LABORATÓRIO NACIONAL
DE ENGENHARIA CIVIL

International Symposium
Stone Consolidation in Cultural Heritage

Special Volume
Short stories and personal perspectives on the history of stone conservation

Editor: José Delgado Rodrigues

LNEC, Lisbon, 23-25 March, 2022

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Preface

The history of (stone) conservation is written in the abundant and rich scientific literature, in books and manuals, and in many forgotten (and most of them lost) reports in dark rooms and inaccessible archives. It is also made up of unpublished stories, hidden memories, personal thoughts and so many other events lived but never told by the protagonists.

When preparing to launch the organization of this Symposium, I challenged a group of friends with long careers in the field of conservation to write a few lines about any episodes, events, short stories or simply tell their personal perspectives on how conservation (of stone) has evolved throughout their life. No themes or guidelines were given, and only a brief indication that it was about anything they considered worthy of being known, but which generally does not find space available where it can be published.

Some of them declined the invitation because they were too far from the scientific front (although they were reassured that this would be a positive and not a negative factor) or for other personal reasons, and it a privilege and honour to thank Elena Charola, Andrew Oddy, Giorgio Bonsanti, Clifford Price, Norman Tennent, Jeanne Marie Teutonico, Carlos Rodriguez Navarro and Johannes Weber for their willingness and effort dedicated to this challenge.

The extremely interesting reflections and analyses made demonstrate that even trivial topics, when handled by intelligent people, can provide insightful perspectives and significant contributions.

Lisbon, March 2022

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What time has taught me

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INTRODUCTION

The experience I gained over the years is based on some initial incidents. It all began with the Stone meeting that was held in Louisville, Kentucky, U.S., in 1982. I was sitting next to an Italian colleague and we were listening to the presentations. For one of them, my colleague mentioned that what the speaker was presenting he had already discussed in a publication. It so happened, that I had read that paper (which was published in English), but could not remember that he had discussed it the same way. At the time, I did not say anything, but as soon as I was back home, I reread the paper in question and could not see where he had mentioned it. This puzzled me, since he has explained it clearly to me during the meeting. So, I read the paper over and over, without seeing where the clue was. Until one night I woke up and realized where he had mentioned it. It took me one week to realize where the problem was and how, in his translation into English, this key point was missed.

The origin of these events is that our brains are not mass-produced, they are unique, and our perception of things depends upon them. Therefore, each one of us has a special talent, in one field or another, and it is seldom that two people will have exactly the same talents. Thus, the way we interpret what we read will be the result of how our mind follows its reasoning. And that certainly depends on our previous experience. Hence the need to make sure, when we write, to be clear in those points that may be misunderstood.

This showed me how important it was to write clearly, especially not being a native English speaker, to allow others to follow the reasoning. It made me aware of the issues of translations from a different language and the ensuing results. Years later, another incident occurred: a student of mine was writing her thesis, where she discussed a paper of mine concluding that the treatment under study had not produced a negative result. When I read this, I could not remember having made that assertion, so I reread my paper; and indeed, I never suggested such a possibility, and had not even considered a negative result. Once more, this showed how statements can be easily be distorted.

BACKGROUND

One of the problems in writing papers for publication, is that English is the preferred language, and this makes it more difficult for non-native English speakers. One of the first papers I submitted to a Journal was accepted, but it was sent to me with the corrections included. I called the Journal up about this, and they said that all I had to do was to copy the final version and resubmit it. I was thankful to the reviewer who helped correct my English to make it easier to read. And since then, I have tried to help correct the English in papers that I have been asked to review. I remember particularly one paper, which was excellent, and only needed some minor changes to make it easier to follow. When I returned the review, they were upset because I had included corrections, which apparently was not expected from a reviewer, but I managed to convince them that this would improve the reading of the paper, and they finally accepted it.

Most of the time, there is no problem, but in many cases, there may be. Especially now, with the increasing number of periodicals that are available, published in various countries, some of them not English speaking, so that the paper published may not be quite written in “proper” English. Furthermore, the “requirement” for publications in academia and elsewhere, results in many cases that the same study is published in two or three different journals, with minor changes made to it. This is one of the most serious issues, since it means that one needs to keep up with various journals to make sure one does not miss an important study. And this approach is both time consuming and costly. Furthermore, the number of journals that require payment for publishing a paper has increased significantly; and although the papers are sent to reviewers, doubts remain about this process. Thus, questions can be raised as to the validity of these “paid” publications: How thorough is the reviewing process? How many reviewers check a given paper? These are points that need to be considered.

On a more general level, the number of journals has increased significantly over the past ten years. And more are being launched daily, reflecting both a booming business and flourishing enterprises. Not only that, but the way the papers are published is being changed: many journals require now a graphic summary of the contents of the paper (so that the readers can immediately know what the paper is about) thus in many cases eliminating the need to “read” the complete paper.

CONCLUSIONS

The world has “broadened” significantly during the last part of the 20th century and the beginning of the current one. And with that broadening, inevitably there will be overlapping of research, studies and experimental work. This implies that to keep up with the research being carried out world-wide, a lot of time is required resulting in less time to do actual research thus losing productivity. This is the current dilemma. And the easiest solution is to disregard research from newer sources and focusing on the established research centers.

We cannot predict what the future will bring, as we could not predict the COVID-19 pandemic, which significantly affected most of the countries in the world. We still do not know how we are to survive it, and when an effective vaccine will be developed. But that will not prevent other problems to occur, the main one being the climate change that resulted from all the combined actions of man.

Polymers in Conservation Research in the 1960s: a brief retrospective review

Andrew Oddy

I joined the British Museum Research Laboratory in October 1966 after a year spent in chemical industry following a university degree in chemistry. The conservation 'Bible' at that time was Harold Plenderleith's ***The Conservation of Antiquities and Works of Art*** (Oxford, 1956), supplemented by the papers published in ***Studies in Conservation*** and one or two other European journals. The practice of conservation in the British Museum had just passed a milestone with the recognition of 'conservator' as a special skill by the civil service. Until the early 1960s, all conservator's in the British Museum had been regarded as 'craftsmen' and they had all trained 'on the job'. But in 1960, the Institute of Archaeology of London University started to produce conservators with a diploma in practical archaeological conservation. At last, those treating antiquities were being taught to question the traditional methods of treatment and to think carefully about any procedure and materials they were proposing – or being told – to apply.

As a scientist coming into conservation I was dependent upon this new professional breed of conservator to educate me into what needed to be done by a scientist. I followed in the footsteps of Robert Organ who had emigrated, first Canada and then to the Smithsonian Institute in Washington DC. Robert left behind very little in the way of archives apart from his published papers and the results of his metallurgical examinations of antiquities. But he did leave behind a reputation for thorough research work. So much so, that the room I occupied, was still known as "Mr Organ's room" for several years after I arrived! I wonder if my colleagues expected him to reappear as a ghostly wraith.

Twenty years after the end of the Second World War, the scientific world was still buzzing with discoveries of new materials made as a result of the investment in research on war work. Many of these materials had not been tested for their suitability for use on antiquities, but they were applied by scientists who were picking up the pieces of Museum research-work in the late 1940s and 1950s who had themselves been trained in research during the war.

By the mid-1960s, if not earlier, a number of polymers was seen as miracle substances and four spring to mind from my own experience:

- Epoxy resins
- Polyester resins
- Soluble nylon
- Polyethylene glycol

In a world that until the 1930s had depended upon animal glue, shellac, starch paste, or a solution of cellulose nitrate for repairing objects, epoxy resins appeared to be the answer to a conservator's prayer. The bonds were very strong, and if not exactly colourless, the use of epoxy resins made the repair of glass and thin porcelain more effective. But at this period, nobody had pointed out – or perhaps even realised – that antiquities should never be repaired with an adhesive stronger than the object itself. Thus before the profession knew where it was, epoxy resins were being applied widely and even to low fired and 'crumbly' prehistoric pottery. Slowly the 'clouds began to clear' and it was realised that epoxy resins might be good for some materials but they were certainly not good for others.

Polyester pastes were widely used for repairing automobile damage and they were quickly commandeered by the old-fashioned craftsman as gap fillers for antiquities. But the 'reversibility' mantra was not yet being chanted and so polyesters found their way onto many objects where the old-fashioned gap fillers of plaster of Paris would have been better. Mind you, plaster of Paris can hardly be said to be reversible as it could not be dissolved and had to be picked away under a microscope if a new treatment was needed. But it could be isolated from the antiquity by a separation layer of cellulose nitrate.

Soluble nylon, sold in the UK as Calaton CB, had, I think, being developed as a way of prolonging the life of textiles that were being used to make wind-socks for the RAF. But as an almost colourless polymer that could be applied to powdery services it again seemed to be a miracle substance. Unfortunately, however, at the time it was being widely used no one had been able to investigate long-term ageing properties. Suddenly conservators found that soluble nylon cross linked with time and would no longer dissolve in the solvents used to make the original solution. Soluble nylon had found uses for consolidating prehistoric pottery, but mostly it had been used on organic (ethnographic) objects which were not part of my brief and I was only vaguely aware of the problems until they became acute.[i]

With polyethylene glycol, problems get nearer to home and I enter the 'battlefield'. More or less the first job I was given at the British Museum Research Laboratory was to impregnate a Chinese sandstone stele with polyethylene glycol. I'm not sure what the reasoning was, other than that polyethylene glycol had recently been used with some success for the conservation of waterlogged wood. But flaking sandstone has nothing in common with waterlogged wood. In fact, as I remember, the stele was not really in a bad condition. Some of the surface had flaked away, but a long time in the past, and there was no evidence of an active flaking surface in 1966. Being new to the profession, I did not demur, and we rigged up a temporary oven made from sheets of asbestos board (!!) and heated this stele with arc lamps. As far as I was concerned, that was that, until we had a problem with the washing of Egyptian limestone a few years later. Egyptian limestone contains soluble salt and if this crystallises on the surface it can cause disruption. Furthermore, modern industrial atmospheres were reacting with the surface of the limestone to create a thin layer of calcium sulphate.

Hence, at some time before my arrival at the British Museum, the Egyptian Department had installed two large tanks to wash their limestone sculptures in order to de-salinate them. All went well for a few months and then one particular lintel started to lose its surface within a few hours of going into the tank. I think it was not noticed for a while and by the time the lintel had been removed from the water large areas of the surface had come loose as thin flakes. Why had we been able to wash several stones without incident, and then suddenly had a disaster?

This started a research project which, in retrospect, was one of our best pieces of conservation research in the early 1970s.ii What we did was to take a small sample by drilling from an inconspicuous area of the surface of the limestone object and subject this sample to measurements for 'acid insoluble' component and 'percentage of soluble chloride'. This produced a very nice correlation because if soluble chloride was <0.1% and acid insoluble was <1% the surface would be in good condition and washing the sculpture in water would be safe. But if soluble chloride was >0.5% and acid insoluble was >5% the surfaces were usually in a fragile condition and soaking in water was harmful.

So far so good and we were able to wash some sculptures safely to remove chlorides from the surface layers. Those that were fragile were carefully cleaned by hand. When cleaning was complete by either process it was decided to consolidate the surface with polyethylene glycol grade 6000. The reason was to prevent the adherence of airborne dirt in the future and the thinking was that, for those stones that had been washed, the PEG could be easily removed by soaking in water if this became necessary.iii

At this juncture, late 1975, I was transferred to work on the scientific investigation of antiquities and said 'goodbye' to conservation until I was unexpectedly put in charge of the Conservation Department in 1981. During these five years some of the impregnated sculptures were put on display and after a while it was noticed that the polyethylene glycol was seeping out of the surface as a result of humidity changes in the museum atmosphere. This was a disaster, but not my problem!!!

The moral of this memoir is that long term testing of new treatments should be mandatory before they are widely applied. If oozing of polyethylene glycol out of consolidated objects was a problem I would have expected the British Museum scientists – that is me and my team – to have known this as it should have been a factor with all the waterlogged wood that had been treated with polyethylene glycol in other museums by the middle 1970s. But I remember nothing like this that would have warned us about a potential problem. Was it negligence on our part – did we not survey the literature well enough? Or were there problems with PEG-treated waterlogged wood that were not being publicised?

At this remove in time, and with no access to a conservation library having moved well away from London in retirement, I am unable to answer this question. It just remains for me to regret that we pushed forward with PEG consolidation of limestone sculptures without sufficient quality control - mea culpa.

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[iii] W A Oddy, Susan M Blackshaw and S Baker, The Consolidation of Limestone Sculptures with Polyethylene Glycol for Indoor Display, in R Rossi-Manerasi (ed), *The Conservation of Stone I*, (Proceedings of the international symposium held in Bologna in 1975), Centro Conservazione Sculture all’ Aperto, Bologna, 1975, 485-497.

A plea for accessible and well-publicised databases of conservation treatments

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KEY-WORDS: consolidant; evaluation; testing; recording; database.

Does it work? Is it safe? Are there any undesirable side-effects? For how long does it remain effective? Are there any circumstances in which it should not be used?

There are many parallels between the development of a stone consolidant and the development of a vaccine. I addressed some of the issues involved in the evaluation of stone preservatives in a paper that I wrote almost forty years ago (Price, 1982); it was the focus of an ICCROM conference in 1995 (ICCROM, 1995); and the topic is still being raised today (Praticò *et al*, 2020). Most people would agree that, ultimately, time is the only true test of a consolidant, or of a vaccine. But even then, a consolidant needs to be tested in a wide variety of conditions and on many different types of stone, just as a vaccine needs to be tested on many different people.

Consolidants have been used for many years, and there should by now be a very extensive body of knowledge regarding their effectiveness. But where is it? Where can one go in order to discover where a particular consolidant has been used, or how well it has performed?

Conservators and conservation scientists are invariably conscientious about their record keeping. Full records are kept of the treatments that are made, and these are lodged with the appropriate authority. But can these records still be found ten or twenty years later? Fifty years? A hundred years? Individuals move on to other jobs, or retire; the records get lost at the back of a filing cabinet and are eventually thrown out. Of course, it is not always like this. But even if the records are held by a professional archivist at a major cathedral, say, other people may not be aware that they exist, or that the treatment to which they refer was ever carried out.

Sadly, we have to accept that there is a large body of knowledge that would be invaluable to us in our evaluation of stone consolidants, but which is either unknown to us, inaccessible, or lost. This is not said in order to find fault with past record-keeping; before the advent of the internet, there was no other means of recording a treatment than to put it on paper. However, we now have the technical means to create a database on which any conservator or conservation scientist could place their records and thereby make them known and accessible to all.

There would be a second benefit of making records widely accessible, which is of comparable importance. At present, conservators are often confronted with decaying stonework in need of treatment. But they may have no idea whether it has ever been treated before, or what it might have been treated with. Knowledge of previous treatments would greatly facilitate the selection of an appropriate treatment now.

The purpose of this paper is to present a plea for relevant bodies to accept the challenge of setting up a database of conservation treatments in their own country, which would then be accessible worldwide. Such a database need not be complex or detailed; indeed, if it were difficult to use, nobody would bother to add any records to it. A database which contained no more than the location of the treated stone, the consolidant used, and the date of treatment, would be a great step forward. The immediate benefit would be small, but the long-term benefit would be enormous.

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Reflections on the History of Stone Consolidation

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It is difficult to point to a precise date for its inception, but the exploration of materials and the implementation methods for the conservation of stone in cultural heritage objects has a long history. The Romans may have attempted to protect and preserve stone with beeswax and the 19th century is littered with examples of the development and use of preservatives for stone. By 1932 it was possible to codify advances in understanding the deterioration and conservation of stone in a monograph – *The Weathering of Natural Building Stones* by R.J. Schaffer. Ensuing decades saw important additional developments, but a significant shift in the production and transmittal of information on these subjects began about fifty years ago with the first conference that brought together participants from several countries to discuss the latest work on stone (and wood) conservation – the *International Institute for Conservation, New York Conference on Conservation of Wood and Stone Objects: 7-13 June 1970.* This conference was quickly followed by *The Treatment of Stone,* Bologna, October 1-3 1971, organized by Giorgio Torraca and Raffaela Rossi-Manaresi, and, the *First International Congress on the Deterioration and Conservation of Stone*, in La Rochelle, France in 1972, organized by V. Romanovsky, which has now seen its 14th iteration in Göttingen 2020. Over the past fifty years these conferences have produced a significant body of knowledge in stone deterioration and conservation in their own right, and spawned other more biodeterioration, consolidation, laser cleaning, and water repellent and surface protection of stone (and other) building materials. specialized conferences on subjects such as stone monuments in the Mediterranean basin, Focusing specifically on the subject of stone consolidation, there are several small histories and reviews of materials for consolidation dating to the 19th century and early 20th century such as Schaffer's book mentioned above, and in more recent decades, Sleater's *Review of Natural Stone Preservation,* Clifton's *Stone Consolidating Materials – A Status Report*, and Amoroso and Fassina's *Stone Decay and Conservation*. These summaries of stone consolidants are remarkably similar and highlight the significant efforts and advances that took place in the 19th century. That century witnessed the inception and development of many of the main ideas and philosophies of preservation and conservation of cultural heritage generally and its constituent materials more specifically. Stone, as one of these materials, received much attention with cleaning and consolidation methods and materials at the forefront.

What began in that century and persists through to today is a strong focus on silicates for stone consolidation. The earliest examples were so-called water glass usually based on either sodium or potassium silicate. They were in some ways trying to model silicate minerals such as quartz and feldspars that persist in nature due to the general stability of the Si-O-Si bond system (silicon is the most abundant element in the earth's crust after oxygen). In addition to silicates, alkaline earth hydroxides such as calcium and barium hydroxide were used as consolidants, the former probably dating back many centuries. Barium hydroxide is still used in limited instances today while calcium hydroxides in forms other than lime water have seen a renaissance in recent decades. The focus on silicates and alkaline earth hydroxides in the 19th century is understandable in that the focus of stone consolidation was often buildings and building stone outdoors. Their use largely pre-dated the many organic resins later used as consolidants both indoors and outdoors – after the advent of modern synthetic organic chemistry that rested largely on the discovery and exploitation of oil in Eastern Europe in the 1830s and in the United States in 1859. Prior to these developments, natural organic materials were used for centuries as adhesives for stone (and other materials): hide (cow), rabbit skin and fish glues; mono-, di- and triterpenoid tree exudates such as rosin and colophony, copal and sandarac, and, mastic and dammar (some mixed with beeswax); drying oils such as linseed oil (and much later, tung oil), insect derived materials such as shellac, waxes such as beeswax (and later synthetically derived) and polysaccharides such as gum arabic. It is not too difficult a stretch of the imagination to think that any of these compounds might have been employed as consolidants as well, although there are few references to that use discovered to date.

While there remained a strong focus on water based silicates such as water glass, attention turned to another silicate material in 1861 – ethyl silicate. Unlike water glass it is immiscible in water without the addition of ethanol but reacts at a reasonable rate with water to produce a stable gel. Like alkaline earth hydroxides their use persists to this day with various refinements over the past 160 years.

One of the earliest organic synthetic resins (or at least semi-synthetic) was cellulose nitrate and later cellulose acetate both of which were used as consolidants in the 20th century in museums. As focus moved to petroleum derived resins, as each resin came into being it eventually made its way into the world of stone conservation, and specifically, consolidation: polyvinyl alcohols (PVA), polyvinyl acetates (PVAC), polyester resins, acrylic resins, fluoropolymers, epoxy resins, polyethylene glycol (PEG), etc. PVAs, PVACs, and acrylics have been used in solvents and as water miscible emulsions, and, PEG as a water miscible consolidant also frequently used for the consolidation of waterlogged wood. These materials are now rarely used in outdoor environments but epoxy resins have persisted to a small degree as consolidants but have an even strong presence as adhesives in many outdoor applications.

From the 1960s forward, alkoxysilane-based consolidants have still dominated in practice. However, recent developments in nano technologies have brought a renewed focus to calcium hydroxide-based consolidants and water-miscible silicates. A significant limitation of alkoxysilane consolidants is their incompatibility with liquid water – whether in the stone being consolidated or with recently treated stone exposed to rainwater or other sources of liquid water. The nanolimes (calcium hydroxide in alcohols) and nanosilicas (waterbased) overcome this problem. For nanolimes an additional advantage is the orders of magnitude increase in concentration achieved through the nano technology – from less than 1% for lime water to up to 50% for nanolimes. Their effectiveness continues to be explored in the literature and the high quantities of VOCs (volatile organic components) make them excluded in some jurisdictions. The nanosilicas are waterbased so have no problems with VOCs. However, most formulations of these nano colloids are stabilized at pHs near 10 or 11 achieved with sodium hydroxide. While lower in concentration than was found in 19th century waterglasses, they suffer from the same problem of forming sodium salts (carbonates and sulfates).

On a separate but equally important track due to their miscibility and compatibility with water are the so-called “reactive” consolidants. These comprise ammonium ion, pH balanced, acids: oxalate (oxalic acid), tartrate (tartaric acid), and, phosphate (phosphoric acid). Tailored specifically for carbonate rocks such as limestones and marbles, ammonium oxalate was originally used for the stabilization of the lime-based substrates of frescoes. All three of these reactive consolidants consume a miniscule part of the calcium carbonate substrate and convert it into a stable calcium derivative: calcium oxalate, calcium tartrate, or one of the forms of calcium hydrogen phosphate.

Over the last four decades there has been somewhat of a retreat from large scale consolidation of stone in monuments, sculptures and buildings. Consolidants are being applied selectively and locally (only on specific elements of a structure) and the choice of consolidants takes into account specific stone types, conditions of the substrate, and the surrounding environment. As stated above, alkoxysilanes still dominate, but practitioners take into account all of the above factors in selecting a consolidant, and, at times apply more than one consolidant to the same set of conditions. Cultural heritage objects in stone are benefitting from this cautious and thoughtful approach to consolidation as we continue to learn more about their application to the many different stone types and conditions that are present.

Stone consolidation: reflections on the relationship between science and field practice

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INTRODUCTION

Surface consolidation of weakened stone substrates is one of the more polarizing issues within the built heritage conservation community. This is not surprising considering that, on the one hand, surface consolidation is very frequently identified as a necessary phase of an overall conservation strategy, and, on the other, that consolidation methodology and assessment is still associated with several unsolved theoretical and operational questions. The inherently irreversible nature of stone consolidation and the technical challenges associated with designing and implementing treatments on extremely complex historic substrates has fostered an incredibly rich and yet controversial corpus of scientific and technical contributions. Looking back at the results of such a long and fertile dialogue between heritage scientists, conservation architects and conservators over the last twenty years (Teutonico et al 1997, Hansen et al 2003, Delgado 2010, and Praticò et al 2020) provides a compelling insight into past and current challenges regarding stone consolidation.

Not surprisingly, the main topics around which debate continues have not changed much. These include but are not limited to:

- the need for effective and reasonably straightforward in situ assessments of treatment performance parameters that can help to inform conservation decisions, such as depth of penetration, relative strength increase, and distribution of consolidant within the stone pore structure;
- efforts to create more systematic, and possibly standardized, operational guidelines for the selection of appropriate treatment products and application procedures;
- challenges in translating widely accepted theoretical requirements - such as compatibility, durability and re-treatability - into operational principles that can be measured and applied with some consistency;
- the persistent gap between research and practice, including the still limited transfer of scientific research results to practitioners, despite a constantly growing number of studies in the field.

This short contribution to the discussion will focus predominantly on the last point, the important relationship between research and field practice, with some reflections on the persistent obstacles limiting effective collaboration and knowledge transfer. Though there is generally consensus on the need for interdisciplinary approaches when dealing with the complexity of built heritage conservation, this rarely translates into truly integrated projects that combine the expertise of both scientists and practitioners. The possible reasons for this can be traced back to methodological issues, practical constraints of cost and time, communication problems, and ultimately, questions of trust.

METHODOLOGICAL DIFFERENCES / PRACTICAL CONSTRAINTS

Considering consolidation in the broader context of stone conservation, there is no doubt that field practice and scientific research desire the same outcome, which is improved effectiveness, durability and compatibility of treatments. However, the working methodologies through which such a final objective is pursued, and some critical associated constraints, are highly discipline-specific and therefore remarkably different.

Despite the unique and irreplaceable values of built heritage sites, the management of conservation projects often involves the strict allocation of limited financial and human resources and rigid timelines to keep interventions within budget. Any activity not strictly related to the conservation treatment that might result in additional costs or time has to be carefully weighed against the direct and short-term contribution to the project's successful completion. Diagnostic and scientific investigation too often fall within the category of *non-crucial actions,* particularly for intervention on non-monumental sites that constitute much of the built heritage worldwide. Conservators and architects invariably have little budgetary margin, and often no scientific support, for developing or fine-tuning treatment procedures or experimenting with innovative solutions. Therefore, decisions regarding consolidation materials and application methodology are often based on previous experiences and personal preferences, trusting that what proved successful in the past will provide reliable and effective performance on a different site. Alternatively (and perhaps worse), materials and methods are chosen based on summary case studies in *grey literature* (i.e., non-peer reviewed information available on the web).

This is why some institutions that provide grants for architectural conservation often have two distinct components of financial aid – enabling grant applicants to carry out scientific and other studies in advance of conservation, so that the latter might be informed and directed by the former preparatory activities. Unfortunately, such enlightened and progressive philanthropy is unavailable in many parts of the world.

Even when resources are available, the timeframe of scientific investigation is an additional issue that can collide with the time constraints of a planned intervention. When heritage scientists are actively involved in planning a consolidation strategy, it is not uncommon for frictions to develop as the practitioners' requests for technical guidance based on laboratory and field-testing results are delayed. Managing these legitimate expectations requires careful communication of the time requirements of the diagnostic phases and clarification of the expected results, and will positively contribute to building trust in this collaborative process. On the other hand, a certain degree of flexibility is needed when planning the testing protocols to account for unexpected circumstances and to ensure that needed information can be provided in keeping with the project's timeline.

As others have noted, initiating the conversation between practitioners and scientists at the early stages of planning is fundamental to ensuring that these different working methodologies are aligned with the project's goals, and that there is agreement on the sequence and duration of various activities, potential risks and expected results. And to state the obvious, providing some allocation of resources for scientific investigation within conservation projects will go a long way toward improving collaborative prospects.

Architectural conservation projects with long logistical lead times before commencement (e.g., when funds have first to be raised through grant applications and the solicitation of donations) can sometimes better accommodate preliminary technical and scientific assessments, and even multi-year trials and evaluations, if planned well in advance and delivered in a timely fashion. Projects can also be broken down into phases, in such a way that the conclusions and recommendations from heritage science activities are programmed for delivery more precisely when needed.

Perhaps the heritage science community might work with the architectural conservation community to establish standard protocols, guidelines and model service level agreements to best articulate work stage definitions, practice methods, resourcing and suggested timescale requirements for common scientific approaches to stone consolidation.

LACK OF STANDARD PROTOCOLS

Obviously, a sound approach for the design and execution of experimental activity supporting consolidation treatment starts with the precise definition of the conservation issues to be addressed and their specific context. This involves the comprehensive characterization of the stone substrate, as well as the type, causes, extent and degree of deterioration. The preliminary investigation should also gather all the relevant information regarding the specific exposure conditions and microclimatic information, which play a key role in damage evolution and in selecting the most appropriate consolidants and treatment procedures. The critical evaluation of this corpus of information will determine whether a consolidation treatment is actually needed and provide a baseline for developing a testing regime.

However, despite an extensive scientific literature, there is still work to be done toward a widely accepted and standardized testing protocol. Thus, each case will warrant an appropriate ad hoc approach, adding to the complexity of the overall collaborative endeavor. From the scientific point of view, an effort has to be made to design the most effective and focused experimental regime, which will keep the duration of the diagnostic activity to a manageable level and achieve good integration with field activities. Similar considerations apply to field testing. The preparation and pre-treatment of pilot areas, trial applications, variable curing times, and a minimum monitoring interval for the assessment of (at least) short-term efficacy all have to be adequately factored in when timing the phases of the intervention. The development of simple and cost-effective in situ assessments would be extremely helpful in this process. And we are desperately in need of more long-term monitoring and evaluation of consolidation treatments (e.g., Martin et al 2002) to better understand their efficacy and the need for/effects of re-treatment.

COMMUNICATION AND KNOWLEDGE TRANSFER

The previous considerations are based on the assumption that diagnostic and testing are crucial resources for an informed selection, fine-tuning and implementation of consolidation treatments. However, to be recognized as such, additional effort is required to effectively communicate the results of scientific activity to practitioners. Many authors have pointed out the importance of knowledge transfer between research and practice, emphasizing how such a process is critical and yet often unsatisfactory for both parties. Effective communication starts with identifying a shared working language capable of conveying all the relevant information, i.e., balancing the need for a scientifically accurate presentation of experimental findings with the importance of reaching a broad practitioners' community that might include professionals from a wide range of disciplines. Moreover, knowledge transfer should not be limited to delivering a collection of diagnostic results at the end of an intervention – as too often happens with final scientific reports whose actual usefulness for practitioners is limited – but has to be managed as a constant exchange of information throughout all phases of a project. This is a two-way process, from which research also has much to gain. Practitioners possess a unique body of knowledge on consolidation practice and a deep understanding of field conditions. Such a combination of skillset and experience is often overlooked or not fully exploited by scientists, to the detriment of both specific interventions and more general research activities.

As has been noted by others, the field would profit from more scientific articles published in journals that are read by practitioners and from greater documentation of practical case studies. Papers written jointly by scientists, architects and conservators are also extremely valuable and often quite rewarding undertakings. Mutual respect for the different forms of knowledge acquisition represented by science and field practice will undoubtedly lead to advances in both realms and to more effective collaboration.

SOME FINAL COMMENTS

Stone consolidation is a very particular type of conservation treatment that brings with it some unique challenges and considerations. However, some of the reflections above could be applied to the heritage conservation field at large. Great advances, both technical and otherwise, have been made in the last several decades. And the field has expanded in scope and in the breadth of professionals that are engaged in it. And yet, heritage conservation still faces many challenges. Financial and human resources for cultural heritage - both governmental and private - remain inadequate. Traditional materials and the craft skills needed to maintain them are often in short supply. Climate change has produced more extreme weather conditions that pose increased risk for heritage generally, and more specifically impact the extent and degree of stone deterioration world-wide. And then, of course, there are the threats internationally from armed conflict, the effects of mass migration and the consequences of pandemics.

Nonetheless, considering the long-term historical development of stone preservatives, protective coatings and consolidants from oils and soaps to alkoxysilanes and synthetic organic polymers, the field of study discussed here has generated an extraordinary array of international research and achievement in a relatively short period of time. It is therefore to be hoped that reflections such as this and others produced for the 2021 symposium on stone consolidation will help steer future actions and innovation for the sustainable benefit of our common cultural heritage and for posterity.

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Short stories, people, and episodes in stone conservation

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INTRODUCTION

Stone conservation, as any other professional discipline, has evolved with the support of bright people, systematic research work, and impactful research findings, but also with the contribution of unpublished and ignored basic works carried out by a population of anonymous professionals following their own paths, with lower or higher relations with the scientific world itself. Heroic personalities, critical discoveries and great achievements are the most easily referenced landmarks and history is mostly written based on them. However, this is only a part of the true story where many other relevant actors and multiple episodes fit, despite not leaving traces strong enough to be visible outside the short circle of direct actors.

The impact is directly visible and measurable within a small circle, the overall result for the broader professional community may be irrelevant to the majority, uninteresting to some, but it can be meaningful and valuable to a few. And “Time” may turn out to show that the hierarchy of relevance and interest is not a static rule, and a minor fact or episode today can become a clue to something tomorrow. A medieval painter's recipe was banal and of mostly private interest a few centuries ago, though it may provide a critical clue in helping to restore a painting today.

Telling short stories, mentioning people who have had an impact on me, and describing episodes of personal interest may be anecdotal to my readers, but it can also inspire others to relate their own life episodes and help to make conservation communication easier. When reaching the end of a career, we realise that our experience was built on a multitude of bases and supported by countless people. Some of these bases can be traced back to published literature and important events, but many (if not most) of them were rooted in diffuse sources and anonymous actors. Bringing to light some of them that I consider significant is the aim of this text.

A FIRST STEP

When, in 1972, Prof. Marc Mamillan paid a visit to our institution, the National Laboratory of Civil Engineering, he was far from imagining how big the impact of his visit would be. His short stay and, above all, his kind and genuine invitation for us (Elda de Castro and myself) to join the RILEM 25PEM group, recently created, profoundly changed our focus and led us to take a step that at that time was clearly greater than our legs. While modest that our contribution to the history of conservation may have been, it is rooted in that person, and by paying homage to his memory, I am witnessing that someone's positive attitude, a brief insightful encounter, or a little pushing given to a colleague can result in dividends that far exceed the investment.

Episodes, anecdotal or not, personal stories, singular and similar events, are outside common scientific subjects and are rarely reported to the general public. And yet, many ideas, research trends, conservation solutions or simply new attitudes of thought have been created or shaped in trivial conversations or occasional episodes.

A second boost in the pace of our research group came, not surprisingly, from an archaeologist, a friend who worked at the national authority for cultural heritage. Dr. Adília Alarcão was director of the Roman site of Conímbriga and a known expert in the Portuguese archaeological heritage. During a working meeting, she presented us with the challenge of directing our research towards the conservation of archaeological heritage in granite. As always, open to accepting new challenges, the group turned its focus to presenting a proposal to the EUROCARE research umbrella, and a second one to the EU FP5 STEP Program. Both were approved and the experience gained from them helped to shape the group's identity and placed it among the pioneers in the research on the conservation of the heritage built of granite.

The scientific results of both projects are widely known and there is no question of revisiting them here. However, these experiences have left a legacy that goes far beyond the published materials and some of the hidden results may be of interest for the scientific community at large and for the young generations in particular. The following notes reflect a personal perspective and seek to reveal the deep feelings that are experienced when a door is opened and a new environment is entered, with new actors and new scripts.

THE *RILEM* AND *ICOMOS* WORKING GROUPS

A young person, from a small country, with modest research facilities and little experience in conservation research is overwhelmed by joining a group of some of Europe's leading conservation researchers, as the RILEM 25PEM[1]. In the 1970s, when “computer” was practically an unknown object, texts were reproduced in cc: (yes, carbon copies, really!), cell phones were unknown even to science fiction, and black and white were the colours available for photography, meeting and talking to such eminent people was an unforgettable experience. It was a big challenge too: how to get into their discussions? What do I need to study to join them? Should I speak or be silent?

Over time, I came to the conclusion that "cultural heritage" was the key to my unexpectedly simple and complete integration into the group: it opens doors and shapes people's character. Prof. Marc Mamillan, the leader of the group, was the personification of kindness, openness and affection and, thus, set the tone for the group, which has always accompanied him in this level of openness and competence.

The technical aspects of the group work have always been easily resolved and the charismatic personality of Prof. Mamillan was certainly a great argument when trying to reach a compromise between the test protocols that had long been rooted in France, Italy, Germany, and the United Kingdom. Having our two proposals (“rock swelling test” and “determination of the pore size distribution with suction methods”) discussed and integrated into the group's portfolio was a small step for the group, but it was a big step for our institution and for ourselves as direct participants.

The benefits of this participation went far beyond these technical details. International contacts were not so easy at that time, travel expenses were a great burden for institutions, missions abroad were carried out at the minimum necessary, and therefore all should be well justified and used. And so they were; work meetings were a permanent learning experience, but also coffee breaks and social gatherings. Participating in discussions about conservation concepts, problems and solutions, and listening to descriptions and comments on real conservation interventions were strong pillars that greatly contributed to my personal training.

The RILEM Recommendations (RILEM-25PEM 1980) are there to testify the seriousness and professionalism of the working group, as one would expect from the high ranking of its members, as the list of co-authors clearly illustrates.

At about the same time, I was invited to join the Petrography group of the ICOMOS-ISC[2]. Initially chaired by Prof. Ragot, the group was later on led by Danniel Jeanette and Andreas Arnold. The defined objective was the analysis of the existing terminology and the elaboration of a glossary adapted to the domain of monuments conservation. Each conservation professional was using their own terminology, virtually without any benchmarking and harmonisation, and finding a unified terminology was an urgent need. The sources used to collect the initial terms were the few published documents on stone conservation, in addition to the multiple documents on petrography, field geology, geomorphology and others. Although all members could suggest terms in their own language, the terms in French, English and German prevailed.

Compared to the RILEM group, harmonising terminology proved to be much more difficult than adapting test protocols. The secular tradition of those three languages in describing geological occurrences proved to be a serious obstacle to this harmonisation, to the point that, despite the enormous amount of work done, the leaders of the group renounced from this “impossible” task. Refusing to give up without fighting, Prof. Fernando Veniale, from Italy, and myself, both indifferent to the language of origin of the concepts, accepted to co-chair the group in a subsequent stage of the work.

Progress had been minimal and leading to a dead end. However, the work already carried out by D. Jeanette and A. Arnold was very valuable and as a new chair we decided to collect a number of terms considered more urgent for the scientific community and assumed the disclosure under our personal responsibility. The result was published in NEWSLETTER (GP Newsletter 1/91) created by the group to make this information available to the scientific and professional community. Although it lacked wide dissemination, it could reach many professionals, showing that the objective of having a widely accepted terminology could be achieved. However, it was not easy to do and it would take almost two decades, until 2008, to finally produce a complete glossary on forms of stone deterioration patterns (ICOMOS-ISCS 2008).

THE GRANITE DOMAIN

When, around 1990, our research group took the initiative to step into the study of conservation of monuments built with granite stones, theoretical knowledge and practical applications known did not go beyond a handful of published articles. Papers dealing with deterioration problems were published by the Trinity College, Dublin, team (Cooper et al. 1989), and indications on successful treatments with an epoxy resin were reported by a team from Venice University (Cavalletti et al. 1985). Very little, if any, was published on granite conservation before that time.

The idea that granite is a highly durable stone is acceptable for certain areas of the globe, but it is far from being true in areas such as the Iberian Peninsula. Here, altered stones were often used in traditional constructions and cases of severe deterioration are common occurrences. The consolidation of deteriorated areas is a problem that conservator-restorers have to face in this region.

Aware of the reported difficulties to study consolidants in limestones and sandstones, often high porosity materials, in the preparation of our research program, the utmost precautions were taken in the definition of the test protocols, as the known difficulties for testing high porosity rocks would certainly be higher in the case of this low-porosity rock. Taking great precautions is never insignificant, but the experience ended up showing that studying the consolidation of low porosity cracked stones, such as granites, is much simpler and more reliable than testing sandstones and limestones.

In fact, the detailed testing program allowed obtaining a bunch of highly meaningful results, and that project has definitely set the bar for other similar studies. An abridged version of the report and several partial papers were published in a EU report (DG XII-Science, Research and Development, Res. Rep. 5).

The production of papers on the deterioration and conservation of granite by the scientific community increased enormously since then and it is now a well-established domain of scientific research.

THE REVIEWING ACTIVITY

With experience and seniority, requests for review of articles and communications increase and this activity can consume a significant part of the researcher's time. This must be seen as a contribution to the scientific community and therefore I have always considered this as mandatory work and refused to do it only when the subject was clearly outside my domain of expertise. In recent times, I had to move away from that attitude and nowadays I decline any invitation coming from some specific journals and publishers. Understanding why this happened can help young people to move in this world of scientific publications, which not always correct and respectful.

After some revisions were made for a specific journal, I sent a manuscript to be published in that same journal. A day or two after submission, I received a note from the editor informing me that the manuscript was rejected because it was not in the scope of the journal. After a few more revisions, I submitted another manuscript, on a different subject, and the response, swift and conclusive, was exactly the same.

An obvious conclusion had necessarily to be drawn from these facts: a researcher who is working in a field that is not covered by the journal cannot be a good reviewer for that journal. I informed the editors of this interpretation and informed them that I had made the decision to decline any future invitation to review manuscripts coming from that journal. By the way, the two manuscripts were submitted to a different journal and were published after a normal serious review process.

Another uncomfortable situation came from a certain editor who sends out invitations and asks for a complete review within a week. They "kindly" inform that this period can be extended upon request, but up to a maximum of 10 (ten) days. As I usually read the manuscript twice with a day or two apart before starting to write the review, a week is too short and I asked for an extension of the deadline. I started the review at my own pace and before the end of the week (!) I received a message informing me that the journal already had two more reviews for that manuscript and that they would proceed without my review if I failed to meet the deadline. As the manuscript was poor research, I was surprised how two reviewers could make their revisions so quickly and decided to speed up my review to meet the deadline.

With a detailed justification (I always spend more time when justifying a rejection) I sent my review proposing that the manuscript should be rejected. A few days later, the editor informed that the manuscript was accepted. The two other reviewers proposed to accept it with minor modifications and the authors answering to my arguments simply commenting that they were not relevant as seen from the full acceptance by the other two reviewers.

This is a publisher with open access journals, so submissions have to be paid for, and this leads to think that they seem to be more concerned with the profit of their business than with the scientific quality of the contents they publish. Since then, as a natural consequence, I refuse any invitation coming from any journal of that publisher.

In recent times, the number of journals accepting Heritage Science topics has increased significantly and the number of published articles has skyrocketed. From this disappointing experience, I fear that the number of insufficiently reviewed articles is increasing, which will raise doubts and perplexities and will contribute to alienate the professionals from the necessary, urgent and essential inter-collaboration with the scientific community.

Journals do exist whether of open or restricted access that follow strict and fair review rules and therefore it is not inevitable to fall into the trap of business-oriented review procedures.

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[1] RILEM (Réunion des Laboratoires d'Essais et des Matériaux), 25PEM (Protection, Érosion, Monuments).

[2] ICOMOS (International Council on Monuments and Sites) – ISCS (International Scientific Committee for Stone).

Stone consolidation in Austria since the 1970s

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SUMMARY: The consolidation of weathered natural stone in Austria's cultural heritage has consistently followed the European developments for the past 50 years. The selection of products largely oriented itself both towards the inorganic group of TEOS, used especially in Germany, and on the acrylic consolidants first developed and used in Italy. Within this half of a century, novel consolidants were only applied in exceptional cases, while new methods of application directed towards increased impregnation depths of the products were eventually developed.

This paper gives a comprehensive overview of specifically Austrian conditions in the field of stone conservation, starting with the most important lithotypes and their characteristic decay features, then describes the most commonly used techniques of cleaning and repair, and finally addressing the issue of consolidation from the 1970s until to date.

KEY-WORDS: Austria, cultural heritage, stone conservation, consolidation

1. STONES OF AUSTRIA'S BUILT HERITAGE

Throughout most of history, the selection and use of building and sculptural stones in the territory of today's Austria has mostly been limited to local sources. In antiquity marble was brought from distant places within and beyond the Alpine provinces of the Roman Empire to important centers like the Pannonian city of Carnuntum, and then, much later, Gothic and especially Renaissance sculptors tended to work on precious limestones eventually transported from remote areas (e.g., Adnet and Untersberg, both in the Salzburg region). Marble, though in principle available in the territory of today's Austria, outcrops far from the most important urban centers and was thus used only on a local level or even by re-using Roman stones before the 16th century. After then it started to be more regularly transported from the South Tyrolean quarries across the Alps. This developed further towards the end of the 17th century thanks to the brothers Strudel, famous sculptors and founders of the first Art Academy in the Empire. They extensively used white crystalline marble from South Tyrol, mostly to serve the needs of Viennese galleries, palaces and gardens owned by the high nobility or the imperial family.

Only in the 19th century were a larger number of different lithotypes exploited from the vast territory of the Austro-Hungarian Empire. This was linked to rapid urban development and the need for stone for building purposes and façades. It was only after the completion of the railway network in the second half of that century that stones from remote areas such as Trieste made their way to emerging centers like Vienna. Meanwhile, the Danube had always enabled easy transport, e.g., of limestone from Bavaria (Kehlheim) or, later, of granites from the north-western areas of Austria, which were even traded down to Budapest.

Regarding alpine stones, it is a well-known fact that today's Austria is largely stretched along the Eastern Alps which contains numerous outcrops of a great variety of different lithotypes, ranging from various crystalline rocks – including a few marbles mostly in Carinthia - to non-metamorphic limestones. It might be less well known that a significant part of the Variscan Bohemian Massif with its granites and other crystalline rocks forms the territories north of the Danube, and that the forelands stretching between the Alps and Bohemian Massif, as well as the lowlands of Eastern Austria, are formed by young sediments of the Paratethys. From the latter area comes a small group of soft carbonate rocks of great importance for the art and architecture of the easternmost provinces (of current Austria) from the Roman times to the 20th century.

Consisting of fossil fragments, these Miocene calcarenites vary in terms of their petrophysical properties: some are fine-grained and highly porous and thus provided excellent sculptural stones, others are compact therefore useful in architecture or engineering. In Austria they are commonly referred to as calcareous sandstones or just sandstones, a somewhat misleading term which has frequently created misapprehension in discussions with conservators from neighboring countries where sandstone is commonly understood as a siliceous rock. Such silicate sandstones do occur also in Austria, partly they were quarried from the Flysch series near Vienna, partly in some local outcrops in the pre-alpine Molasse. Despite their availability especially in the eastern and westernmost provinces of the country, and with the exception of some important medieval buildings, silicate sandstone were never as important in Austria as in neighboring Bohemia and Germany. Already the Romans in Vienna (Vindobona) strongly preferred the calcarenites, even though quarried at a distance of several tens of kilometres, to the Flysch sandstone outcropping at the margins of the ancient town. In principle this choice was kept to over the centuries, probably because of the poor weathering resistance of Flysch sandstone, especially when rich in clay.

Telling the story of stone conservation in most of the historic centers of Austria is thus largely referring to soft limestone, followed by marble, compact limestone and only rarely sandstone. As far as architectural heritage is concerned, natural stones appear relatively rarely as façade materials, especially in the urban architecture of the 19th and early 20th centuries, where renders, stuccoes and plasters based on mortars predominate. Stone exposed to the viewer and the atmosphere is mostly restricted to monuments, churches, and several large public buildings and palaces. Only in a few areas do stones predominate in the vernacular architecture.

Especially since the Baroque times, brick is an important masonry material in many non- or prealpine regions of Austria, however often covered by render. Around the same time people started to paint stone monuments outdoors especially when made of porous limestone, usually by an oil paint with white lead. This was done not only to protect them, but also to yield them the appearance of white marble. This periodically repeated treatment, though discontinued in the 19th century, has seen a kind of revival in stone conservation from the 1970s onwards, now based on lime with fine aggregate rather than oil. Especially in the Eastern provinces of Austria, this approach still plays an important role in the conservation of stone sculptures and façades nowadays.

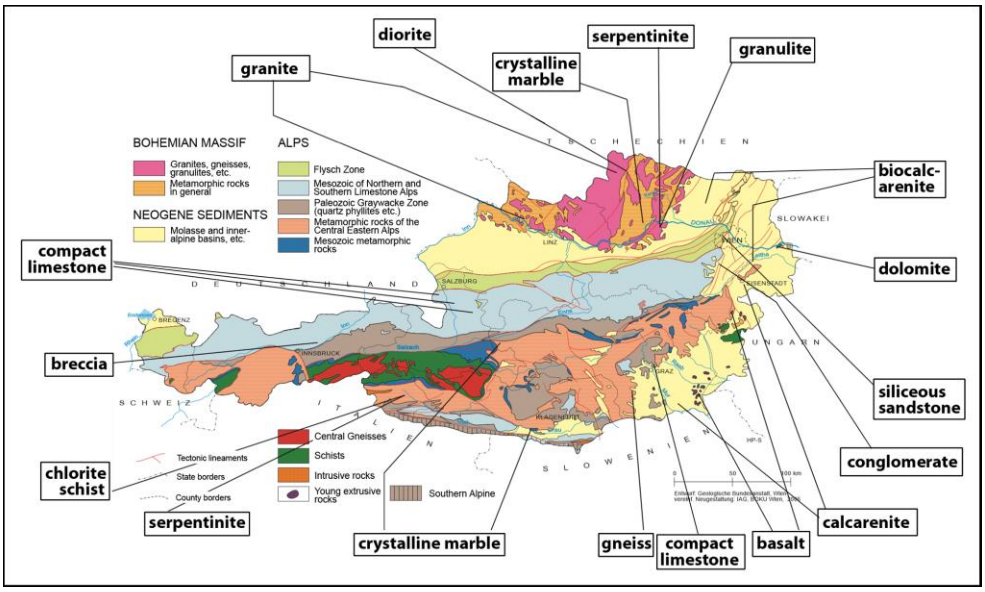

Figure 1: Geological map of Austria, with the provenance of some of the most important heritage lithotypes. (Source: Geologische Bundesanstalt/ Geological Survey of Austria, Geologische Uebersichtskarte der Republik Oesterreich 1:1,500,000, 1999)

Figure 1 gives an overview of the alpine geological units stretching from West to East, with the Danube forming the Southern border of the Variscan Bohemian Massif and acting as important riverway for stone transport from West to East, and the areas of Neogene sediments deposited North and East of the Alps.

2. STONE DETERIORATION

Austria with its temperate climate, apart from the mountainous regions, faces atmospheric impacts on monuments similar to the other Central European countries. Though this is not the place to discuss the effects of atmospheric weathering in detail, a few pieces of information on specific decay phenomena inherent to the most frequently encountered lithotypes may be useful to understand the current approaches of consolidation.

2.1. Porous limestone and calcarenite

Starting with the porous limestones – biocalcarenites as the most important heritage material in Vienna and its larger surroundings, it is beyond doubt that most of these lithotypes are extremely sensitive to acid pollutants and moisture. As everywhere else in the urban areas around the globe, sulfureous compounds were the predominating air pollutant for over a century, thus leading to an extensive sulfurization of calcareous surfaces. Differently from compact limestones or marble, porous calcarenites allow solutions to migrate into and through their pore system. In areas where precipitation or run-off water “washes” the surface, dissolution of calcite wears off giving the surface a clean and unpolluted surface which is often strongly recessed. Upon its migration through the pore system, the water preferentially dissolves the carbonate cement thus steadily weakening the cohesion of the mineral grains and causing sanding and surface losses. The further steps of the process depend on the dimensions and shape of the stone element, and whether it is freely standing, or forming part of the masonry. Isolated, sculptural stone elements on the façade reveal one side protected from the direct impact of rainwater. This is the front of evaporation and deposition, to where the solution migrates by capillarity, precipitating gypsum in the pores near to and on top of that surface. Scaling and black crust formation are the characteristic features of the protected areas of such elements, in which a gradient of significantly different petrophysical conditions between the weathered and protected sides has formed (Figures 2a, b). The same stone type, but placed as ashlar in the masonry, has just one free surface which serves as interface for both processes, moisture infiltration and evaporation, and of course the respective position of the surface has a great impact on the extent of atmospheric weathering. Dissolution, migration and evaporation-driven precipitation of soluble matter are the decisive processes also in these cases, and the superposition of layers of highly different porosity are the consequence. This leads to scale and crust formation above leaching horizons, dependant of the orientation of the wall towards the main direction of wind-driven rain. In synthesis, crusts, counter scaling, and heavy forms of sanding are the typical phenotypes of decayed calcarenites, and they pose two basic problems to any form of consolidation: (1) crusts and scales compacted by gypsum need to be penetrated in order to reach deeper zones of the stone, and (2) a wide range of microstructural defects of significantly different dimensions should be bridged by the consolidant.

The above addressed decay phenotypes and the responsible mechanisms were extensively described before and shortly after WW II (Kieslinger 1932 and 1949), and then more recently by a number of authors (e.g. Pintér 2020). They particularly affect carved sculptural or delicate architectural elements as e.g., those found on the exteriors of Gothic buildings like the Cathedral of Vienna, a building almost entirely made of porous calcarenites. There, the lifetime of such stone elements is not much above 100 years, unless consolidation helps conserve the structure.

The frequent practice of coating these stones in sculpture and, more rarely, in architecture, has often contributed to extend their lifetimes, while in other cases inadequate coatings, e.g., those based on Portland cement, have definitively accelerated their decay.

Figure 2a (top): crab at Vienna Cathedral, biocalcarenite; characteristic features of weathering with gypsum crust in sheltered areas and surface erosion at exposed surfaces.

Figure 2b (right): microstructure of the lithotype shown in Fig. 2a; SEM-BSE image of a polished section from the surface (top) to 1 cm in depth.

2.2. Crystalline marble

White crystalline marbles, which were most frequently used to create figurative sculptures often forming parts of representative buildings, are equally sensitive to the chemical attack by acid pollutants, but due to the lack of efficient porosity they tend to be subjected to surface recession rather than scaling. Nevertheless, their internal microstructure is characterized by de-cohesion and microfissures down to even a centimeter or more from the surface: the processes are usually ascribed to either thermal stresses or frost, or to a combination of both, with the thermic event opening the grain boundaries to an extent that moisture can enter the fabric and create stresses upon freezing. Whatever the mechanisms are, the resulting microstructural defects require consolidation, an often-difficult task since the usually small dimensions of the pore system prevents consolidating solutions from entering the fabric over the course of short terms of application. The use of ultrasound transmission devices can reveal more that microstructural degradation can be present even in the full depth of many sculptures, a deeply concerning problem to heritage managers responsible for the safety of people and objects. The decision to, for example, keep weathered marble sculptures standing on the roof of a building rather than exchanging them with copies, requires a sound risk assessment related to the capability of a consolidation treatment to re-establish sufficient strength to an object in the course of its conservation. Figure 3 illustrates the case of apparently well preserved marble sculptures which, however, were in unsatisfactory microstructural conditions so that ultrasound diagnosis was a crucial means towards the decision to return them to the attic of the parliament building, or rather replace them by copies.

Figure 3: 19th century Carrara and Laas marble sculptures from the attic of the Austrian Parliament building, removed during its refurbishment; the photo was taken after cleaning and conservation; due to their advanced state of microstructural decay even after consolidation, extensive survey by ultrasound transmission had to provide criteria for their re-assembly at the attic of the building.

2.3. Compact limestone

A third group of lithotypes, of significance not only for the countless epitaphs fixed on the outer walls of Austrian churches but also for some of the finest Renaissance and Baroque sculptures (see e.g. Figure 4), are the often-colorful compact limestones, scientifically incorrectly referred to as “marble”. Thanks to the fineness of their micritic calcite crystals as opposed to the much coarser grains of crystalline marble, these stones – some of them revealing extraordinary beauty as long as their polished surfaces are not etched or soiled by outdoor weathering – decay in specific ways much different from calcarenites and marbles. Some of the lithotypes have clayey veins that tend to expand when exposed to moisture, which may result in nodular losses. This affects e.g., the red limestones of the type Rosso di Verona (Figure 5), which were, and still are, quarried in the Salzburg area and widely used under the name of Adnet. Others, being more homogeneous, rather suffer from uniform surface recession by chemical dissolution at a relatively low rate, in some cases associated with the formation of a network of fine fissures. While the former type of weathering often calls for a hydro-repellant treatment, the latter may require a consolidant to penetrate and bridge the fissures. On a whole, compact limestones can be found in the heritage of many other European countries, so that their weathering and approaches of conservation are well studied.

Figure 4: detail of the monumental tombstone of Emperor Friedrich III (finished in 1510) in the interior of Vienna Cathedral; the so-called Rotscheck is amongst the most precious varieties of the Mesozoic Adnet limestone quarried near Salzburg since the Roman times.

Figure 5: detail of an epitaph on the exterior façade of Vienna Cathedral; the photo, taken before conservation, shows four lithotypes of limestone with differing susceptibility to atmospheric impact. The red framing (Adnet limestone, regular variety with clayey veins) reveals the worst state of weathering.

3. STONE CONSERVATION IN AUSTRIA SINCE THE 1970s

As consolidation, the key topic of this contribution, encompasses several other steps of intervention, altogether referred to as conservation, the following presents additional measures that are of particular importance to the practice of stone conservation in Austria.

3.1. Cleaning

Starting from the early approaches of cleaning stone surfaces from dirt and gypsum crusts by using different mechanical and aqueous systems including blast techniques (Koller and Nimmrichter 1996), systematic studies on the efficacy of stone cleaning pastes containing chelating agents such as EDTA (Mora and Mora 1973, Chvatal 1973) encouraged the Austrian conservators to use such systems, usually in the form of commercially available products. Only later in the 1990s, and much less frequently because of a lack of a distributor in Austria, were also ion exchanging resins applied (Matteini et al 1995). Both approaches were rather used in wall painting conservation and only eventually implemented on stone objects. Similar holds true for the ammonium carbonate method as an efficient means of dissolving gypsum (Matteini and Nepoti 1996), possibly followed by a barium hydroxide treatment to convert the gypsum into barium sulphate (Matteini 1987). Practically all the chemical methods addressed above were developed in Italy, and the fact that in Austria they were more readily tested or implemented by wall painting conservators rather than in the field of stone conservation, reflects the lesser degree of contacts with Italian conservators and heritage institutions of the latter group of experts. This started to change in the 1990s, in particular during the conservation of the main portal of the Cathedral of Vienna in 1996-97, when an international team under the guidance of the Federal Monuments Authority (Bundesdenkmalamt – BDA) implemented the laser technique in stone cleaning (Nimmrichter 2006, Koller et al 2008, 199-272). This method has significantly gained importance in Austria’s stone conservation since then.

Once cleaning was understood as an element of stone conservation and restoration, it became common sense in Austria’s heritage preservation that cleaning trials be performed to establish aesthetic and technical criteria before deciding for the whole object to be cleaned in a certain way. However, some important lessons had to be learned by trial and error, such as that the extensive use of water to clean a façade may cause water infiltration through the full depth of the masonry of monumental historic buildings. Water-less dry blasting methods advocated to prevent the above problem were in fact even more harsh on the surface as compared to water-supported blasting, thus leading to the erosion of historic architectural surface details by cleaning.

3.2. Stone repair and copying

Dutchman repair, the filling of losses by the insertion of typically rectangular stone elements, has been the traditional means of stone repair for centuries. Since this technique necessitated the carving of the original stone to produce rectangular cavities, it was used to a steadily lesser extent once specifically trained stone conservators instead of stonemasons started to enter the field of heritage preservation. At the same time, ready-mixed stone repair mortars became available, so that stone repair by the use of mortars became a frequent practice. The usual mortar recipes are based on mineral binders with some organic admixture: pozzolanic (“trass”) lime, hydraulic lime, blends of lime and white cement, and TEOS-based binders are today the most frequently systems employed to repair sculptural heritage. Their long-term performance is as good as the mortar properties comply with the original stone, and as the application is done in accordance with the best practices.

Concerning the aesthetic appearance, the repair of white marble with its often translucent surface still poses problems: while indoor sculptures can be well repaired with mortars based on synthetic resins, outdoors such systems are considered less stable than mineral-based mortars which, however, hardly have, or retain upon aging, the desired appearance of marble.

Dutchman repair in specific cases is still in use, especially where the dimensions of stone surfaces affected by heavy forms of weathering cannot be handled by measures of consolidation and repair, as it is for example the case with parts of the Cathedral of Vienna where decayed stone elements continue to be carved out and closed with stone slabs. Also, missing figural elements, and even whole copies of sculptures, are more often produced out of natural, rather than artificial stone. The involvement of stone sculptors in restoration projects headed by conservators is currently becoming of increasing importance; today most conservation projects are commissioned to academically trained stone conservators while, skilled sculptors get subcontracted to reproduce missing elements or perform full figural copies.

3.3. Stone consolidation

Austria is a relatively small country, and therefore generally tended to watch the international developments in stone conservation and make use of the primary products marketed abroad. This fact, however, did not preclude certain system modifications sometimes developed and tested in the laboratories of the BDA or in other research institutions. In times of competing concepts advocating either synthetic resins, or silicate consolidants to strengthen decayed stone in cultural heritage, Austria kept a somewhat pragmatic approach, well aware of the fact that a great deal of our sculptural and architectural stones – porous detrital limestones - differ from the majority of lithotypes in the heritage of our neighbors, especially German, Bohemia and Italy. Thus, the use of methyl and ethyl silicates, in Central Europe widely applied in the consolidation of silicate sandstones, was not adopted without reservations for the carbonate lithotypes in Austria until it proved useful as consolidant, especially when equipped with specific bonding agents for carbonate substrates. The first use of silicic esters in Austria was nevertheless performed on a silicate sandstone, namely a Flysch sandstone from a Romanesque stone ossuary in Tulln near Vienna, in the year 1971 or 1974. To date TEOS is by far the most widespread group of products used for the microstructural consolidation of weathered stones in Austria. In the above-mentioned case, just like in many other projects following this intervention, water repellent treatments were applied, either as a silicone component of the consolidant, or separately as the a final step of intervention. A survey performed at the Tulln Ossuary after 40 years (Ban et al 2022), revealed the formation of a hard and compact shale above a weakened layer of stone, with a still hydrophobic surface (Figures 6a, b).

Pink - scale formation; Violet - sanding
Grey - salt efflorescence

Figures 6a, b: Flysch sandstone masonry of the Romanesque ossuary in Tulln, Lower Austria; the photo was taken about 40 years after conservation based on alkoxysilane and silicone treatments. The formation of scales, a problem already existing before those interventions, has been traced on the base of percussion tests and then verified for drill cores.

In the 1990s producers, such as Remmers, adapted their range of TEOS products to the specific problems of highly varying permeabilities and pore sizes posed by weathered porous calcarenites and quartzous sandstones constituting parts of the façades of Vienna Cathedral. This was one of the starting points for the modular system of TEOS, which were tailored to a variety of different viscosities at varying rates of active ingredient.

Up to the present, TEOS have kept their key role in the microstructural consolidation of most heritage lithotypes in Austria; only eventually are alternative mineral systems applied, such as silica sols and nano-lime. As is the case virtually anywhere else, the conservation sector is conservative, and the range of scientific means to evaluate a novel consolidant and predict its long-term performance is limited. Though some recent research projects with Austrian participation have shown the shortcomings of TEOS treatments in terms of their limited capacity to bridge larger fissures, due to the high shrinkage rates of the gels (Figure 7), and focused on alternative systems based on inorganic nano products, these results yet have had no major impact on the practice.

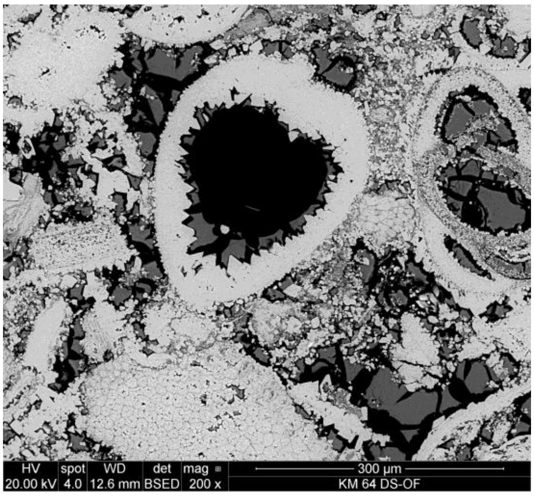

Figure 7: silica gel in the pore space of a biocalcarenite, deposited from a TEOS treatment, by SEM-BSE of a polished section; the observed high rate of shrinkage of the consolidant and its general lack of adherence to the carbonate grains of the substrate are in contrast to the improvement of mechanical strength as evidenced by ultrasound transmission and empirical means.

Starting with the search for methods to provide increased penetration depths of consolidants into the fabric of sculptural marble in the course of in-situ conservation treatments outdoors, a vacuum technology-based method called “Vacuum-Circling Process (VCP)” was developed and patented (Pummer 2016). In principle suitable for any kind of consolidant, the method is currently used in particular for TEOS applications on free standing objects made not only from marble but also from other lithotypes as e.g., porous limestone. A TEOS product with specific accelerating agents was developed to overcome problems related to the low rate of hydrolysis of TEOS in the core areas of stones treated by VCP. Drilling resistance and ultrasound transmission tests performed on stones before and after VCP treatments point to a generally good success of the method.

Attempts to provide full penetration of stone objects by the consolidant through vacuum techniques date back to the late 1970s, when the so-called acrylic-total-impregnation process was developed by W. Ibach in Bamberg, Germany. Based on low-viscous monomeric methylmethacrylate applied to the object under vacuum and polymerized in-situ, this approach seemed to solve all problems posed by heavy microstructural deterioration of marble and other stone types (Wihr 1979). Resulting in totally changed petrophysical and chemical properties, and being of course far from the desired reversibility of conservation treatments, the method was nevertheless applied to many heavily decayed stone objects as an *ultima ratio*. Although based in Germany, Austrian stone conservation practitioners eventually made use of the acrylic-total-impregnation process for a limited number of objects composed of marble, compact limestone and porous calcarenite, a practice which was discontinued around the year 2000. The objects had to be dismounted and transported to Bamberg for treatment, before they came back and were usually returned to the place of origin. Today, a few of the treated objects reveal shale formation on their surfaces, though no systematic studies were performed to fully understand the processes and reasons of post-treatment decay.

Apart from the above-described consolidation process, organic synthetics were first applied on monumental stone in 1980, when the Baroque Plague Column in the center of Vienna was treated with Paraloid B72, an ethyl-methacrylate copolymer widely used in the conservation of stone, mural paintings, and other heritage materials (Koller at al. 1982). Laboratory tests resulted in the use of a threefold solvent mixture by which the polymer was applied in several steps to the Untersberg stone of the monument, a compact limestone revealing microfissures and contour scaling. In order to achieve water repellency, Wacker 190, a silicon resin, was admixed to the Paraloid solution in the last of a number of applications. This approach was inspired by the Italian practice known as "Bologna Cocktail" (Gnudi et al 1981). In general, the 1980's conservation of the Plague Column proved sustainable during a thorough inspection undertaken around the year 2000.

In a trial intervention, a local sandstone from a Romanesque church in Lower Austria was subjected to a treatment with the above system, though this approach was soon abandoned and later continued with TEOS consolidants. Since then, acrylic polymers are generally not used any longer to consolidate sandstones, limestones or calcarenites in Austria.

Critical reviews of the state of art and conservation practices in Austria were eventually published by various authors (Koller 1979, Koller and Prandtstetten 1996, Nimmrichter 2007).

3.4. Post-consolidation surface treatments

As mentioned earlier in Section 1, many sculptures and a considerable number of historic stone structures, especially in the Eastern provinces of Austria, are coated by a sacrificial layer. This often critically discussed approach started to be strongly advocated by the Austria heritage authorities in the 1970s when scientific analyses as well as archival studies evidenced the former practice of the 18th to the early 19th century to whitewash many stone works, likely as a means to embellish and protect the numerous baroque monuments and sculptures, most of them made of porous limestones and calcarenites. During the 19th century aesthetic tastes changed leading to the disapproval of white, or even polychromed stone surfaces. Thus, the majority of objects were then uncovered, or the regular maintenance of renovating this kind of surface treatment was discontinued till the coatings were lost through weathering.

The revival of the concept of heritage preservation of the 20th century was based on two fundamental criteria, one being the reconstruction of the original aesthetic appearance, the other one the idea to provide a protective, or rather sacrificial layer to the chemically sensitive and highly porous limestones and calcarenites to protect them against the acidic pollutants. The original approach using linseed oil with white lead was no longer considered appropriate, so the coatings were now performed with lime. To avoid the formation of a dense surface film which would completely cover the stone, altering its appearance and its physical properties, the wash is usually applied as a water-rich slurry of fine aggregates and lime aimed at a translucent aspect. Figure 8 shows a recent example.

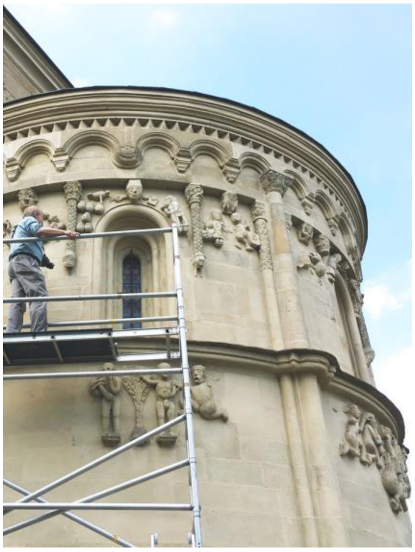

Figure 8: translucent sacrificial lime-sand layer, applied on the sandstone façade of the apse of the Romanesque church of Schöngrabern, Lower Austria, after completion of its conservation. The photograph was taken approx. 20 years later.

During the years, the recipes were eventually modified by adding some amounts of acrylics, or substituting the lime by silicate, NHL, or blends of lime and Portland cement.

More information on this approach which has added a typical feature to stone conservation in Austria can be found elsewhere (e.g. Koller et al. 1996, Ban et al. 2018, Nimmrichter et al 2000, Pintér and Fuchs 2021).

SUMMARY AND OUTLOOK

Learning and exchanging information through international collaborations and congresses has always been of utmost importance for the conservation community in Austria.

The scientific means to evaluate a novel consolidant and predict its long-term performance for a given lithotype in its state of decay are limited. The use of SEM as a technique complementing the existing physio-mechanical test protocols to study all microstructural properties of a given consolidant, or a combination of them, in respect to a decayed stone's pore system has been well developed in the frame of recent EU-funded research projects.

For the past 40-50 years up to present, TEOS have kept their key role in the microstructural consolidation of most heritage lithotypes in our country. The practitioners of building conservation are conservative, and only slowly are alternative mineral systems applied, such as silica sols and nano-lime. As to TEOS, there is a certain gap between empirical and scientific data on their efficacy since research results cannot confirm their usefulness in all cases. Therefore, Austria has participated in several international research projects dealing with inorganic nano products, though the results have yet had no major impact on the conservation practice.

In general, however, the use of consolidants for a given task of conservation is more profoundly considered than in the past, and products as well as their modes of application are selected more critically than this might have been the case in the late 20th century. Given the limited number of consolidants available on the international markets, it is understood that the efficiency of these products in respect to the properties of each of the stone substrates must be more carefully assessed, and combined product applications need to be considered. To this is added the increasing awareness of the utmost importance to use optimum application techniques for a given object. The above marks the focal points of activities as currently envisaged in Austria, a country presumably too small to head for the design and development of new classes of conservation products.

The consolidation of weathered crystalline marble has remained an open question, since proven systems such as Paraloid or TEOS, both when applied alone, seem not to match all demands. For empirical reasons, several interventions have thus been made by use of combined product applications. While empirical results seem to be reasonably good, thorough scientific examination of such a procedure is still pending.

A true paradigm change has been encountered in respect to the surface treatment of stone and architectural surfaces by water-repellents. While until the 2000s most interventions had included a waterproofing application of silicone products, this is now far less the case since the concepts of compatibility in respect to petrophysical properties as well as of re-treatability have been achieving steadily more attention. Nevertheless, it is the authors' opinion that much of these developments is due to current mindset and needs to be confirmed by scientific studies. The attitude of reflexively protecting all surfaces by hydro-repellents is currently giving way to a case-by-case approach based on evidence.

Acknowledgement

Following the groundbreaking works of A. Kieslinger in the pre- and post-WWII decades, a number of persons actively involved in laying the grounds of modern stone conservation in Austria according to international standards must be acknowledged, their names stand also for those who cannot be listed here: M. Koller, H. Paschinger, and A. Rohatsch.

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Weathering and conservation of stone: A personal view

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SUMMARY: Significant progress in the conservation of stone has taking place over the last few decades. In particular, different consolidant and protective materials have been developed to strengthen and protect building and sculptural stone affected by a range of weathering phenomena, chemical, physical and/or biological in nature. However, no conservation treatment seems to have so far been able to achieve a perfect consolidation or protection effect, and several drawbacks have been observed following application of a majority of currently used treatments. In many cases, failure is due to the fact that treatments are physically and/or chemically incompatible with the stone substrate they are applied to, and/or do not tackle the origins of damage but only mask its consequences. To these shortcomings, one has to add the fact that in some instances, treatments are applied without a proper understanding of the damaging mechanism(s) affecting a particular stone. These issues have prompted research aimed at the better understanding of stone weathering mechanisms and the search of novel more effective conservation treatments. Here I present a personal overview on the progress in the understanding of different weathering phenomena and on the basics, uses and performance of traditional and novel conservation materials and methods I have studied and/or witnessed since I started my research career in heritage science back in the early 1990s. I focus this personal overview on the use and limitations of different polymers and alkoxysilanes (and alkylalkoxysilanes) as traditional consolidants and protectives, and then on novel inorganic treatments, as well as on the use of bacterial biomineralization for stone conservation.

KEY-WORDS: Stone decay, salt damage, crystallization inhibitors, clay swelling inhibitors, consolidants, protectives, polymers, alkoxysilanes, nanolime, bacterial consolidation.

INTRODUCTION

Stone used in the built and sculptural heritage is subjected to different anthropogenic and natural weathering processes that endanger the survival of architectural and sculptural masterpieces all over the World (Winkler, 1997; Doehne and Price, 2010; Siegesmund and Snethlage, 2011; Camuffo, 2019). This has prompted the search, testing and application of numerous conservation materials and methods aimed at halting or minimizing the effects of such deleterious weathering processes, while at the same time aiming at increasing the durability of the treated stones by enabling them to regain their lost cohesion and strength (Amoroso and Fassina, 1983; Lazzarini and Tabasso, 1986; Camuffo, 2019; Delgado Rodrigues, 2022). Among such conservation treatments, the application of consolidants and protectives has been the focus of intensive work (Charola,1995; Delgado Rodrigues, 2010, 2022; Praticò et al., 2020). The former are applied to enable the weathered stone to regain, at least in part, the lost cohesion and strength, whereas the latter treatments aim at protecting the treated stone from further damage (particularly water-related decay). In many cases, the development, selection and application of such treatments involved a prior understanding of the decay process(es) affecting these building and sculptural stone elements. This premise is key to develop and apply appropriate conservation treatments to halt or minimize the damaging effects of specific decay processes. However, the latter premise was not fulfilled in many conservation interventions, and treatments were applied without a proper understanding of the damage mechanism affecting a particular stone, resulting in an ineffective protection or consolidation, or even, in exacerbated damage (Rodriguez-Navarro et al., 1997a, 1998). In other cases, the treatments failed because they masked the effects of the weathering process affecting a stone, but did not tackle the cause of damage (Elert et al., 2021).

Here I will present a brief overview of the progress I have witnessed on the conservation of stone since I started my PhD back in the early 1990s studying the decay of stone materials at the Cathedrals of Granada and Jaen (Spain) (Rodriguez-Navarro, 1994). It is therefore not intended to be an exhaustive review of the advances made in the numerous areas of research related to heritage science and/or stone conservation. Rather, this overview focuses on aspects which have been the focus of my own research. I will first present a brief overview on the different weathering mechanisms affecting stone that I have studied, to then narrow the focus on progress I have witnessed on the evolution and application of traditional and novel conservation materials, consolidants and protectives in particular, specific for stone.

PROGRESS IN UNDERSTANDING WEATHERING MECHANISMS

"On the shoulders of giants": in line with Newton's famous quote, we have to acknowledge the fundamental studies on the different mechanisms affecting stone degradation performed during the XIXth c. until the second half of the XXth c. Such pioneering studies set the basis for the current knowledge on and understanding of these topics. See for instance the works and overviews by Hirschwald (1908), Schaffer (1932), Evans (1970), Winkler (1997), Amoroso and Fassina (1983), Price (1996), Kumar and Kumar (1999), Doehne and Price (2010), Siegesmund and Snethlage (2011) and Camuffo (2019). Moreover, there is significant longstanding research on the weathering of minerals and rocks (in nature and in the laboratory) published in the geomorphology and geochemistry literature that has served as a basis to understand weathering of building and sculptural stone. See for instance Ollier (1984), Yatsu (1966), Trenhaile (1987), Goudie and Viles (1997), Stumm and Morgan (2012), or Lasaga (2014), among many others. Most of the recent progress in the understanding of weathering mechanisms of stone would not be possible without such seminal contributions.

Those studies established a division among physical, chemical and biological weathering phenomena. Physical weathering processes, such as salt crystallization damage, freezing of water, differential thermal expansion, or moisture expansion associated with clay swelling, create stresses in porous building materials resulting in crack opening and propagation, ultimately leading to material loss, or even structural failure (Winkler, 1997; Rodriguez-Navarro et al., 1997a, 1998; Rodriguez-Navarro and Doehne, 1999a,b; Scherer, 2004; Ruiz-Agudo et al., 2007; Sebastian et al., 2008; Doehne and Price, 2010; Schiro et al., 2012; Flatt et al., 2017). Chemical weathering processes such as dissolution, hydrolysis, and/or redox reactions (Brantley et al., 2008) associated with the interaction of aqueous solutions with the different mineral component of building materials also result in the weakening of sculpted or built stone structures leading to aesthetic changes and significant material loss (Winkler 1997; Amoroso and Fassina, 1983). This is even more marked in contaminated industrial areas and urban centers where air pollution contributes to chemical weathering upon interaction of acid (pollutant) gasses (i.e., SO_2, NO_x and CO_2) and particulate matter with built structures and/or carved sculptures (Rodriguez-Navarro and Sebastian, 1996). Biodeterioration due to the interplay of chemical and physical weathering processes associated with the development of organisms, specially microorganisms, on and within building and sculptural materials also results in significant damage (Kumar and Kumar, 1999; Warscheid and Braams, 2000: Gadd, 2017). Living organisms, particularly microbial biofilms, can, however, also result in surface protection, as growing evidence is showing (Carter and Viles, 2005; Pinna, 2014). Most of these weathering processes do not normally act alone. Indeed they tend to act together, typically in a synergistic way, leading to positive feed backs that accelerate weathering, resulting in extensive material degradation.

Chemical weathering due to air pollution

When I started my PhD, a main area of research was on the effect of air pollution on stone decay. Numerous studies focused on the role of wet and dry deposition of air pollutants, including SO_2, NO_x and particulate matter, on the decay of stone, particularly carbonate stones such as marble and limestones (Amoroso and Fassina, 1983; Winkler, 1997). I also studied this topic as the carbonate stones in the Cathedrals of Granada and Jaen were affected by the development of black crusts (Rodriguez-Navarro, 1994; Rodriguez-Navarro and Sebastian, 1996). Our research group at the University of Granada (UGR) was able to demonstrate that particulate matter emitted by motor vehicles, including both carbonaceous and metallic particles from diesel and gasoline combustion engines, was key in the catalytic oxidation and hydrolysis of SO_2 to form sulfuric acid, that in turn was responsible for the dissolution of the carbonate stone substrate and the formation of gypsum crusts under dry deposition conditions (Rodriguez-Navarro and Sebastian, 1996). We experimentally observed similar effects in the case of silicate stones such as gabbro, granite and syenite (Simão et al., 2006). In the field, we observed the development of black crusts in a range of historic buildings in Andalucía, including the Cathedrals of Granada and Jaen (Fig. 1). The analysis of the black crusts in this latter building showed that they included abundant gypsum crystals along with fly ash particles (carbonaceous and metallic-rich cenospheres). They also included a range of organics (most likely of microbial origin) along with clays, and, to our surprise, autigenic proto-dolomite and ordered dolomite. Autigenic dolomite was only reported in a single previous case where this phase replaced calcite in a weathered marble monument (Del Monte and Sabioni,1980). Formation of autigenic dolomite was unexpected because dolomite precipitation at Earth surface conditions (low T and P) is almost impossible. This is the origin of the so-called "dolomite problem", rooted on the fact that dolomite is abundant in the ancient geologic record, but almost non-existing in modern carbonate deposits (Lippmann, 1973). Modern dolomite formation has been reported in just a few locations in the world, associated with aqueous environments with a high salinity and strong bacterial activity (Vasconcelos et al., 1995). We proposed that these two conditions could be met in the black crusts of Jaen's Cathedral, resulting in the formation of dolomite (Rodriguez-Navarro et al., 1997b). We also demonstrated that prior to the formation of a black crust, grayish dust deposited on stone surfaces exposed in polluted urban centers included a significant amount of carbonaceous and metallic particles, which ultimately would lead to black crust formation. This prompted us to recommend cleaning of such dust deposits as a preventive conservation measure, and this was done using a pulsed Nd-YAG laser during a conservation intervention at the Cathedral of Granada in the early 1990s.

In recent years the number of publications on this topic have, however, decreased, most likely because stringent pollutant emission control laws have contributed to a significant reduction in their atmospheric concentration. Nonetheless, while a significant reduction in SO_2 emissions has been achieved, other pollutants such as O_3, NO_x and particulate matter, still are produced/emitted at a significant rate, and their effects on stone decay need to be studied in detail (Gibeaux et al., 2018; Falchi et al, 2019). In parallel, the increase in atmospheric CO_2 concentration, besides the effect of this greenhouse gas on climate change and the impact of the latter in cultural heritage (Sesana et al., 2021), being CO_2 an acid gas it might favor chemical weathering as its dissolution in water can reduce the pH, thus increasing the dissolution rate of stones (carbonate stones, in particular) (Bonazza et al., 2009).

Basically, my experience regarding how to deal with chemical weathering of stone due to air pollution involved the implementation of preventive measures: i.e., strict pollutant emission control policies, especially in historic urban centers (including restrictions regarding vehicular traffic, as for instance occurs in the city center of Granada and the surroundings of the Alhambra) and cleaning of dust and crust formed on historic buildings. The latter, typically involved the subsequent application of consolidants and/or protective treatments (with varying effectiveness; see below).

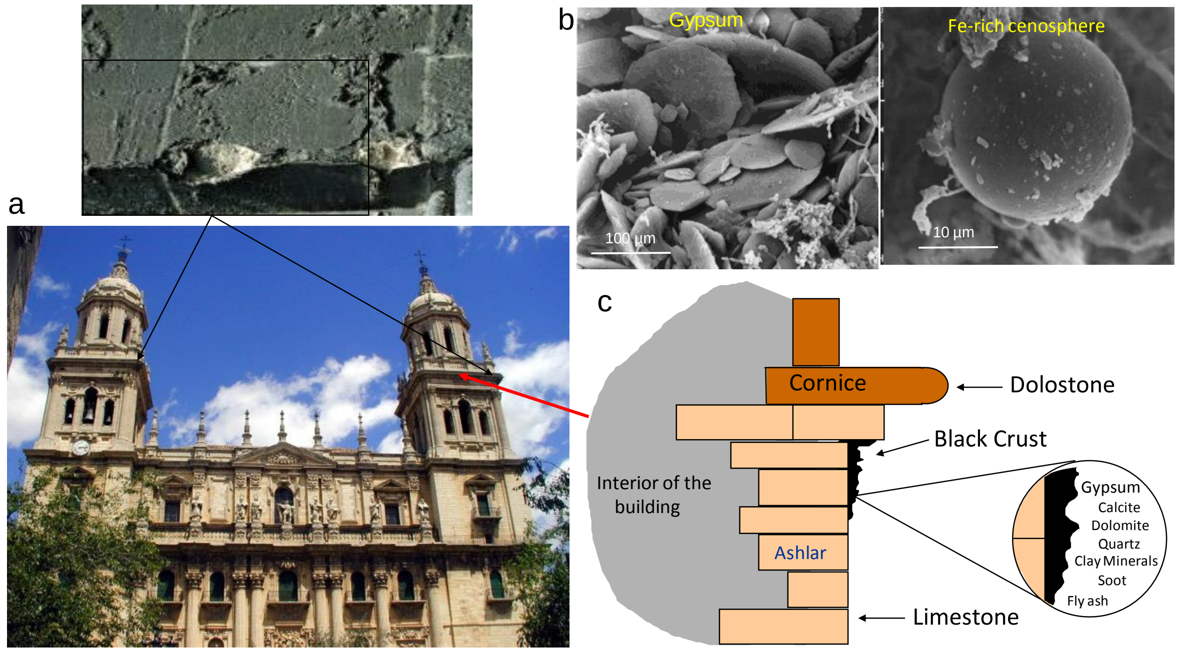
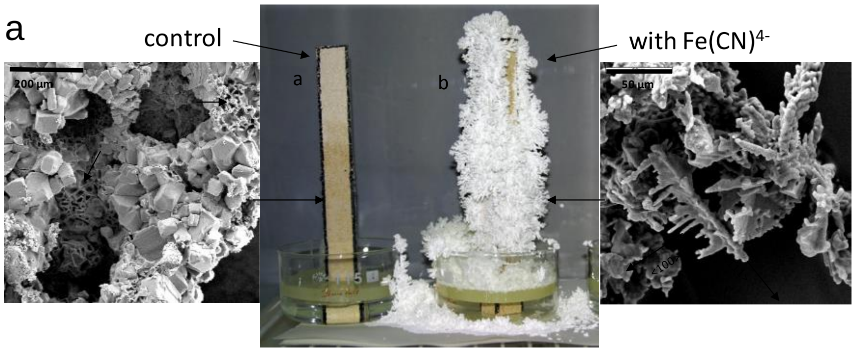


Figure 1. Black crust development at the Cathedral of Jaen (Spain). a) Black crusts developed at sheltered areas on the main façade of the Cathedral of Jaen (see detail in inset); b) SEM photomicrographs of gypsum crystals and Fe-rich cenosphere within the black crust; c) Scheme of the black crust developed due to dry deposition underneath a cornice. Note that chemical weathering (dissolution) of the dolostone making up the cornice is a source of magnesium ions, which enabled the formation of autigenic dolomite in the black crust. Modified from Rodriguez-Navarro (1994).

Salt damage

Salt damage is another area of research which experienced an exponential growth (in term of publications) since the early 1990s. Seminal studies on this highly deleterious process were published back in the XIXth c. and early-mid XXth c. (see overviews by Evans, 1970; Goudie and Viles, 1997; Rodriguez-Navarro and Doehne, 1999a), setting the groundwork for research continued until present. From 1995 until the end of 1998 I had the opportunity to further continue my work on salt weathering started during my PhD at UGR as a postdoctoral researcher at the Getty Conservation Institute (GCI, Los Angeles, USA). There, in collaboration with the GCI staff, we studied several aspects of salt damage to porous stone and novel ways to prevent/minimize its effects. Using state of the art analytical equipments, such as environmental scanning electron microscopy (ESEM) (working with Dr. E. Doehne) and time-lapse video microscopy (set up by Dr. A. Heritage), we were able to visualize how different salts caused damage to stone at multiple scales (from micro- to macro-scale) (Rodriguez-Navarro and Doehne, 1999a,b; Rodriguez-Navarro et al., 2000a) and I tested the use of surfactants as crystallization inhibitors/promoters to minimize damage (Rodriguez-Navarro et al. 2000b). Figure 2 shows an example of the action of a crystallization inhibitor, ferrocyanide ions, in the case of NaCl crystallization within a porous limestone (Selwitz and Doehne, 2002; Rodriguez-Navarro et al., 2002). This additive delays the onset of crystallization of halite, enabling the transport of Na^+ and Cl^- ions in solution to the surface of the stone where evaporation takes place. Following evaporation of the saline solution, crystallization (at very high supersaturation) of NaCl crystals occurs as efflorescence, without damaging the stone substrate (Fig. 2a). This additive can thus be effectively used to prevent damage associated with this specific salt, and can also be used to foster desalination of NaCl-laden porous stones (Fig. 2b).



b

Desalination

- ✓ Application of wet poultices loaded with Fe(CN)$^{4-}$
- ✓ Spraying of a ferrocyanide solution
- ✓ Partial immersion in a ferrocyanide solution

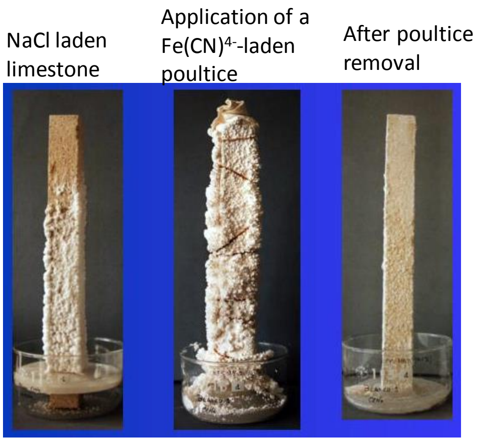


Figure 2. Use of crystallization inhibitors to prevent salt damage and promote desalination. a) Effect of ferrocyanide ions on the crystallization of NaCl within a porous limestone. In the absence of ferrocyanide ions, crystallization of NaCl upon capillary rise and evaporation during partial immersion in a saturated NaCl solution results in the crystallization of halite cubes (near equilibrium shape indicating low supersaturation at the onset of crystallization - see SEM image on the left hand side) mainly as subflorescence (which tends to be deleterious). In contrast, in the presence of mM concentrations of ferrocyanide ions in the saline solution, massive efflorescence is promoted without damage to the substrate. Salt crystals show dendritic/skeletal non-equilibrium shapes indicative of crystallization at a very high supersaturation (demonstrating that the additive is a strong crystallization inhibitor). Figure modified from Rodriguez-Navarro et al. (2002); b) desalination of NaCl-laden porous limestone aided by ferrocyanide ions. Several possibilities for using this desalination method are indicated. On the right hand side it is shown how the application of a wet poultice loaded with an aqueous solution of ferrocyanide (dosed in mM concentration) enabled the nearly complete desalination of the stone (see efflorescence growing on the poultice in the middle picture) without causing any damage.

The use of crystallization inhibitors is a very promising area of research that I continued upon my return to the University of Granada in 1999, specially through the continued collaboration with the GCI, and further collaboration with several international research teams under the umbrella of the European Projects Saltcontrol (2004-2007) and DeltaMin (2009-2012). This research led to the defense of two PhDs at the UGR (Dr. Encarnacion Ruiz-Agudo and Dr. Mara Schiro) and the publication of several papers. We found that the action of crystallization inhibitors/promoters was system- and/or salt-specific. While potent inhibitors such as ferrocyanide ions (see above) were able to effectively delay the crystallization of NaCl, favoring its precipitation as non-damaging efflorescence (Rodriguez-Navarro et al., 2002; Selwitz and Doehne, 2002), other additives such as cationic surfactants (cetyldimethylbenzylammonium chloride), borax, or polyacrylates and phosphonates, were able to promote the in-pore crystallization of sodium sulfate and magnesium sulfate at very low supersaturation, thus minimizing damage (Rodriguez-Navarro et al., 2000b; Ruiz-Agudo and Rodriguez-Navarro,2010; Ruiz-Agudo et al., 2006, 2008, 2013; Schiro et al., 2012; Rodriguez-Navarro and Benning, 2013). The latter two organic additives acted as a template when adsorbed on the pore walls of stone, thereby enabling (via their deprotonated carboxylate or phosphonate functional groups) the heterogeneous oriented nucleation of sulfate salts (Ruiz-Agudo et al., 2013), whereas borax, being isostructural with mirabilite, induced precipitation of this sodium sulfate phase via an heteroepitaxial (seeded nucleation) effect (Ruiz-Agudo and Rodriguez-Navarro, 2010). More recently, in collaboration with Prof. G. W. Scherer and Prof. E. Franzoni groups, we studied the use of natural polymers (biodegradable biopolymers) as crystallization promoters, obtaining very promising results (Andreotti et al., 2019). The use of such biodegradable compounds enabled a greener, more sustainable approach to the conservation of salt damaged stone. Importantly, the combination of these salt damage prevention approach with a biomimetic surface protection using a diammonium phosphate treatment applied to calcitic substrates (see below) yielded the best results in terms of damage reduction following sodium sulfate crystallization tests. Despite their potential, these type of conservation treatments for salt damage prevention/control still are under development and further studies are necessary before widespread application. Considering the recent advances in the understanding of nonclassical crystallization involving prenucleation clusters (PNCs), dense liquid and amorphous precursor phases (Gebauer et al., 2008; Rodriguez-Navarro et al., 2016a), it would be enlightening to study how additives interact with both pre- and post-nucleation species and (precursor) phases during crystallization of different salts, as has been done for the case of calcium carbonate (Gebauer et al., 2009) or calcium oxalate (Ruiz-Agudo et al., 2017), and how such a gained knowledge can be used for the design/selection of best crystallization inhibitors/promoters for each specific salt/case scenario.

Clay swelling damage

Another research topic I addressed in my PhD and continued studying during my stay at the GCI and latter on at UGR was clay swelling damage. It was known that a range of stone types showing surface scaling and flaking, spalling, delamination, drying cracks, and/or contour scaling (Fig. 3a-c), typically included clay minerals, normally in small quantities (<10 wt%) (Delgado Rodrigues, 1976; Wendler et al., 1996; Rodriguez-Navarro et al., 1997a, 1998; Jimenez-Gonzalez and Scherer, 2004; Franzini et al., 2007; Sebastian et al., 2008; Jimenez-Gonzalez et al., 2008; Ruedrich et al., 2011; Wedekind et al., 2013; Elert et al., 2021). Such stones displayed significant hygric and/or hydric expansion (i.e., free swelling strain determined following contact with vapor or liquid water, respectively). Apparently, clay swelling/shrinkage phenomena resulting from wetting-drying cycles led to their degradation (Rodriguez-Navarro et al., 1987, 1998; Delgado Rodrigues, 2001; Veniale et al., 2001, Jimenez-Gonzalez and Scherer, 2004; Elert et al. 2021). Indeed, clay swelling damage is recognized as a highly deleterious stone weathering process (Caner and Seeley, 1978; Ruiz de Argandoña et al. 1995; Rodriguez-Navarro et al., 1997a, 1998; Delgado Rodrigues, 2001; Wedekind et al., 2013).

My PhD study of the clay-induced damage of micritic limestone blocks used in the façade of the Jaen's Cathedral demonstrated that small amounts (< 8 wt%) of smectite concentrated along bedding planes explained the scaling observed in the building following repeated wetting/drying cycles (Rodriguez-Navarro, 1994). By exposing these stones to dimethylsulfoxide (DMSO), a compound that gets intercalated in the interlayer of smectite increasing its d_{001}-spacing from ~14 Å up to ~19 Å, I observed the complete delamination of the stone samples after a few cycles. This experiment showed that crystalline clay swelling (i.e., increase in d_{001}-spacing) was the main culprit for damage development in this particular limestone. Later on, at the GCI, I had the opportunity to study a very interesting related problem affecting ancient Egyptian marly limestone stelae and sculptures of the Phoebe Hearst Museum collection (Berkeley, USA). Such stelae and sculptures, similar to those of the Egyptian collection of the British Museum (London, UK) and the Metropolitan Museum (New York, USA), were heavily damaged, suffering massive delamination and scaling. At the time it was believed that salts (NaCl) were responsible for the damage, so it was a common procedure to desalinate the stone pieces and subsequently subject them to consolidation (first with organic polymers and later on with alkoxysilanes) (Hanna, 1984; Wheeler et al., 1984; Bradley and Hanna, 1986; Bradley and Middleton, 1988; Miller, 1992). All these treatments did not stop the advancement of damage, and in some cases they even exacerbated it. Our study of such stone objects demonstrated that clay swelling (sepiolite and palygorskite) was responsible for the observed damage, explaining why damage continued after desalination and consolidation (Rodriguez-Navarro et al., 1997a, 1998). We proposed a tight environmental control to prevent the development of deleterious wetting/drying cycles resulting in the observed clay damage. This is an illustrative example of the need to properly identify and understand the weathering mechanism(s) affecting a particular stone, in a particular environment, before the application of any conservation treatment.

Upon my return to the UGR in 1999, I continued studying clay swelling damage affecting different stone types. One dramatic case was the massive damage observed in the San Mateo Church at Tarifa (Spain) (Fig. 3a-c). This monument was built using a local sandstone that included ~5 wt% clays. The most abundant clay mineral we identified using XRD was a regular interstratified of chlorite and smectite, named Corrensite (Fig. 3d). These swelling clay particles were concentrated along bedding planes, as shown by polarized light and SEM microscopy (Fig. 3e). The expansive clay was responsible for the observed free swelling strain of up to 0.004, and the resulting damage upon wetting/drying cycles experienced *on site* in this coastal location in Southern Spain (Sebastian et al., 2008; Jimenez-Gonzales et al., 2008). This fundamental study set the basis for the testing of different conservation treatments, both traditional (consolidants) and novel (use of swelling inhibitors) (see below).

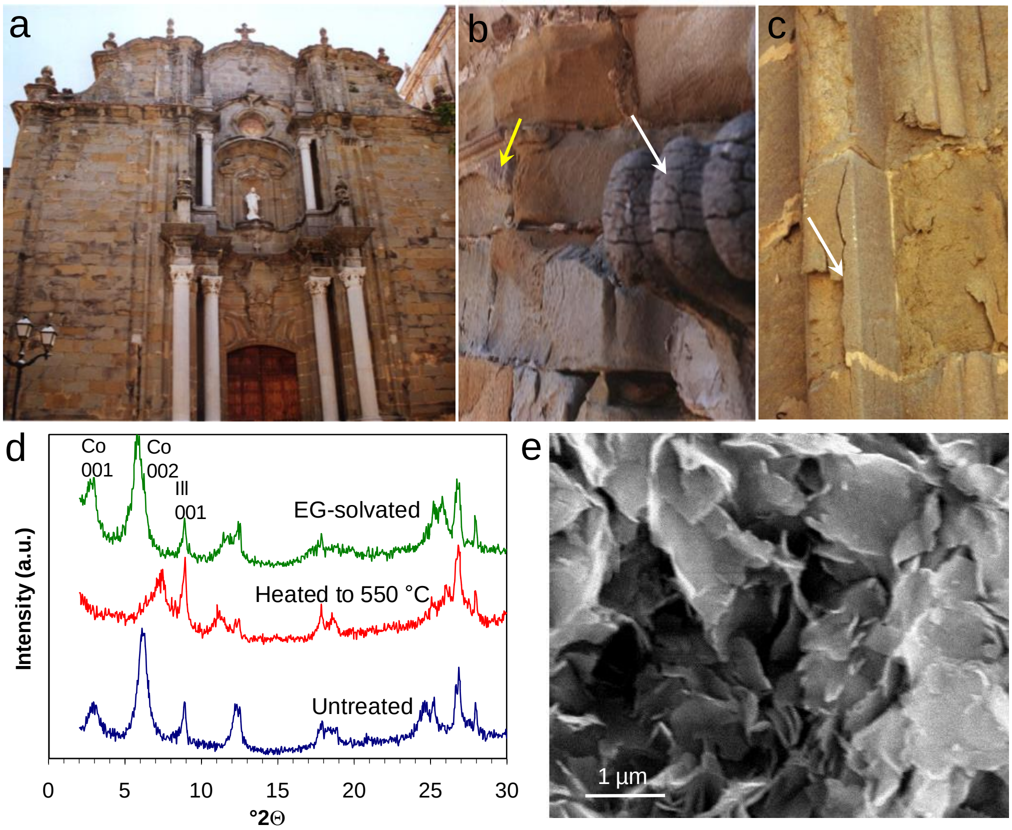


Figure 3. Clay swelling damage at the Church of San Mateo in Tarifa (Spain). a) Overview of the main façade of the church, showing extensive damage (scaling, delamination, contour scaling and drying cracks); b) detail of drying cracks, also known as "mud cracks" (white arrow) and scaling (yellow arrow) of the stone blocks and surface reliefs; c) detail of contour scaling (arrow); d) XRD patterns (Cu Kα radiation) of oriented aggregates of the clay fraction (~5 wt%) of Tarifa sandstone showing Bragg peaks of Corrensite (Co), a regular mixed layer smectite-chlorite (i.e., a swelling clay), and non-swelling Illite (Ill). The d_{001}-spacing of Corrensite expands upon EG solvation from 28 up to 32 Å and collapses to 12 Å upon heat treatment, confirming the presence of such a regular mixed layer clay (Moore and Reynolds, 1989); e) SEM image of the swelling clays within Tarifa sandstone. Modified from Sebastian et al. (2008).

FAILURE OF PREVIOUS CONVENTIONAL CONSERVATION TREATMENTS

During the early 1990s I had the opportunity to attend several international courses and schools (e.g., Pavia 1990; Lago di Garda 1991; Ravello 1993; Poitiers1996) and international congresses on stone conservation (e.g., Int. Congress on Stone Conservation, Lisbon 1992; Int. Symp. Conservation of Monuments in the Mediterranean Basin, Venice 1994, Rhodes 1996). I also performed research stays at several international centers such as Dip.to di Scienze della Terra, University of Pavia, Italy (Prof. U. Zezza and Prof. F. Veniale group), Opificio delle Pietra Dure, Florence, Italy (Dr. C. Manganelli del Fa group), Bayerisches Landesamt für Denkmalpflege, Munich, Germany (Dr. R. Snethlage group), Geologisches Institute, RWTH Aachen University, Aachen, Germany (Dr. B. Fitzner group), and SYREMONT Laboratories, Novara, Italy (Dr. V. Massa group). This was an excellent opportunity to get a broad vision of the understanding and advances, at the time, regarding stone conservation. One point was clear: the high level of decay observed in many building and sculptural stones made that a substantial amount of research and practice centered on the use of consolidants and protective materials (Clifton, 1980; Charola, 1995; Wheeler, 2005; Doehne and Price, 2010; Ruffolo and La Russa, 2019; Praticò et al., 2020; Delgado Rodrigues, 2022). Another point was that the products most studied and applied during the early 1990s were organic polymers, most commonly acrylic resins (such as Paraloid B72) and alkoxysilanes (mainly tetraethoxysilane, TEOS) as consolidants and different polymers and alkylalkoxysilanes/(poly)siloxanes as protectives (water repellents). Some critical voices regarding the effectiveness of such products were however emerging, and an intense debate started among those who defended and those who criticized the use of such consolidants/ protectives. In some cases, there were researchers that proposed the replacement of heavily decayed stone elements with new ones (from the historic quarries) rather than the application of any consolidant. This was the case of my PhD co-advisor, Prof. Ugo Zezza (University of Pavia), who was very concerned about the side effects of consolidation treatments, having studied the extreme damage created by the application of fluosilicate consolidants/protectives to the carved sandstone façade of the San Michele Church in Pavia (Italy) (Veniale and Zezza, 1988).

The problem with organic consolidants and protectives

Early in the 1960-1990s the consolidants/protectives of choice where typically organic polymers, specially acrylic polymers and their copolymers, vinyl polymers and copolymers, and epoxy resins (Clifton, 1980; Lazzarini and Tabasso, 1986; Horie, 1987; Selwitz, 1992). At the time, it was believed that they could overcome the often reported ineffectiveness of existing inorganic consolidants such as alkali silicates, lime water or fluosilicates, which commonly resulted in the formation of shallow hard crusts, produced soluble salts as by-products, and had a questionable ability of binding particles together (Clifton, 1980). However, organic consolidants and protectives were observed to have the tendency to be incompatible with the inorganic substrates (stone, but also mortars and plasters) they were applied to (Giorgi et al., 2010).

During the early 1990s I tested the effectiveness of novel polymeric materials with a dual protection/consolidation effect. I applied three types of fluorourethanes (FU 50, FU 620W and FUS 650W produced by SYREMONT at Novara, Italy) to the calcarenite stone used in the Cathedral of Granada and the biomicritic stone used in the Cathedral of Jaen. Such products were applied as low viscosity solutions either in organic solvents (buthyl acetate in the case of FU 50) or in water (FU 620W and FUS 650W) (Rodriguez-Navarro et al., 1996). They had the advantage of being fully reversible (a key feature that ideally should fulfill any consolidant or protective product, but it is seldom achieved) and displayed a relatively high water repellency due to the F-C functionality (contact angle >103°, with peak values of 126° for the case of FU 50 applied on Jaen´s biomicritic limestone), plus a high capacity to bond to the stone substrate by the O-H and C-O-N functional groups. After application, all of the treatments significantly reduced the water absorption rate, and increased the resistance to abrasion of the treated stones. However, one of this product (FU 50) led to a marked color change (ΔE = 8), whereas the water-based products did not have a high penetration (< 1mm) and tended to form surface films, which should negatively affect the water vapor permeability.

Latter on, I also tested the application of Paraloid B72 to Tarifa sandstone (Fig. 3), which was heavily deteriorated due to clay swelling damage. The treatment was very ineffective. Not only resulted in a significant color variation ($\Delta E > 7$), but also dramatically failed during the standard accelerated salt crystallization test using 14 wt% $Na_2SO_4 \cdot 10H_2O$ solution. After a few cycles, treated stone blocks showed massive weight loss, even higher than that of untreated control blocks (Fig. 4).

As a general rule, polymer treatments tend to form an impervious surface film on the treated stone (Fig. 4a-b) that hampers water vapor transport and eventually can foster salt damage (Fig. 4c). This side effect has been observed by many research groups (Matteini, 2008; Doehne and Price, 2010; Giorgi et al., 2010). Moreover, it has been thoroughly reported that polymeric consolidants and protectives may lead to several problems in addition to limited penetration and surface film formation, including yellowing by ultraviolet rays, and biodeterioration owing to bacterial and fungal growth (Sassoni et al., 2011). To these problems one has to add the issue regarding the assumed reversibility of organic treatments (as opposed to the irreversibility of inorganic treatments). It seems that such a reversibility is basically a myth: upon ageing, organic polymers typically become insoluble, which makes their removal after application quite complex or even impossible (Favaro et al., 2006).

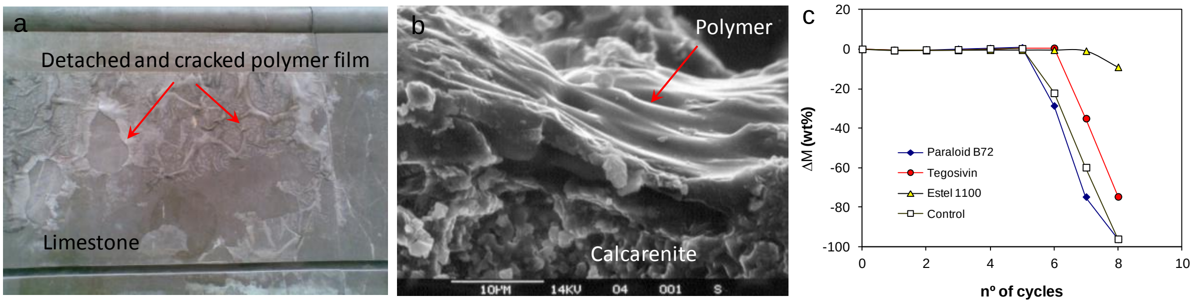


Figure 4. Undesired side effects of organic polymer treatments. a) Failed polymer protective coating applied to Sierra Elvira grey limestone (Granada, Spain). Note the detachment of the surface coating which shows dramatic bulging, wrinkling, cracking and lacunae; b) Formation of an impervious surface film on calcarenite stone from the Cathedral of Granada after application of Mowilith (modified from Rodriguez-Navarro and Ruiz-Agudo, 2018); c) Weight loss vs. number of salt crystallization cycles (using 14 wt% $Na_2SO_4 \cdot 10H_2O$ solutions) of Tarifa sandstone blocks subjected to different consolidation/protection treatments. Note that the treatment with Paraloid B72 increases the weight loss rate as compared with the control (untreated stone blocks).

The alkoxysilane boom

The generally observed incompatibility and poor performance of organic polymeric conservation materials when applied to stone or other inorganic substrates (Giorgi et al., 2010; Doehne and Price, 2010) resulted in their almost complete phasing out during the late 1990s and early 2000s, and their widespread replacement by (mainly) alkoxysilanes/(poly)siloxanes as the consolidants/protectives of choice for stone treatment (Wheeler, 2005; Xu et al., 2019). This was at least the case in conservation interventions in Spain. Alkoxysilanes are a broad family of compounds that include Si bound to alkoxy groups (RO-, where R is an alkyl group, such as for instance methyl, ethyl, propyl or isopropyl). They have been used since the XIXth c.: Wheeler (2005) reports that back in 1861 A. W. von Hoffman proposed the use of ethyl silicate for the treatment of deteriorating limestone in the Houses of Parliament (London). Basically, alkoxysilanes are very fluid (low viscosity), which facilitates a good penetration when applied to porous stone as they basically are monomeric or dimeric solutions (Charola,1995). However, they can undergo different degree of (pre)polymerization via the formation of siloxane (Si-O-Si) bonds. The latter explains the wide range of products available for consolidation and protection of stone derived from the basic alkoxysilane moieties, including siloxane oligomers and polymers, which typically have a higher viscosity and lower penetration than the basic alkoxysilanes. Upon application, and in contact with humidity, alkoxysilanes undergo hydrolysis of the alkoxy bonds followed by polycondensation of silica tetrahedra (via siloxane bond formation) in a process that involves a sol-gel transition and the formation of silica gel as final cementing agent (Wheeler, 2005). This silica cement establish bonds with the OH groups in the treated stone substrate. An example of alkoxysilane used in the consolidation of stone is tetraethoxysilane (TEOS) also known as ethyl silicate. If one or more alkoxy group is replaced by a methyl or ethyl group, which are non reactive (i.e., do not undergo hydrolysis) an alkylalkoxysilane (or alkylsiloxane) is obtained. Upon hydrolysis and polycondensation a silica gel is produced, but in this case the presence of alkyl groups (e.g., methyl or ethyl, or other hydrophobic group) imparts hydrophobicity to the consolidant. This is why such compounds are used as consolidant and protectives in stone conservation. Examples of these products are methyltrimethoxysilane (MTMOS) and methyltriethoxysilane (MTEOS) which have been applied to a range of stones (Wheeler, 2005). Different functional groups, typically hydrophobic, are added to the alkyl chain of these products when they are used as protectives (i.e., water repellent treatments). In this case the most common product are polysiloxanes (Charola, 1995).

Despite their widespread use as consolidants and/or protectives of choice after the observation of the shortcomings of organic polymeric materials, alkoxysilanes and alkylalkoxysilanes/(poly)siloxanes did not resulted in an effective, long-lasting consolidation or protection in some cases. For instance, in the case of carbonate stones, the lack of bonding between the carbonate minerals in the substrate (lacking OH surface groups) and the silica gel formed upon the alkoxysilane treatment results in a very poor consolidation effect (Wheeler, 2005). This issue can be partly solved by using a coupling agent (Praticò et al., 2020) or some specific nanoparticles (see below).

Another generally observed shortcoming of alkoxysilanes is related to the formation of cracks during the drying of the silica gel (Wheeler, 2005). Such drying cracks render the treatment ineffective as a consolidant. This is shown in Figure 5 for the case of the application of TEOS to the highly degraded surface of the Macael marble columns at the Lion's Court in the Alhambra Palaces (Granada, Spain). The treatment had very low penetration, was unable to provide cohesion to the loosed calcite grains, and to make mater worse, the areas without cracks acted as a film barrier that fostered salt damage due to crystallization of gypsum underneath.

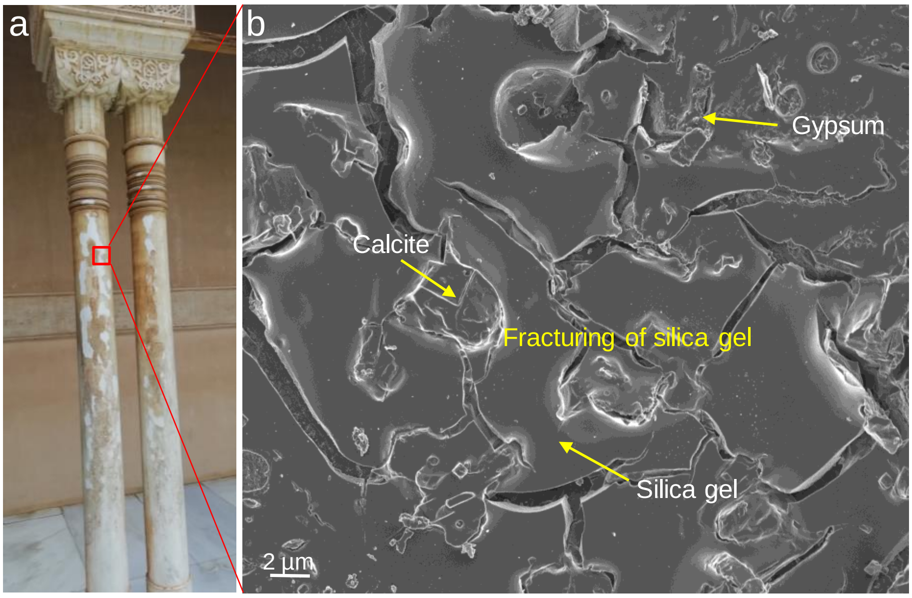


Figure 5. Treatment of Alhambra's marble columns with alkoxysilane (Granada, Spain). a) Macael marble columns at the Lions' Court showing scaling and granular disintegration; b) Extensive cracking of the silica gel surface coating, showing underneath loose calcite grains and newly formed gypsum. The latter contributes to the detachment of consolidated areas.

Recent research focused on ways to prevent formation of drying cracks and to impart some elasticity to the silica gel adding either nanoparticles (e.g., SiO_2, $CaC_2O_4{\cdot}nH_2O$, or TiO_2) or using additives such as polydimethylsiloxane (PDMS) that could also provide some functionality, such as self-cleaning or superhydrophobicity (Miliani et al., 2007; Pinho and Mosquera, 2011; Verganelaki et al., 2015; Ruffolo and La Russa, 2019; Xu et al., 2019). Following a biomimetic approach our group studied the effect of the addition of amorphous calcium carbonate (ACC) and amorphous calcium oxalate (ACO) (precursor for calcium carbonate and calcium oxalate biominerals, respectively) as nanoparticle additives to TEOS, obtaining very promising results when these cocktails were applied on a range of substrates (calcarenite, marble and gypsum plaster) (Burgos-Cara et al., 2019). By using PDMS during the synthesis of the amorphous nanoparticles, their early transformation into crystalline phases was prevented. Upon application to the substrates along with the TEOS solution, the nanoparticles prevented the formation of drying cracks, and their transformation into crystalline $CaCO_3$ and $CaC_2O_4{\cdot}H_2O$ via a dissolution-precipitation mechanism enabled the establishment of an excellent bond with the substrate minerals (epitaxial growth) thereby acting as a coupling (anchoring) agent for the silica gel, and provided micro-rugosity to the surface, fostering hydrophobicity (i.e., Lotus leave effect).

Another shortcoming of alkoxysilane treatments is their observed ineffectiveness following application to stones affected by clay swelling damage (Praticò et al., 2020). Alkoxysilane treatments applied to clay-containing stones such as sandstones loosed effectiveness after a few wetting/drying cycles (Felix and Furlan, 1995; Wheeler, 2005). Swelling/shrinking of expansive clays (e.g., smectites) resulted in damaging stress generation that affected the matrix of treated stones. This typically led to decohesion among the stone's mineral phases and the silica gel. We studied the consolidation of clay-containing Tarifa sandstone using (in addition to Paraloid B72; see above) an ethoxy-siloxane oligomer (Tegosivin HL100) and a mix of TEOS + oligomeric polysiloxane (Estel 1100). While some water-repellency and consolidation effects were observed, particularly in the case of the latter product, the salt crystallization test showed that upon a few cycles, significant material loss was observed, in one case (Tegosivin HL100) similar to that of the untreated control (Fig. 4c).

In these cases, failure of such conventional treatments was likely due to the fact that they did not tackle the cause of the decay (clay swelling) but rather dealt with its effects. This prompted the search of novel conservation approaches involving the use of swelling inhibitors alone or in combination with alkoxysilanes. Wendler et al. (1996) successfully applied a dialkyl ammonium surfactant (diaminobutane dihydrochloride) as a swelling inhibitor to reduce the hydric/hygric expansion of the smectite-rich tuff making up the Moai statues in Easter Island. In the same line, during the course of her PhD research co-directed by Prof. G. W. Scherer, Dr. G. Wheeler, and myself, Dr. I. Jimenez-Gonzales used a cationic surfactant, diaminoethane dihydrochloride as a swelling inhibitor for Tarifa sandstone (Jimenez-Gonzalez and Scherer,2004; Jimenez-Gonzalez et al., 2008). A ~50% reduction in free swelling strain was observed after treatment (Jimenez-Gonzalez et al., 2008). Subsequently, Caruso et al. (2012) demonstrated that the application of such swelling inhibitors before TEOS consolidation reduced swelling damage of Villarlod molasse over several wet/dry cycles. These are very promising results, but much research in this direction is still necessary before this combined approach can be broadly applied.

INORGANIC CONSOLIDANTS AND PROTECTIVES

Over the last two decades, inorganic consolidant and protective materials experienced a revival as an alternative to polymeric- and alkoxysilane-based treatments, particularly for the conservation of carbonate stones where the effectiveness of other conservation materials, including alkoxysilanes, was limited. The rationale behind their application was basically their *a priori* compatibility with the inorganic substrate they were applied to. They have, however, the shortcoming of being basically irreversible. But as discussed above, this is a general issue in nearly all conservation treatments. Indeed, there is a school of thought that states that any conservation intervention is intrinsically irreversible (what is done will irreversibly change the future behavior and evolution of the treated object), and even if the decision is not to apply any conservation treatment, this latter action will also by irreversible (it will affect how the object evolves, without the possibility of getting back to the original situation).

There is a long history regarding the use of inorganic materials for stone conservation. For instance, lime water, which upon contact with atmospheric CO_2 results in the formation of $CaCO_3$, was used since centuries for the consolidation of stone and even mural painting. However, this treatment has very limited consolidation capacity mainly due to the limited amount of calcium in a saturated solution of $Ca(OH)_2$, the need to apply huge volumes of such an aqueous solution in order to introduce a sufficiently high amount of calcium carbonate cement in the treated substrate, and the reported limited consolidation achieved (Clifton, 1980; Price et al, 1988; Hansen et al., 2003). Similarly, other consolidation methods based on the use of alkaline-earth metal hydroxide solutions have some draw backs. This is the case of $Ba(OH)_2$ solutions (the so-called Church's method), with or without addition of glycerin and urea (i.e., Lewin´s method), or with the modifications introduced by Matteini (2008) involving the initial application of ammonium carbonate followed by the $Ba(OH)_2$ treatment. While they resulted in the precipitation of insoluble cementing whitherite ($BaCO_3$), or barite ($BaSO_4$) in the presence of sulfates, they tended to show poor penetration, formation of hardened crusts, and increased surface reflectance due to the higher refractive index of the newly formed phases, and there was the issue of the high toxicity of the $Ba(OH)_2$ solution (Clifton, 1980). Other inorganic materials used in the past included aluminum stearates, aluminum sulfates, phosphoric acid, phosphates and hydrofluoric acid (Clifton, 1980). However, their effectiveness was not clearly established. All in all, these shortcomings prompted the search in recent years of more effective and compatible inorganic treatments (Hansen et al., 2003).

Nanolimes

Considering the limitations of the traditional lime water method, Prof. Baglioni's group proposed the use of alcohol dispersions of $Ca(OH)_2$ particles for the consolidation of (calcareous) stone and lime-based mural painting. First they used slaked lime dispersed in alcohol to avoid introducing water into the substrate and to increase the colloidal stability of the dispersions in order to enhance penetration and prevent surface glazing (Giorgi et al, 2000), but the relatively large portlandite crystals typically present in slaked lime could led to non-optimal results. Subsequently the same group synthesized nanoparticles of $Ca(OH)_2$ via different routes, developing what it is now known as a "nanolime" (Ambrosi et al., 2001; Salvadori and Dei, 2001; Chelazzi et al., 2013; Baglioni et al., 2014). Nanolimes, which are dispersion of $Ca(OH)_2$ nanoparticles (with size typically < 200 nm) in short-chain aliphatic alcohols (ethanol, propanol or isopropanol), have found extensive application in the conservation of stone heritage (Fig. 6) (Rodriguez-Navarro and Ruiz-Agudo, 2018).

Our group at UGR explored different aspects of the synthesis and application of $Ca(OH)_2$ nanoparticles dispersed in alcohol and their effectiveness as consolidants (Rodriguez-Navarro and Ruiz-Agudo, 2018). We found that depending on the pore characteristics of the stone (e.g., high porosity, large pores), aged slaked lime or carbide lime dispersed in alcohol could results in an even better consolidation than commercial nanolimes (Rodriguez-Navarro et al., 2013). We also discovered that over time nanolimes dispersed in alcohol, which were considered inert, could partially transform into calcium alkoxides (Rodriguez-Navarro et al., 2013; 2016b), yet the latter could undergo hydrolysis and convert back into $Ca(OH)_2$ and carbonate as standard nanolime once applied to a stone substrate. This is the basic idea behind the application of calcium alkoxides for the consolidation of stone (Favaro et al., 2008). We also studied the kinetics of nanolime carbonation and phase evolution during this reaction, demonstrating that amorphous calcium carbonate (ACC) nanoparticles were a precursor for crystalline $CaCO_3$ (Fig. 6) (Rodriguez-Navarro et al., 2016c). Interestingly, we observed that the presence of adsorbed alcohol during the amorphous to crystalline phase transition favored the formation of metastable vaterite and aragonite prior to the formation of stable calcite. The latter could have implications in the actual level of consolidation achieved during such phase transitions. We also observed that the carbonation of nanolime followed (pseudo)first order kinetics. Currently we are exploring ways to synthesize, via a modified solvothermal route, $Ca(OH)_2$ nanoparticles with extremely high surface area (> 70 $m^2 g^{-1}$), reduced particle size (<< 200 nm), and enhanced carbonation rates for a more effective consolidation of porous stone.

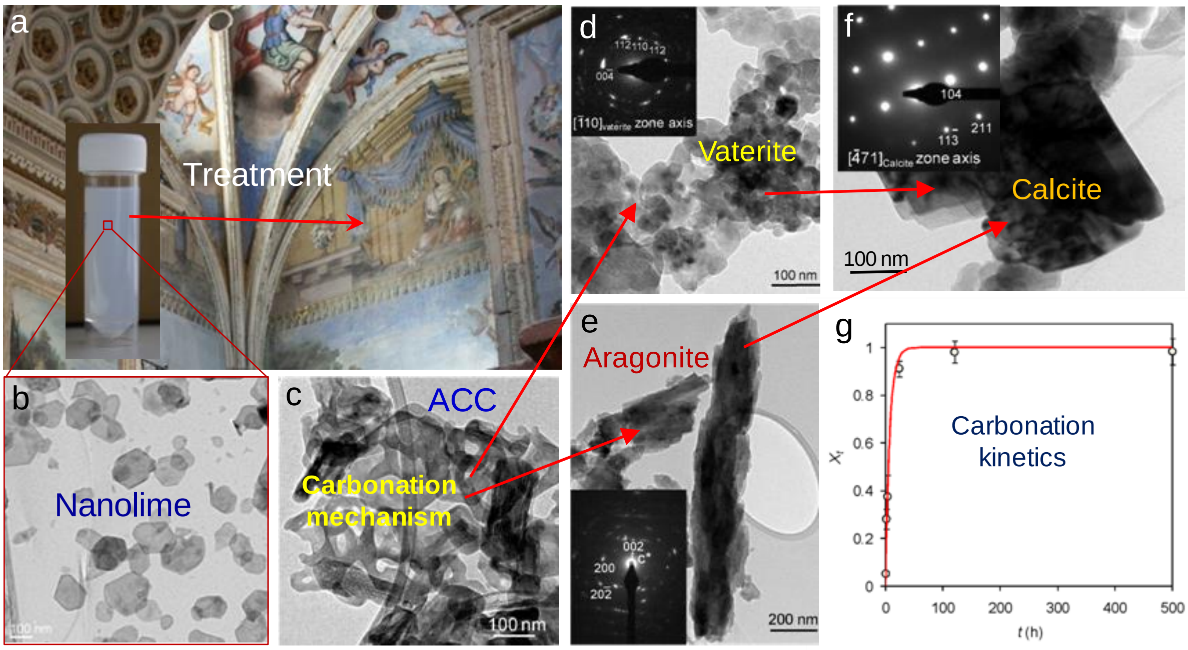


Figure 6. Nanolime for heritage conservation. a) Alcohol dispersion of nanolime for consolidation of mural painting; b) TEM image of commercial nanolime (portlandite) particles (Calosil E25); c) Carbonation of nanolime via a nonclassical crystallization mechanism initially forming an amorphous calcium carbonate (ACC) precursor (TEM image); d) vaterite and e) aragonite metastable phases formed after ACC observed under the TEM (SAED patterns in inset); f) TEM image of stable calcite formed after vaterite and aragonite (SAED pattern in inset); g) fractional conversion (X_f) of portlandite vs. time (t) during the carbonation of nanolime following (pseudo)first order kinetics. Modified from Rodriguez-Navarro et al. (2016c).

Oxalate conversion layers

Matteini et al. (1994) suggested that marble could be protected by coating its surface with a layer of calcium oxalate following reaction of calcite grains with a solution of ammonium oxalate. Such a reaction results in the formation of calcium oxalate monohydrate (whewellite, $CaC_2O_4 \cdot H_2O$) and di-hydrate (weddellite, $CaC_2O_4 \cdot 2H_2O$), which are highly insoluble phases that act as a protective layer against further chemical weathering. The idea behind this treatment was the observation that calcium oxalate-rich patina (scialbatura) naturally developed on marble sculptures (e.g., Trajan's column in Rome) resulted to be highly effective in preventing marble weathering in polluted environments (Del Monte and Sabbioni, 1987).

Our group studied ways to improve the formation of calcium oxalate layers on white calcitic marble and yellowish dolomitic marble (Burgos-Cara et al., 2017a). We observed that in several cases, the newly formed calcium oxalate surface layer was not continuous, which resulted in an inefficient protection against chemical (acid) weathering. That happened when there was no coupling between the dissolution of calcite and the precipitation of calcium oxalate, preventing a pseudomorphic replacement (Burgos-Cara et al., 2017b). This typically occurs at the alkaline pH achieved when using the standard ammonium oxalate treatment. Our study using diluted oxalic acid solutions with pH 1.7 demonstrated that a perfect interface coupling between the dissolution of the calcite substrate in the marble and the precipitation of calcium oxalate could be achieved, resulting in the epitaxial growth of whewellite in perfect crystallographic register with the underlying calcite crystals (i.e., resulting in a pseudomorphic replacement of calcite by whewellite). This led to a full coverage of the marble substrate with a calcium oxalate film 10-30 µm in thickness, resulting in a huge increase in the resistance of the treated marble to acid attack. Importantly, no significant color changes (Δ*E*<<5) nor a reduction in water vapor permeability were observed after treatment (Burgos-Cara et al., 2017a). The observation that organic additives such as citrate can modify the dynamics of the conversion reaction, fostering epitaxial growth of the oxalate phases on calcite and achieving a full surface coverage (Burgos-Cara et al., 2017b), opens new possibilities to tailor and optimize this protection strategy. Further research should steer in that direction.

Other conversion layers

Weiss et al. (2000) proposed the use of tartaric acid to dissolve a thin layer of calcium carbonate and subsequently induce the generation of a surface layer of highly insoluble calcium tartrate onto a calcitic stone substrate. The aim of this surface treatment initially was to create a good coupling between the carbonate substrate and an alkoxysilane treatment. Note that as opposed to $CaCO_3$, calcium tartrate has surface OH groups that can readily bond the silica gel formed after the application of the alkoxysilane. Interestingly, the authors observed that the resulting calcium tartrate surface layer significantly increased the acid resistance of the stone and also its (surface) strength. This opened the possibility of using such a treatment for the surface protection of marble and other carbonate stones (Hansen et al., 2003). Despite its potential, this type of treatment has not seen widespread application in recent years.

The same principle, but in this case based on the conversion of calcite into highly insoluble calcium phosphate (hydroxyapatite) was proposed by Sassoni et al. (2011) for the protection and surface consolidation of carbonate stones, while an alternative method for the in situ production of calcium phosphate for stone conservation was proposed by Yang et al. (2011). Sassoni et al. (2011) used diammonium phosphate solutions to convert a thin calcium carbonate surface layer into hydroxyapatite. In contrast, Yang et al. (2011) proposed the initial application of nano-$Ca(OH)_2$ as a calcium source followed by the application of diammonium phosphate to generate a surface coating of calcium phosphate on a stone. The main advantage of the treatment proposed by Sassoni et al. (2011) is the fact that it does not require the addition of a Ca source, as the treatment relies on the partial dissolution of the calcium carbonate substrate and the subsequent precipitation of hydroxyapatite. This latter treatment approach has been thoroughly tested since 2011, and the results so far show that it produces a significant surface protection and consolidation to carbonate stones, especially in the case of marble. As indicated above, we have recently explored the combination of this treatment with the application of biopolymers to prevent salt damage obtaining very promising results (Andreotti et al., 2019). Also, members of our group successfully tested the possibility of using this treatment to eliminate gypsum crusts developed on carbonate stones via the transformation of this calcium sulfate salt into a protective and strong calcium phosphate surface layer (Molina et al., 2017).

BACTERIAL PROTECTION AND CONSOLIDATION OF STONE

It has been known for decades that some bacteria can induce the precipitation of calcium carbonates in natural environments. For instance, Boquet et al. (1973) reported that biomineralization of calcium carbonate by soil bacteria was a general phenomenon, and it has been also known that bacteria contribute to the formation of calcium carbonate rocks such as travertines or are involved in the formation of speleothems. Based on this principle, Adolphe et al (1990) patented a method for the consolidation of carbonate stones involving the precipitation of $CaCO_3$ induced by bacteria. According to this commercial so-called CALCITE method, a carbonatogenic bacteria culture along with a nutritional solution, was applied on the treated substrate, and after a few days the newly formed calcium carbonate was able to consolidate the treated (mostly calcareous) porous stone (Le Metayer-Levrel et al., 1999). Some shortcomings of this method, namely the initial use of a potentially pathogenic bacteria (*Bacillus cereus*), the presence of a carbohydrate carbon source that could foster the development of acid-producing bacteria, and the limited protection and consolidation initially achieved, were important handicaps for its widespread adoption by the conservation community.

During the late 1990s and early 2000s, our group at the University of Granada in collaboration with the group of Prof. M.T. Gonzalez-Muñoz (Dept. Microbiology, UGR) studied the ability of non-pathogenic soil bacteria *Myxococcus xanthus* to induce calcium carbonate precipitation in a range of culture media, and within the pore system of calcareous stones (calcarenite and marble). Based on this research we developed a consolidation method involving the application of this bacteria in a liquid culture medium (M-3P) that lacked carbohydrates as a C source. Instead, we targeted the ability of these bacteria to degrade amino acids (from a protein source), resulting in the *in situ* production of CO_2 and NH_3. The latter by-products of bacterial metabolism increase the system alkalinity and carbonate concentration, ultimately inducing the precipitation of $CaCO_3$ (Rodriguez-Navarro et al.,2003). The culture medium also included calcium acetate as a Ca source (with the possibility of the bacteria to use acetate as an additional C and energy source). The tests in the laboratory and its application *in situ* on different historical building of Granada (Hospital Real, Monasterio de San Jeronimo, Capilla Real) made of calcarenite showed that this consolidation treatment was very effective, with no apparent draw backs (Rodriguez-Navarro et al., 2003, 2015; Jroundi et al. 2010, 2017). One key result was the observation that the newly formed calcite grew sintaxially on the calcite crystals of the substrate (Fig. 7a-b), and was more resistant to mechanical stress and chemical weathering than abiotic calcite, likely because bacterial calcite was a biomineral including organic byproducts of bacterial activity (Rodriguez-Navarro et al., 2003; Jroundi et al., 2017). However, this kind of treatment has the important limitation that it required the culture in the laboratory (by specialists) of the bacterial inoculum.

This critical limitation was overcome by a new bacterial conservation treatment developed by our group based on the selective activation of the indigenous carbonatogenic bacteria already present in the treated stone substrates (Jimenez-Lopez et al., 2007). By applying the patented sterile nutritive solution M-3P (Gonzalez-Muñoz et al., 2008), the bacteria able to produce a new $CaCO_3$ cement were activated. Following successive application of such sterile solution for a period of 6 days, we were able to achieve a significant consolidation in the treated stones (both in the laboratory and *in situ*) (Jimenez-Lopez et al., 2007; Rodriguez-Navarro et al., 2015; Jroundi et al., 2017). Delgado Rodrigues and Pinto (2019) tested this method elsewhere and obtained similar positive results. Key for the efficacy of this novel bacterial biomineralization treatment is the fact that in nearly all stone substrates studied so far (in different parts of the world) carbonatogenic bacteria are abundant (Jroundi et al., 2017, 2020). Also critical is the fact that the treatment does not induce the proliferation of deleterious (acid producing) microbiota.

To gauge the efficacy of this treatment, not only when applied to carbonate stones and in European (Mediterranean climate) countries, we recently applied this bacterial biomineralization treatment for the consolidation of volcanic tuff stone used in the construction and carving of the structures, sculptures and stelas of the ancient Maya site of Copan (Honduras), which is exposed to a tropical environment (Jroundi et al., 2020; Elert et al., 2021) (Fig. 7c). This tuff stone suffers extensive damage due to scaling and spalling associated with the presence of swelling clays (smectite in concentrations of up to 8 wt%). Previous consolidation treatments with organic polymers (Paraloid B72 and Mowital) and alkoxysilanes applied in the 1980s and 1990s, were not effective (Caneva et al., 2005; GCI and IHAH report, 2006). We applied our patented bacterial conservation treatment to the tuff stone on a pilot site at Structure 10L-18 in the Copan Acropolis (Main Group), and in our laboratory at the UGR on tuff stone samples collected at the site. By culture dependent and culture independent methods we identified the presence of abundant carbonatogenic bacteria in the tuff stone (Jroundi et al. 2000) and we observed that they were activated by the treatment producing a significant amount of bacterial $CaCO_3$ cement (Fig.7d). This newly formed carbonates consolidated the degraded tuff (in the laboratory and *in situ*) as shown by peeling tape test and drilling resistance measurement (DRMS) results (Elert et al., 2021). Interestingly, the treatment also resulted in a reduction of the swelling strain associated with clay expansion in the presence of water. Moreover, the treatment significantly increased the contact angle of water droplets (from ~0° up to ~90°). These results show that the bacterial biomineralization treatment was not only effective for the consolidation of the stone, but also has a significant protective effect. We believe that such a protective action is linked to the formation of bacterial exopolymeric substances (EPS). Note that EPS and bacterial cells forms biofilms, which in some cases show hydrophobic properties (Epstein et al., 2015). Note also that EPS can interact with swelling clays preventing/limiting their expansion (Alimova et al., 2009).

We also tested a variation of this bacterial conservation treatment for a very challenging weathering scenario: porous calcarenite stone heavily degraded by salt damage (crystallization of syngenite ($K_2Ca(SO_4)_2 \cdot H_2O$), niter (KNO_3), hexahydrite ($MgSO_4 \cdot 6H_2O$), gypsum ($CaSO_4 \cdot 2H_2O$), and halite (NaCl)). The new strategy involved the isolation, identification, and culture in the laboratory of the indigenous carbonatogenic bacteria present in the stone to be treated, followed by the re-application of such isolated (and boosted) carbonatogenic bacterial culture to the degraded calcarenite stone along with the M-3P nutritional broth (Jroundi et al., 2017). Such a third type of bacterial biomineralization treatment resulted in the best consolidation in terms of strengthening of the stone substrate (measured by peeling tape tests and DRMS) as compared with the fist type of treatment (inoculation with an exogenous single bacterial culture) or the second type of bacterial treatment above mentioned (activation of the carbonatogenic bacteria already present in the treated substrate following application of the sterile M-3P solution). This third type of bacterial treatment was more effective than the previous ones likely due to the fact that the isolated carbonatogenic bacteria were already adapted to the saline environment in the degraded calcarenite, so they could easily proliferate and generate abundant $CaCO_3$ cement once they were re-applied at a high concentration onto the salt damaged stone.

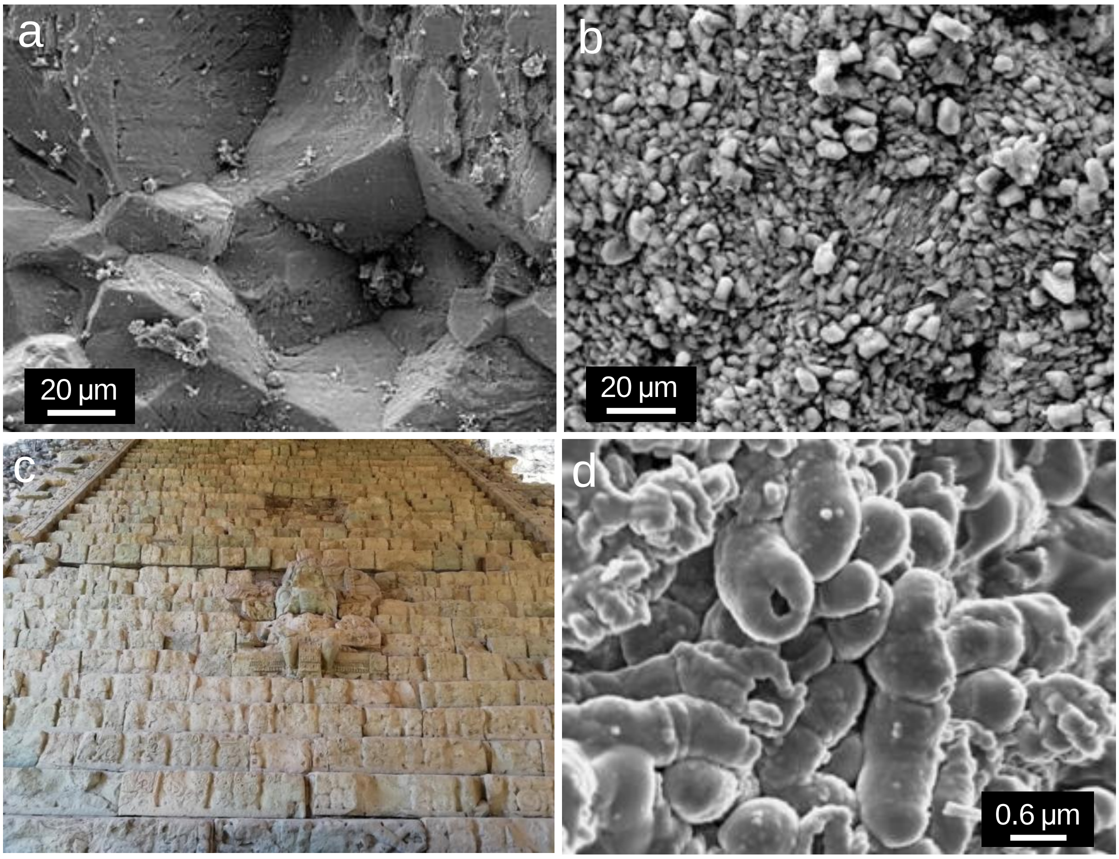


Figure 7. Bacterial protection and consolidation. a) SEM image of Macael marble before and b) after bacterial biomineralization treatment using *M. xanthus*. The epitaxial growth of iso-oriented bacterial calcite crystal on each of the calcite grains forming the substrate is observed. Modified from Rodriguez-Navarro et al. (2011); c) Tuff stone at the Hieroglyphic Stairway of Copan showing extensive damage (manifested by the loss of surface reliefs); d) Bacterial calcium carbonate cementing Copan stone after treatment with sterile M-3P nutritional solution. Note the ellipsoidal shape of fully calcified bacterial cells.

CONCLUSIONS AND OUTLOOK

Here I have shown that despite the significant progress that has taken place over the last three decades in the better understanding of the different weathering mechanisms affecting building and sculptural stone, there are still some aspects of specific weathering processes that are not fully understood. Further research is therefore still necessary if we are to develop more effective stone conservation treatments.

Further studies are needed to better understand the role of pollutants on the chemical weathering of stones, not only carbonate stones but also silicate stones such as sandstones, granites or tuff stones. In particular, it would be necessary to further explore the role of O_3 and NO_x in combination with particulate matter on the accelerated decay of stone. It would also be necessary to evaluate how rising atmospheric CO_2 concentrations affect the dissolution of stones, carbonate ones in particular. This may lead to the development and implementation of more effective preventive measures to avoid chemical weathering of outdoor-exposed stone.

Another area of research that need to be further advanced relates to damage associated with moisture expansion of clay-containing stones. Further studies need to be performed to better understand the parameters that enhance or reduce clay swelling damage, such as clay composition, content and distribution within clay-containing stones, and the interaction with other weathering processes (salt damage and/or thermal expansion). Clay swelling inhibition using different, more effective inhibitors, along or in combination with standard consolidation/protection treatments should also be studied. An aspect that deserves attention is the interaction of natural biopolymers, such as microbial EPS, on the possible swelling inhibition of clay minerals. The promising results of the bacterial bioconsolidation/ protection treatment of clay-containing Copan tuff stone resulting in a significant reduction of free swelling strain, likely associated with the interaction of EPS with smectites, suggest that this is an area deserving further research.

I have also shown that traditional polymeric (organic) as well as alkoxysilane-based treatments have several shortcomings. The former are definitively incompatible with the inorganic substrate of stone, and their use in stone conservation should be carefully re-evaluated. Indeed, further research should be performed regarding novel ways to safely and efficiently eliminate them from stones treated in the past. Regarding the latter products, promising advances have been done using nanoparticles and additives that act as coupling agents, prevent drying cracks generation, and impart specific functionalities to the treatment. Further research should be done in this respect to achieve better performance of alkoxysilane-based treatments, especially when applied to carbonate stones.

The current revival of inorganic treatments is showing that there are many alternatives to traditional consolidant and protective treatments that are in principle more compatible and, possibly, more efficient. In addition to the recently developed inorganic treatments discussed herein, there is ample room for the design and testing of novel green and sustainable bioinspired and/or biomimetic hybrid organic-inorganic treatments. One interesting possibility would be to evaluate the potential of novel biomimetic consolidants based on biomineralization of $CaCO_3$ for carbonate stone conservation, involving the (re)growth of calcite upon attachment of amorphous calcium carbonate in the presence of (bio)macromolecules (Rodriguez-Navarro et al., 2016d). This is an area of research that we are currently exploring, which aims at producing *in situ*, within the pore system of stone, calcium carbonate cement including organics enabling the controlled nucleation and growth of $CaCO_3$, and leading to hybrid cementing materials with the remarkable physical-chemical and mechanical properties of biominerals such as mollusk shells (Rodriguez-Navarro et al., 2016a).

Finally, I want to emphasize that biomineralization of calcium carbonate by the activation of indigenous carbonatogenic bacteria present in degraded stone is a very promising strategy that deserves further research and testing. It would be enlightening if other groups, using other substrates and in different locations, test this novel consolidation and protection approach in order to further validate its effectiveness. This is necessary to foster its application in conservation applications. Note that no matter how much advances are achieved in the design and testing of novel, more effective consolidants and protective treatments, there is always the difficulty to transfer this knowledge from the research community to the field of practical conservation. While there are exceptions, my experience is that in many cases conservators and practitioners are too conservative, not being very kin to adopt and apply novel conservation treatments. Their reluctance is in many cases justified by practical experience showing that many, at the time novel and apparently efficient, conservation treatments failed in the medium- and long-term. It is, therefore, an important part of our work as conservation scientists to present conservators sound and convincing evidence about the effectiveness of the novel consolidation and protection methods and materials we are investigating and developing.

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Notes on Stone Consolidation in Italy, with an appendix on the "Ship of Theseus"

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SUMMARY: The Author examines issues concerning the modernisation of attitudes toward stone conservation as introduced in Italy mainly after the flood in Florence in 1966. Attention is drawn to conferences (such as those held in Bologna in 1969, 1972, 1975, 1981), seminars, figures of significant conservator-restorers. Alternatives between organic- and inorganic consolidants are recalled. At the end, recent research on the artificial recreation of oxalates, cleaning by means of essential oils, consolidation through diphosphates is presented. The opinion is softly expressed that the matter is not so much of producing new substances as much as sharing information and experiences about what is already available in this field

KEY-WORDS: stone conservation, consolidation, artificial oxalates, essential oils, diphosphates.

While reading recently the book by two American conservators about the restoration of Medieval Polychrome wooden Sculpture[1], I took notice of an intelligent observation expressed by the well-known conservator-restorer Stefan Michalski, as quoted by the authors[2] (p. 129): "When one applies consolidant solution to a painting or a sculpture or a pastel, one hopes that capillarity will carry the solution into all the necessary places, that after drying the consolidant will have remained in the necessary places, that the object will be sufficiently strong, and that the appearance will be acceptable. All too often, unfortunately, one sees failure of some or all of those objectives"[3] . Is that really so, I asked myself, that after so many years that conservation science has been working on this sort of problems, still we find ourselves in a situation where uncertainty about the results seems to reign? To address specifically marble- and stone materials: such an uncertainty appears truly paradoxical. Literature devoted to conservation and restoration of stone materials appears to be almost endless, and it would seem that very little is there to add. The bibliography I find in a text to which I use to turn to willingly, "Stone Conservation".

An Overview of Current Research" by Doehne e Price[4], is more than seventy pages long, although I am referring to the second edition, from 2010 (the first is from 1996), that is, by now twelve years "old", and authors only include recent literature. Some lines came to my mind at that moment due to a scholar whom I always admired, the chemist Giorgio Torraca[5]. In his introduction to a well-known volume (not only in Italy), "Il restauro della pietra" by Lorenzo Lazzarini and Marisa Laurenzi Tabasso, Torraca (p. VI) wrote about the difficulty of assembling the enormous dispersed literature[6]. Actually, Torraca rather had in mind restoration reports, but if we consider texts on conservation science, criticalities are still greater. Having said that I am referring to my personal professional experience as an art historian, being neither a scientist nor a conservator-restorer, it seems to me unimaginable that any scholar could keep her/himself truly updated on all the literature being published worldly about stone conservation. But what is it that we need, in order to solve efficiently the series of problems presented by this subject? Doehne and Price, at the end of their very useful and valuable book, wrote: "The key challenge for the future is that resources for applied research, technology transfer, and long-term testing are needed...structural gaps remain between researches and practitioners...in order to preserve our heritage in stone, it is time to build support for large-scale and long-term research and technology transfer projects. In a number of cases, we have exciting solutions to stone conservation problems, but we do not have resources to properly test and implement these solutions" (p. 80). In their opinion there exists therefore a problem of transferring knowledge from researchers to "practitioners", but a problem due to insufficient financing is there as well.

I totally agree on the first point, and I happened to highlight repeatedly this difficulty during the decades when the best part of my professional life has been devoted to conservation; but on the second issue, mine is a rather different belief. It is obvious, and I would never dream to question it, that resources are always insufficient, I should say by default, in that any research would wish to have more and would very well know how to make use of it; but it is also true that the technologies and materials we already have are probably effective enough to take care of most problems offered by specific cases. Should we conclude at this point that Michalski's evaluations we recalled at the beginning are wrong? Surely not, everybody's daily experience demonstrates that; but we must know that no conservation intervention will ever solve all problems entirely and once for all, and no consolidant will ever reach all "necessary places". Our goal will be to improve the existing situation at that moment, to make all the same some steps forward.

This said, it is also true that very probably those responsible for an intervention will not be knowledgeable of all the skills already available about that issue. Partly because it is objectively unthinkable to extricate oneself in such an endless literature as I was referring to (some knowledge is there, but scattered, as Torraca wrote: someone has it, but who, and where?), partly also because of some responsibility on the restorers side, because they did not commit themselves sufficiently to widen their knowledge by reading continuously the specialised publications and attending occasions of specialization such as conferences, seminars and such.

I happened as a consequence to reconsider some decisive moments in the history of conservation of stone materials in Italy, according to my very selective and utterly personal criterion, which I am presenting here in a synthetically. I now have in mind those steps which proved particularly meaningful for my professional life. Starting from the assistance which, at the time of the flood in Florence in 1966, was offered to the Florentine restoration by scientists and restorers knowledgeable in that field coming from other parts of the world. Such a need was real, because a great part of the tradition in marble- and stone restoration in Florence was still mainly devoted to very invasive interventions which would easily resort to simply substituting parts, according to the tradition followed in the past centuries by the workers in the so-called "Opere del Duomo" (Pisa, Siena, Florence). Particularly important proved in that occasion the presence in Florence of Kenneth Hempel, a restorer at the V&A Museum in London, who introduced the use of more modern materials, and most of all helped pushing for a more advanced concept of conservation (surely influencing, for example, the excellent Florentine restorer Guglielmo Galli)[7].

Just a short while after, there began the activity of the "Centro per la Conservazione delle sculture all'aperto" in Bologna, planned by the superintendent Cesare Gnudi and entrusted for the scientific activities to a great chemist, Raffaella Rossi Manaresi (†2011). This Centre promoted a series of conferences and seminars where the major international experts on stone conservation were invited (1969, 1972, 1975, 1981, plus the reports on the conservation of the façade of the church of San Petronio in Bologna, 1979, 1981, and the prothyrum of the Ferrara cathedral, 1981), so that one can judge that it was thanks to those initiatives that Italy entered once for all the modern restoration also for this typology of materials. A participant was a very well-known conservator-restorer, born in Mantua and working in Bologna, Ottorino Nonfarmale (†September 2020), who in the restoration of the facade of San Petronio successfully applied a mixture of silicon and acrylic resins ("successfully" must be interpreted in a relative way, as I shall specify later on). But generally speaking, from the Seventies on, experiences and applications multiplied in Italy, in a context which, I repeat, was by this time totally European.

In 1974 the "Centro di Studio sulle Cause di Deperimento e sui Metodi di Conservazione delle Opere d'Arte del Consiglio Nazionale delle Ricerche (CNR)" was founded in Florence, directed by the chemist Franco Piacenti. This is the structure responsible for making use in conservation, meant as a protective, of a substance first created for aerospace industry, "perfluoropolyether" (on the market as "Fomblin"). In its first formulation, this product had more resistance but less penetration; in a second, as Fomblin Y Met, which allowed its application by sprinkling, more penetration was achieved but minor resistance within the artefact, as could be expected. One has to make a choice, rarely one can have everything at the same moment.

A specific consideration must be granted to the activity as a restorer of the engineer and later architect Piero Sanpaolesi, active in Florence where in 1960 he founded the "Istituto di Restauro dei monumenti" in the Faculty of Architecture. Particularly in the 1960ies, Sanpaolesi restored a series of important historical facades (the Bartolini Salimbeni, Pucci, Rucellai palaces in Florence; Castelnuovo in Naples, Ca' d'Oro in Venice, San Michele in Pavia); but as early as 1941 he had restored with the same methodology Donatello's Pulpit at the cathedral in Prato, not far from Florence. Sanpaolesi used fluosilicates, silicates of fluorine and magnesium, but mainly he undertook attempting a truly total impregnation, which would penetrate as much as possible into the depth (reaching "all the necessary places", as Michalski had it), by creating a vacuum-sealed environment. Many years later (1997), in a conference held in Bath[8], Giorgio Torraca would write that fluosilicates and Portland concrete "are probably the most ill-famed products in the history of conservation". "And yet, he added, there are cases where they seem to have worked properly". "In the Prato Pulpit, he concluded, "Probably the treatment with fluosilicates had more saved than destroyed the reliefs...(possibly) Sanpaolesi's major mistake in 1941 had been to promise that the marble reliefs after treatment would resist any further decay...we might also regret that the marble had not been cleaned before consolidation, but if one thinks how rough were cleaning processes at those times, one can conclude that probably omitting cleaning was rather a lucky event" (pp. 202, 203).

The fluosilicate's functioning has been further studied and explained in the 1990ies by Mauro Matteini and Arcangelo Moles re-examining precisely the Prato Pulpit and Palazzo Rucellai's facade. Concerning the Pulpit[9], their conclusion was that "a treatment with fluosilicates is aggressive because we have an acid attack to the marble, but it would seem that it immediately self-stops, possibly because of the insolubility itself of the transformation products and the very compact screen they would produce...our present belief is that, the total unsuitability of fluosilicates consolidation for ancient marble artefacts being understood...the heavy damages shown by that monument must not be charged to that treatment, being most likely pre-existing to it". And as far as Palazzo Rucellai is concerned[10] (an architecture, remember, by Leon Battista Alberti, one of the Renaissance's major masterpieces), considering that I cannot recount here their reasoning in its entirety, Matteini and Moles' conclusion was that fluosilicates had precipitated upon an exterior layer formed by black crusts existing over the body itself of that artefact, a cleaning operation not having previously been done. Consequently, removing the crusts allowed the aesthetic retrieval of the building. That in other cases the results of fluosilicate treatments was judged quite harmful, having caused a disintegration of the building's facade, such as in the case of the church of San Michele in Pavia, one of the loftiest of the Romanesque period, depended on the fact that the impossible attempt of a total impregnation had led in that case to a hardening which would originate efflorescences inside the monument (built out of sandstone), forming comparatively massive grains. These would stay inside the body of the monument and below the consolidated layers, pressing their way towards the exterior and thus disintegrating the surface.

What I was interested in highlighting here, is a general thought, that more often than not it is not the substance itself applied to a monument to be the origin of a subsequent damage, as much as a lack of understanding of dynamics of a mechanical-physical character carried along as a consequence by that application. This is a consideration worthy always and in every circumstance in stone materials treatments, when bad results are by default blamed to materials, while, being understood that some of those are particularly suitable according to the specific case, damages as a principle come from not having considered globally which processes would arise from the application of that particular substance in that special case.

The commonest error stayed in the trust that consolidation and protection of stone materials could be addressed and fixed by inventing one or more miraculous substances which would magically achieve the desired goal. One used to joke about a “vernice del Soprintendente”, the superintendent’s varnish, ascribing to the civil servants of the State charged with protection and conservation of cultural inheritance, the inadequacy of understanding the complexity of phenomena, and a tendency towards simplifying all problems so as to easily obtain an optimal result. Otherwise, the expression “chemical illusion” had been coined, as if one could entrust chemistry alone with problem solving of all sorts. I myself took over this expression in the title of a contribution of mine, where I examined the concept of “compatibility”[11]. The most reasonable scholars had it clear, that one could never apply the general principle of reversibility when the case was of a consolidating treatment; and I should like to add immediately that they are mistaken, and there is quite a lot of them, who still nowadays attribute this principle to the great theoretician of XXth century restoration Cesare Brandi, who never expressed that. Brandi had spoken instead of the need not to prevent by a restoration the unavoidable future interventions, a principle truly fundamental in conservation which we now commonly define as retreatability or repeatability. More theoretical principles, following the very Italian propensity towards conservation theory, were introduced into the debates on conservation, precisely after considering how irreversible certain treatments prove, that is, how useless would it be to study materials independently from treatments, that is, their behaviour once applied to an artefact. As a consequence, one would appreciate the value of durability, also responding to the much agreed upon principle of minimal intervention (the longer effects endure, so much less will it be necessary to intervene once more); as well as the other already mentioned principle of compatibility (an issue about which Torraca and Matteini had written repeatedly). This last principle meets a condition to be found by default in conservation: that is, that every operation is anyway an approximation of some sorts, and that the specific condition in which a particular artefact is, will always ask for some sort of compromise, as compared to an ideal, solely theoretical project of conservation. This is the reason why, for instance, ethyl silicates have been so very widely employed also in the case of carbonatic, not siliceous, rocks.

It is the principle of compatibility, therefore, that always made me prefer inorganic instead of organic consolidating treatments; apart from many other aspects all the same presented by these latter, such as colour changes. In this case, too, I want to make it quite clear that I am speaking generally, since there are obviously many circumstances when the specificities of artificial resins can meet particular problems more effectively than treatments by inorganic materials. Concerning consolidation in depth of marble statues, for instance, literature registers seemingly optimal results as far as effectiveness and durability are concerned, whenever an impregnation has been accurately done by vacuum-sealing the object[12]. The restorer Gian Luigi Nicola, who in his laboratory in Aramengo d’Asti (Piedmont) had had a big dimensions autoclave built for this purpose, has assured me about the successful results obtained by resorting to this instrument. It is my opinion on the other side that conservation, a field of research and applications notably complicate because of asking for quite different competences, can be conceptually often reduced to simple terms, if only because of the didactic efficacy and the exemplary function offered by a such a procedure. It is because of this that the way of functioning of resins, which in Italy too spread with notably speed in the first years of the Sixties of the past century, both for mural paintings and surfaces as for stone materials, in their most common uses makes them conceptually analogous to the various fixative substances used in the past, such as gommalacca. To say it very rudimentary, the issue is of gluing a surface so as to create a film which would make it compact, and hopefully would impede exchanges with the exterior. But it is precisely this last function which proves damaging and in some cases disastrous, in favouring a more and more harmful decay inside an artefact’s own body. Here too, the problem consists not so much in the material itself, as in the kind of use one makes of it, which can prove counterproductive for lack of understanding physical-mechanical phenomena involved. Restorers in the Nineties and in these first two decades of the new century, found themselves compelled to cope with problems of removal of acrilic or vynilic resins from previous restorations, at least in as much they meant to intervene with different methodologies. I am not spending time here on the applications of barium hydroxide, very influential for mural paintings (here Florence there is a long lasting, meaningful tradition), but not without useful results for stone materials, although consolidation results are only effective for thin superficial layers.

One more issue that in my opinion not always is adequately pondered, is the correct identification of a material's functions, with a frequent confusion between protective and consolidating properties. Sure enough there can be protective treatments also exercising some consolidating function, as well as a successful consolidation treatment can make a surface protection superfluous. But as a principle, it is advisable to always maintain these two functions at least conceptually separate, responding to the principle of simplicity in the operations' project I was referring to above. It is in accordance with the considerations I have been illustrating till now that that one will understand the interest and attention with which researches developed within the Opificio delle Pietre Dure in the 1990ies were saluted, directed to the artificial recreation of oxalate patinas[13]. Calcium oxalates had been very widely discussed, were it because of the ample diffusion with which one found them on monuments of all sort of materials, or for the difficulty of removing them (an operation which one used to consider by default useful and necessary, if only due to aesthetic reasons); as well as because of the debate about identifying their origin (anthropic or natural?).

Now I deem that there exists a sufficiently shared belief that oxalate patinas can very well be kept, if their removal risks provoking considerable damage to an artefact's surface. As for their origin, the matter certainly concerns modifications of protective treatments by means of organic matters applied in the past centuries. To induce their formation artificially upon a stone surface appeared an interesting possibility of providing our monuments with a materially effective and aesthetically uninfluential protection. Sure enough oxalate patinas are colourless: if they show a yellow-brownish colouring it is only because of the impurities embodied in the course of time, a problem which obviously does not exist if they are modernly recreated artificially through a chemical process. I happened to ask myself whether such a treatment would not have been advisable in some cases, in which the principle, surely correct as such, of a programmed conservation by means of periodical maintenance, requires to materially lay our hand upon a monument with repeated frequency. I am thinking, for example, of the XVIth Century Fountain of Neptune in the Piazza della Signoria in Florence. Those responsible for its recent preservation preferred not to proceed with a biocidal treatment of the water, which is re-utilised in a system provided with recycling, foreseeing maintenance operations at close intervals, about every six months. Their intention, I repeat, is well meant, but this signifies that in a range of ten years one will register up to twenty interventions directed to the removal of biologic patinas, which will have embodied carbon compounds from the atmosphere, too.

For this reason I have suggested to realize a protective treatment by recreating artificial calcium oxalates in the case of a collection of XXth Century sculptures belonging to a bank, which is housed outdoors, many of the sculptures located directly below trees and vegetation, in a highly polluted environment in the centre of Milan. One would obtain by this mean that all necessary operations of eliminating biologic and atmospheric damages will not apply directly in contact with an artefact's original surface. In this specific circumstance, moreover, cleaning will be made by means of essential oils, a potentially little invasive technology, which in Italy in the last decade has already been frequently tested[14].

Here I should like to introduce one more issue which I am fond of, the opportunity of distinguishing a cleaning operation from one of removal of unwanted substances, which is a truly different matter. It is mostly Anglo-Saxon languages defining by routine as "cleaning" any intervention meant at recovering a surface, by freeing it from superimposed layers, while in my opinion it would be useful to get used to a more differentiated terminology. To stay in the theme of "soft" cleanings, I point out how in Italy experiences have been made not only, as obvious enough at this time, in the internationally diffused area of laser technology, but also in the use of natural materials such as agar rigid gels, or else the sheets of nanomaterials texted in the Florentine Centre of Piero Baglioni ("Consorzio interuniversitario per lo Sviluppo dei sistemi a Grande Interfase, CSGI"), obtaining a "conservation based on the science of materials and, more particularly, of nanosystems, where a restoration intervention operates directly by inverting the deterioration processes" (so Baglioni). The framework would not be complete, unless one mentioned the excellent results obtained in "traditional" restoration when a fastidious attention to details is applied: the basic principle must be that a cathedral's facade must be treated with the same attention, diligence and accuracy one applies to the surface of a precious painting. Among the high quality results I happened to witness concerning conservation treatments of this kind, I particularly recall those at the facade of the cathedrals in Turin (Nicola, 2001-2003) and Parma (Archè of Simeti and Volta, early 2000es).

The Florentine chemist Mauro Matteini, former director of the scientific laboratory of the Opificio delle Pietre Dure and later of ICVBC-CNR ("Istituto per la Conservazione e Valorizzazione dei Beni Culturali") of CNR ("Consiglio Nazionale delle Ricerche"), responsible for envisaging the technology of artificial re-creation of oxalates, has turned in the last decade also to stone consolidation by employing diphosphates. This technology has already been tested in a series of applications throughout Italy and abroad[15]. This treatment permits reaching consolidation as deep as almost a half centimetre, which in many cases is what was just needed in that specific circumstance. It goes without saying that, where structural interventions are necessary, stone materials restorers are very well aware how to make use of metal elements (rods, pins and such), and of synthetic materials as well, so as to reconstruct an artefact's internal strength. Likewise, it is evident that applications with traditional materials, such as limes and grouts of various sorts, have been extensively used whenever that was the case. A particularly fascinating aspect of stone materials conservation is precisely this collaboration between advanced research and existing traditions, leading to the best obtainable result. As far as I am concerned, I should like to say that in my opinion the matter is not so much of continuing investing in new research, so as to be able to have still more solutions for restoration available: we already have many methodologies and techniques at our disposal. What matters, is to identify those more helpful and suitable in the specific circumstance we are dealing with. And there is the need, this is unquestionable, to have an open, continuous dialogue among all those operating in the world of conservation, exchanging information and sharing experiences: by writing on the specialised press, consulting the literature, attending conferences and seminars, keeping updated.

Most difficulties in a conservation project are often especially of a conceptual nature; while the problem consists mainly in understanding what is advisable to do (in the case of contemporary art, also whether to do something) A technical solution sooner or later can almost always be imagined and realised, considering a possibly questionable principle which however proves in most cases to be sound: that is, that when we are facing a condition of strong deterioration or a real danger of sheer survival, it is always preferable to do something than nothing.

Now, concerning sculpture decorations and damaged architectural parts, it is evident that a traditional alternative to consolidation is represented by substitutions. In the centuries-old works to the great cathedrals, which in a sense never were finished nor will be, a standard mechanism has been, and still is, substituting with copies the original piece, frequently destined to a museum of the cathedral itself. It is advisable however to have it clear, that soon the same problem will involve the copies themselves, considering the acceleration of deterioration processes which we must take notice of in the contemporary times. These mechanisms include methodological and theoretical problems, reiterating questions never settled. Is it legitimate to substitute the elements of an architectonic complex? Also when the case is not of an architecture's serial parts, but of "noble" objects, such as a statue, possibly made by a great sculptor? Which is the concept of "original" we have in mind? Is the originality of an architecture the same as of a single movable art work? The bell-tower of San Marco in Venice collapsed in 1902, could it be rebuilt identically? Is it true, as Cesare Brandi wrote, that the common say "where it was, how it was", is "the denial of the principle of conservation itself, an offence to history and an insult to Aesthetics"?[16] Can we really not consider as "original" a destroyed building, which has been reconstructed following precise existing testimonies (project drawings, architectural surveys, photographic documentation), as in the case of the Barcelona Pavillion by Mies van der Rohe, built in 1929, destroyed in 1930, rebuilt between 1983 and 1986?

It comes to mind the famous puzzle, or paradox, of the Ship of Theseus, as narrated by Plutarch, the object of intellectual lucubration from scholars in history, philosophy, aesthetics. The author of Parallel Lives wrote that "the ship (of Theseus's travels) was preserved by the Athenians down even to the time of Demetrius Phalereus, for they took away the old planks as they decayed, putting in new and stronger timber in their place, insomuch that this ship became a standing example among the philosophers, for the logical question of things that grow; one side holding that the ship remained the same, and the other contending that it was not the same" (Plutarch, Thes. XXIII 1). A first consideration is that this argument can excite our western tradition, because in the eastern it simply would not exist. The document of Nara on authenticity, produced in a conference held in 1994, is focused on the respect of the diversity of traditions; and takes into account the concept of architecture prevailing in the eastern civilizations, foreseeing the progressive and planned substitution of all architectural elements; so that a temple which was finished reconstructing one year earlier, can be defined by a local citizen as two thousand years old.

To the question presented by the puzzle of Theseus, therefore, is that this question is ill-posed, so that inevitably also an answer following its ratio cannot but be wrong. People say normally that a pessimist sees a glass half empty, and the optimist half full. They are both right, in that a glass is at the same time half full and half empty, and not half full or half empty. Precisely from the viewpoint of elementary logic, that glass plays the role of possessing both qualities at the same time. In our epoch, increasingly less problematic and more hasty and dismissive, we find ourselves thinking according to the model of a computer's bits: either zero or one, as alternatives and in reciprocal exclusion (until quantum physics will prevail). But a computer, now we know, is stupid, has no imagination, it only develops inputs received by others and makes no compensations. Reality on the other hand is more complex, and two statements apparently opposing and reciprocally exclusive, can prove both right.

What in our case really matters, is for a consolidating operation to reach its goal without modifying excessively a monument. It will not consolidate it integrally. It will not avoid modifying it to some degree. Our task as conservators and restorers will be to find the balance between these two exigencies. This is why in my opinion the difficulties to overcome are perhaps more conceptual than technical.

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Consolidation of stone. Some observations from laboratory and practice

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SUMMARY: Stone consolidants, with fluates and water glass as examples, have probably first been used during the 19th century. Even ethyl silicate was already invented in the 19th century, but its use as a stone consolidant started only in the 1960's. Originally mainly used on sandstone, nowadays ethyl silicate can be considered the most diffused product for surface consolidation, also in a modified version for other materials such as limestone and mortars. More recently several nanolimes have appeared on the market.

In this paper, first degradation types that can be treated with consolidation via the surface and the depth of degradation as encountered in stone in practice will be described. Effects of consolidants, as assessed with the DRMS profile drill, will be discussed. This paper does not represent a single research project, but rather considerations and sometimes doubts, all deriving from different observations over the years in laboratory and practice.

KEY-WORDS: consolidants, degradation type, DRMS, consolidation effect

INTRODUCTION

The aim of stone consolidation is to re-established the lost coherence at the surface of the stone. This action needs the introduction of a new binder into the degraded layer. The binding agents or consolidants are for this purpose applied in a liquid state on the degraded substrate.

Stone consolidants have probably been used for the first time in the 19th century; fluates and water glass are examples of early products. Even ethyl silicate was invented during the 19th century, but its use as a stone consolidant started only in the 1960's (Nijland & Quist 2017). Originally mainly used on sandstone, ethyl silicate can nowadays be considered the most diffused product for surface consolidation, also for other materials such as limestone and mortars. Recently nanolimes, which are mainly intended for use on limestone and mortars, have appeared on the market.

In this paper first degradation types that can be treated with consolidation via the surface will be described. Then attention is focused on the depth of degradation as occurring in practice and measured with the DRMS profile drill (see: DRMS website Sint Technology). Consequently, also the effects of consolidants, as assessed with the DRMS are discussed. The eventual negative effects of a consolidating treatment and the necessity of side measures are discussed. And finally, some practical guidelines are given.

In this context, the following questions have to be dealt with:

-on which types of stone degradation can a consolidating surface treatment successfully be used;

-which is a usual depth of the degradation and how can it be assessed;

-how can the distribution of the consolidant in the degraded substrate be assessed and judged.

TYPE OF DEGRADATION

Application of consolidants can be performed by brushing, spraying, pouring or even by poulticing. The penetration depth of a product should cover the degraded zone as evenly as possible.

Degradation of stone, which can be treated with a consolidant, concerns mainly types which can be described a loss of cohesion (see also MDCS website an Icomos atlas), such as:

- chalking
- powdering
- sanding

And, up to a certain level:

- crumbling

Other typical degradation forms of stone, like:

- exfoliation, scaling, flaking
- cracking
- bursting
- bulging or blistering

Cannot be treated with a consolidant; it should be added that for crumbling treatability would depend on the particle size of the crumbles, cf. figure 4 and 5.

Figures 1 – 6 show several degradation types that may be observed at stone surfaces.

Fig. 1 Chalking of lime stone surface, photo from MDCS

Fig. 2 Powdering of lime stone, photo from MDCS

Fig. 3 Sanding of stone (sandstone), photo from MDCS

Fig.4 Crumbling of stone, photo from MDCS

Fig. 5 In between stage of sanding and crumbling (ferruginous sandstone); photo from MDCS

Figures 1, 2 and 3 are examples that could be typically treated with a consolidant, whereas 4 is somehow doubtful. The in-between state as shown in fig. 5 might however be treated. In fig. 6, two types of degradation are shown, which in principle cannot be treated with a consolidant.

Fig. 6 Two types of degradation that are not to be treated with a consolidant; left, bulging / blistering, right, exfoliation

Depth of degradation

Typical depths of the degradation phenomena described in the paragraph before, derive from practice. Surface degradation often limited to a depth between 2 and 6 mm. If degradation goes deeper than this, usually loss of material will have occurred. The degradation depth can be made visible by the use of DRMS (drilling resistance measurement).

In fig. 7 – 9 examples are shown of the depth of degradation for different types of limestone, as assessed with the DRMS. Fig. 7 and 8 as well as one of the curves in fig. 9, derive from cases in practice.

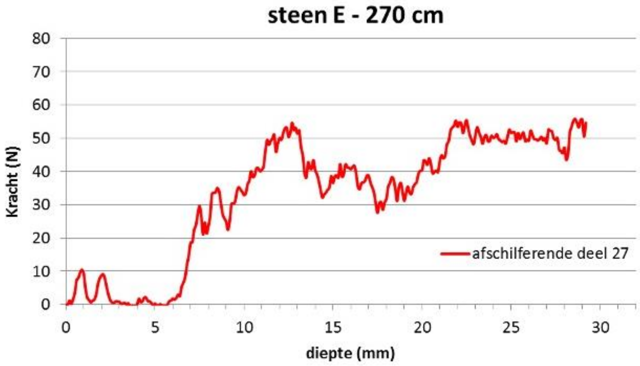

Fig. 7 DRMS profile of Lede sandy limestone, depth of degradation ca. 6 mm

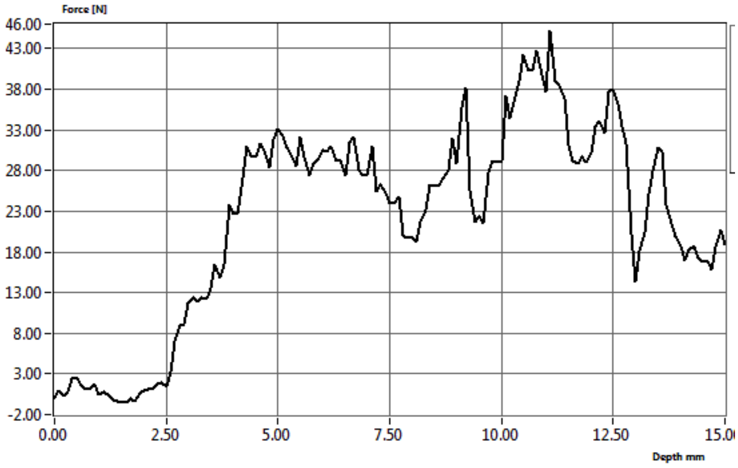

Fig. 8 DRMS profile of Euville limestone, depth of degradation ca. 3 mm (Nijland et al 2016)

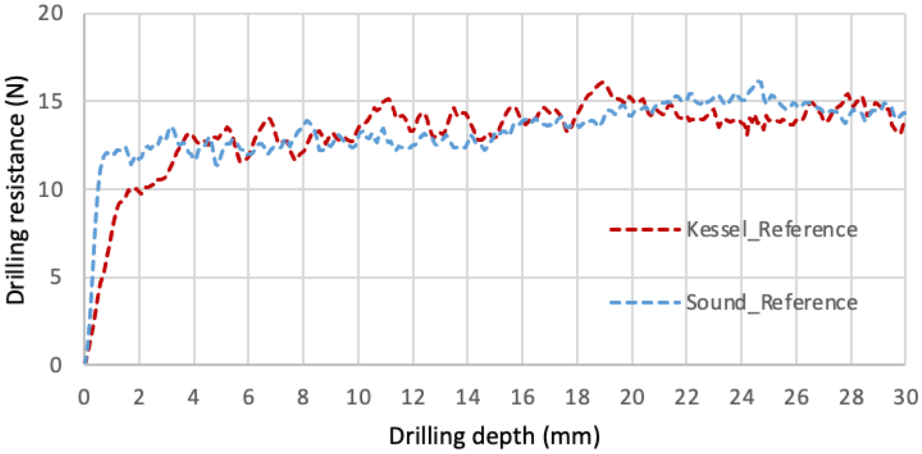

Fig. 9 Maastricht limestone. ‘Sound_reference’, refers to fresh stone, ‘Kessel_reference’ to weathered stone found in practice: a moderate degradation can be seen in the first 3 mm from the surface (Borsoi et al. 2017)

Effects of treatment

In order to study the possible effect of consolidants to be applied in cases as represented by figure 7 – 9, usually a fresh stone of the same type is used. This can however not represent the practice situation. Fig. 10 shows what may happen when a sound stone is treated with a consolidant.

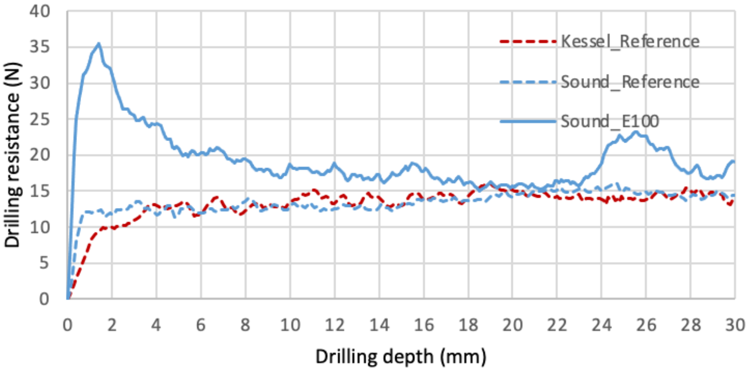

Fig. 10 Laboratory try out with repeated application (7x) of a nanolime consolidant on a sound stone (Borsoi et al. 2017). The surface layer has become too strong, but the question remains how to 'translate' this result to a degraded stone…

Indeed the question is whether the light degree of degradation of the stone in practice justifies treatment with a consolidant. Certainly, the situation represented in figures 6 and 7 is much more severe.

Fig. 11 represents a situation comparable with those of fig. 7 and 8, however it was artificially produced for laboratory purposes. It was intended to study the effect of consolidants on a degraded stone surface. A layer, consisting of reaggregated stone particles, bound together with a lime mortar, was applied on top of a sound substrate of the same stone. The example given here is of Maastricht limestone; the same principle has been developed as well for two types of French limestone, Euville and Savonnières.

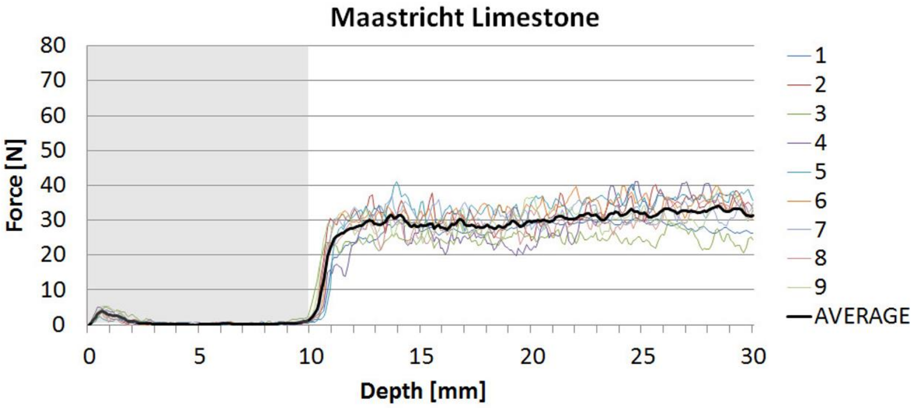

Fig. 11 Maastricht limestone, with 'weathered' surface layer of 10 mm, obtained by applying a re-aggregated layer consisting of particles of Maastricht, bound with a lime mortar. The coherence obtained in this way for the 'degraded' surface layer is comparable with examples found in practice cf. figs. 6 and 7, (Lubelli et al. 2015)

The artificial 'degradation' obtained in this way, results in a higher portion of the pores being coarse than in a sound stone; see fig. 12 (based on Lubelli et al 2015).

Treatment of this laboratory specimen, by brushing twice with 24h interval, with an ethyl silicate, adapted for limestone, Remmers KSE-300 HV, resulted in the following DRMS profile see fig. 13 (Van Hees et al 2017).

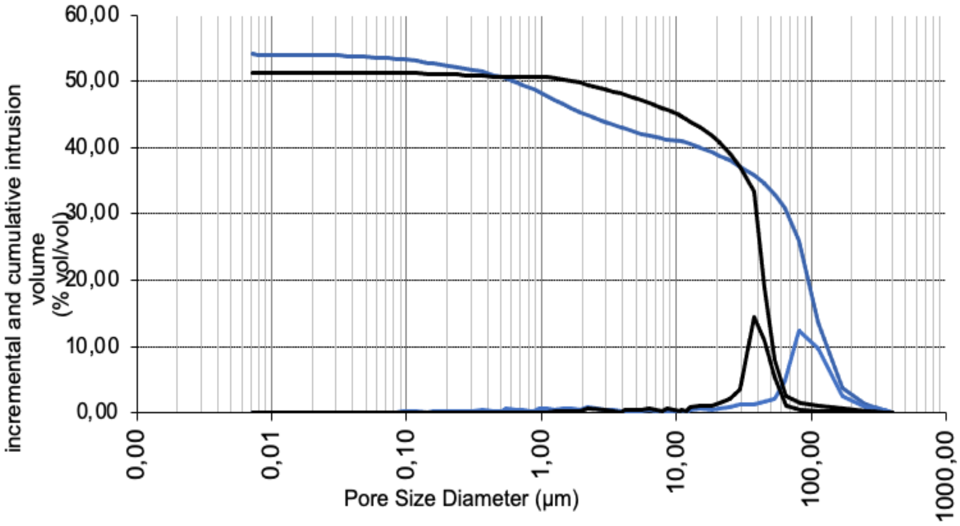

Fig. 12 MIP on Maastricht limestone. Fresh Maastricht (black curve), re-aggregated 1:6 (blue). The total porosity of the re-aggregated layer is slightly higher; most remarkable is the shift in average pore size towards coarser pores (Lubelli et al 2015)

Application of the product was in this case done in a horizontal position. This could imply a risk of percolation of the product through the degraded layer.

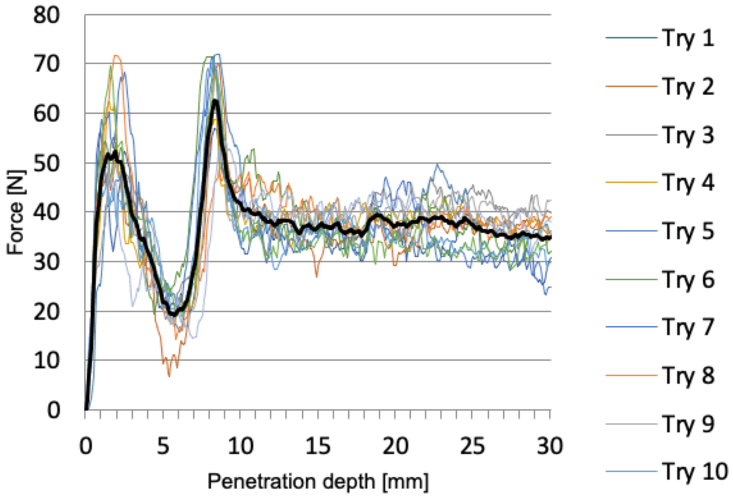

Fig. 13 Effect of treatment of degraded (re-aggregated layer) Maastricht limestone with ethyl silicate (Van Hees et al 2017)

In this case one can observe an accumulation both at the interface between the ‘degraded’ layer and the substrate and near the surface. Although over the full depth there is a consolidation effect visible, this situation seems not ideal. The question is why is it like this? Is this due to the horizontal position of the specimen during treatment? Is it caused by the difference in pore size distribution between reaggregated layer and the sound stone? Or is this anyway the best that can be obtained?

Fact is that at the surface a stronger or less porous layer has been formed, which is a potential weakness.

A possible risk of the formation of a stronger or less porous layer can be observed in a crystallisation experiment with Na_2SO_4, where spalling of the treated layer occurred, see fig. 14.

Fig. 14 Spalling of the reaggregated layer in a salt crystallisation test, after consolidation treatment (Bolhuis 2014)

Both discussed consolidation effects (fig. 10 and fig 13) give rise to speculation on how to obtain a better result. In the first case (fig. 10) a lower number of repeated treatments seems a logical solution, whereas in the second case (fig. 13) try outs with a number of applications in combination with a lower concentration might be the next step to be tried. Another option is to apply the consolidant with the stone in a vertical position.

REFLECTIONS. AVOID RISKS

In all situations of degradation it is necessary to investigate the cause of the damage and to assess if it is possible to stop or mitigate the process causing the damage in order to stop its progress.

If the type of degradation appears treatable, tests should be performed. This can either be done on test panels in situ or in a lab situation. However, one should be aware that try-outs on a sound substrate do not offer the best basis to decide on a treatment.

Although knowledge has increased considerably over the years, there are still uncertainties as comes forward from the observations before and there are risks.

The risk of creating a layer, which is stronger and often less porous or at least of a different pore size distribution, exists and this means that under circumstances, behind such a layer moisture and salts, coming from behind, may accumulate.

Another risk of such a layer at the surface of a wall is that it can behave differently if compared with the underlying not treated material under the influence of temperature and humidity changes. In both risk situations spalling of the treated layer could result.

It is therefore advisable to (1) take additional measures, to avoid moisture and salt entering the construction from behind and (2) to try to strive as much as possible for comparable and thus compatible physical behaviour of treated and untreated material.

Furthermore, before deciding for a consolidation, one should ask oneself if an ongoing degradation process might perhaps be stopped and whether it is then still necessary to consolidate, as any unnecessary treatment should be avoided!

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Retrospective studies of stone consolidation by alkoxy-silanes: treatment notes and long-term performance remarks on three case studies from the 1970s /1980s

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SUMMARY: *Three retrospective studies of organo-silane consolidation treatments of medieval stonework in the UK are described: the sandstone carvings in the tympanum of Aston Eyre Church, the decorative limestone doorway of St Nicholas Church, Barfrestone and a tuffeau stone French doorway in the Burrell Collection, Glasgow. Information is presented on the silane treatment for these three case studies in order to supplement published reports of contemporary consolidation practice in this early period of the use of alkoxy-silanes, in particular Rhône-Poulenc X54-802 and Dow Corning T.40149 methyltrimethoxy silane products and Raccanello E55050 'acrylic silane'. From recent visual inspections involving photographic documentation, comparisons are made with the appearance of the stone surface at the time of consolidation. This four-decade span allows for comments, both positive and negative, on the effectiveness of the three consolidation treatments and enables some of the difficulties of undertaking such retrospective studies to be pinpointed. Proposals are included for additional investigative research which these assessments indicate is warranted.*

KEY-WORDS: alkoxy-silane, Rhône-Poulenc X54-802, Dow Corning T.40149, Raccanello E55050, limestone, sandstone, tuffeau

INTRODUCTION

This paper is devoted to a retrospective assessment of three organo-silane consolidation treatments carried out by one of the present authors (DC) in the 1970s and early '80s. Two of these treatments were executed outdoors for important sandstone and limestone architectural elements in English medieval churches. The third example concerns the tuffeau stone of one of the late Gothic French doorways which form part of the City of Glasgow's Burrell Collection. This retrospective investigation thus deals with stone consolidation treatment and performance in the museum environment as well as the contrasting issues pertaining to exterior treatments for historic buildings. Our study presents information on the application of silane products which reflects current practice in this early period of the use of alkoxy-silanes in the UK. This acts as a reference point for remarks on the stone appearance some 40 years after treatment.

The motivation of our paper is therefore twofold. Firstly, our intention is to document and reflect upon some of the treatment features from that innovative period in the use of alkoxy-silanes. Secondly, our goal is to present an assessment of the visual aspects of silane performance, as exemplified by these case studies, four or more decades after treatment. Our purpose is not only to highlight the value of undertaking such retrospective treatment evaluations but also to consider some of the difficulties involved in so doing.

For one case study (Aston Eyre Church), treatment details were published soon after the consolidation was undertaken (Hempel and Moncrieff, 1976). This information is supplemented below by unpublished notes and recollections of key features of the project. Specific aspects of the consolidation treatments for the other two cases studies (St Nicholas Church, Barfrestone and the Burrell Collection, Glasgow) are published here for the first time, based on a combination of archived documentation and personal recollections.

These retrospective examinations were carried out in 2019 (Barfrestone), 2020 (Aston Eyre) and 2021 (Burrell Collection) and primarily comprise a visual assessment of the appearance of the stone. In the process, new photographic documentation was made for comparison with some still-extant, unpublished photographs taken at the time of the treatments. In the following section, the treatment details serve as an introduction to conclusions on long-term effectiveness of the silane consolidation. No scientific analyses were undertaken as part of this study but the scope for conservation science to give further insights into the consolidation materials, their application and behaviour is discussed.

Previous reassessments of the condition of earlier treatments - despite the regret that they have been an “infrequent occurrence in the field of conservation” (Wheeler, 2005, p6) – have provided valuable information which has extended that of laboratory testing. In addition to a series of studies by Rossi-Manaresi in the 1980s and 1990s, a number of reports attest to the importance of retrospective evaluations of consolidation treatments (see, for example, Thickett et al., 2000; Martin et al., 2002; Haake et al., 2004; Tesser and Antonelli, 2018). Our own work has demonstrated that a simple reassessment, when performed by the conservator who undertook the work and has retained photographic documentation thereof, can provide unique insights into previous treatments (Carthy and Tennent, 2011). It was with this aspiration in mind that the present study was undertaken.

CASE STUDIES

Aston Eyre Church

The treatment for the mid-12th century tympanum at Aston Eyre Church (Figure 1) was carried out in 1974 by Kenneth Hempel, assisted by Deborah Carthy. The tympanum and the arch which it supports are of a greenish-grey, fine grained sandstone or mudstone. It bears a narrative in high relief of Christ, seated on a donkey, entering Jerusalem; to the right a man strews palms in his pathway (Figure 2). The basic treatment methodology, using Rhône-Poulenc X54-802 methyltrimethoxysilane, was described in the article dealing with several projects which followed soon thereafter (Hempel and Moncrieff, 1976). That description is now supported here by additional photographs (Figures 1-5), especially of the consolidated stone surface (Figures 3-5).

Figure 1. Aston Eyre Church showing the entrance porch containing the tympanum sheeted with protective polythene during consolidation in 1974 (photo: Deborah Carthy).

Figure 2 illustrates the tympanum scene in two photographs from the time of the consolidation treatment but the quality of neither is adequate for an assessment of the performance of the silane. Fortuitously, more detailed transparences had been retained since the time of treatment but, curiously, over the passage of more than 40 years they had developed an orange coloration which hindered an ideal comparison with the current state of the same areas (Figure 3). However, by rendering the scanned, discoloured transparences in black and white it was appreciated that in each case little change in the surface appearance had occurred, as exemplified by Figure 4.

In this project, two features of the treatment reflect interesting aspects of 1970s silane treatments in the UK; the so-called ‘gassing’ of the stone with 2-ethoxyethanol prior to consolidation and the use of a sand/silane mortar mix for reinstatement of the original friable lime mortar pointing.

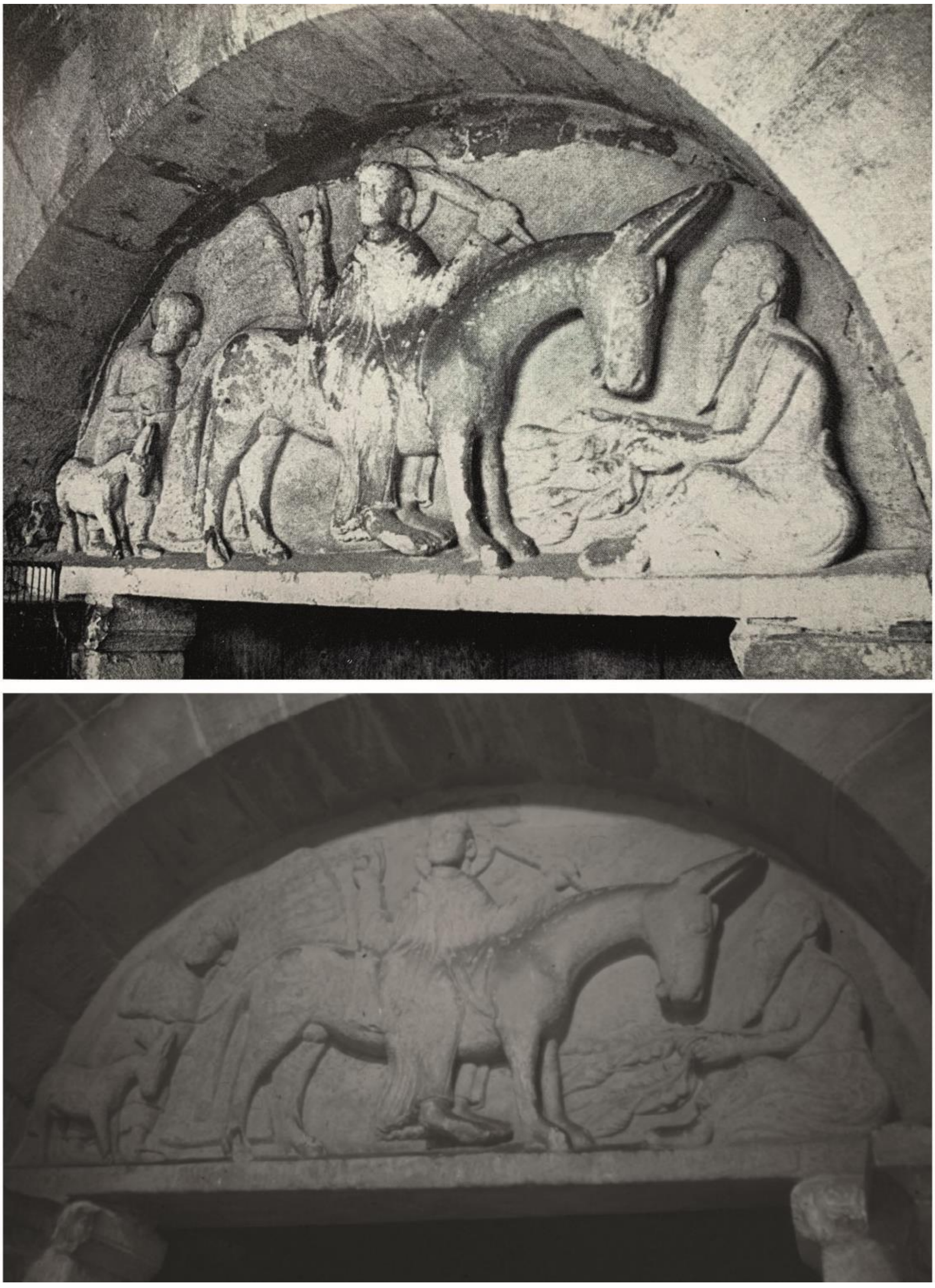

Figure 2. Aston Eyre Church tympanum. Top; in 1974, reproduced from the black and white illustration. Illustration in (Hempel and Moncrieff, 1976), Bottom; photographed in 1974 (photo: Deborah Carthy).

Figure 3. Aston Eyre church tympanum. Left; detail of figure of Christ in discoloured transparency from 1974. Right, photographed in 2020 (photo: Deborah Carthy).

Figure 4. As in Figure 3 but black and white version.

Regarding gassing, in his excellent overview of treatment practice, Larson reports that pre-treatment of the stone with 2-ethoxyethanol not only ensures better penetration of the stone by the silane the following day but also results in greater durability (Larson, 1982). These are intriguing observations for which supportive laboratory experiments seem not to have been published; it would be useful to have corroborating evidence.

Regarding re-pointing with a sand/silane mortar mix, the process carried out at Aston Eyre followed the standard rule of thumb that, when dealing with pointed joints which had deteriorated badly, the existing pointing should be cut out to a minimum depth of 2.5 cm. For the Aston Eyre doorway, lime putty mortar with fine sand had been used in the original building of the stone and in the pointing to the face of the stone. However, directly adjacent to the silane-consolidated tympanum a sand/silane repair mortar mix was chosen to prevent the possibility of ingress of water through the joint, thereby potentially causing a problem at the interface between the consolidated stone and the unconsolidated area of the back of the stone. Various sand/silane proportions were tested to produce a workable silane-rich mix which resulted in a satisfactorily solidified test block. The silane in the mix used in this case was combined with acetone and water in the ratio 100/50/10 (Hempel and Moncrieff, 1976). Though it had somewhat difficult workability for a neat appearance, the mix was used effectively for all areas of pointing, including the aforementioned horizontal joint between the tympanum base and the top of the door jamb (Figure 5).

Figure 5. Aston Eyre Church tympanum. Detail of the sand/silane mortar mix at the base of the sculpture. The arrow shows the cavity where the mortar powdered away when gently probed in 2020 (photo: Deborah Carthy).

During a visit in late 2020, accompanied by the church warden, a small sample of the mortar was delicately removed with a chisel from the point indicated by the arrow. Although the face of the mortar seemed hard and unchanged in appearance, this stable surface in the joint pointing was in fact extremely thin, barely 1 mm in depth. Behind this thin exterior face, the sand was no longer solidified by the silane and fell into a powder once removed from the joint, leaving the cavity illustrated in Figure 5.

St Nicholas Church, Barfrestone

The consolidation of the ornate Caen limestone decorative carvings in the south nave doorway (Figure 6) of this 12th century church was carried out in 1977 using Rhône- Poulenc X54-802 methyltrimethoxysilane. The work was performed during a period of quite intense evaluation of methods of application of silanes in a very conservative attitude towards them in the UK and a more open attitude in Italy.

Figure 6. St Nicholas church, Barfrestone. Main doorway with carved decorative stonework framed for polythene sheeting prior to consolidation treatment in 1977 (photo: Deborah Carthy).

In all general respects, the method of treatment followed the procedures for consolidation of stone in external situations used by Kenneth Hempel and Deborah Carthy during this period of the mid-late 1970s. Since these treatments have not been widely described in publications and are pertinent to the current (and future) assessment of the condition of the Barfrestone doorway, salient features are summarised below from notes prepared at the time of the treatment:

- To allow the stone to dry, it was protected for four weeks by a ventilated black polyethylene covering; the framework for this is shown in Figures 6 and 7. The polythene was hung above the arch to cover the entire area identified for consolidation.
- A covered scaffold was erected to allow good access to all parts of the archway and tympanum of the door. The black polythene cover on the door was then removed to enable the mortar joints to be cut out (to a depth of 2.5 cm).
- A clear, lighter polythene sheeting was then affixed to the top of the frame and the stone was ‘gassed’ (as with the Aston Eyre Church tympanum and other projects) by applying a pre-treatment of 2-ethoxyethanol generously by brush over the entire surface. To reduce evaporation, the clear polythene cover was then dropped down, secured and left overnight.
- Rhône-Poulenc X54-802 methyltrimethoxysilane was applied, by brush, over three days.

Day 1; the silane was applied as a mix of silane/2-ethoxyethanol/water in the ratio 50/50/4. The applications were repeated throughout the day, leaving periods between each application for it to penetrate into the stone. Six applications were achieved over the day. The stone was then covered with polythene overnight to prevent excessive evaporation.

Day 2; the silane was applied with an increase in the amount of silane in the mix (100/50/4) in 6 applications. Once again the stonework was covered with polythene overnight.

Day 3; the silane was applied in a 100/50/4 mix for the first application, after which it was used neat for isolated areas which were still capable of absorbing silane. No attempt was made to remove any excess of silane from the surface.

The doorway was then covered and only uncovered in sections to carry out pointing of joints using stone dust and silver sand mixed with the X54-802 silane and hydrogen peroxide combined in the ratio 50 mL/5 mL. With this mix it was not easy to achieve a neat surface finish (see Figures 8 and 9, right). As a consequence, in subsequent projects, traditional lime mortar was used for pointing which was carried out prior to drying the stone for consolidation, followed by silane treatment of the both the stone and the mortar.

Figure 7. Detail of framework in Figure 6 showing the intimate junction to the stone surface (photo: Deborah Carthy).

Figure 8. St Nicholas Church, Barfrestone. Detail of depiction of Christ in Glory at the doorway apex. Left; in 1977 after raking out the mortar but before consolidation, Right; in 2019 (photo: Left, Deborah Carthy; Right, Richard Cook).

Figure 9. Black and white version of Figure 8.

At the time of the consolidation treatment at Barfrestone, it was felt that the silane should be applied until full saturation of the stone was achieved. This was judged by a visual evaluation, with the end point defined by an excess of silane on the surface. Unlike previous applications in other projects, at St Nicholas Church the excess on the surface was not removed using 2-ethoxyethanol swabs. The intention was that it should be left on the surface to weather off over time, thereby giving superior consolidation of the stone surface. This, however, was a short-lived approach due to the unfavourable reaction of heritage organisations and other parties to the shiny visual appearance of the alkoxysilane-derived gel on the stone surface. In fact, ten years after completion of the treatment, only a slight surface sheen, which in some areas appeared as a thin glaze that could be scraped away with a fingernail, was still apparent. When the present authors visually re-examined the stone surface in 2004, 27 years after treatment, we found that it appeared virtually free from signs of silane (Figure 10). The recent 2019 inspection of the doorway confirmed that the silane had indeed almost totally weathered away (Figures 8 and 9) without any adverse effect of this approach. Figures 8 and 9 also confirm the excellent maintenance of the stone's surface appearance throughout the 42 years since consolidation; the comparison in the black and white version avoids the distraction due to colour variations as a result of camera, film and lighting differences in the 1977 and 2019 photographs.

It is hard to say whether the unique approach described above achieved a better result than that of the standard approach to consolidant application in which the removal of excess silane from the surface leaves a matt, stone-like appearance. As with all consolidation campaigns where no unconsolidated control area is present, this retrospective assessment begs the probably unanswerable question; what would have been the state of preservation had the consolidation treatment not been carried out? A further discussion of this 'unanswerable' question is found in the Conclusions section below. What, nonetheless, does seem beyond conjecture that, in this Barfrestone case study, the present stone condition very closely resembles that in 1977, as exemplified by the pair of photographs Figures 8 and 9 and other similar pairs not reproduced here.

Figure 10. St Nicholas Church, Barfrestone. Detail of one of the many small carvings flanking Christ showing highlights in the photograph of 2004 where only very few small residues of silane were still visible on the surface (photo: Deborah Carthy).

Burrell Collection Gothic doorway (Reg. No. 44/89)

This French 15th-early 16th century doorway (Figure 11) is part of the important collection of medieval architectural stonework which had to be conserved and built into the structure of the new building being constructed in Glasgow in the early 1980s to house Sir William Burrell's private collection of fine and decorative art which had been bequeathed to the city some forty years earlier. These structural architectural items were dealt with according to certain general principles (Carthy, 1985), not least that they should be built in as free-standing units with load-bearing beams above them. A feature of this doorway was that the central stone above the lintel (Figure 12) was in a poor state of preservation. The stone had deep cracks running through it from all sides. An attempt to strengthen it had previously been made using iron cramps; these were traced and removed before consolidation. Below the cramps in the side of the block there was extensive deterioration and the tendency for the stone to spall off in small slithers. It was not possible to move the stone and so it was decided to consolidate it in position, concentrating on the face and the sides as the back was not easy to access safely due to the condition and weight of the stone. Prior to consolidation, the stone was kept covered with polythene for six months to ensure good penetration of the consolidant into dry stone.

Figure 11. Burrell Collection French doorway (Reg. No. 44/89). Darkening of the stone in the upper central fragile area after consolidation (photo: Glasgow Museums).

Figure 12. Burrell Collection French doorway (Reg. No. 44/89). Fragile stonework block photographed in 1981, prior to consolidation (photo: Deborah Carthy).

In line with favoured contemporary practice when the work was undertaken in 1981 (Larson, 1982; Hanna, 1984), the chosen consolidant was Dow Corning T.40149 methyltrimethoxysilane admixed with the so-called ‘acrylic silane’ Raccanello E55050 in varying proportions throughout the treatment; from 5% initially (8 L total in 3 applications in Day 1), through steps of 10% (8 L total in 4 applications in Day 2), 15% (3 L total in 3 applications in Day 3) to, finally, 20% (7 L total in 5 applications in Days 4, followed by 5 L total in 5 applications, applied preferentially to areas which seemed less saturated, over Days 7 and 8). Polythene was applied to make an airtight enclosure between applications and the stone was left covered for two months. It then appeared well-consolidated but had darkened considerably (Figure 11).

The darkening of this section of Burrell doorway as a result of consolidation has remained with no diminution (and, as far as visual evidence shows, also with no intensification) since the treatment. Amongst the various reported consolidation treatments with Dow Corning T.40149 plus a maximum of 20% Raccanello E55050, permanent darkening appears to be a problem unique to this doorway. Although unacceptable darkening in tests with catalysed methyltrimethoxysilane had been observed to occur, the uncatalysed silane, alone or in conjunction with Raccanello E55050, caused no problematic darkening (Bradley 1985; Thickett et al., 2000). Hanna reported that a degree of initial darkening fades during the following 12 months but pointed out that when Raccanello E55050 is present in concentrations greater than 20%, residual darkening results (Hanna, 1984). However, in laboratory experiments with sandstone, Rossi-Manaresi reported that Rhône-Poulenc X54-802 , methylphenylsiloxane and the so-called Bologna Cocktail each resulted in darkening of the stone (Rossi-Manaresi, 1976) and so this apparently contradictory behaviour underlines the view that the factors which give rise to darkening are subtle and may be more variable than generally appreciated.

The Burrell Collection experience raises the question not only of why permanent darkening occurred in this case but also whether any treatment in an attempt to remove consolidant from the surface might ameliorate the darkening effect. Our study was not designed to undertake investigations to probe these questions experimentally but we believe it has highlighted the need for further research on three issues, namely; the role of mineralogical composition on the appearance of consolidated stone, the characterisation of the chemical components of the Raccanello E55050 ‘acrylic silane’ product and the potential to remove surface consolidant from stone which has darkened.

In connection with the first issue - stone petrography - the Burrell Collection French, late Gothic doorway is constructed from tuffeau stone, a sedimentary rock from the Loire valley, comprised primarily of calcite and lesser quantities of opal-CT with more minor quantities of clastic minerals. It is conceivable that the mineralogical composition of tuffeau stone (Dessandier et al., 2000) is distinct enough from that of reported limestone consolidation treatments to result in a post-consolidation darkening. The optical issues which cause stone darkening have been described (Biscontin et al., 1976) but experimental studies which investigate the relationship between the mineralogy and petrophysical properties of stone and consolidation darkening appear to be scanty and deserve to be pursued further. In this case, the high total porosity of tuffeau, up to nearly 50% (Dessandier et al., 2000), may well be relevant.

Regarding the second issue – the chemical composition of Raccanello E55050 – there is lack of unanimity in the conservation literature about the identity of the components of this commercial product. The product is no longer available and during marketing the manufacturers seem to have supplied no technical data giving a breakdown of the active ingredients in this mixture. Wheeler’s comprehensive compendium (Wheeler, 2005) does state (p10, Note 20) that it is “a mixture of methyl phenyl silicone and Paraloid B67 (isobutyl methacrylate homopolymer) in toluene [analysis provided by Susan Bradley of the British Museum]”. However, this is at variance with an unpublished thesis (Porter, 1993) which refers to a personal communication from Eddy De Witte at the Royal Institute for Cultural Heritage (KIK-IRPA) in Brussels that the acrylic polymeric component is a mixture of B72 (methyl acrylate/ethyl methacrylate copolymer) and B67 in methyl phenyl silicone with trichloroethane and toluene (in the ratio 45:55) as solvent. In a later publication, this is also stated to be the composition (Thickett et al., 2000). This commercial product is therefore similar to the 'Bologna Cocktail', previously introduced (Nonfarmale, 1976), and comprising an acrylic resin, a siloxane, and solvent. The attributed description 'acrylic silane' for Raccanello E55050 is a misleading misnomer as, in contrast to some descriptions (Dinsmore, 1987), it contains not a silane, but rather a siloxane (often more commonly known as a silicone oil). Unfortunately, as yet, no confirmatory analytical reports at either the British Museum or the Royal Institute for Cultural Heritage, Brussels, have come to light during the present quest for authoritative details of the chemical analysis of the Raccanello E55050 formulation. The mixture of Paraloid B72 and B67 is certainly a puzzling, difficult to rationalise combination. Indeed, when the product ceased to be marketed a true acrylic silane mix using simply B72 and methyltrimethoxysilane gave satisfactory results (see, for example, Thickett et al., 2000).

With respect to the third issue – the possibility of removal of acrylic resin (and siloxane) components from the surface of stone many years after consolidation - the identity of the acrylic/s and siloxane in Raccanello E55050 has implications for possible remedial action to reduce the darkening in the consolidated area of the Burrell collection doorway. In particular, if the darkening is primarily as a result of the acrylic resin at the stone surface, the long-term ageing behaviour of both Paraloid B67 and B72 applied to stone is important for any attempt to remove the acrylic by means of swabs with solvent. It is therefore disconcerting that laboratory experiments with both B67 and B72 applied to marble surfaces (Favaro et al., 2006) found significant development of insolubility (70% and 60%, respectively) after 2000 hours "photo-oxidative weathering" (of which no further details were given but which may replicate exterior ageing conditions rather than those in a museum environment). This study also reported increasing insolubility (95%) of Dri Film 104 (the siloxane component of the Bologna Cocktail), in contrast to evidence (Rossi-Manaresi et al., 1995) that this acrylic/siloxane formulation will remain soluble.

CONCLUSIONS

This study achieved its main goals but, in addition, it reinforced some well-recognised problems in undertaking retrospective studies of stone consolidation and has brought into focus some special aspects of these problems, the most significant of which concerns the importance of access to extensive, detailed, high quality, archived photographic documentation of treatments.

Although a crucial component of all conservation documentation, photographic records are frequently inadequate for retrospective studies of stone consolidation of large architectural structures for the very good reason that it is often not possible to ensure that sufficient areas are recorded in adequate detail to make telling comparisons of deterioration (or the absence of it) after a span of years. The case studies presented in this paper reinforced the necessity of a good photographic record of the stone surface immediately pre- and post-consolidation. The personal photographs, casually - but fortuitously - stored by one of us (DC) since the treatments were undertaken, compensated nonetheless for the absence of well-designed, suitably archived photographic records, and gave valuable visual information. Despite some deterioration due to the passage of time, the quality of these old photographs was able to be improved so as to enable a useful assessment of the long-term performance of the two church consolidation treatments we document. Be that as it may, retrospective studies should not depend on serendipity for their success. We therefore wish to underline the importance of archiving sufficiently extensive and detailed photographic documentation at the time of consolidation treatments so that future retrospective comparisons can be facilitated.

Furthermore, as an extension of this exhortation, it is timely to point out that almost two decades ago, as part of a perceptive, wide-ranging review, a recommendation was set out (Tabasso, 2004) for enabling effective ongoing assessment of treatments by means of a number of "sample areas", selected on the completion of stone conservation project treatments. It is a moot point how often this has since been accomplished in practice but the wisdom of the proposal has been supported by the present case studies which demonstrated, more than by good luck than by good planning, that valuable information that can be gained in a retrospective comparison by simple photographic comparisons of key sample areas. Beyond that, there is persuasive evidence that such a comparative sample area has actually inadvertently been present in the St Nicholas Church case study.

Figure 13. St Nicholas Church, Barfrestone. The south-facing aspect showing the consolidated doorway and the adjacent, unconsolidated minor doorway in 2019 (photo: Deborah Carthy).

Figure 14. St Nicholas Church, Barfrestone. Extensive stone erosion and significant lichen growth on the stonework of the unconsolidated south-facing doorway in 2019 (photo: Deborah Carthy).

As shown in Figure 13, a smaller blocked doorway also faces south at the same elevation as the main doorway, but it has never been consolidated. This is therefore a good approximation to Tabasso's proposition of "sample areas", in this case as a benchmark to assess the success of the silane consolidation of the main doorway. As can be seen from Figure 14, the general impression is that erosion of the untreated carvings is significantly more advanced than in the main doorway. Unfortunately, at time of the consolidation works in 1977, no photographs were taken of this adjacent doorway which could now have given definitive evidence attesting to the success of the silane consolidation in arresting erosion of the carvings in the main doorway. Also of note is the observation that lichen growth (Figure 14) is more established there than on the treated door. Since lichen requires moisture to survive, this raises the likelihood that the silane treatment has not only prevented erosion but also inhibited lichen growth. These casual but potentially significant observations reinforce our opinion that had sample areas been designated for regular assessment - involving superior documentation, a more diverse range of non-destructive inspection and, where possible, sampling for scientific analysis - a deeper understanding of long-term behaviour of the consolidation treatments we report could have been achieved.

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Microorganisms on stone – damage factors and beneficial impacts

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SUMMARY: Biodeterioration processes on inorganic building materials are based on the interaction of a complex material ecology. This microflora improves the nutrient- and moisture-restricted living conditions on building stones by the formation of protective polymeric biofilms. Based on biogeochemical and biogeophysical mechanisms, microbial biofilms promote even "abiotic" deterioration processes due to the alteration of the minerals as well as thermal and moisture related properties of the rock material. Besides damages, the presence of microbial biofilms might have also beneficial impacts which should be considered before the application of cleaning, biocidal as well as consolidating treatments. A presentation of different case studies from Cambodia and Turkey demonstrates the relevance of microbial impacts on stone. Biodeterioration processes are an important aspect in the interdisciplinary considerations of conservation strategies for the historical objects.

1 INTRODUCTION

Inorganic building materials, such as natural stone, concrete or glass, are susceptible to structural and material changes due to the influence of natural and anthropogenic influences. The deterioration of these materials is controlled by a number of constraints such as the macro- and microclimatic impacts, duration of wetness and hydrolytic processes, precipitation and deposition of corrosive aerosols and their consequent oxidation and reduction. In the course of these process, salts are formed leading to efflorescence phenomena related dissolution, transport and recrystallization. These effects are enhanced in addition by frost-thaw changes. The subsequent occurrence of various forms of "patina" on stone surfaces is characterized by the development of different inorganic and organic based strata which depend on the specific chemical and structural conditions given. This finally leads to the final formation of crusts (crystalline; "protective crusts") and incrustations (crystalline-amorphic; "inner crusts") [1,2].

The development of crusts and incrustations which means to the material an accelerated weakening and deterioration of the matrix is a very complex process of chemical and physical changes in the stone. The crystal structure and composition of minerals, their grain coherence is impacted by the deposition of aerosols and particles on the material's surface, by water vapor diffusion and capillary water uptake as well as by temperature effects. All these result in a decrease in the material's strength. Surface hardening which often leads to a later detachment of shales as well as subsurface sanding processes which a closely related to salt crystallization pressure and frost-thaw-cycling stresses, represent a further step in fatal consequences [3-6]. The alterations of the surface properties of inorganic building materials may question the success of conservation treatments, because the penetration and functional adherence of stone protectives, such as fixatives, water-repellents or coatings, will be additionally impaired [7].

Besides the influences by material properties, climatic conditions and object geometry, the formation of crusts and incrustations on stone is strongly controlled by the intensity and distribution of microbial contamination [8]. The ability of the stone-colonizing microflora to cover and even to penetrate the material surface by the excretion of organic extracellular polymeric substances (EPS) leads to the formation of biofilms in which the microbial cells are immobilized on a substratum which again is embedded in a polymer matrix of microbial origin [9, 10] (Fig. 1 + 2). The occurrence and distribution of these microbial biofilms and their importance for the (bio-)deterioration processes on stones and for conservation treatments will be discussed in the following.

2 BIOFILMS ON INORGANIC BUILDING MATERIALS

Based on their moisture and nutrient demands, the microbial contamination of stones and its biodeterioration activity is closely related to petrological parameters, such as mineral composition, or type of cement as well as porosity and permeability of the material. Thus, both physical and chemical influences of the environment, and the properties of building materials have to be considered the determinants for the initial infection and development of the microbial contaminations of stones consisting of algae, cyanobacteria, fungi and bacteria [11,12].

Fig. 1: Microbial biofilm penetrating into the pore system of a natural stone (e.g. Burgsandstein at Pommersfelden, Bavaria, Germany) as visualized by red PAS-staining.

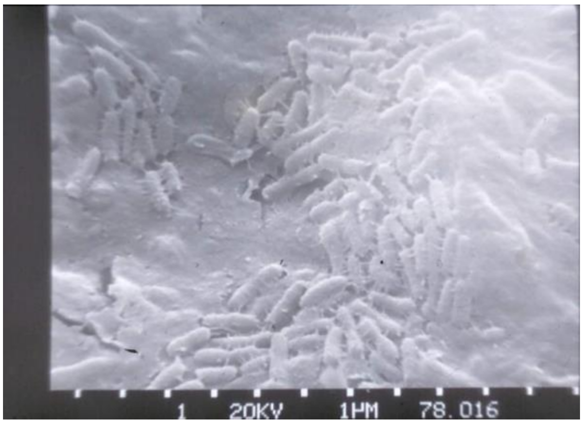

Fig. 2: SEM-micrograph of the microbial biofilm showing rod-shaped bacteria embedded in a slimy extracellular matrix, addressed by the PAS-staining in Fig. 1.

The variously mixed microbial communities which have formed on stones have to face (i) rapid and extreme changes in temperature and moisture conditions, (ii) local ionic respectively osmotic stresses and (iii) a restricted supply in nutrients. Thus, an effective strategy to improve the severe living conditions is the formation of unilaminar up to complex biofilms. Due to the colloidal nature of their EPS which containing polysaccharides, lipopolysaccharides, proteins, glycoproteins, lipids, glycolipids, fatty acids or/and enzymes [13] biofilms are able to balance out extreme changes in moisture and temperature, to buffer osmotic or pH-relevant influences and to provide ion-exchange functions in order to prevent e.g. the penetration of cationic biocidal detergents or antibodies into the biofilm. Furthermore, biofilms may even stimulate the microbial metabolic activity by an extension of the realm for microbial colonization (“inner surface”), by an increase in the supply of nutrients (“storage of energy”), by promoting the microbial nutrient exchange ("cross-feeding"). Thus a complex metabolic "network" (e.g. aerobic and anaerobic zones within the biofilm or biocoenosis of phototrophic algae and copiotrophic bacteria) is established. The stability of an ecological niche is further increased by direct exchanges of genetic information and intercellular communication of the microorganisms which are embedded in a surface-covering biofilm [10].

The process of crustation and incrustation is basically determined by the moisture balance of the stone [3,4]. It controls the distribution and extent of the microbial contamination and biofilms respectively on/in the inorganic materials.

The manifestation of biodeterioration processes on stones can be described looking at the distribution and the extent of microbial biofilms in the profile of various rock types [14]. These biogenic surface alterations are in interaction with the physical and chemical weathering processes. The examples of the "patina types" of which the decay intensity ranges from film-formation to surface-corrosion, and lastly to crust-formation shows this in a perfect manner: the microbial impact which causes discoloration of stone surfaces and erosion including conversion to detrimental crusts is regulated by petrological parameters and the moisture conditions of the specific rock type (Tab. 1). Besides material-specific properties and local expositional condition, the distribution of biofilms in the rock profile depends also on climatic constraints. While the microorganisms colonize the free surfaces of the building stones under moderate climate conditions, in (sub-) tropical zones the biogenic infection takes place in the deeper part of the rocks being better protected against intensive sun radiation and desiccation [16].

Having discussed the ecological occurrences and importance of microbial biofilms on stones so far, their potential impacts by biodeterioration will be shown in the following chapter.

3 DETRIMENTAL EFFECTS OF BIOFILMS ON STONE SURFACES

Biodeterioration has usually been designed to be basically a subsequent degradation process, taking place after surface alterations has been caused by preceding impacts of primarily inorganic agents which have created a conditioned stone surface enriched with inorganic and organic nutrients. In contrast to this, recent investigations, especially on the phenomena of surface-covering biofilms have stressed the fact that in the early stages of stone weathering biodeteriorating effects can be detected even before conditioning processes took place [14,17].

Table1: The formation of different types of “patina” on natural stones with respect to material properties and the consequent microbial colonization, biofilm formation and biodeterioration processes [modified from 15]

PATINA TYPE 1	surface-corrosion (synonyms: granular disintegration, sanding, erosion)
Type of rock:	- coarse-grained, porous stones: tuff, clay-cemented, calcareous or siliceous sandstones, man-made stones (brick, mortar, concrete) - most abundant grain size: > 0,5 mm - porosity: > 18 Vol.-% - inner surface: < 3 m2 / g - pore size: 3 - 8 10 µm
Moisture:	deep penetration (up to 10 cm); frequently changing
Distribution of microflora:	contamination penetrating up to 5 cm deep (mainly dominated by bacteria)
Biodeterioration - processes:	biocorrosion (excretion of inorganic and organic acids) biofilm formation (EPS) narrowing rock pores up to sealing => increase in capillary water uptake (?)
PATINA TYPE 2	crust-formation (synonyms: exfoliation, chipping, shales, flakes)
Type of rock:	- medium-grained sandstones of clay-cemented, calcareous or siliceous rock type - most abundant grain size: 0,1 - 0,5 mm - porosity: 14 - 18 Vol.-% - inner surface: 5 - 7 m^2 / g - pore size: 1 < d < 10 µm
Moisture:	superficial (0,5 to 20 mm); long-lasting dampness
Distribution of microflora:	in the uppermost layers of stone (up to 5 mm depth) and/or behind rock shale (complex and stable microflora ("microbial mat"))
Biodeterioration - processes:	- biocorrosion (excretion of inorganic and organic acids) - biofilm formation (EPS) sealing rock pores ⇨ aerosol deposition and crust formation => reduced capillary water uptake
PATINA TYPE 3	film-formation (synonyms: patina, coating, staining, chromatic

	alteration, deposit)
Type of rock:	- dense and fine-grained stones: siliceous sandstones, granite, basalt, - slate, limestone and metamorphic rocks (gneiss, quartzite, marble) - most abundant grain size: < 0,1 mm - porosity: <14 Vol.-% - inner surface: 3 - 5 m2 / g - pore size: 1 < d < 10 µm
Moisture:	poor penetration (max. up to 1 mm); short time of wetness
Distribution of microflora:	surficial, unilaminar biofilm (mainly dominated by phototrophic microflora and fungi)
Biodeterioration - processes:	- discoloration by pigments and biogenic oxidation of minerals - biofilm formation (EPS) => aerosol deposition and crust formation => rarely reduced capillary water uptake - local biocorrosion ("biopitting")

Depending on the type of rock, exposition and environmental conditions different modification of biofilms may occur (see also Tab. 1). From coloring algae mats to rock incrusted lichen thalli, from macroscopical invisible bacterial infections to fungal controlled contamination, the microbial biofilms tend to reduce the stability of the rock material by acting as basic precursor for the development of crusts. Comparable to a flypaper the biofilm (i) collects airborne particles, like soot and dust (Fig. 3), (ii) modifies the water exchange capacities of the rock (Fig. 4 + 5) and (iii) favors the biocorrosive activities of the rock microflora. Accompanied with the formation of a crust the rock material is hardened on the surface and the uppermost layers below are weakened, implying a gradual loss of coherence of the material leading finally to sanding and shaling off stone fragments [8].

Figure 3: Biofilms force the accumulation of dust and aerosols.

Thus, the microflora on stones acts as a kind of catalysator in the process of crust formation. Furthermore, due to the coloration by biogenic pigments, like chlorophyll, melanin or other light absorbing pigments, the thermal behavior of stones is changed. In addition, the formation of adhesive biofilms leads to an increased adsorption of dust- and soot particles on the stone surface, enforcing changes in the capillary water uptake and the water vapor diffusion in the rock material. This effect is, in addition, increased by the microbial release of surface tension-reducing compounds, such as fatty acids, glycolipids or enzymes. The excretion of inorganic and organic acids conveys the oxidation of mineral-bound iron and manganese which lead again to a further weakening of the stability of the stone matrix [15,18].

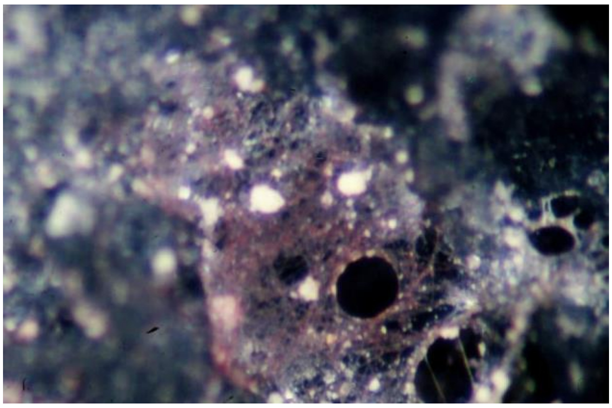

Figure 4: Biofilms modify the capillary water uptake within pores.

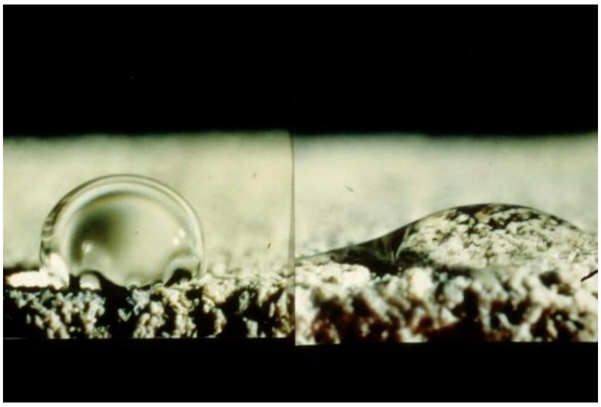

Figure 5: Biofilms increase the wettability of stone surfaces

Not only that the above mentioned biogeochemical (biocorrosion, biooxidation) and biogeophysical (e.g. changes in temperature and hygric properties, mechanical stress) biodeterioration processes promote these primary effects, biofilms may trigger, furthermore, secondary damaging processes related to stresses enforced by frost-thaw-changes and by crystallization pressure of efflorescing salts as well. Besides this, the moisture-conserving biogenic slimes probably increase by the absorption of acidic gases the reaction rate of chemical induced corrosion processes [19]. Moreover, the presence of the extracellular polymeric substances (EPS) induces mechanical stress on the mineral fabric of the stone. This is due to the shrinking and swelling of the colloidal biofilm inside the pore system as well as the penetration of fungal and lichens hyphae inside the inorganic substrate [20]. The consequence of the EPS enrichment is an alteration of the pore size leading again to changes in the moisture circulation and temperature behavior of the material [15]. This means that the microbial contamination acts as a precursor for a later starting formation of crusts on rock surfaces which is caused by the acidolytic and oxido-reductive (bio-) corrosion on the mineral structures [8].

However, it should also be mentioned that recent studies have revealed that microbial biofilms can also provide protective barriers and help to preserve archaeological objects from environmental damages, e.g. from thermal-hygric stresses. Due to the formation of these mainly on the surface located bio-mineralized encrustations it is possible to detect traces of the stone mason carvings, to discover remains of historical pigments and other materials even after centuries.

The assessment of the biodeterioration on cultural artifacts, requires, first of all, an unambiguous prove of a microbial impact, and, then, a differential diagnosis of the actual state of the deterioration process. This necessarily demands the development of integral concepts aiming at a long-term strategy of prevention [21]. The real benefit of an interdisciplinary and complementary cooperation of conservators and microbiologists in the evaluation and handling of biodeterioration impacts on cultural artifacts will be shown in the following examples, in case studies where research activities of our laboratory were performed in close cooperation with the conservation practice.

4 MICROBIOLOGY IN CONSERVATION - CASE STUDIES

4.1 Temple of Angkor Vat / Cambodia

The complex of the temple of Angkor is located near the town of Seam Reap close to the lake „Tonle Sap" in central Cambodia. The region is characterized by a tropical climate of intensive dry and rainy seasons. The buildings were erected between 802 and 1295 AD. This ensemble of temples represents the largest religious monument of the world; more than 100 temples are distributed over an area of 230 square kilometres (Fig. 6).

Figure 6: Natural stone affected by biocorrosive and biofouling microorganisms at the temple of Angkor Vat (Cambodia).

The studies for conservation of the „Apsara"-reliefs which is located in the largest temple of the Angkor complex „Angkor Vat", were performed since 1997. This work is a part of the GACP - German Apsara Conservation Project of the restoration and conservation division at the Polytechnic University of Cologne (Germany).

Due to an extensive corrosion and scaling of the employed sandstone, the „Apsara"-reliefs are extremely endangered. In order to develop an effective conservation strategy, it was necessary to analyse the causes of the stone deterioration and, in this context, to determine and evaluate the influence of the microbial impact.

Based on the experiences and results of previous microbiological studies by French and Japanese scientists [22- 25] most typical sites for biodeterioration processes at the Angkor Vat were selected for a detailed and long-term microbiological study. Further microbiological investigations were performed at Preah Ko, Preah Khan, Bayon and Banteay Srei in order to gain a more comprehensive insight into the biodeterioration processes occurring in that region.

The microbiological studies during 1997 and 2004 implied the assessment of the quantity and quality of microbial infestations by algae, lichens, fungi, bacteria and actinomycetes within stone profiles. The microbial metabolic activity were monitored in dependence of time and climatic conditions. In order to gain a strategy for controlling the biodeterioration processes the role of microorganisms in the stone deterioration was analyzed and conservation tests including biocidal treatments were conducted [26].

The microbiological studies of the GACP-Project at Angkor Vat and surrounding temples of the Angkor site have revealed that the natural microflora on rocks consists of a complex but stable microbial community of algae, cyanobacteria, fungi, lichens and bacteria (Fig. 7 a + b). The microbial films are mainly located in the uppermost layers of rocks, only certain microbes penetrate deeper into the stone. The metabolic activity of the microflora (e.g. respiration, photosynthesis) is very high, especially during rainy season and results potentially in biocorrosive and biooxidation activities due to the excretion of organic acids and the oxidation of iron-containing minerals. Nevertheless, the biodeteriorating activities in mature biofilms (e.g. lichens) indicate a natural, balanced climax status, which should not be interfered without having a conclusive and sound conservation concept, the more, since the natural microbial film is regulating moisture and thermal absorption of the rocks.

Figure 7 a + b: Natural multicolored biofilms of different photosynthetic microorganisms (e.g. lichens, algae and cyanobacteria) on Angkor monuments distinctly separated due to expositional factors and interspecific competition.

The consequences of an uncontrolled removal of the lichen infestations became obvious after a biocidal cleaning campaign which had been performed in the frame of an Indian conservation project at Angkor Vat in the early 90´s. Then, the biogenic contaminations on the stone surfaces were removed by brushes and highly toxic biocides, leading in the following years, however, to an intensive blackening of the treated, grey stone due to the intensive growth of cyanobacteria (Fig. 8 a).

Considering the thermal impact on blackened surfaces, especially under tropical climates, and taking into account the particular hygric stress to be related to the content of swellable clay minerals of that stone material, the contamination by the blackening microorganism is considered a major threat for the stone material. This may explain why the treated and blackened stone shows massive scaling compared to the untouched stone where a bio patina of green algae and multicolored lichens functions as a moisture-balancing protective (Fig. 8 b).

Figure 8 a + b: The removal of the natural biofilms led to an intensive regrowth of blackening cyanobacteria at Angkor Vat with additional thermal-hygric stresses to the sensible clay-containing sandstone resulting in a severe detachment of rock shales from Apsara carvings

Under these aspects, the mature microbial biofilm infestations found at the temples should remain untouched provided that a profound microbiological analysis including a interdisciplinary evaluation has been conducted. Cleaning or biocidal treatments respectively should be applied only if a control of the entire microbial inventory to be found at Angkor Vat has been established. Such treatments might be needed for supporting stone-consolidant treatments or for providing a better visibility of the historic artifacts. Organic and chloride containing biocides should be avoided because of their toxicity and a missing long-term efficacy. In addition, they possibly may have even nutritive effects for the surviving or reoccurring microflora. Synergistic treatments, implying the oxidative destabilization of the microbial biofilms by hydrogen peroxide, soft mechanical cleaning of the stone surfaces and a subsequent application of inorganic biocidal formulations with depot function yielded the most positive effects so far (Fig. 9 a + b).

A further aspect is that, the widespread contamination by fungi requires the application of microbially resistant consolidants in order to get a reasonable durability of the conservation treatment. The application of microbially resistant stone protectives has to be ensured by international standardized testing procedures and an appropriate hygiene at the site. In addition, it is necessary that the conservation activities are supported by a constructive water protection management. Moreover, the long-term effect of any conservation treatment has to be ensured by continuous maintenance for the monuments of Angkor.

The future research activities of the GACP-project with regard to -- the problem of microbiological impacts of the Angkor temple complex will comprise further research activities, such as microbiological ecology studies of the stone-colonizing microflora, determinations of microbial biofilm damage functions by various methods (e.g. determination of dilatation, drilling resistance, hardness etc.). In addition, there are a number practical approaches planned such as the microbiological testing of stone protectives, of mortars and of coatings, a continuation of the started biocide test field operations (e.g. new methodical applications and monitoring) and new applications of bioremediation techniques (e.g. biocalcification, biodesalination) in the ongoing conservation work of GACP.

Figure 9 a + b: Successful application and long-term efficient protection of a specific designed biocidal formulation at the northern bibliotheca at the Angkor Vat within the 3rd enclosure four years after treatment.

4.2 Archaeological site of Milet / Turkey

Milet was one of the largest and most important towns of Asia Minor in the 7th and 6th century B.C., located about 100 km south of Smyrna, the modern town of Izmir. Due to the silting of the gulf by the river Meander, Milet is situated about 10 km away from the seashore today.

During the last century of excavation activities, periodical floodings of the archaeological site of Milet (Turkey) led to a dramatic change of the appearance of marble objects being affected by the fluctuating water level. The excavated marble fragments developed grey/brownish to violet carbonate crusts (Fig. 10).

Figure 10: Spring flooding of the harbor monument within the archaeological site of Milet (Turkey)

These rough, porous but compact crusts are of varying thickness reaching up to 4 mm. Distinctly colored zones can be recognized which seemed related to the fluctuation of the water level: e.g. marble columns show a white-grey appearance in their upper part, while the lower parts at the column foot are brownish-black colored. In spring time, when the water level is sinking, the marble fragments are covered with red to violet layers; their color is changing to grey during the dry summer season.

Microscopical, chemical, petrophysical as well microbiological analysis have revealed a carbonate precipitation on the marble surface (Fig. 11) which is mainly produced by the metabolic activity of photosynthetic algae and cyanobacteria to be found within complex microbial mats. Such mats are typical for the formation of stromatolites in hypersaline marine environments [27].

Figure 11: Surficial carbonate precipitation on the marble columns mainly caused by the metabolic activity of photosynthetic algae and cyanobacteria

The marble fragments covered with those crusts show different forms of damage. In those parts which exhibit thicker crusts extended scaling is observed, while thin crusty parts display a distinct flaking. The crusts are built up from layers similar to annual rings of trees. Compared to the white marble of the object which consists of well sorted large calcite crystals, the grey crusts are characterized by small and badly sorted calcite grains. The crust matrix contains of soil particles, microorganisms and plant residues.

Detailed biological analysis showed the presence of organotrophic bacteria, fermenting microorganisms, photosynthetic algae and cyanobacteria, anoxygenic sulphur bacteria and sulphate reducing bacteria. They represent a complex microbe system also to be observed at stromatolite formation worldwide.

The presence of the microorganisms and the appearance of the crust layers suggest that the crusts are formed by a microbe mat which is activated during the flooding period. The biogenically formed fine calcite grains within this microbial layer, the capture of soil particles and other small compounds of the muddy water are all fixed in the viscous mat. In summer times when the water level is sinking the biological layers will dry (mainly in those areas without sufficient water supply from the ground) and a grey to brownish hard crust is formed. Under these conditions a part of the microbes retreats underneath the stone surface and restarts growing as soon as the environmental conditions improve with the next flood cycle. In cases sufficient water remains available, the red bacteria type will stay on the surface causing an extensive coloring of the objects.

In order to evaluate the possibly detrimental or protective functions of those biogenic carbonate crusts, and to develop conservation strategies, the development of the biogenic precipitations and discolorations were monitored. Their physico-chemical and microbiological properties as well were analyzed in a seven-year lasting study.

All crust samples showed similar mineralogical characteristics. Differences were only given in form of irregular disruptions of the layers, probably caused by dissolution processes. The crusts are of a very porous and weak structure (17 vol%; median pore diameter: about 5 µm) compared to the porosity of the marble (0.3 vol%; median pore diameter about 0.05 µm). This enormous difference in material structure may cause a discrepant thermal expansion behaviour - e.g. the dark areas at the foot of a marble column were warmed up by about 2.5°C more than the upper yellowish white parts. This leads to scaling processes in the thick crusts parts and seems accompanied by a slight deterioration of the underlying marble which is concluded from ultrasonic measurements. A similar mechanism may be inferred for the flaking processes in the white-greyish thin crusts. There were further interesting observations gained by hygric measurements. They revealed that the exterior of the crust forms a water repellent zone at the front side, probably due to microbial biofilms, limiting the desiccation of the microbial microenvironment and protecting this way the marble against a penetration of hypersaline salt waters.

During the field campaign, different cleaning procedures and biocidal treatments (laser, mechanical and chemical procedures) were tested aiming i) at an effective removal of the aesthetically affecting crusts and ii) a control of the microbial infestations on the marble surfaces at site in order to avoid later crust formation. An interdisciplinary evaluation of these conservation treatments is planned in order assess the preservation state of the treated marble fragments and to prognose the sustainability of the interventions performed.

Mechanical treatment (pneumatically operating chisel, a pneumatically dissecting graver and a micro sandblast equipment) have proven to provide a suitable technique with respect to cleaning but also to preserve simultaneously the original marble surface. A problem, however, is the enormous demand of time.

Future research activities will address the analysis of causes and the dynamics of the biocarbonatisation process due to the periodical flooding. In that context also recommendations for the conservation of the historical artifacts in Milet and other places of historical importance in the Mediterranean area as well should be given.

5 PROSPECTIVE NEEDS FOR AN INTERDISCIPLINARY APPROACH IN CONSERVATION MICROBIOLOGY

Based on the fundamentals of microbial impacts on materials and case studies as presented here, any restoration or archaeological activities or conservation intervention at a historical site should pay particular attention to microbial impact features when the deteriorations of cultural artifacts or archaeological sites are studied. Microbial impact features should be an important aspect in any interdisciplinary risk analysis [28].

In this context, a profound microbiological analysis within biodeterioration studies on materials in the restoration and conservation of cultural artifacts is mainly dependent on a timely recognition and evaluation of microbially influenced material damages and their relevance. For such investigations, a number of almost non-destructive detection and analysis methods (e.g. in situ-microscopy, remission spectroscopy, contact agar enrichments and molecular biological techniques) are at hand.

A basic measures in a practice-related conservation of the cultural heritage is the control of environmental parameters which constrain the microbial infections and growth. The preservation of prevailing environmental conditions or changes towards more favorable exposure conditions should always be carefully balanced and analyzed for possible consequences. Moreover, the conservation practice is expected to keep a systematic documentation of their techniques, materials and treatments in order to show their specific significance in controlling biodeterioration processes and to work out specific guidelines. Thus the application of microbicides will be minimized and ecotoxicological aspects are taken into account. Furthermore, good records are very helpful for the biotechnological progress, e.g. for the development of using biogenic desalination and carbonation capabilities in the conservation practice.

Long-term sustainable conservation strategies should be therefore be adequately based on physical, chemical and biological interventions respecting the natural constraints of the archaeological site in question.

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