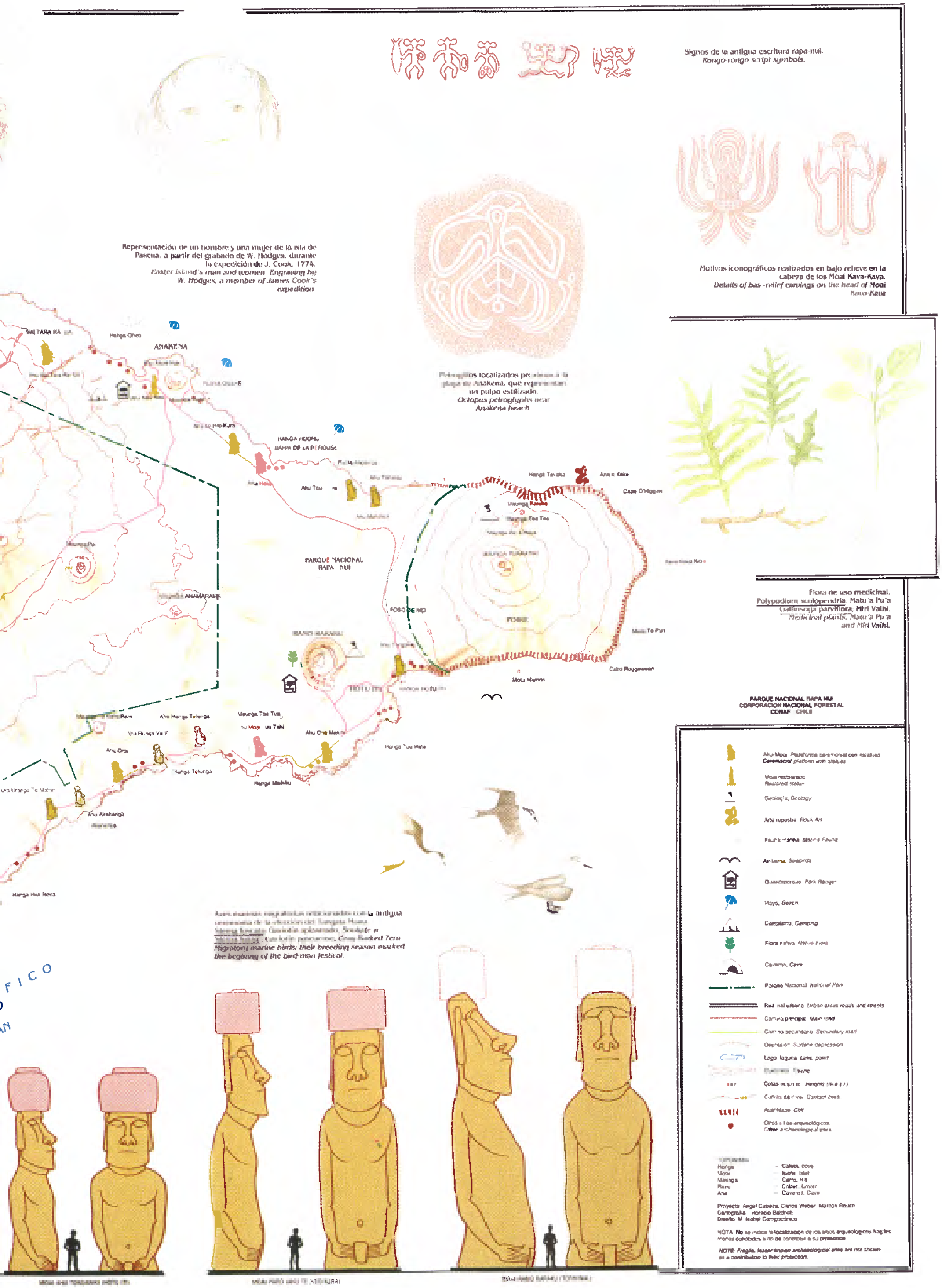
Petroglifos localizados cerca del Ahu Omohi, en la costa Nor-Oeste de la isla.
Petroglyphs (Carved rocks) located near Ahu Omohi, North-West coast of the island.

Petroglifos de la aldea ceremonial de Orongo, que representan al hombre pájaro o Tangata Manu.
Petroglyphs at Orongo ceremonial village, representing the bird-man Tangata Manu.

Moai Tangata: estatuilla masculina estilizada.
Moai Tangata: stylized masculine wood carving






Signos de la antigua escritura rapa-nui.
Rongo-rongo script symbols.
Representación de un hombre y una mujer de la isla de Pascua, a partir del grabado de W. Hodges, durante la expedición de J. Cook, 1774.
Easter Island's man and women. Engraving by W. Hodges, a member of James Cook's expedition
Petroglifos localizados próximos a la playa de Anakena, que representan un pulpo estilizado.
Octopus petroglyphs near Anakena beach.
Motivos iconográficos realizados en bajo relieve en la cabeza de los Moai Kava-Kava.
Details of bas-relief carvings on the head of Moai Kava-Kava
Flora de uso medicinal.
Polypodium scolopendria: Matu'a Pu'a
Galinsoga parviflora: Miri Vaihi.
Medicinal plants, Matu'a Pu'a and Miri Vaihi.
ANAKENA
Hanga Oheo
HANGA HOONU
BAHIA DE LA PEROUSE
PARQUE NACIONAL RAPA NUI
Cabo D'Higgins
Hanga Tavara
POIKE
Cabo Roggeveen
RANO RARAKU
Hanga Hoa Rova
Hanga Tee Tea
Migratory marine birds; their breeding season marked the begining of the bird-man festival.
PARQUE NACIONAL RAPA NUI
CORPORACION NACIONAL FORESTAL
CONAF CHILE
Geología, Geology
Arte rupestre Rock Art
Guardaparque Park Ranger
Playa, Beach
Campismo, Camping
Caverna, Cave
Parque Nacional National Park
Lago laguna Lake, pond
Acantilado Cliff
Hanga - Caleta, cove
Motu - Islote, Islet
Maunga - Cerro, Hill
Rano - Cráter, Crater
Ana - Caverna, Cave
Proyecto: Angel Cabeza, Carlos Weber, Marcos Rauch
Cartografía: Horacio Baldrich
Diseño: M. Isabel Campodónico
NOTA: No se indica la localización de los sitios arqueológicos frágiles menos conocidos a fin de contribuir a su protección.
NOTE: Fragile, lesser known archaeological sites are not shown as a contribution to their protection.

RAPA NUI:
RISE AND FALL OF A MEGALITHIC CULTURE

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ABSTRACT

This paper tries to explain, in part, the mystery of Rapa Nui. It is based on results of recent archaeological investigations and documentary sources.
The evidence is analysed from an anthropo-ecological point of view to try to understand the grandiose historico-cultural process that occurred under such special conditions. At the same time this process has many elements in common with the beginnings of neolithic civilizations elsewhere and at other times.

16.1 INTRODUCTION

For many, the mystery of Easter Island centres around how the hundreds of monumental stone images (the *moai*) were made and moved, rather than how the Rapanui society developed to the stage it did.

What is really fascinating about Rapa Nui is how such a complex society developed in one of the most isolated places of the world, and why it collapsed.

To paraphrase a common expression, it could be said that the Rapa Nui forest cannot be seen because of the moai. The hundreds of moai, and close to three hundred megalithic altars (*ahu*) built around the island, are the most spectacular manifestation of and evidence for one of the most advanced cultures in the world at the neolithic level. The historical, environmental and social conditions responsible for that process and its various phases were buried by the internal changes of their own culture and the foreign impact on the Rapanui peoples, which were practically exterminated by the second half of the nineteenth century.

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Since 1955, the systematic archaeological studies carried out, together with documentary and ethnographic sources, have contributed to give a fairly coherent picture of the Rapa Nui past.

16.2 THE ORIGIN

The present archaeological, ethnographic, linguistic and even biological evidence points to the Marquesas Islands as the most probable departure point of the settlers of Rapa Nui – *Te Pito O Te Henua* [the navel of the world] to them.

This small piece of land was the last link in a chain that had its origins thousands of years earlier, in southeast Asia, and had reached Tonga-Samoa, the centre of Polynesian culture, around 1000 BC. Later the Society Islands and the Marquesas Islands constituted the eastern nucleus of Polynesian culture, and from there settlers proceeded north towards Hawaii, southwest towards New Zealand, and east towards Rapa Nui.

Thus megalithism as an expression of an ancestor-oriented cult did not originate spontaneously in Rapa Nui, it simply reached there its greatest level of expression. This can be attributed to the particular environmental conditions and socio-political development in such an isolated place.

Tradition recounts, and scientific evidence so far supports, a planned trip from Marae Renga, in Hiva, led by the legendary King Hotu Matu'a. At present, no direct archaeological traces have been found of this first settlement, which has been estimated to have occurred around AD 300.

16.3 THE ENVIRONMENT

The settlers from oriental Polynesia had taken with them plants: breadfruit tree (*Artocarpus communis*), coconut (*Cocos nucifera*), taro (*Colocasia esculenta*), yams (*Dioscorea* spp.), sweet potato (*Ipomoea batatas*), plantain or banana (*Musa* spp.), sugar cane (*Saccharum officinarum*), mahute or paper mulberry (*Broussonetia papyrifera*), gourds (*Lagenaria siceraria*), *toromiro* (*Sophora toromiro*) and totora reed (*Scirpus californicus*), and animals: pigs, dogs and hens. Due to the length of the journey, it is surmised that pigs did not survive. Recently, dog bones were found at the lowest occupational level during excavations in Anakena. This confirms they survived the journey, but were unable to multiply.

The subtropical climate of the island, at 27° S latitude, precluded the establishment of the breadfruit and coconut. The settlers did not find the luxurious plant growth they had left behind them: instead there was an island of barely 166 km^2, of low and undulating terrain, and where rainwater filtered quickly through the porous volcanic rock. However, there were growths of palm and toromiro, and the lakes in the bottom of three of the craters had sufficient sweet water to allow the totora reed to grow there. No animal existed on the island then, so that the imported hens, plus lizards and rats that accompanied them, were the only ones until contact with the rest of the world occurred. Hens acquired great importance as a prestige object, far beyond their economic value.

Sea birds arrived periodically at the coast of the island, and the sea contributed a large variety of animal species. Nevertheless, due to the isolation of the island and its lack of a surrounding coral reef, the abundance and accessibility of the sea fauna was limited compared to other islands of eastern Polynesia.

The island offered a wide variety of lithic materials: from the crystalline obsidian to the hardest and finest basalt. Consequently, these materials provided the means to express the people's beliefs, and stimulated engineering, working techniques and arts, which developed to a level never seen before.

16.4 THE SOCIETY

The basis of cultural development was a social order headed by a religious aristocracy: the King (*ariki henúa*); the royal family (*ariki paka*); and the priests (*ivi atúa*). Then came the warriors (*matatoa*); the crafts experts (*maori*); and the important men or heads of lineages (*tangata honui*). Finally, the common people (*huru manu*) and the servants (*kio*).

The justification of this rigid hierarchy was to be found in the divine origin of the ariki, direct descendant of Tangaroa and Rongo, the gods of creation. His lineage (*miru*) would maintain this order for centuries, through right of primogeniture. The authority and prestige of the ariki was given through supernatural power (*mana*) that allowed him to have influence in life and death, in the fertility of plants and animals, in control of agricultural production, and in ceremonies. He was separated from the rest of the population by strict laws of *tapu* – the forbidden.

This prestige was fundamental to obtaining the necessary manpower to carry out the monumental works and sustain the privileges of his lineage.

In a society of this type, the two basic mechanisms for maintaining the system were regulation of access to maritime resources of higher economic value, and control of planting and harvesting dates. Access to marine resources was effected by a tapu that restricted the fishing of larger fish on the high sea to miru specialists, and then only for consumption of the aristocracy during the summer months. Planting and harvesting dates were determined by the scientific and ritualized calendar established by the astronomer priests of royal lineage. It also allowed the generous re-distribution of excess on the occasion of ceremonies and great festivities.

The system could only function with a high density population, organized in relatively autonomous groups that were self-sufficient and that dominated a clearly demarcated territory.

Twelve clans (*mata*) and their respective territories have been identified. The basic unit was an extended family (*ivi* or *paenga*) settled loosely in the common ground of the clan. Different families with a common ancestor formed a lineage (*ure*) and had a joint ceremonial centre for their cult.

16.5 DOMESTIC AND MONUMENTAL ARCHITECTURE

Large ceremonial constructions were located by the shore, where the aristocracy lived. The most common living quarters were the so-called boathouses (*hare paenga*). These were of elliptical plan, outlined by elongated basalt blocks on which a structure of branches and leaves was mounted, giving the shape of an upturned boat. They had only one low and narrow entrance in the centre of one of the sides. A pavement of rounded stones was sometimes laid in a half circle in front of the boat house. The average length was between 10 and 15 m, but some larger ones, up to 40 m, have also been found.

Towards the interior of the island, by the cultivated lands, other, less elaborate boat houses have been found, together with houses of a round or rectangular plan, associated with the exploitation of various resources.

The excavated hearths (*umu pae*) used for cooking, were usually lined with basalt slabs.

Another typical structure found along the coast is the *tupa*, a tower-like structure built of stone, with an inner chamber 2 to 4 m in diameter and about 2 to 3 m high, that, according to tradition, served as observation posts to watch for the arrival of the sea turtles.

The greatest architectural achievements were the ahu, the platforms or altars destined to receive the images of the ancestors, the founders of the various lineages.

Figure 16.1 Ahu Naunau.

These megalithic altars can be found in all of eastern Polynesia. In Rapa Nui, by 700, the old Polynesian prototype (*marae*) was complemented with a sloping front ramp (*tahua*), a pavement of rounded boulders, wide lateral wings, crematories and stone images of a unique style: the *moai*.

During a period of nearly one thousand years, the great construction masters built around 300 ahu, most of them along the coast. With time, successive enlargements and re-modellings took place, increasing their beauty and size. In the case of Ahu Tongariki, it ultimately extended over 160 m, and its central platform supported fifteen large moai with their respective head-dresses, *pukao*, in red pumice. Architectonic development reached its culmination with the constructions of Ahu Vinapú by 1200, and Ahu Akivi, by 1445.

About a dozen of these ahu show astronomical orientations to solstices and equinoxes, which cannot be ascribed to chance. This is especially the case for one of the inland ahus: the Huri A Urenga.

16.6 THE MOAI

To begin with, the monumental images of the lineage-founding ancestors were carved from various materials – red pumice, trachyte, or vesicular basalt – but later the preferred material was the tuff of the volcano Rano Raraku.

Between 1000 and 1500, about 164 moai cut in that quarry were taken to various ahu along the coast and the few in the interior. The older statues were coarse and of smaller size, but with time they evolved from the old Polynesian prototype to the fine stylization unique to Rapa Nui.

The southwest corner of the crater was the site for the cutting of these images. The average size of the statues is a little more than 4 m in height. The largest moai actually moved to its site, the Ahu Te Pito Kura, is 10 m high and weighs about 85 tons. According to William Mulloy, thirty men for one year were required for cutting it, ninety men for two months to move it from the quarry to the ahu, some 6 km away on the north coast near the bay of La Pérouse, and ninety men for five months were needed to install it on the platform.

The volcanic tuff was carved and polished with picks and adzes of basalt (*toki*). Thousands of these artifacts were left on site in the quarry, as well as 394 moai at different stages of carving, including a giant of 22 m, estimated to weigh about 200 tons.

The statues were slid down the side of the volcano into a hole prepared at its base, where the back of the figure was finished.

Thus it was in position to "walk" – as tradition has it – to its place on the ahu, thanks to the mana of the ariki.

It is possible that various moving techniques were used, according to the size and weight of each figure, but the fact that the statue is designed to be erect, with a low center of gravity, seems to give credit to the hypothesis of moving the standing statue

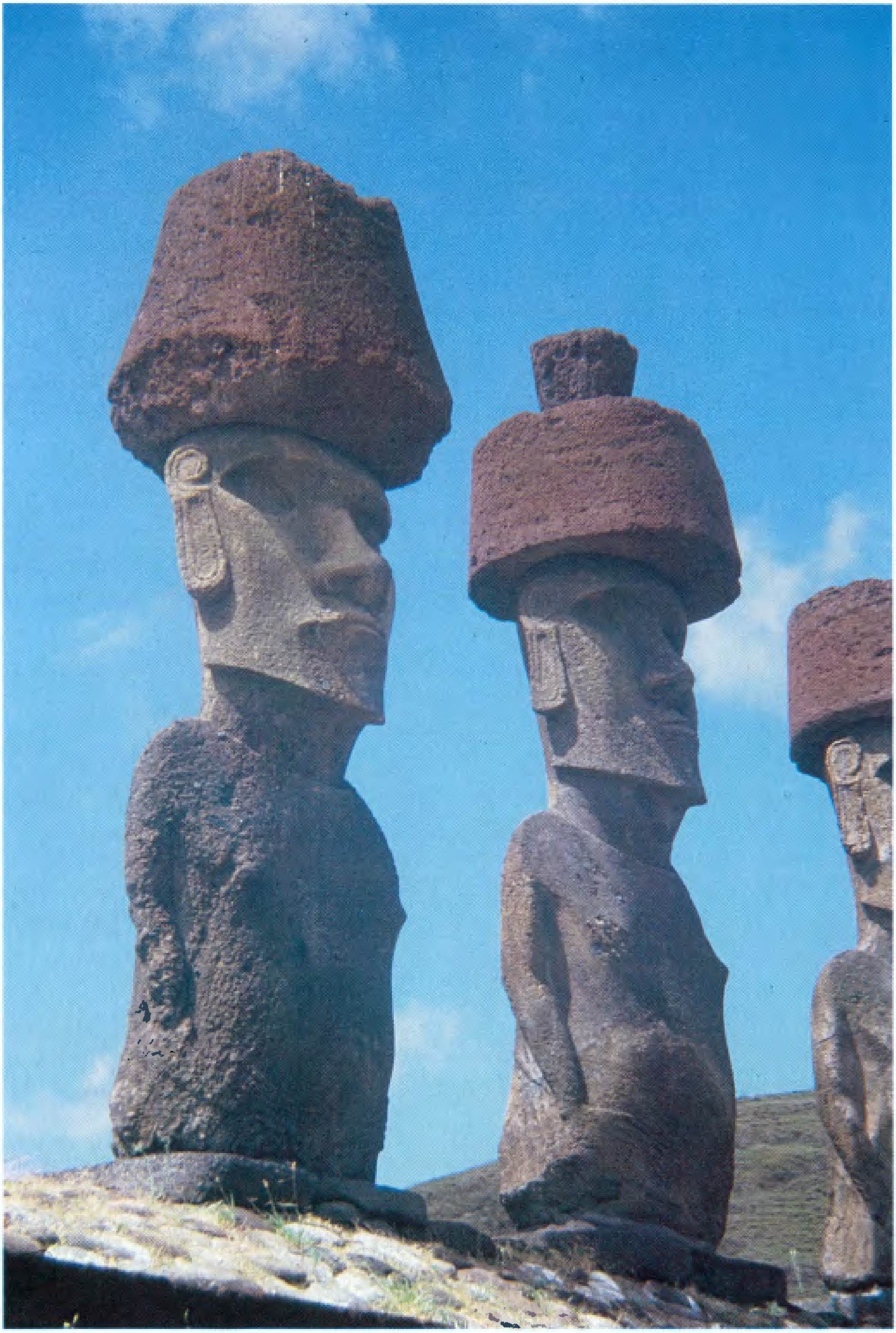

Figure 16.2 **Ahu Naunau. Moai with pukao.**

by means of ropes which alternately shifted the statue to one side and the other, as if it were taking small steps. Obviously, the smaller the base of the statue, the smaller the strength needed to move it.

In any case, they must have used a lot of wood and vegetable fibre ropes to protect the delicately carved details, and in particular the two critical points of the hands and the nose, whilst moving over the hilly, stone-strewn roads. There were some paths commonly used for moving the moai, especially one that begins at the west side of the quarry and follows the south coast.

Finally, the culminating moment of this long process, once the statue had been set up on the platform, was the installation of the eyes, carved in coral and with obsidian or red pumice pupils. At that moment the stone statue was transformed into the living image (*aringa ora*) of an ancestor, it received its name, and began to project mana on its descendants and its territory.

At the height of the cultural development of Rapa Nui, the most important groups installed enormous cylinders of red pumice, the pukao, on the heads of 58 of the 164 moai that were erected at some time or other on an ahu. These pukao represented the bow that the ariki made with his long hair, stained with red earth (*kiea*), the sacred colour.

16.7 THE CRISIS

About 1500, with a population that could well have been approaching ten thousand inhabitants, over-exploitation of the fragile ecosystem of Rapa Nui brought matters to a critical state.

The unique response to the need for productive lands, under the environmentally critical conditions arrived at by the cutting and grazing agricultural techniques that impoverished the sustaining capacity of the land, was compulsive insistence on the cult of the ancestors.

The social order of a thousand years was not able to adapt to new circumstances. The necessary technical solutions were not available, and nor was there the possibility of reducing demographic pressure by means of massive migration. The Rapanui society could only turn to the mana of its ancestors. But this was also exhausted, like the island.

The search for a new equilibrium was very painful. War and destruction of the megalithic monuments were the most dramatic consequences. It is possible that the known legend of the "Long Ears" (*hanau eepe*) and the "Short Ears" (*hanau momoko*) is related to the conflict between the aristocracy, where ears were extended as a symbol of rank, and the lower class, which ended with the extermination of the aristocracy. The interpretation that these were two different races that arrived in successive migrations does not have any substantiation from archaeological evidence.

When one group vanquished another they plundered and killed, and also destroyed the moai that had protected that territory, trying to break the necks of the statues as they were toppled over, and removing their eyes.

This was the time of glory for the warriors, the matatoa, who passed from a secondary position to a dominant one. Even though the royal family managed to avoid getting involved in the conflicts, protected by the inviolable lands at Anakena, the situation of the clans in the interior of the island changed radically.

Hunger was the origin of these cruel wars, reactivated by the need for vengeance. At one point the island was divided between two large confederations: *Ko Tu'u Aro* to the west, and *Ko Hotu Iti* to the East. The weapon characteristic of the time was the deadly *Mata'a*, a hand-held mace or projectile, made out of obsidian.

Agriculture was devastated and a lack of boats limited fishing; under these conditions subsistence reached critical levels. The situation got so desperate that battles had as their principal object the hunting of human victims – it was the time of cannibalism.

Archaeological data for this period show intensified gathering of small molluscs; the extensive use of caves (*ana kionga*) as refuge sites from the fighting; the re-modelling, disguising or re-use of the ahu as ossuaries, with special chambers for the bones of the members of the lineage; the construction of cultivation terraces in protected spaces, such as the interior of the volcano Rano Kau; the construction of circular stone walls (*manavai*), both above and below ground to protect plants from wind and to conserve soil moisture; and the construction of hen houses in stone (*hare moa*) – fortresses to protect the hens from being stolen.

The most obvious sign of this era is the abandonment of megalithism as an expression of the millennium-old socio-political and religious order.

16.8 THE NEW CULT

On leaving megalithism behind and with the resulting relief from pressure on the production resources, the hierarchy of the Ariki gives place to a temporary leadership, chosen from among the warrior chieftains of the main clans. This occurs through a cult centered on the magic of fertility and the rites of the first fruits: the god of creation *Make Make* and the ceremony of the bird-man, *Tangata Manu*.

The ritual, which before the wars had been held periodically at the ahu of each lineage, was now carried out at the ceremonial centre of Orongo, on the top edge of the Rano Kau volcano at the southern tip of the Island.

The centre – of a style unique on the island – comprises 53 elliptical houses. These have walls made with basalt slabs and are covered by a false vault of larger slabs. They are ranged linearly along the slope that looks onto the islets of Motu Kao Kao, Motu Iti and Motu Nui.

Each spring, for about three centuries, all the people on the island gathered there for the big feast of the election of the politico-religious leader, the *Tangata Manu*. The

Figure 16.3 Orongo. View of three motu.

election was carried out through a ritual competition for the egg of the *manutara*, the sooty tern (*Sterna fuscata*), that used to nest on Motu Nui, about one kilometre off the cliff at Orongo.

The youths chosen from each participating group had to swim to that islet, helped by a floater of totora reeds, *pora*, and wait there until the birds laid their eggs. The first one to return with one of the eggs gave the chief of his group the honour of being invested as Tangata Manu.

The new Tangata Manu, incarnating the divine power, was shaved and painted with red and black colours, and received the ceremonial double paddle, *ao*, representing power. In a triumphal procession, he came down to Mataveri and from there he was led to his site of seclusion for the next six months, as he was tapu. The site was either Anakena, if he belonged to the clans of the west, or Rano Raraku, if he belonged to those of the east. His clan gained several privileges for that year, including exploitation of their traditional enemies. The last Tangata Manu was chosen in 1867.

At Orongo, hundreds of images of the Tangata Manu and of Make Make have been carved on the basalt boulders of the ceremonial site. Paintings of the Manutara can be found in the nearby cave of Ana Kai Tangata, where the men who participated in the competition ate, or where the victims were eaten.

In spite of the drastic change from the previous order and notwithstanding the particularly cruel process, the strength and continuity of Rapanui culture can be appreciated by the fact that the direct descendants of Hotu Matu'a kept their prestige. This is well expressed in the moai called Hoa Haka Nana Ia, the "wave breaker," that

Figure 16.4

The cave of Ana Kai Tangata.

Figure 16.5 Rock paintings in Ana Kai Tangata.

Figure 16.6 Birdman petroglyph.

used to stand in Orongo. This moai, of classic style but carved in basalt, clearly shows the transition to the new order. Its back is decorated with bas-reliefs representing the ao, Tangata Manu and vulva signs symbolizing fertility, *komari*. The moai was in Orongo until 1868, when it was taken to the British Museum, where it now stands.

16.9 CONTACT WITH EUROPE

On 5 April 1722 – Easter Sunday – Roggeveen introduced yet another factor, the influence of Europe, to the complex socio-economic situation on the island.

At first, the contacts were few and brief, in the spirit of the great explorers of the eighteenth century such as Cook and La Pérouse. But the nineteenth century brought with it the worse aspects of western civilization, in the form of colonial exploitation. By 1877, the slave trade, combined with accidentally introduced plagues, had reduced the population to a low of 111.

In 1864, the first Christian missionary, brother Eugene Eyraud, arrived on the island. He was the first to describe the wooden tablets with hieroglyphic script: the *rongo rongo*. Only 28 wooden pieces with rongo rongo script are left in the whole world, divided between various museums and private collections. Not one of them remains on the island.

To date, their origin and significance continues to be one of the mysteries of Easter Island. Experts agree that it is a pictographic script which only a few initiates could follow and intended to guide the recitation of texts. According to tradition, the tablets came to the island with Hotu Matu'a, but some experts consider that these tablets were created after the contact with European culture.

Neither of these hypotheses seems likely. There is no record of this type of script in either Polynesia or the Americas. That something so complex could have developed during that critical period in the history of the island does not appear probable. Furthermore, at that time – after the discovery by European explorers – those that possibly had the ability no longer had the prestige or the support from the religious aristocracy. It is more likely that by the time the Europeans arrived the meaning of the rongo rongo script was only partly known through mechanical repetition. The clues to their meaning have been lost forever with the loss of the native experts.

The island was incorporated by Chile on 9 September 1888. During most of the last century, it was still as isolated as before, but inevitably affected by a distant and foreign world. The opening to the outside world brought material advances and new perspectives to the Rapanui people, but also deterioration of their culture, just as there was deterioration of their monuments.

Yet the islanders are very concerned about saving their cultural heritage – monuments, old traditions and language – as images of a glorious past, and also as symbols of their present identity.

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RESUMEN

El presente trabajo intenta explicar en parte el 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 módelo antropo-ecológico, con el objeto de acercarse al espectacular proceso histórico cultural en condiciones tan especiales, pero que tiene muchos ingredientes reconocibles en el início de las civilizaciones neolíticas de diferentes tiempos y lugares.

RESUME

Le présent article tente d'expliquer en partie le mystère de Rapa Nui en s'appuyant sur les résultats des recherches archéologiques les plus récentes et sur des sources de documentation.
Les témoignages sont analysés d'un point de vue anthropo-écologique dans le but de comprendre le formidable processus historico-culturel qui s'est déroulé dans des conditions exceptionnelles. Ce processus a toutefois beaucoup de points communs avec les débuts des civilisations néolithiques qui se sont développées ailleurs et dans d'autres temps.

KURZFASSUNG

Die vorliegende Arbeit versucht, einen Beitrag zur Klärung des Geheimnisses von Rapa Nui zu liefern. Sie gründet sich auf Ergebnisse der jüngsten archäologischen Forschung und auf schriftliche Quellen.
Die Befunde werden aus anthropo-ökologischer Sicht analysiert, um ein besseres Verständnis des großartigen kulturhistorischen Prozesses zu ermöglichen, der unter solch einzigartigen Bedingungen ablaufen konnte. Anderseits läßt die Entwicklung auf Rapa Nui viele Parallelen zu den Anfängen anderer neolithischer Zivilisationen erkennen.

GEOLOGICAL OUTLINE OF EASTER ISLAND AND PETROGRAPHICO-STRUCTURAL FEATURES OF ITS LITHIC MONUMENTS

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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 – *moai, pukao* and *ahu* – 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.

17.1 INTRODUCTION

Easter Island is the summit of a submarine volcanic complex which is located 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, rising to 506 metres above sea level, covers the northern and central part of the island; Poike stands at the eastern corner and Rano Kao is located at the southwestern corner (Figure 17.1).

The island measures about 22 by 11 km; covers an area of 166 km^2; and is located on the Nazca Plate, 4000 km west from the coast of Chile.

A geological map of the island at 1:100 000 was first published by Baker, Buckley and Holland [1] and at 1:50 000 scale by Gonzalez Ferrán and Baker [2], both in 1974. Earlier studies, mainly related to the petrography and geochemistry of the volcanic rocks, include those of Verlain [3], Tilley [4], Rosenbusch and Ossan [5], and Lacroix [6]. Some geological data were added through the studies by Chubb [7] and Bandy [8]. A more recent and complete geological study of the island was made by Baker [9].

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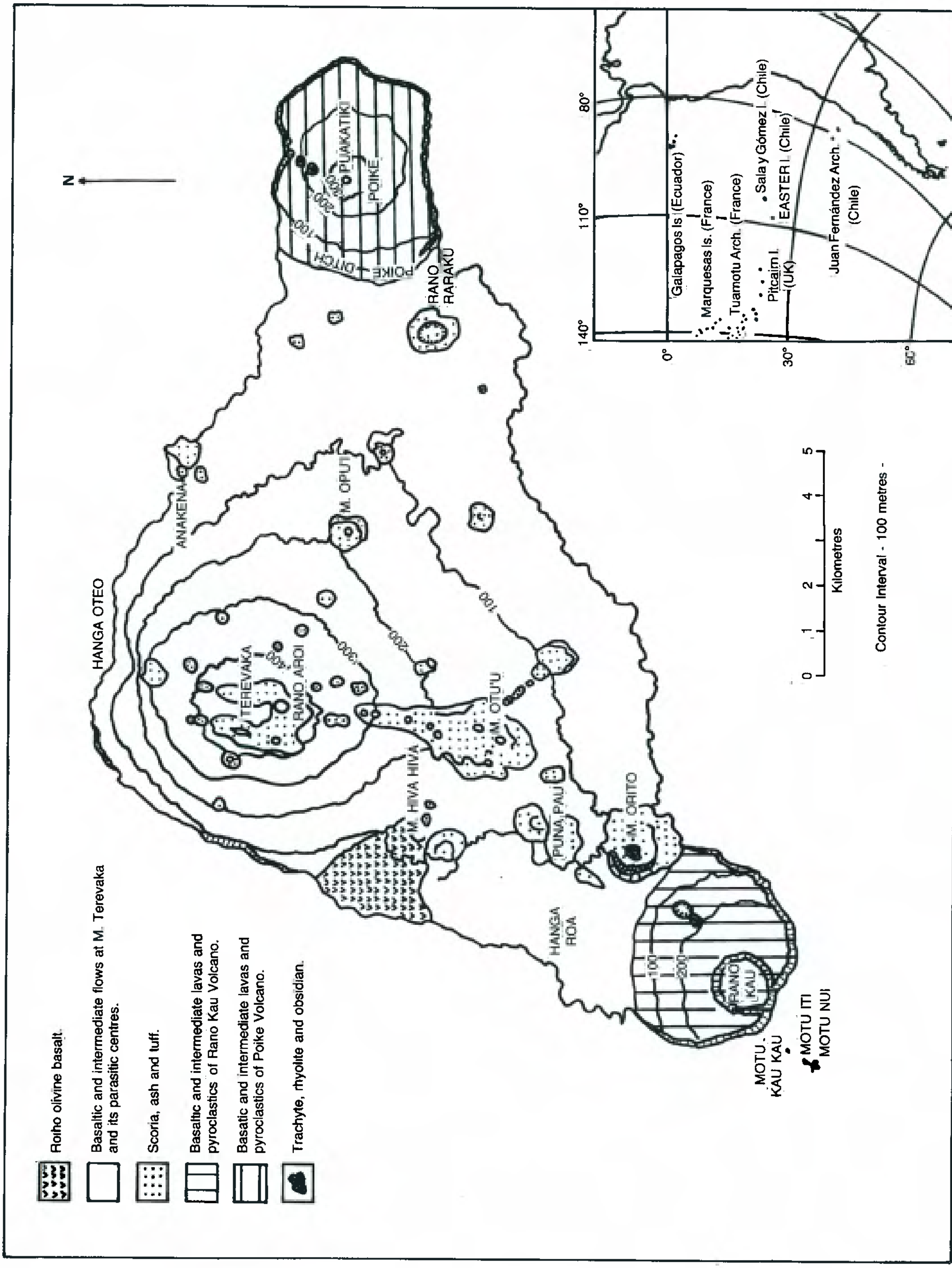

Figure 17.1 **Simplified geological sketch map of Easter Island, with insert of the South-East Pacific showing location of the island.**
(Source: Baker, 1967 [9]).

17.2 GEOLOGICAL OUTLINE

The 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 the volcanoes can be classified as belonging to shield volcanoes, scoria cones and lava domes. The volcanic topography of the island is mostly well preserved, although wave action has deeply eroded the three main volcanic slopes, forming steep sea-cliffs.

17.2.1 Terevaka volcanic group

This volcanic group covers almost 100 km^2 of Easter Island and consists of a main shield volcano forming the mid-northern part of the island, with scoria cones either scattered and isolated, or aligned in radial fissures striking N 10°E and N 60°W. The slopes of Terevaka consist of basalt and hawaiite lava flows.

According to González Ferrán and Baker [2], the main bulk formed in three stages. The oldest stage forms most of the shield volcano and is composed of basalt and hawaiite lava flows with little pyroclasts of aphiric basalt.

The middle stage is represented by porphyritic basaltic lava flows erupted from the western N 10°E summit fissure, and which flowed down to cover the western slopes of the volcano. About 14 scoria cones built up on this 2.5 km-long fissure.

The youngest stage consists of extensive lava flows that erupted from the eastern N 10°E summit fissure and flowed down, covering the northeastern slopes of the volcano.

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

The Tangaroa scoria cones that belong to the middle stage provided the material from which were cut the head-dresses, *pukao*, for the moai. This is the Puna Pau site where the outcrop consists of lapilli and bomb agglutinates and agglomerates, reddish coloured due to haematite precipitates. The quarry appears to be located in the vent pipe, surrounded by layers of tuff and agglomerates.

The youngest lava flows of the island seem to be those associated with the small Hiva Hiva scoria cones. Many lava tubes were observed and in one of them was found a cylindrical structure of about 30 to 40 cm in diameter and 5 m long, bearing tree-bark marks. Along the coastal cliff and overlaying a reddish, sandy paleosoil there is a hawaiite lava flow with 20 tree moulds and probably a turtle cast. This discovery shows that a forest – probably of palm trees – was destroyed by the eruption in relatively recent times.

17.2.2 Rano Kao Volcano

Located at the southwest corner of Easter Island, this volcano has a small caldera of 1.6 km in diameter and 250 m deep. Almost three-quarters of the volcano has been eroded by wave action, forming steep sea-cliffs that reach 300 m in height. Most of these cliffs show a succession of hawaiite and basaltic lava flows corresponding to the middle stage. A pumice-flow deposit forms a 3 to 5 m-thick layer that covers the benmorite lavas and is probably related to the caldera formation during the youngest stage.

Contemporaneously with the second-stage benmorite lava flows, three rhyolite lava domes (obsidian), were formed, deriving from a N 45°E fracture.

17.2.3 Poike Volcano

Located at the extreme eastern end of Easter Island, the Poike volcano is a typical shield volcano, rising to 365 m above sea level. The volcano ends in high sea-cliffs to the north, east and south, caused by marine erosion. The cliffs reveal numerous basalt to hawaiite lava flows. On the northeastern flank, three trachyte lava domes striking N 30°E can be seen.

17.2.4 Ages of the Volcanoes

According to Gonzalez Ferrán, Cordiani, and Halpern [10], the samples analysed from Terevaka, Rano Kao, Poike and their associated parasitic scoria cones and lava domes, all belong to the Upper Pleistocene – less than 0.47 million years before the present. It is hard to say which volcano is the oldest and which the youngest, but geological methods establish that the Terevaka volcano and its parasitic centres form the youngest volcano group. Among them, the Hiva Hiva scoria cones and related lava flows seem to be very recent, perhaps from the Holocene.

17.3 PETROGRAPHICO-STRUCTURAL FEATURES OF THE MONUMENTS

The monuments studied on Easter Island were the statues, *moai*, the head-dresses, *pukao*, and the platforms on which they stand, the *ahu* [11].

17.3.1 The moai

Almost all of the moai were carved from the Rano Raraku lapilli tuff. Most of them were cut along the tephra bedding, others were cut at an angle or perpendicularly to the bedding. The quarry shows thin horizontal to 30° dipping layers, composed of coarse, medium and fine grain sized lapilli, interbedded with coarse ash. The various pyroclastic particles (and their grain sizes) are: bombs and blocks($\varnothing > 65$ mm); coarse lapilli (65 mm $> \varnothing >$ 32 mm); medium lapilli (32 mm $> \varnothing >$ 16 mm); fine lapilli (16 mm $> \varnothing >$ 2 mm); coarse ash (2 mm $> \varnothing >$ 0.25 mm); medium ash (0.25 mm $> \varnothing$ $>$ 0.03 mm); and fine ash ($\varnothing <$ 0.03 mm). Some bombs and blocks of up to 45 cm in diameter were found. The carving tools used, the *toki*, were dense basalt fragments.

The statues exhibit different degrees of weathering. The main erosional agents seem to be the rain and, to a lesser extent, the wind. Distinct degrees of deterioration are correlated with the apparent age of the statue, structural conditions and textural features. In general terms, the youngest moai show least damage. In most cases, the statues cut along the bedding exhibit less deterioration than those cut at an angle or perpendicularly. Statues cut from tuff composed of ash with fine lapilli fragments are better preserved than those with coarse to medium lapilli.

17.3.2 The pukao

The pukao were carved from the scoria of the Puna Pau quarry, located in a volcanic pipe. The outcrops show medium to coarse, scoriaceous lapilli and spatter type bombs, which form red-coloured agglutinates and agglomerates. Lapilli are abundant and vary from 5 to 60 mm in size. In contrast, bombs can reach up to 200 mm in diameter.

The pyroclastic rock density was estimated to be about 1.5 g/cm^3, hence, the weights of the pukao vary from about 9 up to 20 tons.

17.3.3 The ahu

Most of the ahu are composed of blocks of vesicular basalt, dense basalt and brecciated-lava blocks, alone or in combination. 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 from which the wind has removed the loose material.

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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 describe la naturaleza petrográfica de los principales monumentos líticos: los moai, los pukao y los ahu. Se analiza la influencia de la orientación de corte en cantera de las estatuas con respecto a su deterioro.

RESUME

Un aperçu géologique de l'Ile de Pâques décrit brièvement les trois principaux groupes volcaniques: Terevaka, Rano Kao et Poike.
La nature pétrographique des principaux monuments lithiques – moai, pukao et ahu – est exposée. La détérioration des statues est analysée en fonction de l'influence de l'orientation de la stratification pendant le découpage des statues à partir de la carrière.

KURZFASSUNG

In einem Abriß der Geologie der Osterinsel werden die drei vulkanischen Hauptgruppen – Terevaka, Rano Kao und Poike – kurz beschrieben.
Es folgt eine Beschreibung der Petrographie der drei wichtigsten Kategorien von steinernen Monumenten, d.h. derjenigen der Moai, der Pukao und der Ahu. Die Verwitterungsschäden der Statuen werden in Bezug auf den Einfluß der Gefügeorientierung bei der Gewinnung im Bruch diskutiert.

THE RAPA NUI NATIONAL PARK: MANAGEMENT AND MAINTENANCE OF THE ARCHAEOLOGICAL HERITAGE OF EASTER ISLAND

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ABSTRACT

The historical background of the Rapa Nui National Park is briefly outlined. The present aims and objectives of the park and its management plan are described. The problems of dealing with the preservation of the archaeological heritage of the island are discussed. The need for interdisciplinary collaboration and cooperation among government agencies, research institutions, the local population and the tourist industry is stressed.

18.1 INTRODUCTION

The National Parks and Reserves of Chile were initially established on the basis of their natural characteristics: environmental biodiversity, natural resources, and specific flora and fauna. With time, the importance of cultural heritage was also recognized, and several parks and reserves were created to protect this. Rapa Nui National Park is one of these, its value being mainly based on the archaeological heritage it encompasses.

The inclusion of a given site into the National Park system assures that it will receive the support of an institution that has acquired with time extensive practical expertise in the protection and administration of sites harbouring heritage of special interest. The management agency, backed by a legislative mandate, also provides the trained personnel necessary for the functioning of the park.

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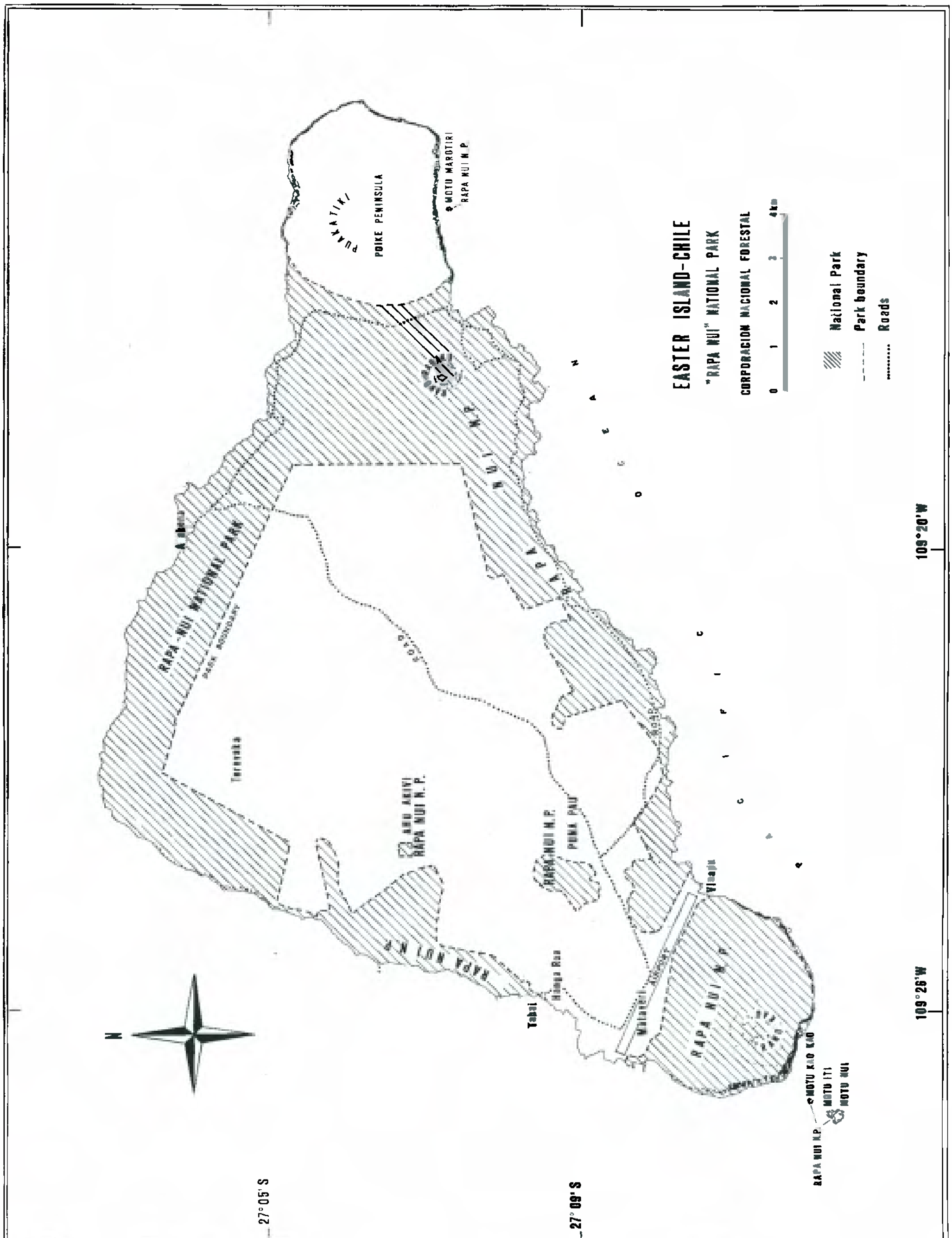

Figure 18.1 Map of Easter Island, showing park boundaries.

The Rapa Nui National Park is famous for its archaeological heritage – statues and other archaeological sites – that are set in a landscape that enhances their monumental nature. This has attracted tourism to Easter Island, tourism that over years has been increasing steadily. It is at present the main source of income for the inhabitants. It is of fundamental importance to protect this heritage from the damage that results from the circulation of large numbers of visitors.

18.2 HISTORICAL BACKGROUND

The history of the Rapa Nui National Park falls into three parts: its creation; the establishment of personnel on the island; and the formal development of management planning.

The park's creation can be traced back to 1935 when all the island was declared a National Park [1]. That same year the island was also declared an Historical Monument [2]. Both these declarations were purely formal, with no action actually taking place on Easter Island itself.

In 1966, a field management system, under the Ministry of Agriculture, was established on the island. An administrator and local personnel were in charge of the park, with initial emphasis placed on forestation of eroded areas and increasing tourism. These efforts, localized in specific sections of the island, and the fact that areas for urban development, agriculture and related public works were needed for the local inhabitants, brought about a reduction in the area of the park [3; 4; 5]. The park was divided into a Rano Kau section and a Maunga Terevaka section.

In 1972, responsibility for the management of all of Chile's national parks and reserves was assigned to the newly created Forest Service, *Corporación Nacional Forestal* (CONAF), under the Ministry of Agriculture. This enabled the development of a new focus in the management of the park, which now stressed management planning as a tool for the protection of special sites.

Following development of the first management plan, the boundaries of the park were modified in 1976 [6], as it was realized that management and protection of the archaeological heritage could not be effected unless the park was extended to include those areas with the highest concentration of monumental archaeological features. The need to include their surrounding landscape so that they could be effectively protected and appreciated was also realized. Thus most of the coastal area, small inland areas around Ahu Akivi and Puna Pau, and the small islands of Motu Nui, Motu Iti and Motu Kau Kau off the SW corner, and Motu Marotiri off the south coast of the Poike Peninsula, were included.

The present area and boundaries of the park were established in 1983 [7]. The National Park at present occupies 66.66 km^2 – approximately 42% of the total surface of the island. It is divided into five areas: the coastal section (54.03 km^2), the Rano Kau section (11.29 km^2), the Ahu Akivi section (0.09 km^2), the Puna Pau section (1.18 km^2) and the small islands (0.05 km^2 altogether), as shown in Figure 18.1.

The park contains most of the monumental archaeological heritage, but less spectacular sites and artifacts, identified during archaeological surveys carried out in the 1970s and 1980s [8; 9] have been found in the interior of the island and are not currently inside the park. This issue will have to be taken into consideration in future revisions of the park boundaries, although these sites are far less liable to deterioration as they usually pass unnoticed by visitors. At present, there are approximately 12 000 identified surface archeological features within the park, among which are the 900-plus *moai* statues and the 300 *ahu* memorial platforms.

18.3 MANAGEMENT

When the first park administration was established on the island the main interest of the government was to control erosion through a forestation programme, with eucalyptus as the main type of tree planted. Management of the existing wooded areas, control of fires and directions for fire application were also introduced. Only in the Rano Raraku area was some attention given to the interpretation, control and protection of the archaeological area.

Almost twenty years ago the concept of a management plan was developed as a means of establishing a coherent, long-term set of actions and measures, in order to achieve the conservation goals needed for the given sites with a minimum of financial and environmental cost. Management plans are drawn up by an inter-disciplinary group of specialists and have a defined time span. Thus, periodic revisions occur, which should improve the management of the sites by taking into account the changes that inevitably occur.

In 1976, the first Management Plan for the Rapa Nui National Park was implemented [10]. Its general objective was the conservation, protection and interpretation of the natural and cultural resources within its boundaries. The Management Plan is a document that contains a description and analysis of all the resources present, gives a definition of the objectives, and prescribes the norms and actions necessary to achieve these objectives.

The second Management Plan is currently [1990] being published (11). It is based on the first plan, and includes the present development needs of the local community. The aims of the plan are to be achieved through a number of management programmes:

- Conservation and management of the archaeological and historical heritage of the Rapanui culture and of Easter Island.
- Cultural identity.
- Environmental education, interpretation and recreation.
- Natural resources management.
- Protection and recovery of the native flora – both the original and that introduced during the Polynesian colonization.
- Design, construction and maintenance of civil works.

- Fire management.
- Research support.
- Tourism support.

The park is divided into four zones: intensive use, preservation, special use and extensive use. Zones of intensive use are those in which a heavy concentration of the public is allowed, as adequate facilities exist to handle it. Usually these areas are created around natural attractions such as beaches, or man-made attractions such as restored sites. Preservation zones are those to which public access is limited. In the Rapa Nui National Park it corresponds to the northwest coast, which has no roads. Special-use zones include areas for administrative facilities, and the coves used by local fishermen. The extensive-use zone covers the rest of the park.

Currently, local staff on the island consists of one park manager, one archaeologist-*cum*-conservator, seven rangers, three clerical staff and six maintenance staff.

18.4 PRESERVATION OF THE ARCHAEOLOGICAL HERITAGE

18.4.1 Outline of the problems

The task of assuring the preservation of the archaeological heritage is complex and delicate. It needs the contributions of several disciplines to establish an adequate conservation methodology and initiate long-term maintenance to ensure its future survival. The financial, material and human support is always less than that actually needed to carry out such a task. As the preservation of a site is based partially on a subjective evaluation of the way it should be presented to the public, widely differing opinions can be found. Hence, in places like Easter Island, proposals for the construction of hotels, restaurants, new roads or recreation areas can interfere with the actual preservation of a site containing archaeological heritage of a delicate nature. Even government agencies do not always take into account the problems that their activities or the establishment of new constructions can create for the preservation of the heritage on the site.

Scientists carrying out research on the island sometimes fail to consider the post-investigation conservation needs of a site and, in some instances, ignore the fact that a site can suffer irreversible damage if not properly treated. Also, in any archaeological excavation, part of the original information is inevitably lost; that is why archaeological sites should be defined as a non-renewable resource. Even when adequate conservation measures are considered, the long-term maintenance needed after completion of the investigation is not taken into account. Institutions responsible for such studies are sometimes not even willing to recognize the existence of these future costs.

The general public is attracted to archaeological sites, especially when these have been restored or reconstructed, or the studies carried out have reached a wide audience through the mass media. Thus, tourists and local inhabitants can become an additional damaging element by their mere presence and number on the site. Most damage results from the acute massive tourism brought by ships that stop at the island for a day. About eight hundred visitors, in proportion nearly one-third of the local population, can thus "invade" the island. This can only be mitigated by adequate education programmes, sensible regulations and facilities establishing safe access and circulation patterns on the site.

The park is visited yearly by 7 000 to 8 000 visitors, not counting the local population of about 3 000 which also visits these sites very often. The local inhabitants act as tourist guides without having had adequate training. They are therefore mostly in ignorance of the fragility of this heritage, and can cause severe damage to it, such as by incising worn petroglyphs for tourists to photograph. Under present legislation, no restriction or licensing system can be imposed on these self-appointed guides. Through their colourful tales, mis-information regarding the history of Rapa Nui and of Rapanui culture is kept alive among the general public.

The island is covered mainly by grasslands, and the regular burning of these to improve grazing was introduced when sheep were brought at the turn of the century. Although no sheep remain, the inhabitants continue the practice for the benefit of the few cattle on the island. These fires cause substantial damage to the archaeological heritage and the sites, requiring continuous fire control efforts.

Natural weathering factors also must be taken into account. Erosion through wind, rain, sea spray or even flooding; changes in temperature and relative humidity; forest and grassland fires; the presence of biological deterioration agents such as algae and lichens, or the circulation of cattle, can all contribute to the deterioration of the archaeological heritage.

18.4.2 Conservation strategies

The preservation of large sites needs considerable coordination and planning. This applies to attention to and control of visitors; the design of the site access and facilities; its administration; and its constant surveillance. It also implies appropriate legislation and enactment regulations covering land acquisition and use. The management must also be aware of the economic evaluation and social impact assessment of any actions on such a site. Furthermore, it needs archaeological research to provide the historical background and information, and scientific investigation of the materials and their conservation needs.

The planning and coordination of all these activities is extremely important, as the objectives and general guidelines for the preservation of the site need to be established. An evaluation of the socio-economic impact of development of the surrounding region must also be carried out [12]. If reconstruction is to be considered on a site, this will definitely turn it into a tourist attraction, and hence the deterioration pressure on the site is bound to increase.

Therefore, before any restoration or reconstruction is carried out, the increase in visitor numbers to the site needs to be taken into account. This implies forecasting the effect of increased traffic on roads and consequent possible need for their improvement or re-design, and the need for parking areas, information centres and visitor facilities, lodgings and restaurants. The amount of irreversible damage that can be done by heavy, uncontrolled circulation of visitors is well-known from experience worldwide.

18.4.3 Conservation and management programme

The Programme for the Conservation and Management of the Archaeological Heritage of the Rapa Nui National Park is coordinated with the other eight Management Programmes of the park and takes into account its zoning.

The programme has four basic objectives:

- The preservation, conservation and maintenance of archaeological, historical and architectural heritage.
- The evaluation of the archaeological and historical heritage according to its scientific, ethnological, interpretational and environmental value.
- The determination of the general problems concerning conservation, protection and management of the archaeological and historical heritage.
- The maintaining of an up-to-date record of the conservation and maintenance problems of the archaeological and historical sites.

To meet these objectives several actions have been designed, ranging from recording of sites and compilation of all previous legislation, to the re-design of roads and access points for some sites of special interest, as well as the civil engineering works needed for public circulation on fragile sites where visitors tend to concentrate.

The programme gives a set of norms to guide the activities of the park administrators and the park rangers. It also provides the guidelines for any scientific or development-related activities that might need to be carried out within the confines of the park.

The programme also establishes the personnel, equipment and infrastructure required to implement the outlined objectives.

18.5 CONCLUSIONS

Archaeological sites are fragile and their survival depends on the interaction of various factors – factors which usually bear no relation to the site's archaeological nature. These factors include, *inter alia*, the use and ownership of the land; the management of visitors who will crowd the site if it is turned into an attraction; the impact of natural weathering agents; coordination with other government agencies; the availability of long-term funding for recurrent expenses; the permanent supervision of the site; and the ability to coordinate research activities in the various relevant fields. A national park provides an effective and efficient way to integrate all of these in order to achieve a worthwhile goal: the preservation of a nation's heritage.

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RESUMEN

Se presenta un breve resumen de la creación y pasado del Parque Nacional Rapa Nui. Se describen los objetivos y metas del Parque y de su plan de gestión. Se resumen los problemas concernientes a la preservación del patrimonio arqueológico de la Isla remarcando la necesidad de colaboración interdisciplinaria y cooperación entre entidades gubernamentales, instituciones de investigación, la población local y el turismo.

RESUME

L'historique du Parc National Rapa Nui est brièvement esquissé. Les visées et objectifs actuels du Parc et son plan de gestion sont décrits. Les problèmes ayant trait à la préservation du patrimoine archéologique de l'île sont analysés. La double nécessité d'une collaboration interdisciplinaire et d'une coopération entre agences gouvernementales, instituts de recherches, population locale et tourisme est soulignée.

KURZFASSUNG

Es wird eine kurze Darstellung der Geschichte des Rapa-Nui-Nationalparks gegeben, wobei auch die derzeitigen Zielsetzungen und der Verwaltungsplan beschrieben werden. Die Probleme in Verbindung mit der Erhaltung des archäologischen Erbes der Insel werden angesprochen. Besonders wird auf die Notwendigkeit interdisziplinärer Zusammenarbeit und eines abgestimmten Vorgehens von Regierungsstellen, Forschungsinstituten und der lokalen Bevölkerung unter Einbeziehung touristischer Aspekte hingewiesen.

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

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ABSTRACT

Rock carvings (petroglyphs) on Easter Island are found on lava flows, 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 due to man. This paper discusses problems of erosion, effects of visitors to the island, and vandalism. Also of significance is the damage to petroglyphs and carved statues that resulted from various experiments and museum projects in efforts to obtain replicas for display purposes.

19.1 INTRODUCTION

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

Designs were also carved into 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 symbolic or decorative element on certain ahu, were additionally carved with designs, even though this type of relatively soft stone is a very poor surface for petroglyphs.

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Figure 19.1 Petroglyphs on the sea wall at Ahu Iho Arero, Anakena, which are beginning to be affected by lichen growth.

Figure 19.2 Lichen growth can be so extensive as to practically cover all details of a petroglyph, of which a part of one can be seen in the lower right corner of the photo.

19.2 DOCUMENTATION

Over 5 000 petroglyphs have been documented on Easter Island. They range in size from a few centimetres to 12 metres in length. Rock carvings are undoubtedly one of the more important artifacts of ancient cultures. 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 outside world [1].

Where petroglyphs have been added to statues, pukao, and the red scoria facia of ahu, we have evidence for a re-use of the sacred, because these motifs have, for the most part, been carved after the statues and pukao were thrown down in the intra-island wars that decimated the old society [2]. The designs on these surfaces are thus time-related, possibly occurring after AD 1550.

The rock art recording project began documenting the petroglyphs (and paintings) on Easter Island in 1981. As the project has spanned 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 of approximately 20 × 20 cm was placed over the rock surface. 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 being drawn, 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, or areas that were affected by foot traffic from either man or beast.

Thus, over the years, the constant re-visiting of sites revealed changes. The natural process of weathering is inexorable and continuing; it is also slow and not obviously noticeable in the short term. 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 compared with present conditions; such comparison revealed significant modifications over time.

19.3 THE PROBLEMS

19.3.1 Natural deterioration

Petroglyph panels suffer as the stone erodes through weathering, but the main cause of their deterioration is the growth of lichens. Several fine examples of petroglyphs are literally covered with them. Eventually these growths will destroy the stone and the designs upon it. The occurrence of lichens varies with the micro-environments 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 19.1 and 19.2 show lichen growth on various petroglyph panels.

Figure 19.4 A north-coast petroglyph that is rarely visited and which is in an area not frequented by livestock. The design retains its sharp edges and clear lines.

Figure 19.5 The great panel at Tongariki has been severely affected by foot traffic. This site is close to the road and receives a great number of visitors. The bas-relief pictures are visibly worn down.

Figure 19.6 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.

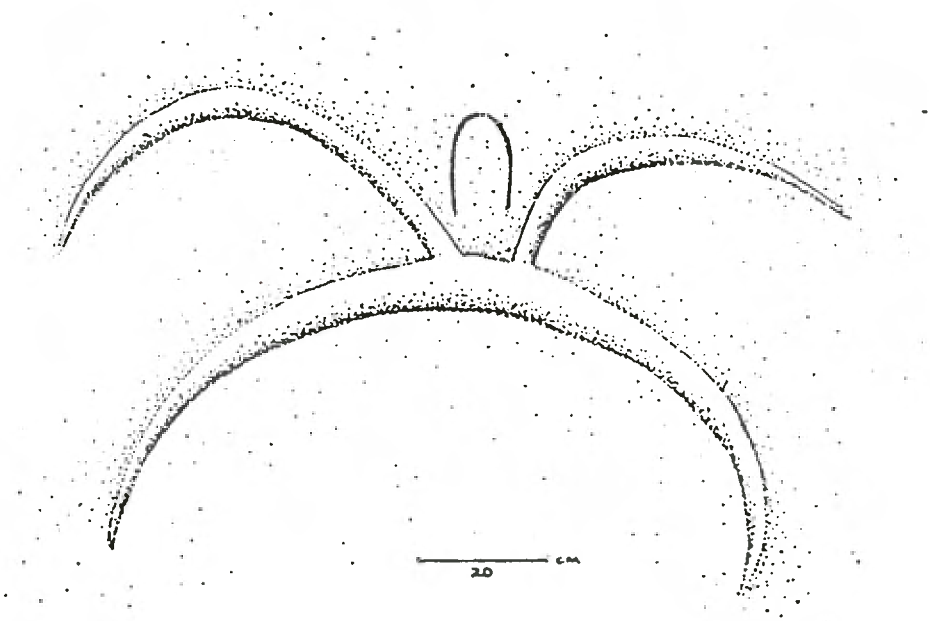

Figure 19.7 A bas-relief petroglyph has been changed in recent years by the addition of a head. This was done by the islanders scraping or scoring the incisions with stones.

Figure 19.8

One of the two moai at Rano Raraku later damaged in the process of making moulds for producing museum replicas. This view is from 1986.

Figure 19.9

The same moai as shown in Figure 19.8, but after the cast had been made. This view is from 1990.

excavations, make replicas, test various products, or conduct experiments in order to prove various theories.

Heyerdahl's excavations of statues at Rano Raraku in 1955 left them exposed to the elements, and they have deteriorated from weathering. Other damaging effects from the Heyerdahl expedition can be seen at Ahu Tepeu [9] where a portion of the magnificent sea wall collapsed because an excavation pit was not backfilled.

Experiments conducted on moai by Heyerdahl [10], who attempted to prove a theory regarding their transport, were detrimental to the statues. The statues chosen were poorly suited for testing, their bases had been altered by restoration efforts, the stone was weathered and since they were not in their original location the validity of the experiments is highly questionable. In addition, they were adversely affected by the experimental procedures, and the statue at Tongariki was left unstabilized in an upright position [11].

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. However, the making of a replica is a delicate, specialized process and must be performed 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 taking moulds from petroglyph panels at Tongariki and Vai Tara Kai Ua, a variety of substances have 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 which has seeped into the 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 copied to provide casts for an exhibition in Europe, the removal of the moulds also removed patination plus some of the stone surface from the weathered, west sides of the moai (Figures 19.8 and 19.9) [12]. Also in the quarry, another moai with a ship petroglyph on its chest was marred by attempts to take a mould. 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 [13], museum experts involved in these processes must take the responsibility of studying the problem with greater care before attempting to produce cast replicas. A beautiful replica does not justify irrevocable damage to the original work of art [14].

A test treatment was applied to a moai to evaluate the effectiveness of these chemicals for the preservation of the volcanic tuff statues. This was conducted in recent years by the Centro Nacional de Restauración, Chile, and the Wacker Chemical Company of Germany [15]. Though the treatment procedure was carefully tested in the laboratory, and adequately documented in the field, no *in situ* testing was carried out. One wonders why a highly visible, restored statue such as that at Hanga Kio'e was selected for experimental trials rather than an obscure fragment of one out of the public eye.

Some justification can be found for a carefully planned and documented test, but what should not be tolerated are casual test treatments, such as were applied in 1987 by a Hawaiian firm, International Chemical Systems. A product said to contain vinyl and acrylic resins was sprayed on volcanic tuff statue fragments at Anakena. By chance the author witnessed this application which turned the stone a blue-grey color. The fragment has been monitored photographically by the author on subsequent trips to the island. No documentation on the applied product is available, and no further studies were made. This cannot be considered a professional activity – merely vandalism.

(iv) *Vandalism*

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.

In 1991, deliberate destruction occurred of the rock art in one of the caves on the island of Motu Nui. The painting, on the ceiling of the cave, is a unique example of rock art in Oceania. It has been damaged beyond repair. At the same time, other petroglyphs on the walls of the cave were damaged and new petroglyphs carved.

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.

19.4 THE SOLUTIONS

19.4.1 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.

19.4.2 Education

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.

19.4.3 Providing guards

An excellent means of preventing damage to sites is to have someone with authority monitoring the site. However, the problems of monitoring sites on an island-wide basis are enormous, as is finding the funding to hire guards.

19.4.4 Physical restraints

The designation of petroglyph areas as marked archaeological sites will help in their preservation. Simple walls or fences around sites should keep animals and motorcycles off, and low-key signs requesting that artifacts 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 significance as it indicates that a site is special and protected [16].

19.4.5 Conservation

Undoubtedly, the technology exists to stabilize or even repair many of the basalt papa upon which carvings occur. A pilot programme to study the feasibility of stabilization should be initiated; however, any conservation treatments should first be field tested *in situ* on similar papa without petroglyphs – not on the actual artifact.

19.4.6 Graffiti removal

It is a proven fact that graffiti attract 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 ensure survival of the petroglyphs.

19.4.7 Official policy

Tighter control over requests and permits to make replicas or to do other scientific experiments should be a simple matter to implement, and damage from such 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 conservators and archaeologists; lay persons may not be aware of potential hazards to the cultural heritage.

19.4.8 Documentation

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

19.5 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 amongst the island's inhabitants must be intensified. 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 caused by heavy tourist traffic, 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 at the navel of the world.

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RESUMEN

Los petroglifos de Isla de Pascua fueron esculpidos 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. De manera significativa, gran parte de los daños han sido resultado de diversos experimentos y proyectos de museos a fin de obtener réplicas para la exposición al público.

RESUME

Les pétroglyphes de l'Ile de Pâques sont taillés sur des coulées de lave, des affleurements et blocs de basalte, du tuf volcanique et des scories rouges. Malgré les marques d'érosion et les pertes d'éléments graphiques dues aux intempéries, à la croissance de lichens et à l'effritement superficiel des roches, les dommages les plus graves sont causés par l'homme. Cet article décrit les problèmes d'érosion, l'impact des visiteurs sur l'île et les effets du vandalisme. Il est également observé que les pétroglyphes et les statues ont été sensiblement endommagés par suite d'essais divers et de projets muséologiques dans le cadre desquels on s'est efforcé de réaliser des répliques aux fins d'exposition.

KURZFASSUNG

Die Felsritzungen (Petroglyphen) der Osterinsel finden sich auf Lavagesteinen, Basaltblöcken und -aufschlüssen, vulkanischem Tuff und roten Schlackengesteinen. Neben der offensichtlichen Wirkung natürlicher Erosion und dem Verlust von Teilen der Zeichnungen unter dem Einfluß von Witterung, Flechtenbefall und einer oberflächlichen Abschuppung des Gesteins ist es vorwiegend der Mensch, der eine Bedrohung der Petroglyphen darstellt. Diese Arbeit diskutiert die Probleme von Erosion, der Einwirkung durch den Tourismus und den Vandalismus. Kennzeichnenderweise geht ein großer Teil der Schäden auf verschiedene Experimente und Museumsprojekte zurück, die der Herstellung von Kopien für Ausstellungszwecke dienten.

WEATHERING OF EASTER ISLAND TUFFS AND PROPOSED CONSERVATION TREATMENTS

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ABSTRACT

Microscopy and X-ray diffraction analysis were used to investigate 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 and solvent absorption, drying and capillarity) were measured in view of the two most important parameters for *in situ* conservation of the *moai* statues (moisture and physical characteristics of the crusts). Measurements of surface moisture on moai were made to locate the damp areas. Selection of treatment depends on these conditions. Treatments have to be developed in laboratory trials. Several products (consolidants and/or water repellents) were tested using artificial weathering to simulate meteorological conditions. The final selection was based on the results from classical tests. Some conditions for *in situ* treatment are defined.

20.1 EASTER ISLAND TUFF AND ITS WEATHERING

The deterioration of the tuff from Easter Island has already been addressed in some studies [1; 2]. These studies were complemented by the examination of twelve specimens, presumably from a broken moai, which could be divided into fine- and coarse-grained tuff. Both are quite similar, the difference being mainly in the lapilli size and concentration. The fine-grained part has few lapilli and these are about 0.5±0.2 mm long. The coarse-grained part has numerous lapilli and these can reach lengths of 20 mm.

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The water absorption characteristics of the stone can be explained on the basis of the various pores in it:

- pores in the vitreous cement, which account for approximately three-fifths of the porosity and, due to their large size, give a high imbibition speed; and
- pores in the lapilli and surrounding aureole, which account for about two-fifths of the porosity and, due to their smaller size, have a low absorption speed.

Petrographic analysis was carried out on both the deeper, unweathered part of the tuff and on its weathering crust. X-ray diffraction analysis shows the presence of smectites, even in unweathered samples, thus giving evidence for the ongoing deterioration process.

20.1.1 Unweathered rock

The samples were taken at depths of over 6 cm. Two colours of vitreous cement could be observed: light brown and dark brown glass. The areas of light brown colour show few vacuoles and these have woolly edges. The lapilli in these areas are also light brown in colour.

The dark brown areas enclose many vacuoles with well-defined edges, showing no alteration products. The lapilli in these areas are dark brown and are edged by a dark aureole probably formed at the time of the eruption or shortly thereafter [3; 4]. There is a high content of iron oxides (magnetite and goethite).

The phenoclasts are olivine – sometimes partly deteriorated into iddingsite – and plagioclase – labradorite according to the anorthite content of 50-65% – often Carlsbad-twinned. Some scarce aegirinic augites are also present. The previously reported [1] bowlingite has not been found.

The glass cementing the lapilli is clear in plain light, and the small-diameter pores have good edges.

The shape of the vacuoles varies from round or slightly flattened (about 90% of all vacuoles) to very flattened (about 10%). Some intermediate cases can also be observed. This variation in structure is due to differences in the setting temperature.

The rock could be classified as a basalt rather than a trachyandesite.

20.1.2 Weathered rock

The samples were taken from the surface, less than 2 cm in depth. They can be divided into low and high deterioration areas.

(i) *Low deterioration*

The weathering is limited to the vitreous cement bonding the lapilli, which remain unaltered. The light-brown glass turns greenish- or blueish-brown (probably zeolites). It loses its clearness and becomes almost completely opaque when observed in plain light. The weathering begins at the walls of the pores, which lose their sharpness.

(ii) *High deterioration*

In this case the lapilli are also weathered. The vitreous cement around the lapilli is very altered, changing into a cloudy or opaque mass. The pores enlarge, and some very thin walls, formed by magnetite crystals, remain.

The lapilli-containing vacuoles enlarge and anastomosis takes place due to the breaking down of the walls. In larger vacuoles, free plagioclases can be seen, sometimes bridging the vacuole. Olivine is seen increasingly transformed into iddingsite, sometimes forming perfect pseudomorphs. The dark brownish lapilli are more resistant to weathering, which begins by a localized thinning of the dark aureole.

20.1.3 Honeycomb weathering

Honeycomb weathering is fairly frequent on the south coast, where it has been found in the stone blocks used for the construction of *ahu*, such as Ahu Akahanga. There it is found on the surfaces facing the sea (southeast orientation). The cups are about 2-5 cm long and 1-3 cm deep. The basalt cobbles and boulders lying around the ahu also show honeycomb weathering on the upper face: this is true for the heavier stones, down to about 20 kg in weight. The smaller cobbles are easily turned over by man or cattle, and therefore show alteration on both sides. This type of deterioration has been previously described [5; 6]. The soluble salt concentration was found to range from 1.4 to 2.0% in these pits.

On the red top-knots, *pukao*, the particular structure of that lava leads to a curious morphology: hemispheric holes of about 5-8 cm diameter. An accidental origin of these holes seems unlikely. The holes are usually found on the vertical surfaces. They can be observed on pukao that have fallen and where the original vertical surface is now a horizontal one (e.g., pukao 568, 555 or the half-buried 554 at Ahu Aka Hanga).

In the cases of pukao which remained resting on their base after the toppling over of the moai, two lines of holes can be seen, one formed in the original orientation and the second forming in the present orientation. This is the case for pukao 601 at Ahu Poukura, the westward great holes were formed originally, while on the eastward, sea-facing side, small holes are currently developing. This can be used as an indication of the original orientation of the pukao. Similar observations hold for pukao 556, 561 and 554 at Ahu Aka Hanga. At Tongariki, the site that was affected by the 1960 tsunami, the ahu and its thirty statues were scattered around. Therefore the statues have had three positions: the original erect on the ahu, the toppled over on their face, and then the overturning by the tsunami. The white silica varnish that formed on the eye holes is decaying on the statues that now face the sea, and the morphological development of this deterioration is similar to the early phases of honeycomb deterioration on a calcin hardened limestone.

20.1.4 Surface crusts

At Rano Raraku, in the rock alcove where moai 230 was being carved, the whole wall is covered with small yellowish or reddish crusts. These are about 2 mm in diameter and separate very easily from the underlying rock which is usually damp and covered with greenish algae. These crusts contain about 2% silica and 14.6% soluble salts. This morphology and chemical composition is similar to that of crusts found on calcin-covered limestones in La Rochelle, France, which appear to be in the early stages of honeycomb formation.

These siliceous crusts form due to the seepage of rainwater through the porous structure of the stone. In a second stage, the crusts break up due to the presence of soluble salts. The amount of damage induced by soluble salts is dependent on their concentration and the area where crystallization occurs relative to the height above ground level on the vertical, half-buried moai.

20.2 WATER TRANSPORT

20.2.1 Drying curves

The evaporation rate of samples wetted to different degrees was assessed under laboratory conditions. Five samples were brought back from Easter Island. There were three fine-grained and two coarse-grained samples, and they were wet from two days of rain on Easter Island. The samples were carried back in closed polyethylene containers, and were dried in the laboratory at 25°C and 50% RH. It was observed that the evaporation rate changed as a function of the relative water content, $((\boldsymbol{S}_w\ \boldsymbol{S}_d) / \boldsymbol{S}_d) \times 100$, i.e., the percentage of water left in the sample. The data are given in Table 20.1.

Table 20.1 Evaporation rate ($g/m^2.h$) as a function of relative water content (%) for fine- and coarse-grained samples of Easter Island tuff

Water content %	Evaporation rate ($g/m^2.h$)				
	Fine-grained			Coarse-grained	
	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

Two of the above specimens, one fine-grained and one coarse-grained, were saturated with distilled water – the fine-grained one by applying a standardized water-pipe [7] to the surface of the sample, keeping it in a moisture-saturated atmosphere and letting water soak into it until the sample reached constant weight. The coarse-grained specimen was first wetted through capillary rise and then saturated by submerging it totally in water for six months. The samples were then dried at 20°C and 60% RH. The drying curves for these samples were similar regardless of how the samples were saturated with water. It was noticed that coarse-grained specimens gave more dispersed data for the evaporation rate than the fine-grained specimens. The dispersion of data is larger than can be accounted for from temperature and RH variations during the drying process.

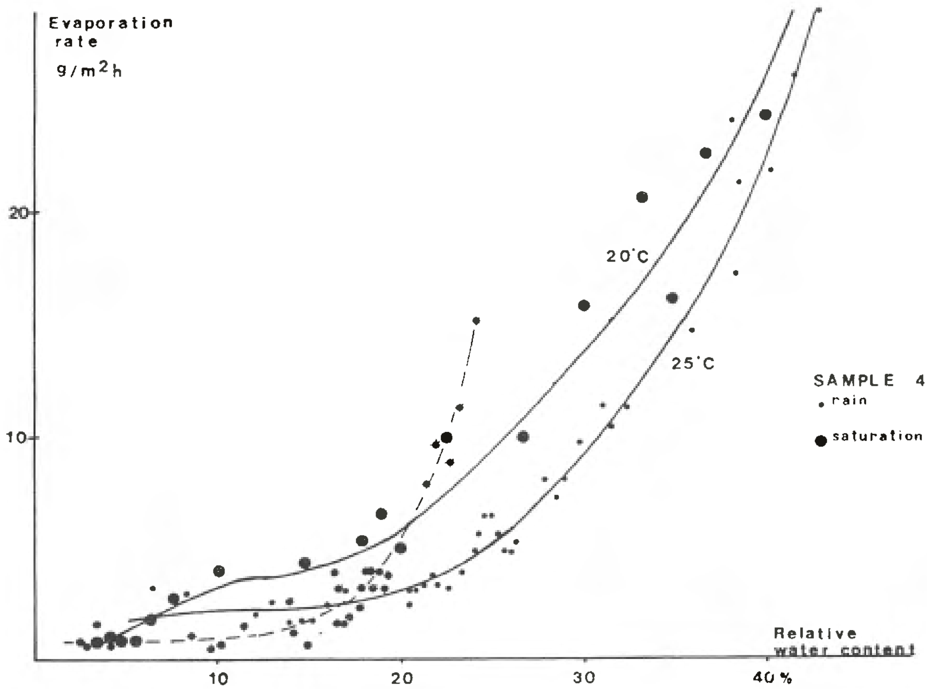

Figure 20.1 Comparative drying curves for a coarse-grained sample (N° 4) wetted first by rain and, in a second experiment, by saturation. Also included is the drying curve for a fine-grained sample (N° 1) wetted by rain.

Evaporation curves from the rain-wetted specimen and from the same specimen saturated with distilled water in the laboratory are given in Figure 20.1.

The differences in evaporation rate can explained as a function of the location of the water within the sample. For short-term wettings, such as occurs during rainfall or at the beginning of the capillary rise, water fills mainly the pores in the vitreous matrix. This water evaporates quickly when the water content is higher than a critical value. When the sample is thoroughly saturated, water fills both the vitreous matrix pores and those in the lapilli and surrounding aureoles. Upon drying, the water from the matrix evaporates first, while the water in the lapilli diffuses in an irregular manner through the matrix before evaporating. This can be attributed to the retention of water by the clays surrounding the lapilli and explains the erratic nature of the data observed.

20.2.2 Surface moisture

The surface moisture of the samples was measured during the drying cycles by means of two different two-point moisture gauges. These gauges (a *Protimeter Humitest SM 13-28* and a *Protimeter Architectonic D5785*) were chosen as being suitable for the rough surface of the samples in question. Apart from the samples used for the drying curves, a flat sample of unweathered tuff, 7 mm thick and with an area of 40 cm, and which had been treated with a biocide in order to eliminate algae, was used as reference. These measurements permitted the calibration of the meters so that *in situ* readings could be converted to relative water content.

Different readings were obtained, depending on whether or not the specimen had a moderate growth of algae on the surface. The presence of such biological growth produced higher readings with the meters. The specimens with biological growth changed colour as they dried: the surface was black when the stone had a water content above 90%. It then changed to grey, and finally to yellow when the water content fell below 60%. Also to be noted is that siliceous crusts on specimens gave "dry" readings except when the measurements were taken immediately after very heavy rain.

It was seen that the water tends to accumulate in the lower part of the samples. This cannot be attributed to heterogeneity as when the drying was repeated a second time with the sample inverted, the same effect was observed.

The surface moisture readings of saturated and rain-wetted specimens correlated well to the values for the drying curves. It was seen that for samples with approximately 20% water content, those that had been wetted by rain gave higher readings than those that had been saturated with water. This confirms that rainwater tends to remain only in the pores of the glassy matrix, while during the drying of saturated samples, the water is diffusing out of the pores in the lapilli and the surrounding aureole into those of the glassy matrix.

20.2.3 Capillary rise

The capillary rise was measured on samples that were in hygroscopic equilibrium at 25°C and 50% RH. The value for the 30-minute capillary absorption coefficient was 285 $g/dm^2h^{0.5}$, while after 48 hours this coefficient had decreased to 35.5 $g/dm^2h^{0.5}$. A tuff with about 40% porosity has about a quarter of it filled with hygroscopic water; half of it will be filled in less than an hour, while total saturation takes a very long time.

It was observed that the ascending water front was not uniform. The water rose faster in the glassy matrix than in areas with lapilli. These could take one to two hours longer to wet than the glassy matrix.

In situ moai will therefore have a 25% void volume filled with moisture, and this moisture is equivalent to 7% in weight, while values of 60% to 80% of relative water content can be expected after heavy rains. Buried statues, or areas of those that become watertight through the formation of siliceous crusts, can exceed 80% water content and reach saturation.

20.2.4 Water migration

In order to study the migration of water, de-ionized water was sprayed on the surface of a sample at regular intervals (5 sprayings over 20 hours). The sample was weighed periodically and the surface moisture measured at nine different points. The first measurements to establish the drying curve were started 30 seconds after the spraying.

It was seen that little water is needed to saturate the surface, and that the evaporation rate is slow. Fifteen hours after the last spraying the relative water content was 47% according to the meter.

For a given amount of water (e.g., 0.5 l/m^2), as measured by weighing, the readings obtained with the moisture meters during the first drying curve were totally different from those obtained during the last drying curve. In the first case, the surface moisture reading gave a 73% relative water content, while for the last curve, there having been time for the water to migrate to the interior of the sample, the surface moisture reading corresponded to a 54% relative water content.

20.2.5 Water absorption under pressure

To be able to measure the absorption capacity and the water content of both superficial crusts and underlying stone, the water-pipe method was used [7]. The maximum pressure exerted by the water column corresponds to the dynamic pressure created by a 140 km/h wind. This wind velocity is not unusual and therefore allows an evaluation of the water absorption of moai during driving rain.

This is an appropriate method to evaluate the degree of weathering or the efficiency of applied treatments.

The kinetics of the absorption process depends on the pore structure of the stone, its surface state and its nature. The absorption pattern is typical of that for a diffusion process [7; 8], but when modifications are introduced, as in the case of hydrophobization treatments, absorption tends to follow a logarithmic pattern [9].

The water absorption coefficient, $\boldsymbol{B}$ (in $cm^3/cm^2.min^{0.5}$) of most stones, as measured with the pipe method, remains constant regardless the number of times the pipe is filled with water. However, in the case of the tuff, it was found that $\boldsymbol{B}$ increased to a maximum until the relative water content of the stone was about 28%. Then the coefficient decreased as the relative water content increased. This change in $\boldsymbol{B}$ can be explained by the two different pore systems in the stone. As long as the relative water content is below 28%, $\boldsymbol{B}$ increases because an important part of the water diffuses only into the pores of the glassy matrix. After these are saturated the water diffuses from the glassy matrix, through the surrounding aureole and fills the pores in the lapilli.

For the period during which $\boldsymbol{B}$ increased, the water absorption, $\boldsymbol{D}$, (in cm^3/cm^2) could be seen to follow a logarithmic law:

$$\boldsymbol{D} = \boldsymbol{D}_1 . t^a, \text{ or } \log_{10}\boldsymbol{D} = \log_{10}\boldsymbol{D}_1 + a.\log_{10}t.$$

However, after the sixth test, approximately a fortnight after the start of the experiment, the coefficient did not show that maximum, but decreased as the relative water content increased. This confirmed our earlier findings that the water from the pores of the glassy matrix evaporated faster than that retained in the pores of the lapilli.

It is interesting to note that the swelling of the clays occurred after about two weeks from the first humidification of the stone and that the relative water content of 28% was nearly the critical water content as defined by Vos [10].

The water absorption curves obtained for a dry stone, for a barely moist stone, and for one with a relative water content above 40% are shown in Figure 20.2.

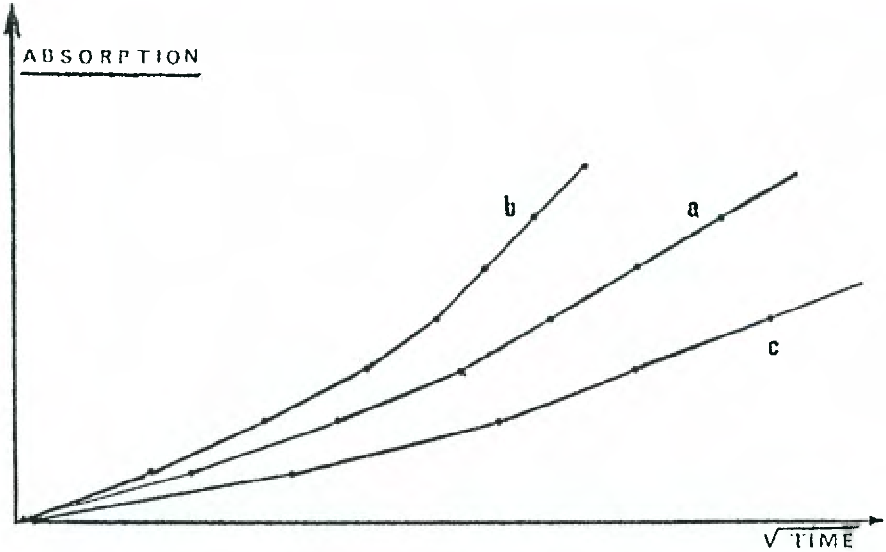

Figure 20.2 Water absorption curves for a tuff sample with different amounts of moisture: (a) dry, i.e., in hygroscopic equilibrium; (b) damp, i.e., water content about 30%; and (c) wet, i.e., water content above 40%.

20.2.6 Hygroscopicity

The variation in weight of a 3 kg basalt boulder from Easter Island under measured thermo-hygrometric conditions (between 18° and 29°C, and between 45 and 91% RH) was followed for three months. It was found that the most frequent variations were in the 0.1 to 0.4 $g/m^2h^{0.5}$ range, reaching 1 to 2 $g/m^2h^{0.5}$ in the case of high RH variations. The total variation of hygroscopicity was about 40 g/m^2, similar to that found for French limestones and sandstones containing about 1 to 5% soluble salts. It is interesting to note that the hygroscopicity values are similar, even though the porosity of the Easter Island basalt, less than 1%, is much smaller than that of the French stones.

The variations in weight of the five Easter Island tuff samples were also monitored for three months. Regardless of the type of tuff, coarse- or fine-grained, a good correlation was observed between the variations in weight and the temperature. The variations were proportional to about 1 to 2% of the total porosity of the stone. If the sample is not uniformly dry, the variations can reach up to 4 $g/m^2h^{0.5}$. If this is extrapolated for a moai, the weight variations could be of the order of 3 to 10 kg.

20.3 *IN SITU* MEASUREMENTS

These measurements should be considered in combination with the climatological data for Easter Island presented as Appendix A of this paper.

20.3.1 Surface Moisture

The measured surface moisture readings were converted into relative water content on the basis of the calibration curves obtained during the drying cycles of the laboratory samples (Section 20.2.2 above).

It was observed that the relative water content is high (about 85 to 100%) in areas above cement mortars, such as the lower part of the statue or the lower part of the head where these have been put back in place with cement mortar. The stone immediately under the mortar is drier (about 35% relative water content). Figure 20.3 shows measurements carried out before and on consecutive days after a two-day rain period. After heavy, driving rain the surface moisture reaches 80 to 90%, or even 100%. After the rain the surfaces directly exposed to the sun dry quickly, but the others remain wet and their rate of drying is similar to that observed in the laboratory.

The moai at Hanga Kio'e showed a residual moisture greater than the hygroscopic content and it always has an area where moisture accumulates, in the region 30 to 40 cm above the base of the statue.

The ground in which some of the moai are half buried probably acts as an impermeable barrier. For example, moai 272, which is half buried in a vertical position in the SW sector of the Rano Raraku site, is fairly typical. This moai has, from ground level up to 40 cm high above ground level, a clay-like crust, 10 mm thick. This crust tends to swell and fall off. The middle part of the statue, immediately above the area with the crust, already shows signs of some deterioration by the presence of reddish clay-like areas among the beds of lapilli, while the top part shows beds of lapilli and some crusts. These observations apply to the north-north-west orientation. To the south, siliceous crusts have formed under the chin and other projections, with lichens down to 1 m from the ground. The west and south-west sides show lichens except in the protected areas: eye-holes, nostrils and under the chin.

Before any treatment is considered, the movement of water within a moai – and the actual source of that water, whether capillary rise from the ground, descending humidity and infiltration from rains, or both, and in what proportions at what times – needs to be established.

20.3.2 Water Absorption

In situ water absorption measurements were carried out on various moai by means of the water-pipe method [7]. It was observed that fine-grained tuffs followed the general capillarity absorption pattern ($\boldsymbol{D} = \boldsymbol{B}.t^{0.5}$). On the other hand, coarse-grained tuffs with lapilli of about 1 cm in length tended mainly to follow a logarithmic curve ($\boldsymbol{D} = \boldsymbol{D}_1.t^{a}$). The data gathered on different days on moai 103 at Ahu Naunau, (see Figure 20.3), are summarized in Table 20.2.

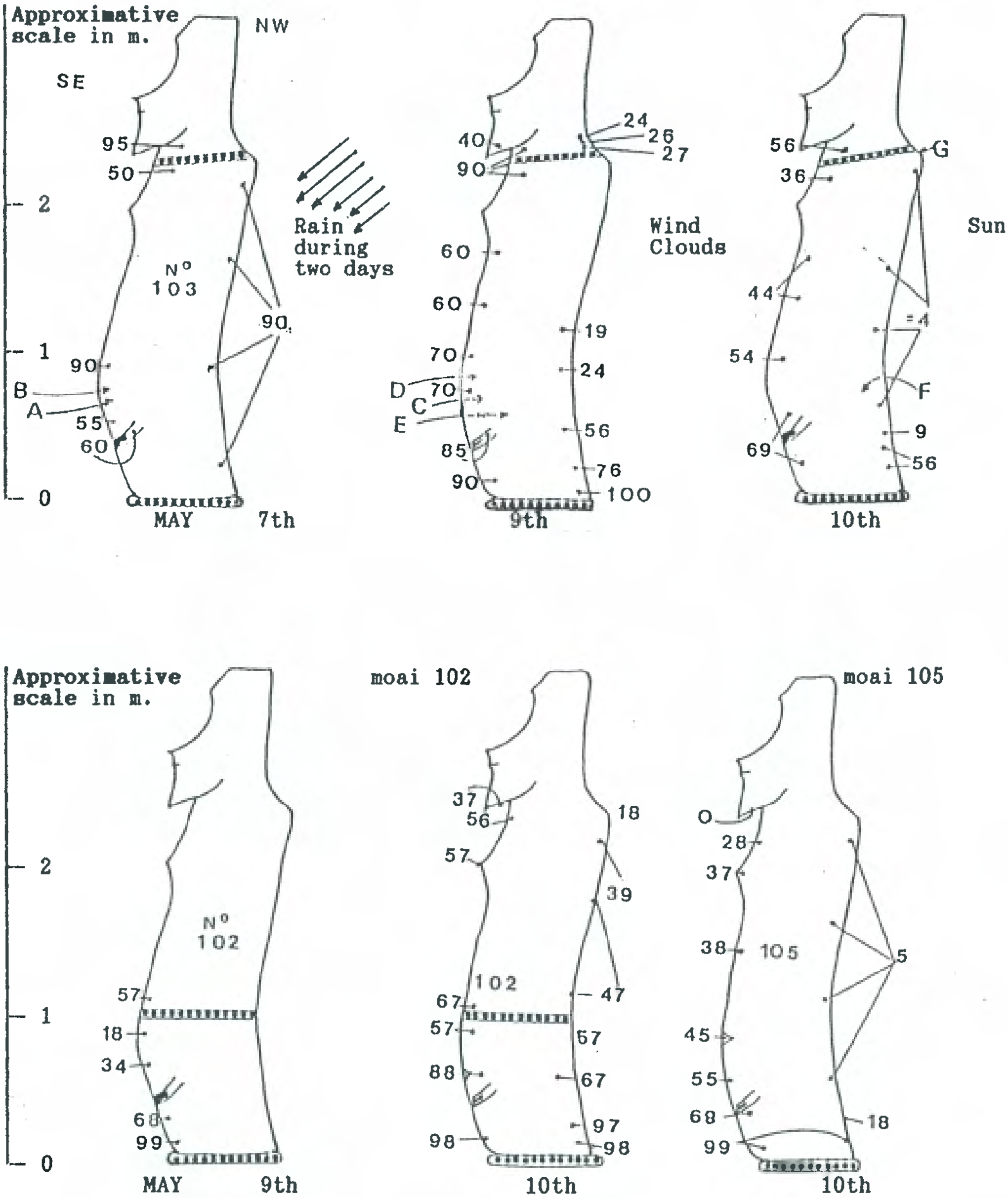

Figure 20.3 Relative water contents, from surface moisture measurements on successive days, in different moai at Ahu Naunau, Anakena.

Table 20.2 **Absorption curves for various points on moai 103, Ahu Naunau, on different days** (see Figure 20.3 for location of points of measurement)

Date	Point	Form of curve	Comments
May 7	A	$D = 0.8 \times t^{0.5}$	yellow, watertight area
May 7	B	$D = 2.65 \times t^{1.02}$	non-watertight area
May 9	C	$D = 0.16 \times t^{1.16}$ for $0<t<21$ minutes $D = 0.016 \times t^{1.70}$ for $21<t<30$ minutes	yellow area
May 9	D	$D = 0.56 \times t^{1.044}$	clay-coated lapilli
May 9	E	No water absorption after 36 min	white, watertight crust
May 10	G	$D = 0.25 \times t^{0.99}$	weathered area
May 10	F	$D = 1.15 \times t^{0.50}$ for $0<t<24$ minutes $D = 0.75 \times t^{0.90}$ for $24<t<70$ minutes	north-facing, eroded area

The absorption data obtained by Domaslowski [2] was also analysed, and it was found that most of curves were logarithmic of the form $D = D_1 \times t^a$. Within those data, three distinct patterns could be observed: for unweathered stone ($a>0.98$); for weathered, impervious stone ($0.6<a<0.8$); and an intermediate state ($0.8<a<0.98$). The absorption of white spirit was twelve times as great as that of water. The data comparing water and white spirit absorption are summarized in Table 20.3.

Table 20.3 **Comparison of the absorption of water and white spirit at different heights on statues** (data from Domaslowski [2])

Region measured	Absorption		Ratio	WS/Water
	Water	White spirit	D_1	*a*
Top	$0.44 \times t^{0.69}$	$0.94 \times t^{1.30}$ (1st phase) $2.1 \times t^{0.75}$ (2nd phase)	2	2
Middle	$0.34 \times t^{0.78}$	$3.4 \times t^{1}$	10	1.3
Bottom	$0.06 \times t^{0.81}$	$0.8 \times t^{0.81}$	12.3	1

The change in absorption can be explained as a function of the water content of the statue: the water tends to collect at the bottom, as already mentioned in Section 20.2.2. Hence water is not absorbed as fast at the bottom as at the top. The absorption curve for the bottom is similar to that of samples that had reached their critical water content (see Section 20.2.5).

20.4 PROTECTIVE TREATMENTS

20.4.1 General Observations

The choice of the resin or other impregnation material, the solvent and the application concentration has to take into account a number of facts.

- Heterogeneity of the stone can lead to an uneven treatment.

- The high water content (about 25%) and the low drying velocity require solvents capable of displacing the water, or that at least are not hindered in their penetration by the presence of water.
- The local high mean temperatures and high wind velocities (see Appendix 20-A of this paper) do not allow the use of volatile solvents.
- The low permeability of the surface crusts on the moai determines the choice of solvents.
- The low mechanical strength of this type of stone, even in its sound state, requires the use of pliable resins.
- Due to the depth of alteration of the stone, the treatment has to be carried out through successive applications.
- The key factor in the mechanism of deterioration of the stone – the breaking down of the glass matrix, the movement of the solubilized silica, and to a lesser degree the crystallization of salts contributed by marine spray – is water. Hence a water-repellent treatment is necessary, in addition to any consolidation treatment considered.

20.4.2 Treatment Evaluation

The treatments were evaluated by the following tests:

- water-drop absorption: time to absorb twenty, 0.05 ml drops;
- water absorption using the water-pipe technique: change in the absorption coefficient $\boldsymbol{B}$ before and after treatment, expressed as an improvement index $\boldsymbol{I}$, where $\boldsymbol{I} = \boldsymbol{B}_{\text{before}} / \boldsymbol{B}_{\text{after}}$;
- water vapour permeability: difference between before and after treatment;
- score width test: because of the heterogeneity of the tuff samples, the results need careful statistical analysis to be useful; and
- abrasion resistance test: measurement of the length of the imprint every 5 or 10 turns is needed. The type of erosion induced has also to be noted. In some cases the test needs to extend past the standard 75 turns.

20.4.3 Choice of formulations

From preliminary studies and tests carried out, some of which are briefly summarized in Appendix 20-B, a number of conclusions could be drawn:

- the solvent has to have low volatility, with high solubility for the chosen resin; and
- to obtain a homogeneous treatment, the hydrorepellent has to be added together with the consolidant.

For testing on Easter Island tuff samples and for the artificial weathering tests the following formulations were chosen:

- *Wacker H* (WH);
- urethane oil at 16% concentration (UO16) in white spirit;

- a mixture of urethane oil and methyl silicone (*Rhône Poulenc 4518*) in white spirit (UO16+4);
- *Paraloid B-72* (B72) dissolved in white spirit; and
- *Acryloid A21LV* (A21) at a 5.6% concentration in a mixture of ethyl and isopropyl acetates.

The samples on Easter Island were treated through their weathering crusts, and after eliminating any biological growth with a biocide (0.2 l/m^2 of a *Fongivore* solution).

As it was found that four successive applications of a given product were the minimum to produce a satisfactory impregnation, the test samples were treated by five successive applications, without letting the sample dry between applications.

20.4.4 Artificial Ageing

The cycle followed was that of Auger [11], and consisted of holding the temperature at 40°C, the RH at 30%, and daily spraying of the sample not only with 20 ml of seawater (about 0.6 g of salts), but also with 20 ml of distilled water to wash away the loosening debris from the samples.

Changes in the samples were monitored by visual observation, photography, weighing and measurements of sound velocity. These last measurements had only relative value as they were carried out on non-geometrical sample shapes and through the weathered, treated surfaces.

20.4.5 Results

The depth of penetration and the water vapour permeability data for some of the products tested on Easter Island tuff samples are reported in Table 20.4.

The poor penetration of the A21 resin, and the fact that it tends to varnish the surface after the second or third application, does not recommend it for treatments. The B72 resin does not provide good water repellency, even though the surface hardening, as measured by the score width, is fairly good, regardless of how many applications are made. On the other hand, the abrasion resistance clearly improves after the fourth application and remains constant for up to ten applications.

The results of the score width test for samples treated with some of the products tested are plotted in Figure 20.4. It is interesting to note that the products tested harden the weathered surface, reducing the score width, but except for urethane oil, this is still wider than the unweathered, untreated stone.

From the above data the products can be ranked according to:

- the increasing depth of penetration: A21 << WH < UO16+4;
- the decrease in permeability: UO16+4, A21 >> WH; and
- the decreasing score width: WH >> B72 >> UO16.

Artificial ageing produced rapid deterioration in the control specimen. At first both the weight and the sound velocity increased ($\Delta w = +15\%$; $\Delta V_s = +15.3\%$). This is due to water absorption by the sample, and the higher water content results in a higher sound velocity. The sound velocity then decreases ($\Delta V_s = -5.6\%$) and finally stabilizes ($\Delta V_s = -6$ to -8%) while the weight decreases as the surface of the sample deteriorates. Two months after the beginning of the test, the control sample had lost about 15% in weight.

Table 20.4 **Products applied and the resulting depth of penetration and water vapour permeability**

Sample	100 f *	101 c *	104 f	105 c	107 f	108 c
Product	UO 16/4	UO 16/4	WH	WH	A 21	A 21
Quantity Applied**						
Q (kg/m^2)	1.816	2.262	2.459	2.065	1.550	1.419
Q_1 (kg/m^2)	0.34	0.45	0.50	0.56	0.62	0.48
c	1.033	1.020	1.008	0.82	0.58	0.68
Penetration depth		{22}	{18}			
min. (mm)	10	22	10	10	1	2
max. (mm)	13	>22	18	15	9	7
mean (mm)	11	22	12	12.5	4	4
Permeability (g/m^2.h$^{0.5}$)						
before	7.49	5.79	7.85	7.01	8.05	6.08
after	4.28	3.73	5.76	5.08	5.71	3.66
% loss	42.9	35.5	26.4	27.6	29.1	39.7
% loss/mm	3.9	1.61	2.2	2.2	7.3	9.9

Where: * f = fine-grained tuff; c = coarse-grained tuff.
** Applied Quantity $\boldsymbol{Q} = \boldsymbol{Q_1}.\boldsymbol{n}^{\mathbf{c}}$, where $\boldsymbol{Q_1}$ is the amount applied in the first application, ***n*** is the number of applications, and **c** is an index that expresses the ability of the product to penetrate into the stone. A low value for **c** indicates poor penetration.
{22} and {18} indicate the thickness (in mm) of the particular sample used in the test.

The specimen treated with WH shows a gradual deterioration of the cement, leaving the lapilli to detach from the surface. The weight increases slightly ($\Delta w = +0.8\%$) while the sound velocity decreases slightly ($\Delta V_s = -3.3\%$).

The fast deterioration of the specimen treated with UO16 alone confirmed the need for a water repellent capable of resisting water absorption under pressure. The sample lost the treated surface, absorbed water until saturation and the sound velocity increased ($\Delta V_s = +6.6\%$).

The specimen treated with UO16+4 had an early deterioration phase but later stabilized and resisted for a long time.

The results of the artificial ageing showed that the deterioration rate decreased in the direction: control >>> UO16 > UO16+4 > WH.

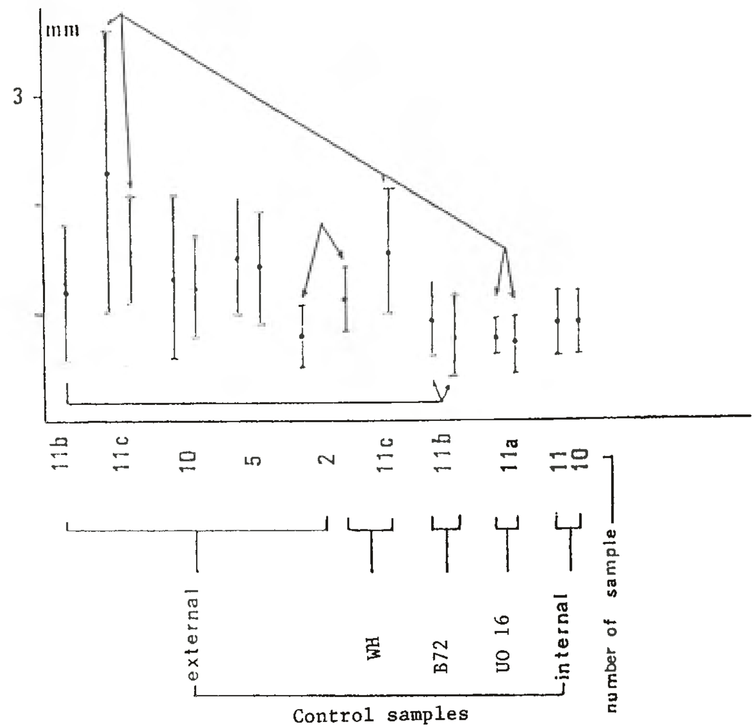

Figure 20.4 **Score width on Easter Island tuff samples, untreated and treated with different products. Upper and lower arrows mark results obtained with the same sample.**

20.5 CONCLUSIONS

Any conservation treatment that is to be applied to Easter Island statues has to take into account the nature of the stone and the conditions *in situ*, implying a need for careful choice of consolidation and hydrophobization treatment and the solvent system.

The stone used to carve the statues of Easter Island has a high degree of heterogeneity: the presence of coarse- and fine-grained areas, and the difference between the porosity of the glassy matrix and that of the lapilli produces varying behaviours with regard to absorption of liquids. This heterogeneity is increased through the weathering process and the formation of clayey or siliceous crusts. The high water content of the stone (about 25% v/v of its porosity) is also an important factor.

The conditions *in situ* will determine the application technique used for the treatment. The following points have to be considered:

- the recording of all possible non-destructive measurements before the treatment so as to adapt treatment to the particular moai;
- the protection of the moai before and during treatment;
- the monitoring of the moai during and after treatment; and

- the elimination of any constant water source, such as contact with soil or the ground. This last condition precludes the treatment of any moai standing on the ground, half buried or still in the quarry niche.

Further points to be taken into account are the necessity of applying a biocide before any consolidation, hydrophobization or combined treatment is applied, and last – but not least – the use of Portland cement mortars in restorations should be minimized, with lime-cement mortars used instead.

From the experiments carried out it was found that the *Fongivore* solution applied by spray at 0.2 l/m^2 (or 0.4 l/m^2 for heavy infestation or very porous tuff) allowed elimination of the biological growth by brushing two days later. The elimination of the growth could also be carried out by relatively low-pressure water spray (<20 kg/cm^2).

Two formulations of consolidant + water repellent mixtures – UO16+4 and WH – gave the best results for protection of the Easter Island tuff. Of the solvents tested, white spirit proved to give the best penetration depth, and the most efficient application technique relied on successive applications without letting the stone dry out between them.

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APPENDIX 20-A

CLIMATE

Data on the climate of Easter Island were collected from two primary sources [12; 13] and are summarized in Table 20-A.1 below.

Table 20-A.1 Climatological data for Easter Island (Sources: [12] & [13])

	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
Temp (°C)												
max.	28.9	28.9	28.9	27.8	27.8	25.0	23.9	25.0	25.0	26.1	26.1	28.9
min.	20.0	21.1	21.1	17.8	16.1	15.0	12.0	12.9	15.0	15.0	15.0	17.2
mean	23.6	24.1	23.5	21.8	20.4	18.7	18.2	18.0	18.7	19.7	19.7	22.3
Rain (mm)	122	94	116	106	117	109	90	77	68	94	117	125
Wind*	E	E	E	E	NW	E	NW	NW	N	E	E	E

MEAN ANNUAL VALUES	Temperature (°C)			Rain (mm)
	Maximum	Minimum	Mean	
	26.9	17.2	20.8	1234.1

* Prevailing wind direction

20-A.1 Insolation and Temperature

During the southern summer at the latitude of Easter Island, 27°19′ S, the quasi-E-W trajectory of the sun (at 12:00 on 21 December the altitude of the sun is 86°) implies that on north-facing vertical surfaces the angle of incidence and the flux of direct solar radiation are very low. Thus, short projections (such as the chins of the statues) cast shadows on large areas of any north-facing vertical surfaces.

On the other hand, during the winter (at 12:00 on 21 June the altitude of the sun is 40°) all the north-facing surfaces are directly exposed to full solar radiation, and large differences in temperature between the air and the surface of the stone can develop.

20-A.2 Salt deposits from sea spray

It has been shown at other sites [11; 14] that the amount of salts deposited on a wall close to the sea depends on the height of the waves:

$$Q_{Cl} = k \times \Sigma h^2$$

where: Q_{Cl} is the amount of chlorides deposited; k is an empirical factor; h is average wave height; and Σh is summation over a given time.

From charts of the monthly frequency of wave heights, the Σh^2 value can be calculated for each direction of origin of the waves. For the three coasts of Easter Island, the relative values found were: N-NE = 43, S-SE = 146, and N-NW = 100. It follows then that the deposits of soluble salts will be more important on the S-SW coast, while on the N-NE coast these should be at a minimum.

20-A.3 Rains

The information on the amount of rain refers to a horizontal surface, but does not give an indication of the amount received by a vertical surface. From previous studies, a formula was developed that linked this amount to that received by a horizontal surface through a factor depending on the direction and velocity of the wind [15]. If the site factor is not known, only a rain index can be obtained [16; 17]. In the case of Easter Island, it was found that the wind velocity distribution was similar to that of Chassiron, close to La Rochelle [18], so that the same site factor (0.05) was used tentatively. On this basis the monthly amount of rain received by vertical surfaces depending on the wind direction has been calculated, and is reported in Table 20-A.2.

From the table it can be seen that vertical surfaces will get more rain from the N, NW, NE and E directions, while they receive almost no rain from the SE and S.

20-A.4 Summary

Combining the information on salt deposited by sea-spray with the washing of vertical surfaces according to the wind directions, month by month, using arbitrary units for both, a set of graphs for each major wind direction can be obtained (Figure 20-A.1).

This combined information can be superimposed on the map of Easter Island for better visualization (Figure 20-A.2).

From the above data, three areas can be defined on the Island:

- E, NE, N & NW – receive low salt deposits and frequent rain washing
- W & SE – receive medium salt deposits and medium washing
- S & SW – receive high salt deposits and practically no washing

Table 20-A.2 Calculated monthly amount of rain reaching vertical surfaces according to wind direction, in arbitrary units.

	Rain (mm)	E	NE	N	NW	W	SW	S	SE	Max. 0.05
JAN	121.4	2280	522	369	22	22	22	22	22	114(E)
FEB	94.0	1907	2052	425	1663	19	19	19	19	103(NE)
MAR	115.6	2252	1831	3117	35	35	35	35	35	156(N)
APR	105.9	770	2481	19	3113	19	19	19	1396	155(NW)
MAY	117.2	193	275	138	1515	633	26	26	26	76(NW)
JUN	109.3	24	24	1467	24	24	24	24	24	73(N)
JUL	90.0	259	173	19	825	825	168	19	548	42(NW)
AUG	114.0	291	14	333	498	1477	15	15	15	74(W)
SEP	68.0	409	12	172	895	812	12	12	280	45(NW)
OCT	93.6	270	1951	957	11	11	11	11	1103	98(NE)
NOV	116.9	1561	5	1482	5	5	980	5	5	78(E)
DEC	124.8	1047	14	372	149	14	14	14	14	52(E)
	Total ×0.05	563	468	371	510	195	67	11	174	

The location of a given moai is critical with respect to the amount of sea spray to which it is exposed and the amount of washing it will receive. For example, the east-facing surface of a moai located on the west coast will not receive as much salt as the face of a moai located on the SE coast. The distance of the moai from the sea is also important; locations further than 2 km from the coast will receive no salts unless the breaking waves are very high. The occurrence of honeycombs on the southeast coast (see Section 20.1.3), similar to the "taffoni" in Corsica [6] can be explained on the basis of these data.

APPENDIX 20-B

PRELIMINARY TESTS

A preliminary study had been carried out to evaluate the quality of hydrophobization and consolidation treatments as a function of the solvent used, the surface moisture level, the number of applications, the time between applications, the residue left in the stone, the depth of penetration, etc. The study used some French tuffs for the tests [19]. These were:

- Neschers, a trachytic pumice which disintegrates within minutes of immersion in water, and
- Servières, a fairly homogeneous tuff with high concentration of clays, and relatively similar to the Easter Island stone.

The Servières tuff has an porosity of approximately 57% in the unweathered state. The absorption coefficient varies, depending on the grain size of the tuff. The values range from $\boldsymbol{B}$ = 1.9 $cm^3/cm^2.min^{0.5}$ for the coarse-grained tuff, through approximately 0.6 $cm^3/cm^2.min^{0.5}$ for the medium-grained tuff, to 6 $cm^3/cm^2.min^{0.5}$ for the fine-grained tuff.

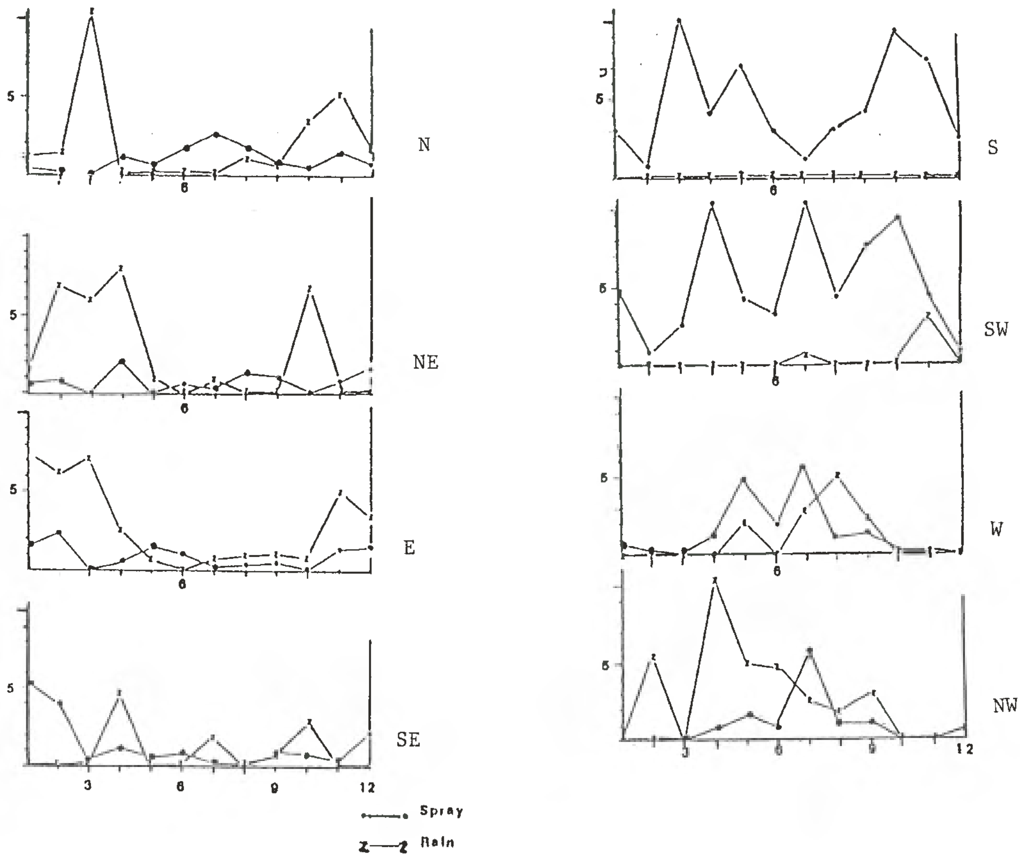

Figure 20-A.1 Representation, in arbitrary units, of calculated amount of salt deposited by sea spray and the washing of vertical surfaces by rains according to the wind direction.

The weathering can take different forms: superficial, or deep and homogeneous. The water absorption of homogeneous samples, weathered or unweathered, approximates to a normal diffusion pattern, but for heterogeneous samples, the absorption mechanism is more complicated, as was also found for the Easter Island tuff.

For the tests, the following hydrorepellents were chosen:

- aluminum stearate (St) in white spirit, as the presence of goethite in the tuffs could promote its fixation;
- methyl triethoxysilane (Sil) in white spirit (*Dow Corning Z 6070*); and
- methyl silicone (4) in white spirit (*Rhône Poulenc 4518*);

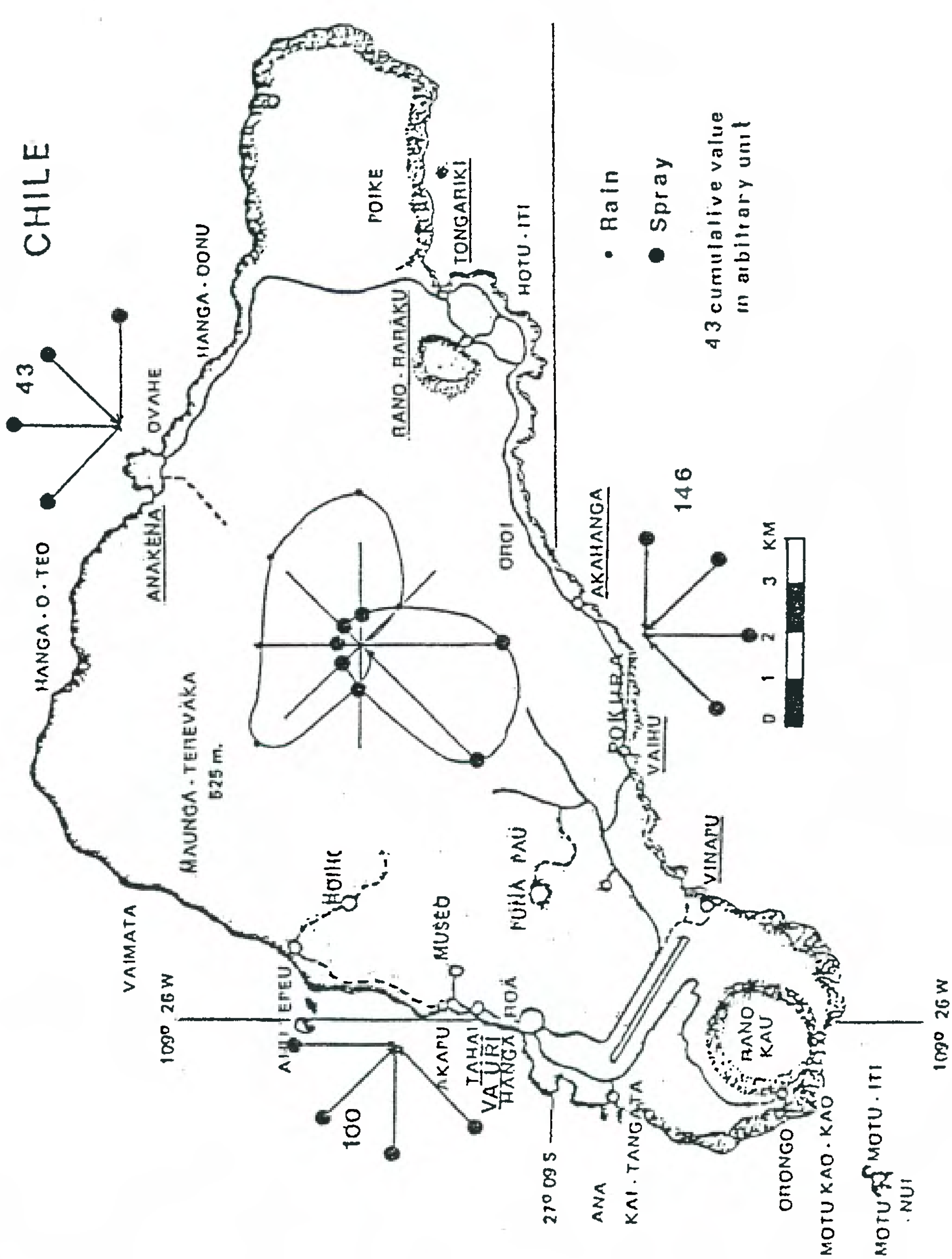

Figure 20-A.2 **Map of Easter Island showing the direction and intensity of salt deposits from sea spray and driving rains according to wind direction.**

and five consolidants were also chosen:

- urethane oil (UO) (oxidation drying) in white spirit at either 16% or 25% concentrations;
- alkyl alkoxy silane (WOH) in ethyl alcohol (*Wacker OH*);
- alkyl alkoxy silane + alkyl silane (WH) in ethyl alcohol (*Wacker H*);
- isobutyl methacrylate (IBA25) in white spirit (soft resin); and
- *Paraloid B-72* (B72) in white spirit and *Acryloid A 21* (A21) in ethyl acetate and isopropyl acetate (hard resin).

The capillary rise of the various products was tested on both the Servières tuff and the Neschers pumice. It was found that the silane (Sil) had the highest absorption rate, while B-72 and the mixture UO16 + St have the lowest absorption rate. The higher concentration of urethane oil (25%) rises at a slower rate. Only B-72 in the Servières sample, and the IBA25 in the Neschers pumice, did not reach the top of the prismatic sample (2 × 2 × 10 cm), even after 20 hours in contact with the solution.

Even though the penetration of the UO16+4 mixture proved satisfactory, and the score width and abrasion tests showed an adequate hardening of the surface, the water absorption under pressure was only delayed for some time, then reaching values as for the untreated specimen. This phenomenon has been described previously [20; 21; 22; 23].

This mixture was therefore not considered and the water repellent was replaced by the methyl silicone resin.

As the surface moisture is a critical parameter, samples were sometimes sprayed with water before treatment application. The treatment was then evaluated by the water drop absorption test, the improvement index ***I***. Table 20-B.1 gives the results for UO16 applied on the Servières tuff.

Table 20-B.1 Evaluation of treatment UO16 applied on surfaces sprayed with different amounts of water

Sample	Water applied (l/m^2)	Water content (%)	Applications	Product applied (g/m^2)	Time (min.)	*I*
S1	0	6	1	50	240	35
S4	0.12	26	1	40	130	12
S8	0.11	45	2	80	390	7
S3	0.54	98	1	50	100	1
S6	1.23	99	1	20	8	1

where:
Time gives the minutes taken in the water-drop absorption test (See Section 20.4.2)
I = improvement index (B_{before} / B_{after}) (See Section 20.4.2)

It can be seen that spraying the surface with more than 0.6 l/m of water hinders the penetration of the resin, thus resulting in poor water repellency and in no improvement in the water absorption. When the water content is above the critical level, as in S8, a twofold application improves the water-repellency, but does not provide significant protection against water under pressure.

Similar results were obtained with the other products. The quality of any treatment decreased when the surface water content reached the critical water content (about 30%). This fact has to be taken into account in the implementation of any proposed *in situ* treatments.

It is important to be able to estimate the amount of resin that is introduced into the sample, as the required penetration depth of at least 1 or 2 cm from any given point of the surface of the statue has to be reached. The amount of resin introduced, Q, can be calculated as a function of the amount introduced in a first application, Q_1 and the number of treatments applied:

$$Q = Q_1 \times \mathbf{n}^{\mathbf{c}},$$

where **n** is the number of applications, and **c** is the penetration index, ranging from 0.5 for poor penetration to 1 for good penetration.

The value of this penetration index depends on the solvent used. Table 20-B.2 gives the value for the Easter Island tuff.

Table 20-B.2 Value of index *c* for the Easter Island tuff and different solvents

Solvent	very volatile	ethanol	white spirit	water
Easter Island tuff type				
fine-grained	0.59	1.01	1.03	1.00
coarse-grained	0.68	0.82	0.82	0.90

The poor penetration with a very volatile solvent is due to pore-blocking during the first application. This can be overcome in part by reducing the time between applications. The relationship between the penetration index and the time between applications is represented in Figure 20-B.1. It was found that the best application procedure was to treat the sample with successive applications separated by 15 to 30 minutes, so that the sample did not dry out between applications.

For any given tuff, the order in which solvents improve penetration of a given resin is the same. The increasing order of penetration has been found to be: B-72 < WOH < St, Sil < UO25 < UO16. The amount of resin introduced varies also, according to the combination of resin and tuff.

The amount of water in the sample will decrease the amount introduced in the first application but will increase the penetration index.

APPENDIX 20-C

MATERIALS USED

- *Acryloid A 21 LV*; Rohm, Boulogne Billancourt, France; formulated by J.P.Pauly
- Urethane Oil, consisting of two components: Saturateur (16%) and Durcisseur (20%); ONIP, Le Kremlin Bicêtre, France
- Isobutyl Acrylate; Rohm & Haas, Paris, France
- *Paraloid B-72*; Rohm & Haas, Paris, France
- *Wacker OH*; Wacker Chemie, Munich, Germany
- *Wacker H*; Wacker Chemie, Munich, Germany
- Methyl triethoxyisilane; Dow Corning Z 6070
- Methyl silicone; Rhône Poulenc 4518
- *Fongivore*; formulated and manufactured by ONIP, Le Kremlin Bicêtre, based on *Bardac 22* (didecyl dimethyl ammonium) produced by Lonza, Nanterre, France

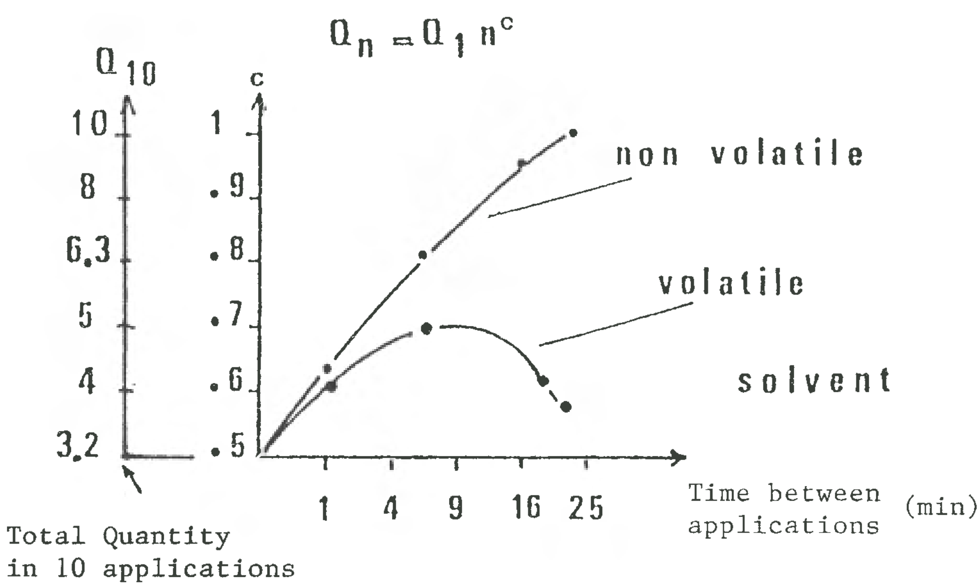

Figure 20-B.1 Influence of the solvent on the relationship between penetration index and the time between applications.

RESUMEN

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

RESUME

Des recherches (microscopie et diffraction rayons-X) ont été effectuées sur des roches saines (tufs trachytiques et trachyandésitiques et pierres ponces) et des parties altérées (croûtes et alvéoles). Les caractéristiques physiques (absorption d'eau et de solvant, séchage et capillarité) d'échantillons altérés et non altérés ont été mesurées en fonction des deux paramètres les plus importants pour la conservation *in situ* des statues moai (humidité et caractéristiques physiques des croûtes). L'humidité superficielle relevée sur les moai a été mesurée pour localiser les plages humides et choisir les traitements, qui doivent être mis au point par des essais de laboratoire. Plusieurs produits (consolidants, hydrofuges) ont été testés en procédant à des dégradations artificielles pour simuler les conditions météorologiques. La sélection finale s'est fondée sur les résultats de tests classiques. Certains procédés s'appliquant au traitement *in situ* sont définis.

KURZFASSUNG

Mittels Mikroskopie und Röntgentechniken wurden Untersuchungen an unverwittertem Gesteinsmaterial (trachytische und trachy-andesitische Tuffe und Bimse) sowie an verwitterten Proben (Krusten und zellenverwitterte Bereiche) durchgeführt. Die physikalischen Kennwerte (Wasser-/Lösungsmittelaufnahme, Trocknungsverhalten und Kapillarität) der verwitterten und unverwitterten Proben wurden im Hinblick auf die beiden für eine *in situ* Konservierung der Moai wichtigsten Parameter (Feuchtigkeitsgehalt und physikalische Eigenschaften der Kruste) gemessen. An den Moai wurden außerdem Messungen der Oberflächenfeuchte durchgeführt, um Feuchtbereiche zu lokalisieren, die ihrerseits die Bedingungen für eine konservierende Behandlung definieren. Die Ausarbeitung solcher Bedingungen erfolgt im Rahmen von Labortests. Verschiedene Produkte (Konsolidierungs- und/oder Hydrophobierungsmittel) wurden mittels künstlicher Bewitterung, die sich an den Klimadaten orientierte, getestet. Die endgültige Auswahl gründete auf den Ergebnissen aus klassischen Meßverfahren. Einige der Behandlungsbedingungen *in situ* werden definiert.

DETERIORATION PHENOMENA OF LAVAS AND VOLCANIC TUFFS UNDER SUBTROPICAL AND TEMPERATE CONDITIONS:

FIELD AND LABORATORY STUDY USING MULTISEQUENTIAL METHODOLOGY

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ABSTRACT

The petrographic and petrophysical features of lavas and volcanic tuffs are very heterogeneous. They depend on the original volcanic facies, their evolution during cooling, and the geomechanical stresses during movement. Natural outcrops undergo weathering during the course of geological time; the causes and results are varied. Weathering also operates on objects fashioned from these materials when the objects are left exposed to open air. This process is mainly dependent on climatic and microclimatic factors, since they control the hydrochemical and biochemical parameters. The role played by marine sprays is emphasized. Technology transfer from previous studies has permitted development of a specific methodology to study volcanic materials in general and Easter Island statues in particular.

21.1 INTRODUCTION

A brief field and laboratory study was carried out to understand the decay mechanisms that operate on the statues erected on Easter Island. In addition, samples of tuff were obtained from a site 200 km to the east of Bordeaux, France, and placed in the south-west region of France in an environment with climatic conditions that are similar

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to those on Easter Island. The duration of the study (November 1988 to November 1989) corresponded to a complete climatic cycle.

The investigation was based on non-destructive, indirect, multisequential and repetitive measurements. The aim was to identify the factors that affect the decay of exposed carved and engraved stones, and understand the operating mechanisms, with the expectation that elucidation of these points would allow the formulation of adequate conservation measures.

21.2 EXPERIMENTAL RESULTS

21.2.1 Stone samples

On Easter Island, *moai* of different stone types were chosen for the study: one was a tuff and two others were carved out of lava. The tuff moai (sample #1) is at Hanga Kio'e, while the other two samples (#2) and (#3) are at Hanga Roa (moai locally numbered 4 and 5).

The French samples were taken from the Massif Central, a large volcanic area of about 85 000 km^2 (about ⅙ the surface area of France). Four samples were taken, two tuffs (#4 and #5) and two lavas (#6 and #7). These last two were chosen for their visual similarity to the Easter Island samples.

In situ observations and petrographic data of the samples are given in Table 21.1.

The small, medium and large phenocrysts of all samples are commonly oxidized, with a rim of opaque oxidation products. The Easter Island samples show frequent, white, hydrosilicate crusts, while in France, ferruginous encrustations are formed by running water.

The Easter Island rocks, lavas and tuffs, have porosities that range from 42% to 27%, the most frequent values ranging between 31% to 33% [1]. The French tuff samples have a porosity around 30% and the lavas around 6%. More detailed data on these samples are given in Table 21.3.

The chemical analyses of various samples are reported in Table 21.2. The data are drawn from previous published studies (samples 417 & 418 – [1]), those carried out on a sample of the Rano Raraku quarry (volcanic tuff) (sample IP1) and the French lavas and tuffs (#4 and #6).

In Table 21.2, note that sample #6 represents a mineralogical anomaly for a trachyte because of the low alkali content. Anomalies of this kind are to be found in transition systems such as those of the Massif Central.

Table 21.1 Petrophysical characteristics of the rocks

Source	Moai Hanga Kio'e	Moai 4 & 5 Hangaroa	Rock	Rock
Sample ID #	1	2 — 3	4 — 5	6 — 7
Rock type	volc. tuff, breccia	lava, alk.trachyte	Volc. tuff, breccia	lava, trachyte
Sample size (cm)	360×170×85	#2: 214×95×40 #3: 200×100×45	#4: 45×25×20 #5: 30×20×20	#6: 35×20×20 #7: 30×20×20
Structure	macro-granular	micro-granular	macro-granular	granular
Hardness	low to medium	medium to high	low to medium	medium to high
Surface texture	rough	rough	rough	rough
Surface deposits	amorphous silica	lichens	–	–
Cement (Matrix)				
Nature	glass +microliths	plagioclase feldspars	glass +microliths	plagioclase feldspars
State	amorphous dominant	crystallized	amorphous dominant	crystallized
Subordinate minerals	pyroxene	Fe & Mg compounds	?	Fe & Mg compounds
Colour	reddish brown	light brown	reddish brown	light brown
Fissuration	micro-fissures	#2: medium #3: high	micro-fissures	micro-fissures
Inclusions				
Nature	basalt	–	basalt	–
State	microlithic	–	microlithic	–
Appearance	massive	–	slaglike	–
Texture	compact	–	vesicular	–
Colour	bright black	–	dull black	–
Grain size	0.2 – 32 cm	–	0.2 – 6 cm	–

21.2.2 Field Tests

The aim was to elucidate the surface and internal hydrodynamics of exposed objects and the water transport mechanism between two or more rainfall sequences. This was carried out using surface conductance measurements and the transparence process for internal measurements. Iso-conductance maps were then drawn up (see Figure 21.2).

(i) *Temperate climate tests (France)*

One of each kind of stone – volcanic tuff and lava (samples 4 and 6) – were left outdoors in Bordeaux-Pessac, from 2 December 1988 to 15 September 1989. They were then transferred to Royan for marine spray studies but were vandalized on 10 October 1989.

The other two samples, 5 and 7, were left in Bordeaux-Pessac from 2 December 1988 to 22 June 1989, after which they were taken to the laboratory for study.

Two characteristic climate conditions were chosen to monitor the hydrodynamic behaviour of the objects. These were days around a spring storm and around a summer

Table 21.2 Chemical analysis of tuffs and lavas

Sample #	4	6	IP1	417	418
% SiO_2	58.5	57.4	53.6	50.20	48.20
% Al_2O_3	14.8	16.7	14.2	12.75	12.85
% Fe_2O_3	3.6	5.5	4.6	7.30	8.30
% FeO	3.5	2.6	3.6	4.80	4.15
% TiO_2	0.3	0.3	0.8	2.24	2.25
% MnO	0.1	0.1	0.2	0.26	0.27
% MgO	5.8	5.0	6.8	3.10	3.60
% CaO	9.6	8.6	9.7	5.90	4.90
% Na_2O	1.2	1.6	2.8	2.45	2.40
% K_2O	0.9	0.8	1.1	1.00	0.91
Ignition loss <600°C	2.1	1.0	2.8	*	*
TOTAL	100.4	99.6	100.2	99.10	99.13

* the loss of water is given as: #417 – adsorbed water 4.20%, constituent water 4.90%; and #418 – adsorbed water 6.95%, constituent water 4.40%.

thunderstorm. The winter test was unsatisfactory because that year mild weather, with no snow, predominated over SW France.

The spring test was carried out from 18 to 21 April 1989, and the summer test from 18 to 21 June 1989. Data are reported in Figure 21.1. Table 21.3 gives the analyses of the rainwater before and after percolation through samples 4 and 5 during the spring rain. The amount of water that percolated through samples 6 and 7 was too small to allow chemical analysis.

The water that percolated through the samples dissolved some material from the stone, showing enrichment in silica and in soluble salts such as sulphates and bicarbonates of magnesium and calcium, and to a lesser degree of sodium and potassium. Such leaching promotes loss of cohesion of the cement, and the detachment of inclusions, increasing the porosity and permeability of the stone.

The spot measurements of humidity taken the day after the summer rain of 20 June 1989 are reported in Table 21.4, which also lists the petrophysical characteristics of the French lava and tuff samples.

It was observed that three different levels, of variable thickness, could be distinguished on the basis of the measurements carried out on the French samples. These were:

- level 1 = internal part of the rock at ≈10 cm below the surface; does not dry completely even after 5 sunny days.
- level 2 = subsurface, at ≈1 cm below the surface; takes 4 to 5 sunny days to dry.
- level 3 = surface layer, micrometres thick; dries within 1 sunny day.

For each of these levels, the hygric exchanges by evaporation, run-off and gravity are different.

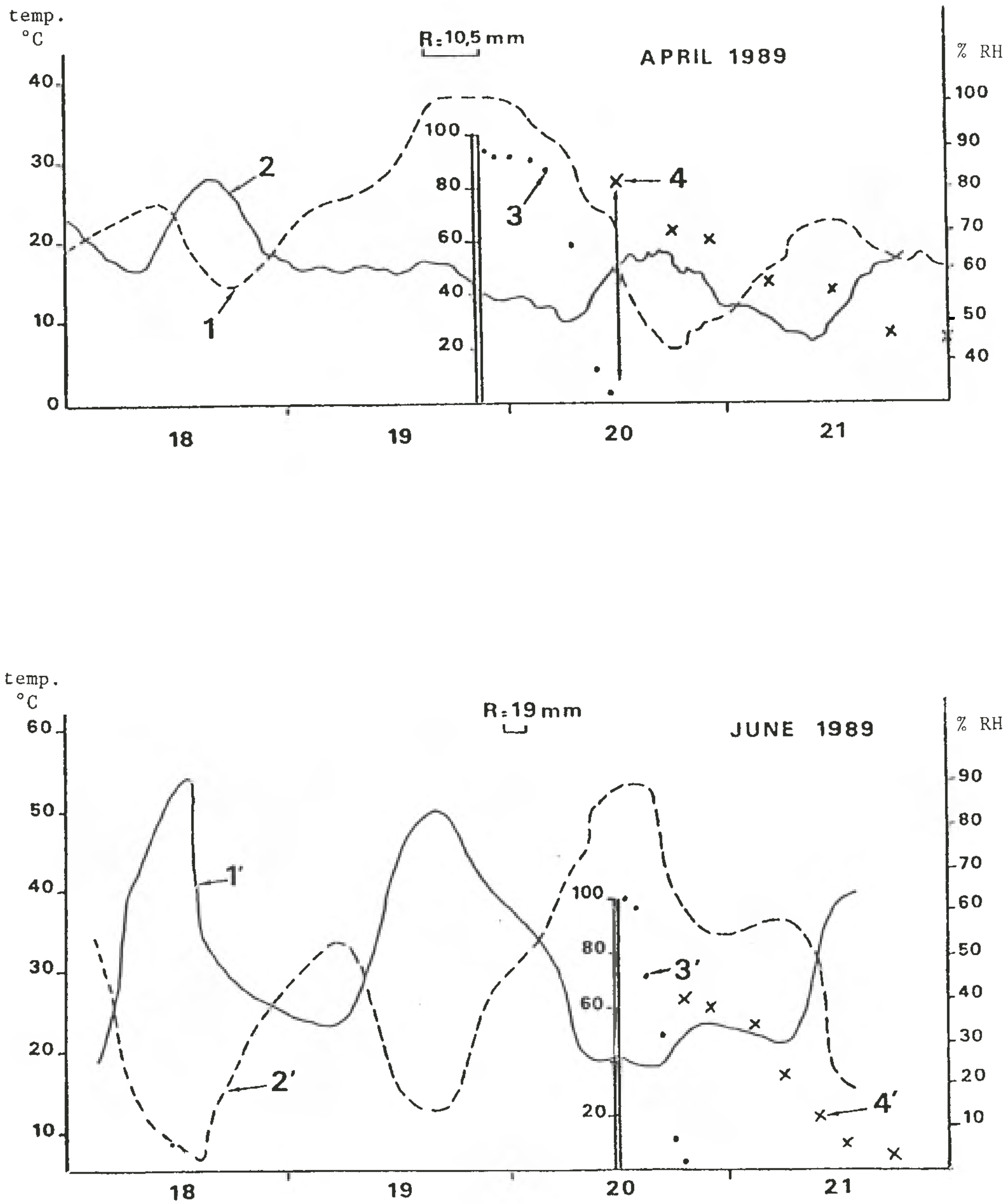


Figure 21.1 **Diagram of variation of water contents of sample 4 as a function of climatic conditions.**

Top graph: spring, rain on 19/04/89. Bottom graph: summer, rain on 20/06/89.
Curves 1 and 1′= surface temperature of the stone (°C).
Curves 2 and 2′= air RH%.
Points 3 and 3′= humidity change in level 3 with time.
Points 4 and 4′= humidity change in level 2 with time and determined through conductance readings.
R = amount of rain.

Table 21.3 Rainwater analysis, before and after percolation through samples #4 and #5. Rain of 19 April 1989.

	Concentration (mg/l)	
	Rainwater	Percolated water
Ca^{++}	4.4	6.0
Mg^{++}	0.6	1.7
Na^{+}	3.1	4.0
K^{+}	1.0	1.8
Fe^{+++}	tr.	0.07
Al^{+++}	tr.	0.5
HCO_3-	9.15	12.2
SO_4- -	3.2	6.0
Si	tr.	12.2
Soluble matter	–	54
Organic matter	tr.	1.4
NH_3	0	0
NO_2	0	0
P_2O_5	tr.	0.33
pH	6.5	6.8
Dry weight (mg)	820*	–

*corresponds to micro-fragments of rock collected at the base of sample #4.

Table 21.4 Petrophysical characteristics of the French volcanic rock samples

Level	Layer	IH%	Porosity (%)	Permeability Coefficient (l/m^2s)
#4 – TUFF				
subsurface d<10 mm	a	3.7	34	1.01
	b	4.3	36	0.34
	c	4.4	39	0.26
internal 10 mm<d<100 mm	a′	5.7	28	0.22
	b′	6.1	32	0.28
	c′	6.3	38	0.19
#6 – LAVA				
subsurface d<10 mm	g	2.2	6.5	0.12
	h	2.2	5.7	0.11
	i	2.3	6.1	0.10
internal 10 mm<d<100 mm	g′	2.1	4.2	0.08
	h′	2.2	6.7	0.11
	i′	2.3	6.4	0.11

where:
IH% is the spot humidity value measured 24 hours after rainfall on 20/6/89.
Porosity (%) was determined by water saturation of the vacuum-evacuated sample.

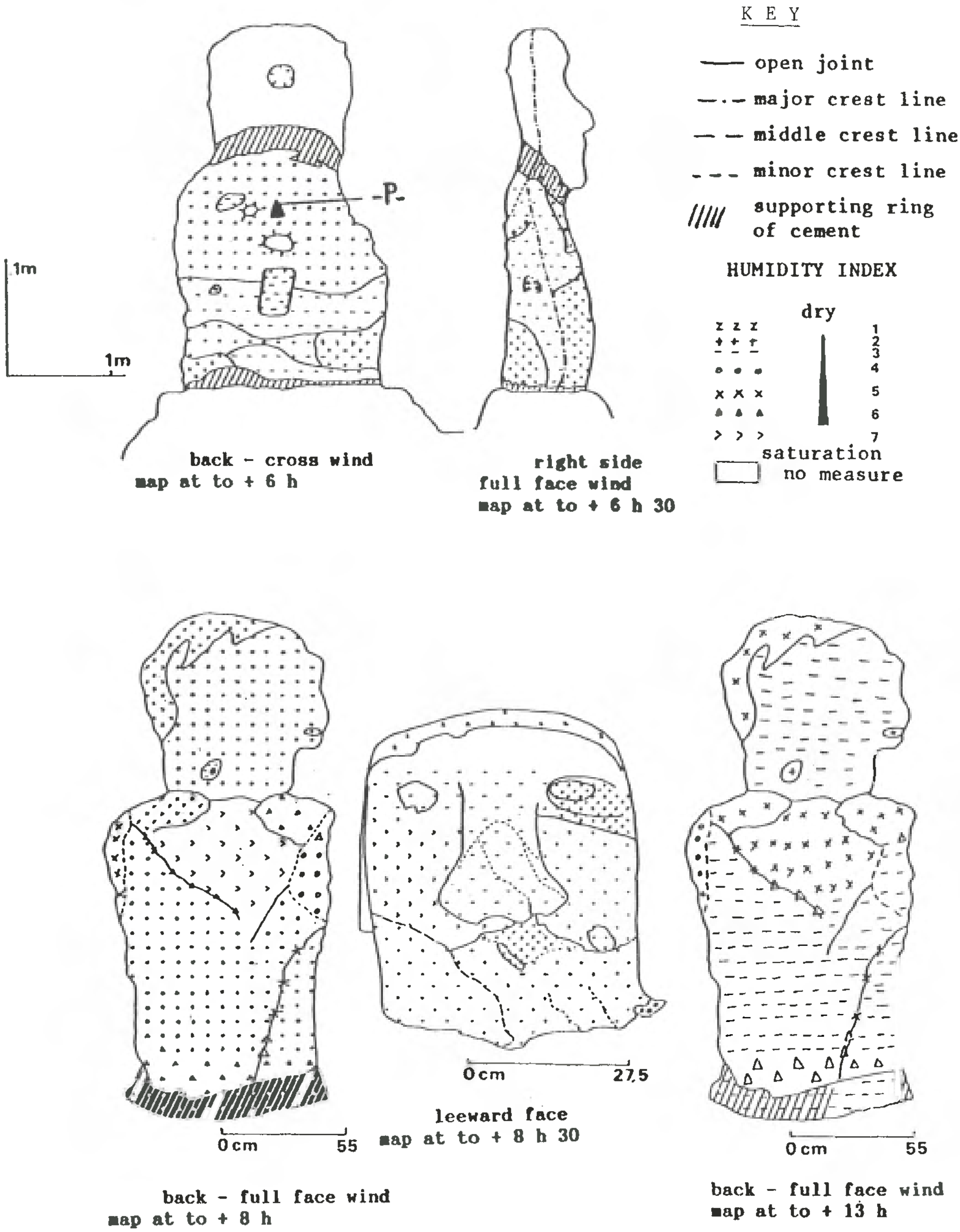


Figure 21.2 **Iso-conductance mapping for two moai on Easter Island showing their hydrodynamic behaviour.**
Top: Hanga Kio'e moai (sample #1) Bottom: moai 4 at Hangaroa (sample #2)
t_0 = end of rainfall; t_0 + h = time at which measurements were taken.
P = indicates area from which sample flake was taken.

The experiments relating to marine spray were cut short on 10 October 1989, when the samples (4 and 6) were thrown into the sea by some vandal. Nonetheless, the observations that had been carried out till then showed that no accretion of sodium chloride salts formed on the windward surfaces or within the microfissures of the stones. This could be explained by the more temperate climate of France, where the evaporation rate is not as high as on Easter Island. Also to be taken into account is the fact that the lee sides of the samples were not reached by the sprays.

(ii) *Subtropical climate tests (Easter Island)*

These were carried out on the moai on Easter Island, samples 1 to 3, between 23 February and 8 March 1988.

The climatic data obtained on 3 March 1988 are given in Table 21.5 and the measurements represented on the iso-conductance mapping for two of the moai are given in Figure 21.2.

Table 21.5 Climatic data for 3 March 1988

Morning	Frequent rainfall alternating with sun, end of rainfall 11:30. Strong wind from WNW.	
Afternoon	Cloudy. Medium and irregular wind from WNW.	
Evening	Short shower (minutes) at about 22:00. Light winds.	
Time	RH	Temperature
08:00	90%	22.2°C
12:00	100%	26.1°C
15:00	88%	26.8°C
17:00	70%	28.0°C
20:00	75%	27.1°C
21:00	81%	26.2°C

The study of the iso-conductance mapping of objects in conjunction with the climatic data allows an evaluation of the surface or internal hydrodynamic phenomena over time. Table 21.6 summarizes the observations carried out on the Hanga Kio'e moai and moai 4 at Hanga Roa, corresponding to the rain on 3 March 1988 (see Figure 21.2).

The effects of marine sprays were followed on Easter Island for the Hanga Kio'e moai (sample 1) which faces inland. With strong winds bringing marine spray from the rough sea it was observed that the spray settled only on part of the back and sides of the statue, and additionally over some parts of the belly (on the lee side) which could be attributed to local turbulence.

In the case of strong winds from the sea bringing marine spray plus rain, after the rain stopped and the sunshine dried the statue, the formation of salty droplets was observed, depending on the gravity flow and the micromorphology of the stone.

Table 21.6 **Evolution of humidity in the moai from Figure 21.2**

SAMPLE 1
Back with cross winds; measurements at surface (level 3) at t_0 + 6 hours; Cement: medium humidity, slow drying Basalt inclusions: low humidity, fast drying Hygric phenomena: imbibition then evaporation
Side with full winds; measured at surface and subsurface (levels 3 and 2) at t_0 + 6½ hours; Cement: fast drying Neck and cracks: medium humidity Hygric phenomena: imbibition, filtration, then evaporation
SAMPLE 2
Face leeward of wind; measurements at t_0 + 8½ hours Eye sockets: high humidity Nose: low humidity Hygric phenomena: imbibition, retention and then fast evaporation
Back measured at surface and subsurface (levels 3 and 2) at t_0 + 13 hours; Top part: fast drying Lichens: humidity equal to cement Bottom part: high humidity Hygric phenomena: imbibition, then evaporation in upper regions; imbibition, then retention and runoff + gravity effect for bottom part.
Body measured at surface, subsurface and internal part (levels 3, 2 and 1) at t_0 + 21 hours (not shown in Figure 21.2) Surface and subsurface: low humidity, i.e., dry Internal part: medium humidity Hygric phenomena: drying and infiltration (?) moisture transfer (??)

A flake taken from the back of the statue (see Figure 21.2) showed the presence of NaCl crystals on its internal surface. The repeated strong abrasion effects of marine sprays facilitates the penetration of salt into the open pores, microcracks and cracks. Part of it is removed through the leaching effect of the rainwater, but some is left behind. The high evaporation rate found in this climate facilitates the crystallization of the salt and the consequent mechanical damage, which leads to scaling and peeling.

21.3 DISCUSSION

The results obtained on Easter Island and in France can be differentiated into:

- established facts,
- poorly defined facts, and
- specific facts.

The established facts are that there is no question that driving rain, water flow and runoff are factors in the mechanical deterioration of the objects. Hydrogeochemistry contributes through the leaching of solubilized matter. The time factor is also to be considered at this point.

Poorly defined facts are the internal structure of the objects, which will determine the thermic and hygric flux transfers. These points need to be well defined for any understanding of the deterioration problems.

Specific facts are the climatic data for the particular object in question: wind strength, hygrometry data, temperature data, thermo-hygrometric changes, etc.

Deterioration of the objects results from the joint action of two or more of these factors. In the specific case of Easter Island, the effect of marine sprays is significant and must not be ignored.

The time factor mentioned previously comes into the equation through comparative studies of the present climate and the paleo-climate. For example, in France the Little Ice Age had an effect, while on Easter Island the paleo-movements and marine transfers, i.e., the El Niño current, and other mega-meteorological and catastrophic phenomena associated with the Central Pacific, are crucial.

All the facts and data need to be collected into a data bank. This is discussed in the next section.

21.4 DATA BANK: THE M.O.A.I. PROJECT

The M.O.A.I.-1 program is entitled *Megalithic Objects Analysis by Imagery*, within a broader version – M.O.A.I.-2, *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 through different, complementary and variably complex procedures.

The full description of these procedures here would be too lengthy, but some examples are given to demonstrate the significance of the research undertaken and the potential provided by such data processing.

The MOAI-1 program combines computer image processing – *Péricolor 2001* software – with the *Géopéricolor* software. At present it is divided into four sub-programs, which could eventually be extended. The sub-programs are designed for:

- acquisition of the natural features of the statues by non-destructive methods at any given time;
- notation of the weathering by comparative analysis;
- notation of spatial-temporal evolution after interventions; and
- acquisition and processing of environmental data.

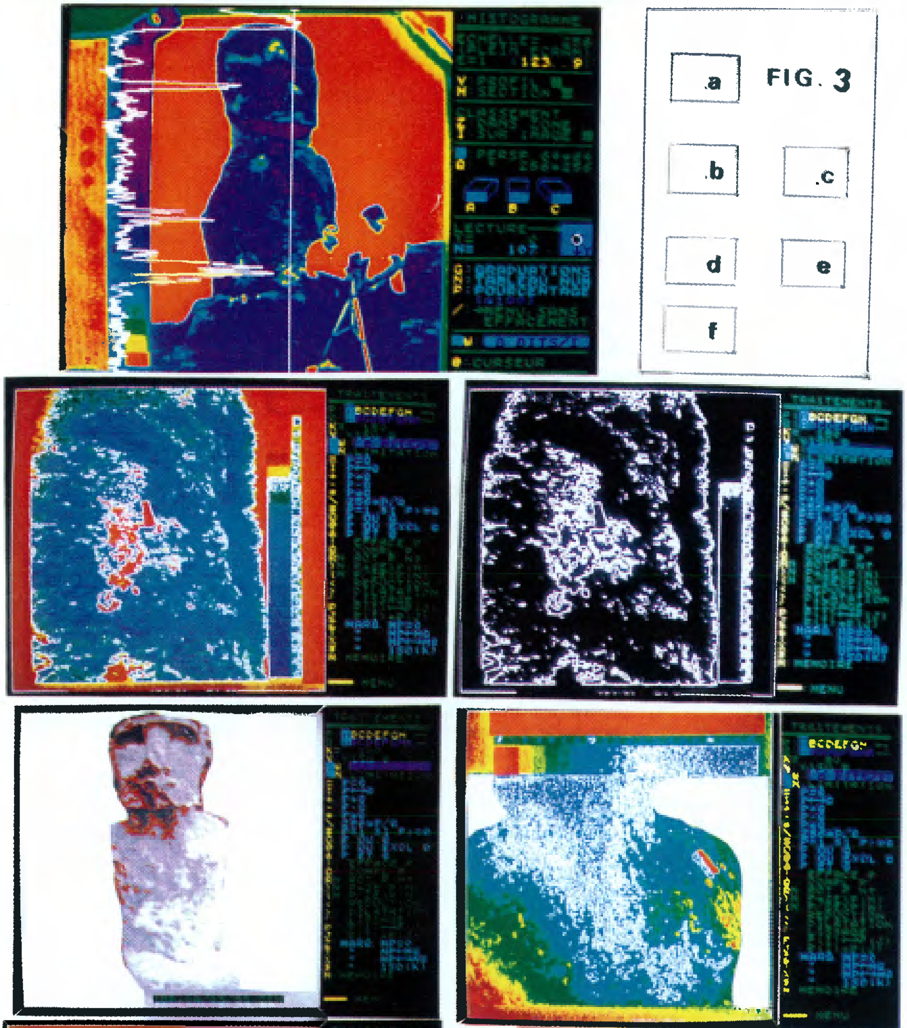
A non-exhaustive list of measurable parameters is currently being prepared. This is based on previous experience, such as the Lascaux problem [2; 3]. The codified parameters are stored in an index which is specific to each statue.

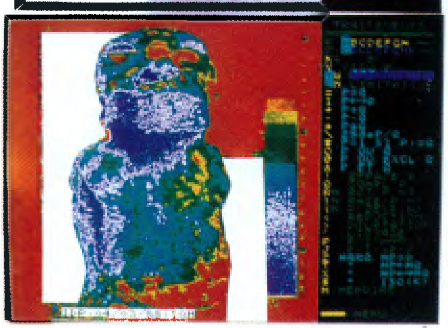
Table 21.7 presents the first codified and numbered results. The sizing of the pixels and the display are made on the basis of image restitution through numerical listings, histograms, statistical analysis, composite imagery, alphanumerical mappings, etc. A photographic illustration of some examples is given in Figure 21.3.

Table 21.7 **Proposed components of the information matrix for the MOAI-1 data bank.**

Objects: LAVAS AND TUFFS					
	Bare rock	Concrete	Encrust-ations	Biological growth	Matrix
Colorimetric identification – grey levels – false colours	 <——— XXXX ———> <——— XXXX ———>				
Index of reflectance	#1 - 62/85 #3 - 67/120	163/259 —	— 97/120	— 127/210	85/104 —
State of surface (S) – rough S. – smooth S.	Line transects and stereo-diagrams <——— XXXX ———> <——— XXXX ———>				
Morphology	<——— XXXX ———>				
Superficial humidity level 3	– no tests on #1, #2 & #3 – tests in the laboratory on #4 & #5 <——— XXXX ———>				
Imagery definition	<——— 8 megapixels ———> <——— 16 megapixels ———>				
Thematic mapping	<—— XXXX ——>		XXX	<—— XXXX ——>	
Inverse	<——— XXXX ———>				
Imagery superimposition	Samples #1 & #4 <——— XXXX ———>				
Animation	<——— XXXX ———>				

Notes:
62/85 = spectral values of the index of reflectance.
Quality of the tests: X = inadequate; XX = poor; XXX = medium; XXXX = good.





a. Hanga Kio'e moai false-colour cartography and linear analysis (line transect) of hydro-chemical and superficial anomalies.
b. Hanga Kio'e moai (sample #1), abdomen, micro-cartography of encrustations.
c. Hanga Kio'e moai (sample #1), abdomen, inverse micro-cartography.
d. Moai 4 (sample #2), cartography of algae.
e. Moai 4 (sample #2), breast, micro-cartography of wet surface (white) and lichens (green and yellow).
f. Moai 5 (sample #3), biological stains and rain trails.

Figure 21.3 Examples of computer imaging.

21.5 CONCLUSIONS

Volcanic tuffs and lavas are porous, permeable, and heterogeneous materials which need further study for their complete understanding.

The hydrodynamic and hydrogeological phenomena and transport of material that affect these stones are influenced directly and indirectly to varying degrees by the climatic and environmental parameters associated with the objects.

Further studies, both in the field and in the laboratory are needed for a better understanding of the deterioration mechanisms. For this purpose, some statues will have to be selected and numerous samples, of comparable mineralogy, will have to be taken for further study. The temporal unit of these studies should be the climatic cycle or a multiple thereof. The spatial unit should be a statue and its near environment.

The creation of a scientific data bank is absolutely necessary to be able to handle both field and laboratory data.

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RESUMEN

Las propiedades petrográficas 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 tambien 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 bioquímicos. Se recalca la importancia de la niebla salina. La transferencia de tecnología de previos estudios permitió la elaboración de una metodología específica para el estudio de los materiales volcánicos en general y las estatuas de Isla de Pascua en particular.

RESUME

Les caractéristiques pétrographiques et pétrophysiques des laves et des tufs volcaniques sont très hétérogènes. Elles dépendent du faciès volcanique d'origine, de l'évolution au cours du refroidissement et des contraintes géomécaniques pendant le mouvement. Les affleurements naturels s'altèrent au cours du temps géologique; les causes et les résultats sont divers. L'altération affecte aussi les "objets" façonnés par l'homme à partir de ces matériaux s'ils sont laissés à l'extérieur. Ce processus repose principalement sur des facteurs climatiques et microclimatiques, puisqu'ils définissent les paramètres hydro- et biochimiques. Le rôle joué par les embruns marins est souligné. Le transfert de technologie à partir d'études antérieures a permis de développer une méthodologie spécifique applicable aux matériaux volcaniques en général et aux statues de l'Ile de Pâques en particulier.

KURZFASSUNG

Die petrographischen und physikalischen Eigenschaften von Lavagesteinen und vulkanischen Tuffen sind sehr verschiedenartig. Sie hängen ab vom Chemismus des Ausgangsmagmas, dem Verlauf des Abkühlvorganges und dem geomechanischen Kräftefeld während der Magmawanderung. Gesteine in Naturaufschlüssen sind im Verlauf geologischer Zeiträume der Verwitterung unterworfen, deren Ursachen und Auswirkungen sehr unterschiedlich sind. Ebenso wirkt die Verwitterung auf die vom Menschen bearbeiteten Objekte aus diesen Materialien, wenn sie sich im Freien befinden. Dieser Prozess wird meist durch klimatische und mikroklimatische Faktoren gesteuert, da diese die hydro- und biochemischen Parameter kontrollieren. Hervorzuheben ist die Rolle des marinen Sprühwassers. Eine Übertragung der Arbeitweise aus früheren Untersuchungen ermöglichte die Entwicklung einer eigenen Methodik zum Studium vulkanischen Gesteinsmaterials allgemein und der Statuen der Osterinsel im besonderen.

CONSERVATION TREATMENT OF A MOAI ON EASTER ISLAND: A LABORATORY EVALUATION

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ABSTRACT

Deterioration of the statues of Easter Island is an exponential process clearly apparent today. It is the result of the combination of 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 and UNESCO, the advice of international experts in the field and the sponsorship of the manufacturer of the product used.
The treatment carried out was later evaluated by artificial ageing of samples in the laboratory. The results show the effectiveness of ethyl silicate as a consolidant for volcanic tuff.

22.1 INTRODUCTION

The statues, *moai*, of Easter Island are endangered. For centuries they have been suffering a progressive and irreversible deterioration whose exponential effect is an evident fact today.

Since their creation they have been exposed to the weathering effects of rain, wind and sea spray, all of which are a permanent aggression to the constituent material – a volcanic tuff with poor characteristics. The result has been a steady deterioration, which today is obvious as surface loss (to a depth of several centimetres in places), powdering, flaking, cracking, fissuring, efflorescence, silica deposition, build-up of microflora, etc.

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In the hope of preserving this important heritage a plan was developed, within PNUD/UNESCO/DIBAM project CHI/79/013, involving study, diagnosis and an experimental intervention on a statue. The object was to determine adequate conservation measures, compatible with the material of the moai and appropriate to the environmental conditions on the island.

22.2 CONSERVATION TREATMENT OF THE MOAI

In 1980, within the framework of the above-mentioned project, Prof. W. Domaslowski, as UNESCO expert, was asked to carry out a study on the causes of deterioration of Easter Island tuffs, and to suggest conservation procedures for the statues. The study concluded that a consolidation treatment, based on ethyl silicate, followed by a hydrophobization treatment, based on a rubber-type silicone resin, was needed [1].

This proposal, after discussions with various experts, was slightly modified by changing the suggested hydrophobization agent to a silicone resin-based treatment which would not seal off the surface of the stone: water vapour would still be able to pass through.

22.2.1 The Hanga Kio'e Moai

For the purpose of the project, the moai at Hanga Kio'e was chosen. The choice was based on the fact that this statue presented nearly all the various types of deterioration phenomena observed on moai. Its proximity to the museum facilitated the execution of the treatment and its follow-up. A thorough survey was carried out and the actual state of preservation was duly documented [2]. The most relevant deterioration phenomena observed were:

- surface loss on the back and both sides, approximately 5 cm in depth
- loss of an important part of the right shoulder
- thick, white silica deposits on the forehead, nose and lower parts of the statue
- fissures and microfissures on the whole statue
- presence of biological organisms
- surface powdering on the back, which faces the sea, and on both sides

A factor contributing to its deterioration was the restoration that was carried out in the 1970s [3]. At that time the moai was lying face down on the ground, its head separated from the body, and on its back two circular holes, approximately 20 cm in diameter, had been made. The restoration had consisted essentially of putting the head back on the body, using iron bars and cement mortar, and standing the statue up on the reconstructed *ahu*. The statue was stabilized on the ahu by means of a thick layer of the cement mortar.

Due to the low porosity of the mortar, the stone immediately above the mortar layer has deteriorated proportionally more because humidity concentrates in it, keeping it permanently moist.

In addition, the iron bars used in the restoration could, as a result of their corrosion process, have induced the microfissuring of the moai that was observed in the present study.

22.2.2 The Treatment

The treatment carried out has already been reported in various publications [4; 5; 6]. Some details are given in the first part of the Appendix to this paper. The treatment consisted of three stages:

- **Insulation and surface cleaning**
  To carry out the consolidation it was necessary to protect the moai from rain and marine spray. This was done by setting up a tent around the statue. During the drying-out period the surface was cleaned of lichens and salt efflorescence.
- **Consolidation**
  The moai was completely wrapped up in various layers of cellulose wadding, wound tightly around the body, then enveloped in a polyethylene sheet to avoid solvent evaporation. The consolidant was applied from the top and percolated through the body by gravity.
- **Salt extraction and hydrophobization**
  Approximately two months after consolidation, any remaining soluble salts were removed by poulticing. The hydrophobization product was applied by surface spraying.

The effectiveness of this last treatment was already apparent during a short shower on the day following the application. The treatment as a whole has, so far, been successful. The surface is no longer powdering, no lichens have re-established, and the moai shows the original colour of the stone rather than the black algal patina it had prior to the treatment.

22.3 EVALUATION OF TREATMENT AFTER ARTIFICIAL AGEING

To evaluate the performance of the products used in the conservation of the moai at Hanga Kio'e, a laboratory study was carried out. Samples of untreated (**U**) volcanic tuff, consolidated samples (**C**) and samples treated with the consolidant and water repellent (**C+WR**) were artificially aged and subjected to various resistance tests.

22.3.1 Sample preparation

From a specimen of volcanic tuff taken from the Rano Raraku quarry, about 100 prismatic samples, 40 × 40 × 60 mm, were cut. The X-ray fluorescence analysis of this tuff is given in Table 22.1.

To obtain a homogeneous body of samples, only those from the unweathered internal part of the specimen were used. Of these 57 samples, 22 were left untreated (**U**) to serve as controls, 22 were treated with only the consolidant (**C**), and 13 were treated with both the consolidant and the water repellent (**C+WR**).

Table 22.1 **Chemical composition of the volcanic tuff, determined using X-ray fluorescence data. Values given as %** w/w of dry sample

MAIN COMPONENTS				ALSO DETECTED	
Fe_2O_3	12.8	MnO	0.3	Sr	0.03
TiO_2	2.5	MgO	3.4	Zr	0.05
CaO	6.0	Na_2O	2.1	Y	0.01
K_2O	1.3	P_2O_5	0.5	Nb	0.01
SiO_2	52.0	SO_3	0.1	Zn	0.03
Al_2O_3	14.0				
Loss by calcination at 1000°C = 3.7%					

The consolidant was applied to the 35 samples by partial immersion (standing in half a centimetre of the liquid) and they were allowed to become totally saturated through capillary rise. The samples were dried for three weeks in ambient outdoor conditions, but under cover. The water repellent was applied to 13 of these samples by immersion. The treated samples were allowed to dry, under the same conditions, for another three weeks.

22.3.2 Tests applied

The samples were subjected to three different artificial weathering procedures and then evaluated by means of abrasion resistance, compression and water absorption tests. The three ageing systems used were: UV radiation and water spray (xenotest); high temperature and oxygen pressure (HTOP); and salt spray. Details of the ageing procedures and the tests applied are given in the Appendix to this paper.

The abrasion resistance test was applied to unweathered samples and those aged by xenotest and by HTOP.

The compression and water absorption tests were applied to unweathered samples and those aged by all three procedures.

22.4 RESULTS

22.4.1 Abrasion resistance test

This test was carried out according to ASTM D 968-51. Particular details are given in the third part of the Appendix to this paper. The test was applied to unweathered samples, and those weathered by xenotest and HTOP.

The results for unweathered samples are shown in Figure 22.1, and, for those weathered by xenotest and by HTOP, in Figures 22.2 and 22.3, respectively.

In all cases studied, the highest weight loss was seen in the untreated samples. Unweathered samples showed an increase in abrasion resistance in the order **U**, **C**, **C+WR**, while the ranking for weathered samples was **U**, **C+WR**, with **C** being the most resistant.

Samples aged by xenotest showed little change from unweathered material. This result agreed with the expected behaviour of the treatment which, by its nature, should not be susceptible to UV radiation.

Samples aged by HTOP showed the highest resistance to abrasion.

22.4.2 Compression test

This test was carried out according to Chilean Norm NCh 1037. Details are given in the third part of the Appendix to this paper. The test was applied to unweathered samples and those weathered by all three procedures. The data obtained are given in Table 22.2.

Table 22.2 Compression test data for unweathered and weathered samples (in kg/cm^2)

	Untreated (**U**)	Treated (**C**)	Treated (**C+WR**)
Unweathered	68 ± 15	104 ± 10	–
Xenotest	97 ± 20	120 ± 10	–
HTOP	123 ± 15	167 ± 7	–
Salt spray	–	174 ± 5	149 ± 1

The data show that consolidated samples are more resistant than the untreated ones. Though only data for samples weathered in salt spray are available, it would appear that the presence of the water repellent diminishes somewhat the resistance of the consolidated samples.

It is interesting to note that the dispersion of data diminishes for treated specimens. This would indicate that an apparently more homogeneous material is obtained upon treatment.

22.4.3 Water absorption test

This test was carried out by measuring the capillary water absorption 24 hours after treatment. The data are given in Table 22.3.

As expected, untreated samples absorbed the highest amount of water while those treated with consolidant and water repellent absorbed the least.

Table 22.3 Water absorption data (% increase in weight)

	Untreated (**U**)	Treated (**C**)	Treated (**C+WR**)
Unweathered	10.50	7.00	0.31
Xenotest	12.50	5.70	0.29
HTOP	10.70	10.00	0.26
Salt spray	12.30	8.11	0.37

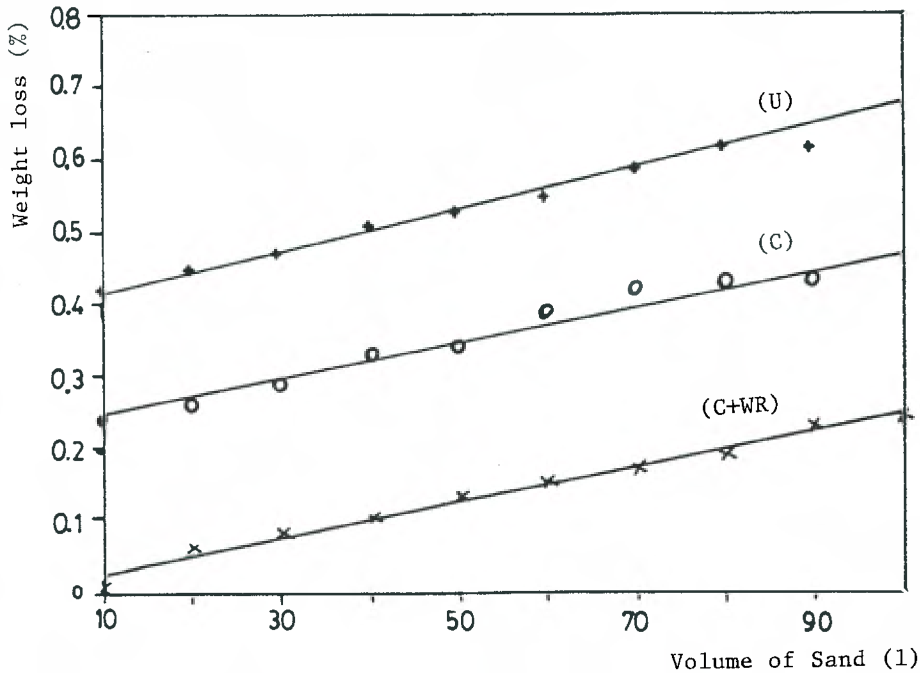

Figure 22.1 Abrasion resistance test for unweathered samples: untreated (U); consolidated (C); consolidated + water repellent (C+WR)

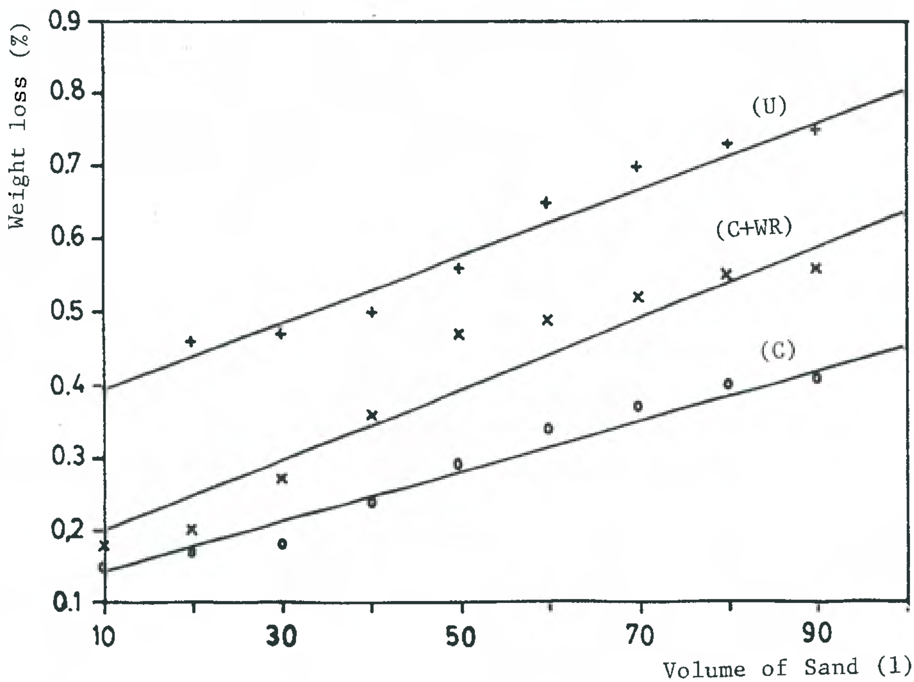

Figure 22.2 Abrasion resistance test for samples weathered by xenotest: untreated (U); consolidated (C); consolidated + water repellent (C+WR)

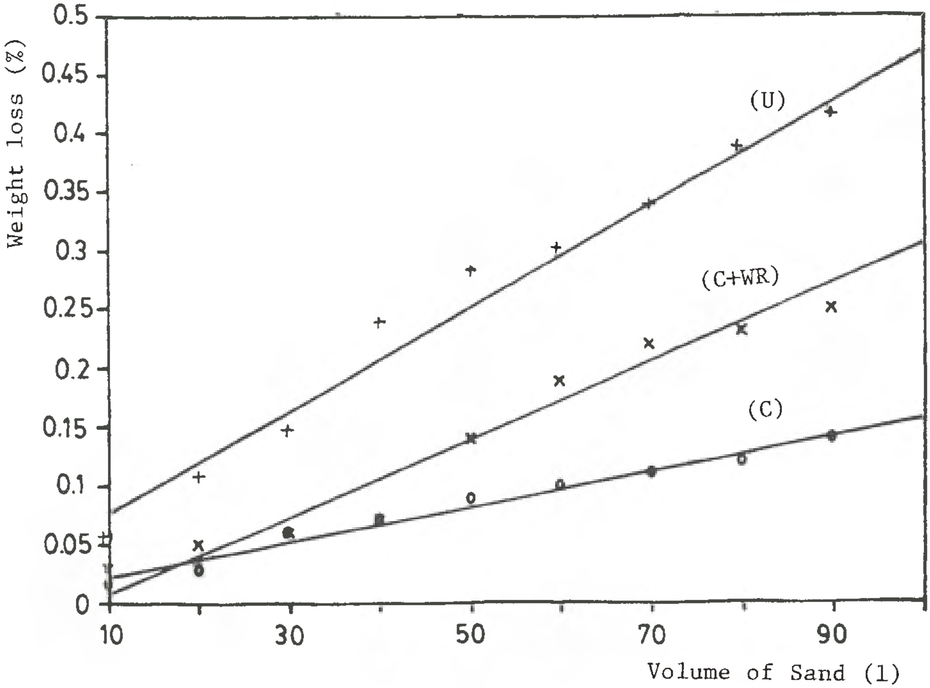

Figure 22.3 **Abrasion resistance test for samples weathered by HTOP: untreated (U); consolidated (C); consolidated + water repellent (C+WR)**

22.5 CONCLUSIONS

The weathering treatments used in this study tried to reproduce, in an accelerated fashion, the conditions to which the moai are exposed over time.

Even though the hydrophobization treatment appears to diminish the mechanical resistance of the consolidated stone, the improvement in terms of reducing water absorption fully justifies its use.

The evaluation of the treatment after weathering under high temperature and oxygen pressure, which would accelerate any further reaction of the consolidating and water-repellent product, appears to indicate that, upon ageing, the system will improve its resistance.

The results obtained appear to vindicate the choice of treatment.

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Thanks are due to the CESMEC Laboratory, and in particular to Mr Manuel Zuñiga, for the tests carried out.

APPENDIX 22-A

22-A.1 Products utilized

It is important to point out that the first field tests carried out (summer 1985 and summer 1986) with *Wacker OH*, the product recommended by Domaslowski, were not successful. The solvent evaporated too quickly, precipitating silica on the surface of the stone.

The tests were suspended and the manufacturer, Wacker Chemie, modified the product by using a different solvent system that would be appropriate to the climatic conditions on the island. They also modified the water repellent, *W 090 S*, that was used for the hydrophobization of the statue.

The surface cleaning of the moai was carried out at the beginning of 1986. The tent was set up around the moai at the time and was left until the consolidation treatment was applied toward the end of that year. The water repellent was applied in February 1987.

22-A.2 Artificial weathering conditions

- **Xenotest:** carried out according to DIN 54005 standard. The samples were exposed for 500 hours. The cycles alternated light and dark, with a 3-minute water spray every half hour. The UV source was a xenon lamp (XE 1500) whose spectrum covers the 300 to 700 nm range.
- **High temperature and oxygen pressure (HTOP):** carried out for one month, holding the samples at 100°C and under an oxygen pressure of 25 kg/cm^2.
- **Saline spray:** carried out according to ASTM B117 standard. The temperature was held at 38°±1°C, using a concentration of 5% NaCl in the water spray.

22-A.3 Tests

- **Abrasion resistance test** (ASTM D 968-51): the sand used had 80% of the particles between sizes 600 μm and 850 μm. The flow of sand was 2 litres in 2.5 seconds. The sand was dropped at an angle of 45°.
- **Compression test** (NCh 1037): the equipment used was an Instrom testing press with a capacity up to 10 000 kg.
  The charge was applied continuously and without impact at the uniform rate specified by the norm. Results are given in kg/cm^2.
- **Water absorption test:** the dried and weighed samples were set upon a water-saturated polyurethane foam support, covered, and re-weighed after 24 hours.

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 ha 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, la asesoría de expertos internacionales en el área y la subvención del fabricante del producto utilizado. El tratamiento realizado fue sometido a una evaluación posterior en laboratorio mediante envejecimiento artificial del material tratado. Los resultados muestran la eficacia del silicato de etilo en procesos de consolidación de la toba volcánica.

RESUME

Les statues de l'Ile de Pâques souffrent d'un processus accéléré de détérioration dont l'effet exponentiel est aujourd'hui évident. Il est principalement dû aux conditions climatiques conjuguées aux caractéristiques du matériau fragile (tuf volcanique). Dans le but de sauvegarder ce témoignage culturel, on a réalisé une intervention expérimentale avec l'appui du PNUD-UNESCO, les conseils d'experts internationaux dans ce domaine et le parrainage du fabriquant du produit utilisé. Le traitement a été plus tard évalué en laboratoire par vieillissement artificiel d'échantillons traités. Les résultats montrent l'efficacité du silicate d'éthyle comme consolidant du tuf volcanique.

KURZFASSUNG

Die Statuen der Osterinsel sind einem Zerfallsprozess unterworfen, dessen exponentialer Verlauf heute eine sichtbare Tatsache darstellt. Die Witterungsverhältnisse im Zusammenspiel mit den Eigenschaften des Gesteins (ein vulkanischer Tuff) sind die hauptverantwortlichen Faktoren für den gegenwärtigen Zustand der Statuen.

Mit Blickpunkt auf eine Erhaltung dieses Kulturerbes ist eine Versuchsbehandlung mit Unterstützung von UNDP-UNESCO, unter der Anleitung internationaler Fachleute und mit Beihilfe der Herstellerfirma der angewandten Produkte durchgeführt worden. Die dabei vorgenommene Konservierung wurde im nachhinein mittels Laborbewitterung an Proben bewertet. Die Ergebnisse sprechen für die Eignung von Ethyl-Kieselsäureester zur Festigung des vulkanischen Tuffs.

HYDROPHOBIZATION TREATMENTS: PRELIMINARY TESTS ON THE EASTER ISLAND TUFF

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ABSTRACT

The deterioration of the Easter Island statues is mainly due to the action of water: chemical dissolution of the vitreous matrix and mechanical erosion by driving rain. The protection of the statues must therefore rely on a good hydrophobization treatment. In a first study, three water repellents were tested: two siloxanes dissolved in solvents, and one water-soluble silane system. The artificial ageing was based on wet/dry cycles, with the wet cycles providing a water spray to simulate driving rain. No significant differences in efficacy were found for the three products tested. These preliminary results need to be complemented by *in situ* tests to adequately evaluate their performance. The aim of applying a protective treatment is to avoid further deterioration and a future need for consolidation treatments.

23.1 INTRODUCTION

The deterioration of the tuff used for the carving of the statues of Easter Island is caused by many factors [1; 2; 3]. The primary factor is the action of water which, through chemical dissolution or mechanical erosion, rapidly weathers this stone.

Given the number of statues on the island and their generally poor condition, most of the previous studies addressed consolidation of the stone [2; 4; 5; 6]. Those studies placed only minor emphasis on hydrophobization treatments.

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In view of the great number of very weathered statues present on the island, and the questions that only time will answer regarding the ultimate efficacy of the tested consolidation treatment [2], it was considered important to start a research project that would address the protection of the few well-preserved examples remaining, such as those statues at Ahu Naunau in Anakena.

23.2 PREVIOUS STUDIES

An assessment of four water repellents was carried out on a red sandstone from the Jura. These were:

- *Tegosivin HL 100* (Goldschmidt). A methyl ethoxysilane dissolved in white spirit to a concentration of 7%. Before application, 2% of a catalyst – *Tegosivin HLK* – was added.
- *VP 1311* (Wacker). An experimental methyl-octyl ethoxysiloxane dispersed in water to a 7% concentration just before application.
- *C 300* (Sylvania). An acrylic resin mixed with the catalyst before application, following the manufacturer's instructions.
- *Sigmasil* (Sigma). A mixture of methyl ethoxysiloxane and aluminum stearate, dissolved in white spirits to a 7% concentration.

The products were applied by a flow technique to prismatic samples. The surface was treated until no more visual uptake of the product was apparent. In general this was achieved after 2 to 4 seconds. After a 5-minute drying period, a second application was carried out. The amount of material absorbed averaged around 135 g/m^2 for *HL 100* and *VP 1311*, while 349 g/m^2 of *C 300* was absorbed, leaving a film on the surface and darkening the stone considerably. An average of 142 g/m^2 of *Sigmasil* was absorbed.

The samples were aged under two different systems: the first with a water spray, the second with moisture condensation. The water-spray system had constant UV irradiation and a weathering cycle of 2 hours light at 40°C + 2 hours light with rain at 25°C (eight rain events and four 5-minute heatings at 65°C (after every second rain)). The moisture-condensation system also had constant UV irradiation, with a weathering cycle of 2 hours at 40°C and 95% RH with sample cooling, followed by 4 hours at 40°C and 40% RH with no cooling.

Water absorption was measured using the RILEM II.4 method, with the "pipe" or Karsten tube. It was found that two weeks of weathering under the moisture condensation cycles produced results equivalent to 6 weeks (1 000 hours) with the water-spray system.

From these preliminary tests it was concluded that *HL 100* maintained its water repellency the best after the 1 000 hours of weathering under water-spray conditions, while the other products lost some of their effectiveness. In the case of *C 300*, the film coating had yellowed visibly. The poorest results were obtained with the *Sigmasil*, although the treated surfaces dried much faster than the untreated ones. Under moisture condensation cycling, after 4 weeks (672 hours) of artificial ageing, the water repellency of the *HL 100* and the *VP 1131* treatments were similar, while the *Sigmasil* and the *C 300* had lost some of their efficacy.

The results obtained served to narrow down the selection of the products to be tested on the Easter Island samples to siloxanes dissolved in solvents.

23.3 EXPERIMENTAL DETAILS

23.3.1 Stone samples

Samples of the tuff from the Rano Raraku volcano were taken from an outcrop mound. Three big blocks were taken, which broke into smaller pieces as the material dried. The moisture content of these samples was between 10 and 25%.

The samples were sawn into 5 × 5 × 5 cm cubes. As the material was very friable, many samples broke during the wet sawing process.

23.3.2 Products tested

Three water repellents were tested:

- *Wacker 290*, a methyl-octyl methoxysiloxane at 7% in white spirit,
- *Wacker 090*, a methyl ethoxysiloxane at 7% in white spirit, and
- *Dynasylan BSM 100W*, a water-soluble propyl methoxysilane. The pure silane is diluted in water in a 10% v/v concentration. After 4 to 8 minutes, the solution becomes clear and has to be used within 6 hours.

The products were applied by spraying for 30 seconds.

23.3.3 Artificial ageing

Only water-spray weathering cycles were used for this study. Several reasons prompted this choice: (a) results from the first survey showed the loss of water-repellency from both types of ageing could be equated; (b) the fact that the mechanical erosion of the rain is an important factor in deterioration of the Easter Island statues; and (c) the limited availability of stones from the island, which forced a choice for this study. The cycles consisted of 2 hours at 45°C and 20% RH + 2 hours with rain at 20°C (eight rain events and four 5-minute heatings at 65°C after every second rain). The exposed surfaces received constant UV irradiation during the 840 hours (5 weeks) of the ageing, giving a total of 561 kJ/m^2 at 340 nm.

23.4 RESULTS

The water absorption coefficient of a freshly sawn surface and of a naturally weathered surface was measured following the RILEM II.6 procedures. The values of the absorption coefficients for the products tested were also measured. The results are given in Table 23.1.

Table 23.1 Absorption coefficients for both water and the hydrophobization products tested, for freshly sawn surfaces and naturally weathered surfaces.

Product	Surface	Absorption Coefficient ($kg/m^2.s^{0.5}$) 0 – 4 minutes	4 – 15 minutes
Water	A	0.433	
	B	0.545	
W 290	A	0.373	0.189
	B	0.344	0.234
W 090	A	0.373	0.189
	B	0.344	0.234
BSM 100W	A	0.486	0.222
	B	0.486	0.222
where: A = freshly sawn surface, and B = naturally weathered surface			

From the above data it can be seen that water-based hydrophobization agents penetrate initially at the same rate as water, but slow down after 4 minutes. The products dissolved in organic solvents show a lower penetration rate at all times.

The data suggested that the products should be applied to the test samples by spraying for 30 seconds. The amount of material absorbed was determined by weight differences, and the depth of penetration was measured on the samples that remained whole after the artificial ageing cycles were completed. The samples that had been used for the absorption tests (duration 15 minutes) were also subjected to artificial ageing. The results are reported in Table 23.2.

Every week capillary water absorption was measured for samples with naturally weathered surfaces and the water absorption by means of the pipe method was determined for those with freshly sawn surfaces. As these last surfaces deteriorated during the ageing process, especially those treated by spray for 30 seconds, not all data could be obtained for the full duration of the experiment. The samples treated by absorption for 15 minutes resisted better than those treated for less time. No significant differences were detected between the two Wacker products.

The capillary water absorption data obtained during the five weeks of artificial weathering are reported in Table 23.3.

The distribution of the products within the matrix of the stone was examined by scanning electron microscopy (SEM). The two solvent-based siloxanes left a homogeneous coating on the pore surfaces, as shown in Figures 23.1 and 23.2. The water-soluble product appeared not to have as good a covering power, as shown in Figure 23.3. These observations are in accordance with the water absorption data obtained.

Table 23.2 Amount of hydrophobization product absorbed and penetration depth.

Product	Application mode	Surface	Consumption (kg/m^2)	Impregnation depth (mm)
W 290	Spray	A	4.34	25
		B	3.70	15
	Absorption	A	6.89	25
		B	15.3	75
W 090	Spray	A	4.32	30
		A	2.54	21
		B	3.68	15
	Absorption	A	7.91	40
		B	14.8	65
100 W	Spray	A	2.21	10
		B	4.22	2 - 30
		B	1.30	11
	Absorption	A	10.1	40
		B	11.7	40

Table 23.3 Capillary water absorption of naturally weathered surfaces after exposure to artificial ageing.

Product	Absorption mode	Water absorbed in 2 hours (kg/m^2) after ageing for (weeks)					
		0	1	2	3	4	5
Ref. #1		22.6	18.5	23.4	19.3	15.2	18.4
Ref. #2		13.5	12.0	13.6	13.1	10.8	13.4
W 290	Absorption	1.3	0.9	1.5	1.7	1.2	1.7
	Spray	1.1	–	–	–	–	1.3
W 090	Absorption	1.4	1.0	1.6	1.4	1.1	1.5
	Spray #1	0.5	0.6	0.8	0.8	0.9	0.9
	Spray #2	1.4	1.7	2.1	2.6	1.9	3.4
100 W	Absorption	1.4	0.9	1.3	1.3	0.8	1.4
	Spray #1	2.6	1.7	2.6	3.2	1.9	2.0
	Spray #2	13.8	11.6	14.3	12.5	9.9	12.4

Figure 23.1 **SEM photomicrograph of a fracture surface. The area shown was about 0.5 mm below the treated surface. Note the homogeneous distribution of the *W 290* resin over the pore surface.**

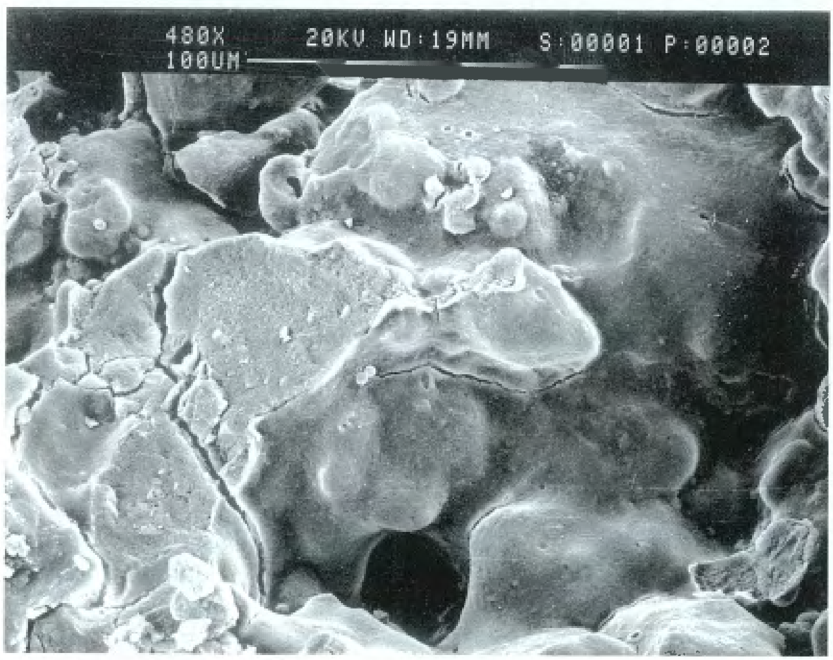

Figure 23.2 **SEM photomicrograph of a fracture surface. The area shown was approximately 1 mm below the treated surface. The *W 090* product leaves a uniform coating over the stone matrix.**

Figure 23.3 SEM photomicrograph of a fracture surface. The area shown was approximately 0.2 mm below the surface treated with *BSM 100 W*. Note the uncoated, platelike minerals on the left side of the photograph.

23.5 DISCUSSION AND CONCLUSIONS

The products tested did not show any important decrease in effectiveness after the five weeks of artificial ageing. The main differences observed were due to the heterogeneity of the material and to fissures and cracks in the weathered surfaces. Another factor contributing to the dispersion of the data is the water level maintained during the absorption measurements (the naturally weathered surfaces were not flat and hence the water level adjustment was difficult). A small difference in this water level can cause variations of up to 4 kg/m^2 in values recorded. Nonetheless, it would appear that the products using solvents gave a slightly better hydrophobization than the water-dissolved product.

During the artificial ageing the exposed surfaces lost their "pearling" effect. However, when the samples were broken up at the end of the five weeks, all three products still showed a perfect pearling effect on the freshly broken surfaces. Hence, the products were still effective under the exposed surface.

Given the positive results obtained on samples that were far more deteriorated than the tuff of the statues at Ahu Naunau, the distinct possibility of protecting these by means of a hydophobization treatment exists. Nevertheless, *in situ* testing is needed before a given product can be applied to these statues. It is hoped that if the hydrophobization treatment is effective, and a good routine maintenance programme of re-applications is developed, deterioration of these statues can be prevented. This would then eliminate the need for future consolidation treatments.

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RESUMEN

La deterioración de las estatuas de Isla de Pascua se debe fundamentalmente a la acción del agua: la disolución química de la matriz vítrea y la erosión mecánica de las lluvias batientes. La protección de las estatuas se basa, por lo tanto, en una buena hidrofobización. En un primer estudio, tres productos hidrorepelentes fueron ensayados: dos siloxanos disueltos en solventes y un sistema de silanos soluble en agua. El envejecimiento artificial se basó en ciclos húmedo-seco, con una rociada de agua en los ciclos húmedo simulando las lluvias batientes. No se encontraron diferencias en la efectividad de estos tres productos. Estos resultados preliminares necesitan ser complementados con ensayos *in situ* para evaluar adecuadamente su comportamiento. El objetivo de la aplicación de un tratamiento protectivo es el de evitar la futura deterioración y consecuentemente un ulterior tratamiento de consolidación.

RESUME

La détérioration des statues de l'Ile de Pâques est principalement due à l'action de l'eau: dissolution chimique de la gaine vitreuse et érosion mécanique par des pluies battantes. La protection des statues doit par conséquent miser sur un bon traitement d'hydrofugation. Dans une première étude, trois hydrofuges ont été testés: deux siloxanes dissous dans des solvants et un silane soluble dans l'eau. Le vieillissement artificiel a été obtenu par répétition de cycles de mouillage-séchage, le mouillage étant effectué par jet d'eau pour simuler les pluies battantes. Aucune différence sensible d'efficacité n'a été constatée pour les trois produits testés. Ces résultats préliminaires doivent être complétés par des tests *in situ* pour établir un bilan précis. Le traitement de protection a pour but d'arrêter le processus de détérioration et d'éviter d'avoir à procéder à des traitements de consolidation.

KURZFASSUNG

Die Verwitterung der Steinfiguren der Osterinsel ist zum Großteil auf die Einwirkung von Wasser zurückzuführen, nämlich auf eine chemische Lösung der glasigen Tuffmatrix und die mechanische Erosion durch Schlagregen. Eine Schutzbehandlung der Steine muß daher auf einer geeigneten Hydrophobierung beruhen. In einem ersten Untersuchungsprogramm wurden drei Hydrophobierungsmittel getestet: zwei Siloxane in Lösungsmitteln und ein wasserlösliches Silansystem. Die künstliche Bewitterung der behandelten Prüfkörper beruhte auf Feucht-Trocken-Zyklen, wobei die Feuchtphasen aus einer Beregnung bestanden, die den Schlagregen simulieren sollte. Für die drei getesteten Produkte konnten bezüglich ihrer Wirksamkeit keine signifikanten Unterschiede festgestellt werden. Die Voruntersuchungen müssen durch Versuche vor Ort bestätigt und weitergeführt werden. Das Ziel einer Schutzbehandlung ist die Verhinderung der weiteren Zerstörung und der Notwendigkeit von Festigungsbehandlungen.

Part Six

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS AND RECOMMENDATIONS OF THE INTERNATIONAL MEETING ON "LAVAS AND VOLCANIC TUFFS"

The International Meeting on Lavas and Volcanic Tuffs was held on Easter Island from October 25th to 31st, 1990. The Meeting was organized by:

- the Dirección de Bibliotecas, Archivos y Museos (DIBAM) of Chile, through its Centro Nacional de Restauración;
- the Corporación Nacional Forestal (CONAF) – as administrator of the Rapa Nui National Park and other protected areas;
- ICCROM (International Centre for the Study of the Preservation and Restoration of Cultural Property); and
- the World Monuments Fund (WMF).

A group of international experts participated in this meeting. These scientists – geologists, chemists, biologists, engineers and physicists – all specializing in the conservation of stone – had previously prepared studies dealing with relevant problems of lavas and volcanic tuffs. Those studies were published in a preliminary volume, prior to the meeting.

This group of experts, after five days of field work on Easter Island and several inter- and intradisciplinary discussion sessions, prepared the following, based on conclusions reached. This document presents a set of recommendations that emphasizes the urgent need for adoption of a comprehensive plan for the conservation of the archaeological heritage of Easter Island.

Lavas and Volcanic Tuffs: Proceedings of the International Meeting. Easter Island, Chile, 25-31 October 1990. Edited by A.E. Charola, R.J. Koestler and G. Lombardi.

ISBN 92-9077-115-1

The participants in the International Meeting on Lavas and Volcanic Tuffs:

– **recognizing** that the stone used for carving of the moai is extremely heterogeneous and its characteristics vary extensively with the location from which it was taken in the quarry;

– **recognizing** that the climatic conditions favour weathering both directly (due to the heavy and frequent rains and the strong winds) and indirectly (through development of lichens, algae and other biological organisms);

– **recognizing** the negative effects of human activity, such as the unrestrained movement of tourists, their actions and those of accompanying persons, the direct and indirect effects of cattle, and the fires in grasslands;

– **considering** that the archaeological heritage of Easter Island, comprising the well-known monumental statues – the moai; the petroglyphs; the living and ceremonial centres; and the rock paintings represents a unique cultural heritage, both for the Rapanui community and for the whole world;

– **considering** that this heritage is in a critical conservation state due to the progressive deterioration of the stone;

– **considering** that the conservation problem is compounded by the fact that this heritage is made up of approximately a thousand moai, three hundred ahu (ceremonial platforms), and many other archaeological artifacts distributed over thousands of sites on the 166 square kilometres of the island;

– **being convinced** that immediate action is needed due to the serious and progressive nature of the deterioration affecting the lithic material, and the extensiveness of the conservation problem;

– **recommend** that the authorities adopt a comprehensive plan for the conservation of the archaeological heritage of Easter Island, and that that plan should include a scientific and technical programme, as briefly outlined below;

– **recommend** the adoption of complementary measures that will allow the development of the comprehensive plan for the conservation of the archaeological heritage, as described below;

– **recommend** some specific actions in view of the urgency for immediate conservation measures, as listed at the end of this document; and

– **recommend** that any action involving archaeological objects and taken for study or conservation purposes should be part of the comprehensive plan, and that the sampling needed for all these studies and tests be carried out on a statistical basis to ensure that the smallest number of representative samples is taken.

SCIENTIFIC AND TECHNICAL PROGRAMME

The following scientific and technical programme for the conservation of the archaeological heritage of Easter Island, developed on the basis of previous studies carried out by the participants, was prepared during the International Meeting on Lavas and Volcanic Tuffs. The programme has been structured on the basis of two simultaneous activities: base-line studies and *in situ* testing.

1. **Base-line studies**

- Completion of the documentation relative to the state of conservation of the heterogeneous stone materials used in the different archaeological objects.
- Compilation and critical analysis of the results of previous research.
- Petrographical, mineralogical and geochemical characterization of the stone materials.
- Physico-mechanical characterization of the stone materials.
- Compilation and elaboration of climatological data and study of the microclimate in specific areas.
- Identification, characterization and quantitative analysis of the biological species present on the stone materials.
- Study of the morphology, causes and mechanisms of the deterioration processes, including simulation tests and measurements on samples in the laboratory.
- Determination of the deterioration rate in specific areas through periodic and systematic measurements, carried out on the surface of stone elements (statues, petroglyphs, etc.).

2. ***In situ* Testing**

- Evaluation of the effect that the change in position of a moai (from horizontal to vertical, such as occurs during restoration) has on the type and rate of deterioration of the stone.
- Environmental protection of sites through the development of protective structures and the evaluation of their efficacy.
- Evaluation of biocide systems for the control or elimination of algae and lichens.
- Evaluation of consolidation or hydrophobization products, or both, carried out simultaneously with laboratory testing and including quality control of the tested products.

COMPLEMENTARY MEASURES

The participants to the International Meeting on Lavas and Volcanic Tuffs consider of critical importance the adoption of the complementary measures described below. These measures provide for the qualified personnel, public awareness and installations necessary for development of the comprehensive plan for the conservation of the archaeological heritage.

The measures proposed are:

- development of training courses on deterioration problems of and conservation techniques applicable to the archaeological heritage, for teachers at the local elementary and high schools;
- training of park rangers and other technical support staff to help in projects related to deterioration studies and in conservation programmes for archaeological objects in stone;
- training of tourist guides in subjects relating to conservation of archaeological heritage;
- appointment of one or more professional conservators trained in the conservation problems specific to Easter Island and residing on the island;
- improvement in management and control of archaeological sites and an increase in staff available for security and assistance to the public; and
- establishment of a support centre on Easter Island for use by all scientists collaborating in the different conservation projects. The centre should include a basic laboratory with a mobile unit, storage space, lodging space, and transport units.

SPECIFIC ACTIONS

The participants in the International Meeting on Lavas and Volcanic Tuffs, in view of the urgent need for some immediate conservation measures to preserve the archaeological heritage of Easter Island, recommend the following specific actions:

- improvement in management and control of archaeological sites, taking into account their design and minor installations, as well as an increase in staff available for security and for public assitance. It is suggested that this measure be carried out at the following sites: Orongo, Rano Raraku, Ana Kai Tangata and Anakena;
- hydrophobization treatment of the best-preserved moai. It is suggested that this measure be carried out on the moai of Ahu Naunau;
- design and installation of protection structures, which also might serve as observation points, around the perimeters of the petroglyphs carved on

the rock outcrops called *papa*. It is suggested that this measure be carried out for the petroglyphs at Tongariki, Ra'ai and Pu hakanini mako'i;

- construction of temporary shelters to cover specific sites. Their design should take into account all the existing information from other archaeological sites in similar climatic areas. It is suggested that this measure be carried out on one or more of the moai along the so-called "moai road" in the neighbourhood of the Toa-toa hill; and
- preservation of one or more moai by relocation into the local museum. These objects should be maintained under professional, scientific control to assure their proper conservation. It is suggested that this measure be carried out on the moai called Tuturi.

Hanga Roa, Easter Island, Chile,
October 31st, 1990

Part Seven

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MAILING ADDRESSES

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