Natural stone, weathering phenomena, conservation strategies and case studies: introduction

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The weathering of historical buildings, as well as that of any monument or sculpture using natural stone (or man-made porous inorganic materials) is a problem identified since antiquity. Although much of the observed world-wide destruction of these monuments can be ascribed to war and vandalism, many other factors can contribute significantly to their deterioration. These threaten the preservation of the current inventory of historically, artistically or culturally valuable buildings and monuments. Furthermore, a drastic increase in deterioration has been observed on these structures during the past century. This prompted Winkler (1973) to make a pessimistic prediction, that at the end of the last millennium these structures would largely be destroyed because of predominantly anthropogenic environmental influences. Fortunately, this has proven not to be the case.

There is a general belief that natural building stones are durable, and not for nothing does the Bible refer to the Rock of Ages. However, all rocks will weather and eventually turn to dust. If rocks are cut and used in buildings, the chance of deterioration increases because other factors come into play. To understand the complex interaction that the stone in a building suffers with its near environment, (i.e., the building, and the macro environment, the local climate and atmospheric conditions), requires an interdisciplinary approach with the work of geologists, mineralogists, material scientists, physicists, chemists, biologists, architects and art historians.

Although most historical buildings use natural stone as the main construction material, other materials, such as mortars for masonry or rendering and ceramic roof tiles, to name a few, may interact as well with the building stones. These materials, if not chosen correctly can also be a source of eventual deterioration.

What characterizes natural stones, geomaterials, apart from the chemico-mineralogical composition and texture, is their very heterogeneous and anisotropic fabric. This originates from a varying, polyphase formation (e.g. crystallization from a melt, sedimentation, diagenesis, metamorphism and deformation) over long geological time periods, i.e. millions of years. The particular rock fabric determines the variability in the observed weathering and deterioration patterns and processes. To find an appropriate approach for reducing these deterioration processes, cutting-edge research is needed to elucidate the actual mechanisms. Knowledge of the properties of geomaterials, of their weathering processes and of subsequent material changes is a basic requirement to understand the complex mechanisms involved in producing the eventual deterioration.

All geomaterials at the Earth's surface, exposed as a natural outcrop or in a building, are subject to the destructive physical, chemical and biological aspects of weathering. Moreover, when they are part of a building, anthropogenic influences will increase significantly – after all the building is a result of that influence – affecting both material properties, for example thickness of the cut block will influence its mechanical resistance, and the weathering processes. These cannot be viewed as independent processes since complex interactions operate between them.

Physical weathering is caused specifically by freeze-thaw processes, salt weathering as well as hygric, thermal and wet-dry cycling. As a result of these processes, the stone undergoes a progressive fragmentation along preferred anisotropic surfaces, for example, intra- and intercrystalline microcracks, cleavage planes, twin lamellae and joints etc.

Chemical weathering can essentially be understood as resulting from the reactions that are induced on mineral constituents of the stone by water, carbon dioxide and oxygen from the air. This chemical disintegration largely takes place at the sub-microscopic level, and therefore exposed stone surfaces containing complex systems of pores, fracture surfaces and grain boundaries provide the surfaces where these chemical reactions can occur.

The most significant single environmental factor is the presence of moisture on and in the stone. Not only can water induce some chemical

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reactions, but under thermal cycling it can cause physical damage through freeze-thaw, hygric cycling and controls salt crystallization when soluble salts are present. Furthermore, it is a necessary component for biological colonization. Microorganisms in turn will generate acids and chelating agents that can corrode and attack the minerals present in the stone.

Anthropogenic influences begin already during the quarrying process. Rocks are then subjected to the effects of the actual quarrying techniques as well as the resulting changes of environment. These can be very significant for the material properties and weathering processes that the stone will eventually show once it is included in the masonry. An anthropogenic influence will also affect changes in the environment by air pollution from industry or car exhausts. These, in general, acid pollutants were the main cause of some of the most dramatic deterioration observed during the mid-twentieth century and served to call world wide attention to the need for preservation of this stone-made cultural heritage.

Natural stone conservation in conjunction with restoration is an old theme. Already in Roman times the principle that regular stone or building maintenance is necessary was recognized, especially if long-term preservation of the building was desired. Also, traditional conservation measures were essentially based on protecting the building stones from water. For this purpose, either specific construction measures, such as coverings or canopies to prevent water from direct contact with the water were used, or sacrificial coatings or protective treatments were applied.

The protection of our architectural heritage has both cultural and historical importance, as well as a substantial economic and ecological value. Large sums of money are being spent world-wide on measures for the preservation of monuments and historical buildings. The economic and ecological commitment to the preservation of monuments and historical buildings requires, however, a prudent handling of the appropriate funds. This demands an optimization of damage analysis procedures and damage process controls as well as the development of monitoring and early warning systems for damage prevention. Therefore, the goal needs to be the implementation of permanent preservation measures, which requires long-term maintenance. This is ultimately controlled by the limited economic resources and the increased number of cultural assets that are recognized as of value to be preserved.

The process of uncontrolled building construction appears to be over – at least in the western world. The demands for resource protection on the already existing inventory of buildings leads to the situation where more and more architects have to deal with question of how to handle the older inventory of historic buildings and even monuments rather than design of new construction. Awareness of the importance of the safeguarding of our architectural heritage has increased significantly and it is hoped that it will lead eventually to a means of achieving a sustainable, long-term preservation.

The present volume combines review articles with reports on recent progress in our research field. The first section of papers is dedicated to weathering of natural building stones.

Weathering of natural building stones

Weathering is the natural way of stone decay into smaller particles. Weathering is a slow, continuous process that affects all substances exposed to the atmosphere, especially marble. As well as chemical weathering mechanical weathering causes stones to lose their strength. There are several causes of mechanical weathering. Changes in temperature and freeze thaw successions are some examples. Expansion and contraction in the stone texture is the result of variations in temperature. Frost action, as discussed by **Ondrasina, Kirchner & Siegesmund**, occurs when water enters tiny cracks in the stone and freezes at lower temperatures. When the ice expands it will weaken the stone fabric after a period of time. Much of our marble looks just as fresh today as on the day it was installed. In some areas, however, the marble has badly deteriorated. This deterioration occurs in areas where the marble is repeatedly wetted. The mechanism for these proceedings will be discussed in this paper.

But temperature changes are also important for other rock types. Alsatian monuments are built with two types of Buntsandstein sandstone (**Thomachot & Jeannette**). Their different pore structures cause them to have mixed petrophysical properties and occasion a different response to frost. To understand these differences, frost simulations where absorption/drying periods are not allowed, have been carried out. These experiments have demonstrated the importance of wetting/drying periods in changing the porous network, which can then lead to material damage. It seems that most of the damage, usually attributed to frost action, cannot be imputed to ice formation. Wetting–drying cycles accentuated by freezing, are probably the main cause of stone weathering.

The evident differences in weathering between the Soll and Franka stone types of the Globerigina Limestone Formation are related to the mineralogy, geochemistry and porosity of these building stones by **Cassar**. The weathering of the more marly rocks depends mainly on exposure to atmospheric conditions especially in the near-shore environment. The weathering process of Globigerina Limestone in general, and Franka in particular, has been explained as a sequence of steps, from formation of a thick and compact superficial crust, to the loss of this crust and to the initiation of alveolar weathering. No crust forms in the Soll type, and severe deterioration occurs here at an early stage in the weathering process.

Weathering processes

A special weathering factor is salt weathering, since it may be caused both naturally and anthropogenically. A literature review on the effects of salt weathering is provided by **Doehne**. Salts have long been known to damage porous materials, mainly through the production of physical stress resulting from the crystallisation of salts in pores. Salts can also damage stone through a range of other mechanisms, such as differential thermal expansion, osmotic swelling of clays, and enhanced wet/dry cycling due to deliquescent salts. The review combines views from geomorphology, environmental science, geotechnical and material science, geochemistry and conservation.

The magnitude and dynamics of thermally induced weathering are addressed in the paper by **Zeisig, Siegesmund & Weiss**. They give a unique compilation of thermal degradation in marble. Different types of commercially used marbles composed of calcite and/or dolomite are investigated by thermal expansion measurements. The marbles do not only vary in composition but also in texture, grain shape and grain size. Special emphasis is placed on the magnitude and directional dependence of thermal degradation and its correlation with fabric observations. The basic outcome is that all fabric parameters have to be considered for the assessment and understanding of the proneness to weathering of a marble.

The current condition of many building facades and historical monuments clearly reveals that they are not immune to the impact of weathering and associated deterioration. The effect of thermal stress on porosity change for two types of marble has been investigated by **Malaga-Starzec, Lindqvist and Schouenbourg**. The results indicate that inter-granular decohesion starts already between 40°C and 50°C. This temperature is easily reached on building surfaces in most European countries during summer time. Damage diagnosis of natural stone based on investigations of porosity changes could diminish not only aesthetical but also economical problems.

The assessment of the intensity of rock degradation is one of the most important aims for preservation and conservation purposes. Ultrasonic wave velocities are frequently used for a non-destructive diagnosis of marble deterioration. The paper by **Weiss, Rasolofosaon & Siegesmund** gives a quantitative determination of the reduction of ultrasonic wave velocities as a function of pre-existing and thermally induced microcracks with special emphasis on anisotropy. Thermally induced microcracks lower ultrasonic wave velocities significantly and a correlation with the microfabric of marble is evident. Thus, ultrasonic wave velocities have been proven to be an efficient tool for the non-destructive determination of marble degradation.

Fabric dependence of physical properties

Rock fabric determines significantly the properties of different building stones. A new integrative approach presented by **Weber & Lepper** deals with the complex interrelations between the geological background on the one hand and specific dimension stone properties on the other hand: Weathering resistance and petrophysical properties of siliciclastic dimension stones are governed by depositional environment (type of fluvial architecture) and diagenesis (quartz cement and clay matrix contents). This is evidenced by two contrary examples of historical exterior use (former monastery churches). For the actual use of siliciclastic dimension stones, these relevant aspects should be considered.

This approach is valid for sedimentary rocks, while comparable correlations can be observed for metamorphic rocks. Every natural building stone represents an anisotropic and heterogeneous system. Degree and type of a fabric anisotropy may vary and are characterized by grain shape preferred orientations, microcrack systems and preferred orientations of the rock-forming minerals (here referred to as texture). The fabric dependence of mechanical rock properties like compressive, tensile and abrasive strength and their development due to an increasing mylonitic deformation is discussed by **Strohmeyer & Siegesmund**. With regard to mica bearing rocks as investigated in this study the mica texture is the most prominent factor influencing the mechanical behaviour.

Particular fabric properties may even lead to very unconventional material properties. Itacolumites are very special rocks due to their high flexibility. The flexibility is mainly related to a penetrative network of open grain boundaries that enable a limited body rotation of individual quartz grains (**Siegesmund, Vollbrecht & Hulka**). Continuous layers of white mica display deformation features indicative of shear along its layer-parallel cleavage planes. As demonstrated by simple bending experiments, flexibility is a highly anisotropic phenomenon. Solution along grain boundaries, volumetric strain by thermal contraction of quartz and bulk extension are processes discussed for the origin of the extreme values of secondary grain boundary porosity.

Computer simulations may help to understand observations and the processes behind them. Natural building stones like marbles are in general heterogeneous and anisotropic materials. Up to now there has been a lack of knowledge on the effect of different fabric and material properties on marble degradation. Thus, an alternative approach to simulate and understand marble weathering is presented in the paper of **Weiss, Siegesmund & Fuller**. A finite element analysis of marble degradation reveals that besides different single crystal properties of calcite and dolomite, the main rock forming minerals in marble, the texture has an important effect on marble weathering. Since identical microstructures are used for the modelling, the effect of single crystal properties and the texture could be quantified. Scattering in the stress distributions, finally leading to microcracking, due to different textures is larger than the difference between calcite and dolomite marbles without textural changes.

Not only the rock itself but connecting materials may be the source of deterioration or places subjected to degradation. The use of calcium sulphate based mortars has a very long tradition and was used at the Pyramid of Cheops, Towers of Jericho as well as on sacred buildings in Germany. **Middendorf** discusses the difficulties for restoration and conservation of those historic buildings since the information about composition including the admixtures and additives used are missing. He presents results on studies of historic calcium sulphate based mortars which will form the basis to develop mortars for restoration purposes. His focus is on the improvement of the water resistance of calcium sulphate based restoration mortars. The increase of water resistance can be achieved by chemical additives or hydraulic and/or latent hydraulic admixtures.

Biodeterioration

A number of different papers address biodeterioration. This effect is ubiquitous and widely not considered in past times. The colonisation by endolithic microorganisms such as cyanobacteria, chlorophycaceae, fungi and lichens on natural carbonate rock surfaces as well as carbonate building stones is discussed by **Pohl & Schneider**. Under a residual and protective carbonate rock layer (150 to 300μm beneath the surface) photobiontic microorganisms occupy more then 60% of the dissolved rock volume. Deeper beneath the substrate an initially dense, then progressively diminishing hyphal network of mycobionts develops. On natural carbonate rock surfaces no grain loss or exfoliation was observed as is often found on silicate rocks. After an initial material loss underneath the carbonate surfaces, a more protective rather than destructive impact of endolithic biofilms on carbonate rock substrates is suggested.

The importance of biodeterioration for granitic and calcareous building stones is outlined in the paper by **Schiavon**. He concludes that the combined effect of physical degradation by lichen hyphae, penetrating in a rock, and chemical attack by organic acid with associated growth of inorganic salts leads to accelerated weathering. Different types of weathering patinas are observed which are clearly associated with fungal and bacterial activities. They lead to extensive corrosion and dissolution of mineral surfaces beneath them. As it is the case with soiling patinas from air pollution, the biological patinas observed by **Schiavon** never form a protective layer on the stone surface and, thus, their careful removal is always suggested.

Basically all types of building material are colonizable by microorganisms. Often, surfaces are covered with a rigid layer composed of microbial cells and extracellular biopolymers (biofilm). Biodeterioration of building material is determined by the metabolic activities of the cells as well as the impact of the extracellular biopolymers. In order to elucidate the mechanisms of biodeterioration, preparation techniques have been designed by **Hoppert, Kämper, Pohl, Flies, Berker, Ströbel & Schneider** to preserve the cellular and extracellular structures of the biofilm down to the micrometer scale.

Quality assessment and conservation of stones

Systematic descriptions of damage szenarios and their quantification are required to assess the degree of degradation on a monument. Phenomenological observations may, therefore, be combined with laboratory analyses. Studies on weathering of building stones were carried out by **Fitzner, Heinrichs & La Bouchardiere** comprising laboratory analysis and in situ investigations, the latter including detailed survey of weathering forms, registration and evaluation of weathering forms by means of monument mapping and in situ measurements. For historical monuments made from limestones in the centre of Cairo the weathering forms, weathering products and weathering profiles show a clear correlation between the damage and salt loading of the limestones as a consequence of air pollution and rising humidity. The deterioration characteristics of many historical stone monuments in Cairo is alarming and needs a control like rising humidity, desalination, cleaning, stone repair, fixation or consolidation of loose stone material, structural reinforcements and stone replacement.

Comprehensive knowledge about the situation on-site is indispensable for an appropriate conservation strategy. Before attempting any restoration project on monuments and historic buildings, characterization of the stone must be carried out, and the causes of stone deterioration need to be established in order to eliminate or mitigate them effectively. The assessment of the efficiency and durability of some preservation treatments with water-repellent effects is discussed by **Alvarez de Buergo & Fort** on the basis of a two-year project carried out at the Palace of Nuevo Baztán, a state-designated historic monument built in the early eighteenth century in Madrid, Central Spain, whose façades are mainly built in limestone. Two siloxane-based products were ultimately determined to be the most effective on the basis of chromatic variables, water vapour permeability, water-stone contact angle, SEM observations and durability (artificial ageing tests).

Due to the frequent utilization of marble as a building and monumental stone, its conservation and preservation is an important challenge in the saving of our cultural heritage. The change of thermoelastic behaviour of marble upon consolidation is discussed by **Ruedrich, Weiss & Siegesmund**. Based on the comparison of weathered and consolidated marbles, the influence of the rock fabric and the stone consolidant on thermal weathering of marbles is considered. For the directional dependence and intensity of marble weathering, the texture, the grain boundary geometry and the preferred grain boundary orientation are of crucial importance. The different properties of consolidants, like their adhesion properties and their glass transition temperatures significantly affect the thermoelastic behaviour of marbles.

Stone decay processes are controlled by multiple factors inherent to the rocks (and their natural heterogeneity and variability) and related to the surrounding environment. The theoretical and laboratory modelling of these processes is hindered by the complex interactions between these diverse factors. **Matias & Alves** try to cast light in these relationships and the influence of diverse factors by the study of decay patterns (established from detailed observation of stone decay features and their distribution) in thirty-nine monuments built with granitic stones.

Extensive conservation and reconstruction effort of historical buildings and cultural monuments has led to an increasing demand for detailed information on the ancient stone material. Knowledge about provenance and technical properties of building material is required to evaluate weathering processes and successfully preserve and reconstruct historical buildings. The results of a case study on ancient building sandstones from the Görlitz/Zittau area in Eastern Germany by **Michalsky, Götze, Siedel & Heimann** show that it is possible to assign unequivocally historically used material to specific sandstone occurrences. A combination of macroscopic rock description, thin section and CL microscopy coupled with image analysis, scanning electron microscopy, and analysis of technical parameters (e.g., Hg porosimetry, total water uptake) is very useful for this purpose.

Particular emphasis may be placed also on recent architecture and its problems. The use of natural stone panels or cladding material for building facades has led to some durability problems, especially with marble slabs. The most spectacular phenomenon is the bowing of marble panels. The influence of intrinsic and extrinsic parameters is discussed by **Koch & Siegesmund** on the basis of a detailed study performed on the Oeconomicum Building at the University of Goettingen. Particularly, rock fabric is detected as a key parameter contributing to the deterioration of marble and the final degree of bowing. Rock fabric controls the mechanical and physical properties such as porosity, permeability, Young's modulus and thermal expansion.

Mechanical properties are important when using rocks as building materials. **Sahlin, Stigh & Schouenbourg** discuss the bending strength properties of eight different rock types. Conventional dimension stone tiles are normally untreated and at least 10 mm thick. However, a production method has been developed that makes it possible to produce dimension stone tiles only 4 mm thick without high amounts of waste material. The tiles are impregnated with a mixture of potassium-based waterglass, water, colloidal silica, and Berol 048 (non-ionic surfactant), using a repeated cycling between vacuum and atmospheric pressure.

Environmental conditions

A number of papers address the importance of the environment for stone alteration. Study of the decay of stone and glass by atmospheric pollution carried out by LISA in Europe since the early 1980s is reviewed by **Lefèvre & Ausset**. The authors make a nice explanation of two different types of gypsum development, i.e., above and below the surface. The quantification of the effects of atmospheric pollution on stone raises the question, whether the SO_2 contents in stone can be directly related to quantifiable damage rates. A significant advance particularly in theory regarding the modelling of alteration of building materials is presented based on the UN-ECE-ICP "Materials" study and an attempt made to map SO_2 and potential damage.

The decay dynamics of sandstones in a polluted maritime environment was investigated by **Smith, Turkington, Warke, Basheer, McAlister, Meneely & Curran**. Visible decay is triggered by the delamination of surface layers associated with the near-surface accumulation of chloride and sulphate salts, particularly gypsum. These simulation studies show that after the initial state of weathering the continuous salt weathering and rapid loss of surface material are of critical importance to understand the subsequent decay pathway and control the conservation strategies.

The continental climate and severe air pollution causes major damage to 'sensitive' stones such as limestones. In a study of buildings in Budapest **Török** has demonstrated that the interaction of atmospheric pollutants and oolitic limestone leads to the formation of weathering crusts. A range of black and white crusts are described including their mineralogical composition and physical properties. The increased values of surface strength and decreased water absorption are described in detail with models of crust formation. The rate of crust strengthening and mineralization is controlled by wind/rain exposure and pollution concentration.

The mechanisms of gypsum formation and accumulation on Venetian monuments are reported by **Fassina, Favaro & Naccari**. The different forms of decay (white washing, dirt accumulation and dirt wetting) were used for a simplified model controlled by the degree in sulphation. The most extensive sulphate formation occurs in the black dendrite-shaped crust restricted to the interface between the white washing areas and the sheltered ones. Gypsum formation strongly depends on the mineralogical composition and the rock fabric. In compact limestones gypsum appears only at the surface while in marbles these effects are more penetrative.

An important point in the elucidation of deterioration mechanisms is the correlation between the deterioration factor dose and the resulting damage. The role of acid deposition in the deterioration of stone is discussed in the overview by **Charola & Ware**. Specifically, dry and wet deposition are considered along with their resulting deterioration mechanisms. Key factors in this process are dry deposition of gaseous pollutants, the nature of the stone, including structure and porosity, and the presence of surface moisture as moderated by time of wetness.

The global climate has, over geological time, experienced great change over a range of time span. The implication of future climate changes for stone deterioration over the next 100 years is discussed by **Viles**. Based on a range of scenarios of future emissions of greenhouse gases, and on a range of climatic models the global average temperature and sea level are projected to rise over the twenty-first century. The complex interaction of chemical, physical and biological weathering processes on stone decay may change for example in Mid-Europe due to much more warmer and wetter winters and warmer and drier summers.

The formation of sulphate salts caused by direct attack of polluted air and rain water on the stone surface is a main factor for its deterioration in monuments. In some cases the sources of sulphur could be more complex involving building material or ground water, soil etc. **Klemm & Siedel** demonstrate the use of the sulphur isotope ratio in sulphate salts as a fingerprint to evaluate the influence of potential sulphur sources. The dominant role of anthropogenic factors was found as well as the locally differing situation in an industrial region of Central Europe.

The cation exchange capacities of sandstones

(CEC) have been studied by **Schäfer & Steiger**. Clay minerals occuring as very small particles in sandstones are the most likely single contributor to the cation exchange capacities. For weathered sandstones significantly different cation exchange capacities were observed along profiles close to the exposed surface. Even after a relatively short exposure time in a heavily polluted atmosphere the CEC in the weathering zone is only about half of the value compared with the unweathered ones.

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