

Schutz für karbonatische Natursteine in Zeiten des Klimawandels –präventive und invasive
Maßnahmen

**Protection for Calcareous Stones in Times of Climate Change - Preventive and
Interventive Conservation Measures**

Dissertation zur Erlangung des akademischen Grades
einer Doktorin der Naturwissenschaften
eingereicht an der Universität für angewandte Kunst Wien

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Wien, im Februar 2026

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A handwritten signature in blue ink, appearing to read 'Marija Milchin', written in a cursive style.

Acknowledgements:

I would like to express my sincere gratitude to all the students and colleagues who contributed to different parts of this thesis by sharing their knowledge and supporting me throughout the various phases of the research process.

In particular, I would like to thank my supervisors, Johannes Weber and Gabriela Krist, for their guidance, expertise, and continuous support. I am also grateful to my colleagues Katharina Fuchs, Andrea Hackel, Farkas Pintér, and Johann Nimmrichter, as well as to all the co-authors of the publications presented in the appendix of this thesis, for their valuable contributions and collaboration. Special thanks are due to the students of the “Stone Class” for their engagement, patience, humour, and the positivity they share with me.

I would like to thank Jana Korunovska for her assistance with the statistical analyses, Johannes Falkeis for the insightful discussions and support, and my son Ilija Milchin for his encouragement and for creating the illustration of a sensor used in this thesis.

I would also like to acknowledge all my colleagues from the STECCI project who contributed to the production and on-site installation of the sensor racks, especially Siniša Bizjak and Krešimir Bosnić. Furthermore, I thank Stefan Simon and Véronique Vergès-Belmin for their valuable input regarding the design of the exposure racks.

There are many more people who supported this work in one way or another. I thank you all sincerely for your help, patience, and encouragement.

Funding acknowledgment:

The sensors and exposure racks used in the final phase of this dissertation are financially supported by the European Union through the EU HORIZON project STECCI - STone monument Ensembles and the Climate Change Impact (Project number: 101094822).

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Abstract

Climate change and ongoing alterations in atmospheric composition pose increasing challenges to the preservation of cultural heritage, particularly for stone materials exposed to outdoor environments. This doctoral thesis investigates these challenges with a specific focus on calcareous stone heritage, aiming to bridge scientific research and practical conservation decision-making.

The thesis begins by outlining the broader context of climate-related risks to cultural heritage, explaining why changing environmental conditions represent a significant threat to stone monuments and reviewing strategies currently discussed within the heritage sector. Calcareous stones are examined in detail, considering their historical use, material properties, and importance as heritage materials. Building on this foundation, the principal deterioration mechanisms affecting outdoor calcareous stones are analysed, with particular attention given to how these processes are expected to evolve under future climatic conditions.

A central contribution of this work is the development and evaluation of methodologies for quantifying surface recession in calcareous stones. The design of material sensors and exposure protocols presented in this thesis enables the assessment of changes in decay rates and forms the methodological core of the research, linking conservation science and practice.

The final part of the thesis addresses practical conservation approaches. Selected preventive and interventive measures relevant to emerging challenges are discussed, with particular emphasis on winter shelters, shelter coats, and water-repellent treatments. Their advantages, limitations, and potential risks are evaluated and illustrated through examples from practice. The thesis concludes with a case study demonstrating a structured approach to conservation decision-making for an existing monument.

Keywords: climate change, calcareous stones, surface recession, material sensors, protection, conservation, restoration, outdoor monuments

Zusammenfassung

Der Klimawandel und fortlaufende Veränderungen der atmosphärischen Zusammensetzung stellen zunehmende Herausforderungen für den Erhalt des kulturellen Erbes dar, insbesondere für Steinobjekte im Außenbereich. Diese Dissertation untersucht diese Herausforderungen mit einem spezifischen Fokus auf karbonatische Natursteine und verfolgt das Ziel, wissenschaftliche Forschung mit praxisorientierter Entscheidungsfindung in der Konservierung zu verbinden.

Zu Beginn wird der übergeordnete Kontext klimabedingter Risiken für das Kulturerbe dargestellt. Dabei wird erläutert, warum sich verändernde Umweltbedingungen ein Risiko für Steindenkmäler darstellen, und es wird ein Überblick über aktuell diskutierte Strategien im Kulturerbesektor gegeben. Karbonatische Natursteine werden hinsichtlich ihrer historischen Nutzung, ihrer Materialeigenschaften und ihrer Bedeutung für das Kulturerbe untersucht. Darauf aufbauend werden relevante Schadensmechanismen beschrieben, die im Außenbereich wirken, mit besonderem Augenmerk darauf, wie sich diese Prozesse unter zukünftigen klimatischen Bedingungen voraussichtlich verändern werden.

Ein zentraler Beitrag dieser Arbeit ist die Entwicklung und Evaluierung von Methoden zur Quantifizierung des Oberflächenabtrags karbonatischer Gesteine. Die vorgestellten Materialsensoren und die dazugehörigen Expositionsprotokolle ermöglichen die Erfassung von Veränderungen in der Verwitterungsintensität und bilden den methodischen Kern der Dissertation, der Konservierungswissenschaft und -praxis miteinander verknüpft.

Der abschließende Teil der Arbeit widmet sich der praktischen Konservierung. Es werden ausgewählte Maßnahmen im Hinblick auf neue Herausforderungen diskutiert, wobei Wintereinhausungen, Schlämmen und Hydrophobierungen im Mittelpunkt stehen. Deren Vorteile, Grenzen und potenzielle Risiken werden anhand von Praxisbeispielen bewertet. Den Abschluss bildet eine Fallstudie, die ein strukturiertes Vorgehen zur konservatorischen Entscheidungsfindung für ein bestehendes Denkmal demonstriert.

Schlagwörter: Klimawandel, karbonatische Steine, Oberflächenabtrag, Materialsensoren, Schutz, Konservierung, Restaurierung, Außenbereich

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List of abbreviations:

AR — Assessment Report

CDR — Carbon Dioxide Removal

CVI — Climate Vulnerability Index

GHG —Green House Gases

GU — Gloss Units

HVAC — Heating, Ventilation and Air Conditioning

ICOM-CC — International Council of Museums – Committee for Conservation

ICOMOS-ISCS — International Council on Monuments and Sites – International Scientific Committee for Stone

IoC — Institute of Conservation

IPCC — Intergovernmental Panel on Climate Change

IPM — Integrated Pest Management

SAI — Stratospheric Aerosol Injection

SRM — Solar Radiation Modification

STECCI — Stone Monument Ensembles and the Climate Change Impact

TEOS — Tetraethyl Orthosilicate

Introduction

The lithosphere and atmosphere of our planet, along with their associated rock formations and climates, will undoubtedly outlast our civilization. Cultural heritage and climate change impact humanity in much shorter time frames.

As highlighted in the latest report (2023) of the Intergovernmental Panel on Climate Change (IPCC) and recognized by the scientific community, our climate is undergoing significant changes due to anthropogenic emissions of greenhouse gases (GHGs). How these climatic changes affect cultural heritage has been increasingly studied in recent years. Predictions for the changing risks to cultural heritage were drafted as part of different research projects. Forecasts relate to multiple parameters affecting i.e. the solubility of carbonates in outdoor environments. In this context, changes in temperature, precipitation and atmospheric CO₂ concentration are of particular interest.

This cumulative doctoral thesis examines the expected impacts of climate change on cultural heritage in Central Europe, with a particular focus on Austria. It addresses key challenges in the preservation of stone heritage, emphasizing calcareous lithotypes exposed to outdoor environments. In response to anticipated climatic changes, a methodology is proposed to quantify variations in decay rates — specifically surface recession — and the protective potential of both preventive and interventive conservation measures is evaluated.

My professional background is in stone conservation. Although academically speaking relatively young, the field existed long before the establishment of a formal academic framework and was traditionally dominated by craftspeople and artists. Since the late twentieth century, stone conservation has become increasingly academic, enabling a more detailed, scientific approach to understanding materials and their decay processes. However, this scientific strategy focuses primarily on fundamental principles, whereas conservator-restorers require object-specific answers. While the contribution of (heritage or conservation) science to understanding decay and deterioration processes is indispensable, practical conservation goes one step further by applying this knowledge to individual objects in their specific setting and exposure. This tension between theory and practice has accompanied my studies and professional career, and although the interface between the two has improved significantly, further development is still needed. This consideration constitutes one of the main motivations for writing this thesis.

The structure of the thesis reflects the nature of the underlying research process. The work is divided into two parts: core part and an appendix. The appendix contains six publications, all of which focus on calcareous stone monuments in outdoor environments. In the aforementioned core part of the thesis, the narrative connecting the contents of these publications is presented. The work has been written in a way that aims to be useful to both stone conservators and scientists working in the field. As is typical of interdisciplinary research, differences in disciplinary perspectives must be acknowledged. Consequently, some chapters may appear superficial or unnecessary to one group of readers but of use for another

group. I have sought a balanced approach to these complex issues and thus hope that the result will be of interest to all those dealing with scientific and practical issues of stone conservation.

The first chapter addresses the broader context of the issue: why changing climate conditions and air composition represent a relevant threat to cultural heritage in general, and to stone heritage in particular, and which broad strategies exist to address these challenges in the heritage sector. The second chapter focuses on calcareous stones, examining their use and significance as heritage materials. The third chapter presents the fundamental deterioration mechanisms affecting outdoor calcareous stones and discusses how these mechanisms are expected to change in the coming years and decades. The fourth chapter explores methods for measuring surface recession in calcareous stones, as well as the design of the sensors and protocols used in this work. This chapter forms the core of the thesis and occupies the central position between conservation science and practical conservation. Chapter 5 is more closely aligned with practical conservation. First, the conservation terminology used in the thesis is defined in relation to the terminology established in the ICOM-CC Resolution on Terminology from 2008. This is followed by exemplary preventive and interventive measures that may have potential when addressing emerging challenges. Particular emphasis is placed on winter shelters, shelter coats, and water repellents, with their advantages, disadvantages, and limitations discussed in detail. Where appropriate, these discussions are supported by examples from practice. The main part of the thesis concludes with a case study illustrating one possible approach to decision-making when dealing with an actual monument.

The publications included in the appendix, together with additional referenced works, constitute the scientific foundation of the thesis. These are:

- 1) Milchin, M., Krist G. (2020), Herausforderung Steinrestaurierung. Vergangenheit, Gegenwart, Zukunft / *Challenges in Stone Conservation: Past, Present, and Future* (in German)
- 2) Milchin, M., Haselberger M. & Krist, G. (2023), Maßnahmen zur Erhaltung des baukulturellen Erbes – Monitoring, Schutz und Pflege als Behandlungsstrategien / *Measures for the Preservation of our Built Cultural Heritage – Monitoring, protection, and care as treatment strategies* (in German and English)
- 3) Milchin, M., Weber, J. & Krist G. (2023), Sensor Materials for the Deterioration of Carbonates in a Changing Outdoor Environment
- 4) Milchin, M., Weber, J., & Krist, G. (2023), Material Sensors for the Surface Recession of Calcareous Stones: Understanding Present and Future Decay
- 5) Milchin, M., Haselberger, M. & Krist, G. (2020), Preventive Conservation Measures for Stone Statuary in the Outdoor Environment: Three Case Studies from Austria
- 6) Milchin, M., Pesce, C., Weber, J., Krist, G., Ban, M. & Anghelone, M. (2020), An evaluation of shelter coats for the protection of outdoor stones

Publication (1) addresses the past, present, and future of stone conservation, focusing on the major problems affecting stone in outdoor environments over time. It discusses potential future developments, with particular emphasis on challenges arising from changes in air quality and climate change, as well as possible responses. Paper (2) targets climate change and cultural heritage, with a focus on possible coping strategies from the field of conservation. The following two publications (3) and (4) address the use of the so-called material sensors, to better understand the rate of surface recession of calcareous stones, an aspect which is also given broad space in the core part of the present work. The material sensors presented here aim to bridge the gap between the knowledge generated by (conservation) science and the object-specific focus required in practical conservation. They are designed to answer questions concerning the rate of decay of specific monuments in their particular settings and exposures, thereby supporting preservation-related decision-making processes. The final two publications (5) and (6) of the appendix discuss possible conservation responses to new challenges arising from shifts in air quality and climate change. Existing measures are reviewed, and approaches with potential relevance under new environmental conditions investigated. Two of these, shelter coats and winter shelters, are in the focus of these publications.

1. Contextual framework: cultural heritage, climate and pollution

The interaction between cultural heritage, tangible and intangible, and climate is multifaceted. Climate change impacts, and will continue to impact different forms of cultural heritage in all regions of the world. Works of architecture should be considered exemplary in this context. They represent one of the most significant categories of tangible heritage. The primary role of architecture is to provide shelter from the outdoor elements for humans and their possessions, placing buildings at the forefront of climatic pressures.

The design of (traditional) buildings often correlates with the needs deriving from certain types of climates. For example, the typical vernacular Newar buildings in the Kathmandu Valley, Nepal, feature projecting roofs and elevated 'ground floors' (Fig.1) designed to give protection against flooding and water ingress during monsoon rains (Bodach, Lang and Hamhaber 2014). In alpine regions, projecting roofs are also part of the traditional architecture (Fig.2), their task here being mostly to keep snow away from the direct vicinity of the walls.



Fig. 1 and 2: Vernacular architecture in Katmandu Valley, Nepal (left) and in Tyrol, Austria (right)

Similarly, the choice of building materials often directly addresses climate and predominant weather conditions. The frequent use of earthen materials (i.e. adobe) in arid regions (Richards et al. 2020) or the use of wood in northern countries (Proft, Brebbia and Connor 2018) can be regarded as exemplary.

From another perspective, climate and weather directly influence the preservation of tangible heritage, both being responsible for many deterioration mechanisms, widely known as "weathering". The "ICOMOS-ISCS Illustrated Glossary on Stone Deterioration Patterns" defines the term **weathering** as:

*"Any chemical or mechanical process by which stones exposed to the **weather** undergo changes in character and deteriorate."* (Cartwright and Vergès-Belmin 2008)

For example, in wet climates, dissolution is often the predominant weathering mechanism, while in arid

regions, thermal stress and mechanical weathering may be the most significant deterioration mechanisms.

Lithic materials undergo weathering not only on monuments but also within the landscape, constituting a crucial process in geology. 'Peltier's diagram' (Fig. 3) best illustrates how climate change poses risks to heritage stones. While initially designed to illustrate geological weathering in landscapes, 'Peltier's diagram' also provides valuable insights into the predominant deterioration mechanisms affecting heritage stones and other mineral building materials in outdoor environments across various climates. It illustrates the dependence of weathering on different climate parameters i.e. average annual temperature and precipitation. It thus shows how shifts in temperature and precipitation can alter the predominant weathering mechanisms for certain materials in specific regions.

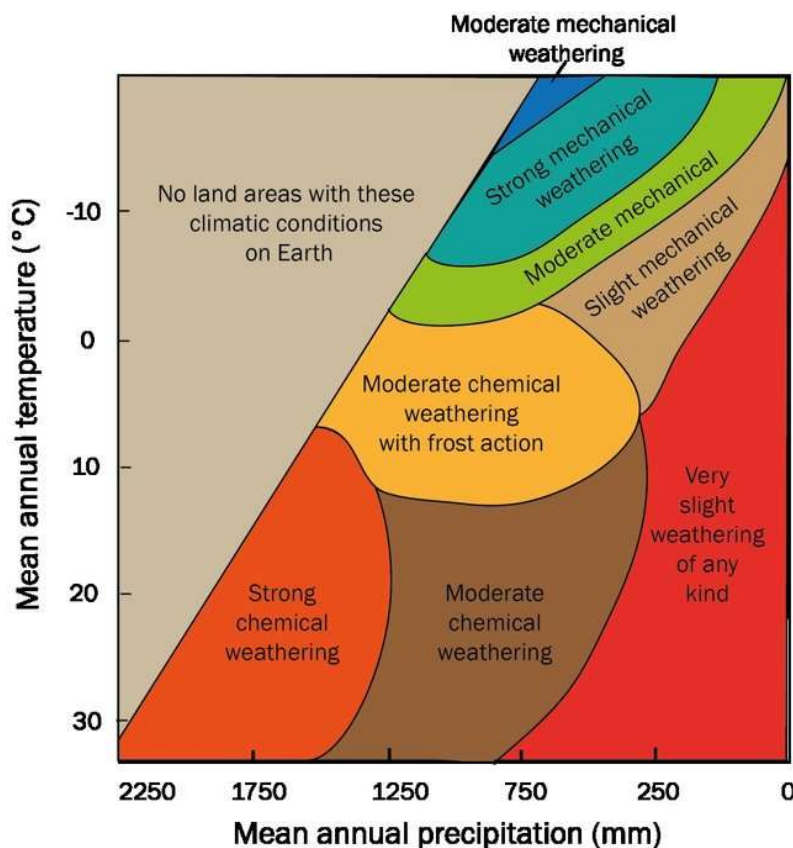


Fig. 3: Peltier's diagram (© J. Eduardo Marquez, after Nagel 2000)

It seems important to note that the diagram primarily distinguishes between mechanical and chemical weathering. However, in conservation practice, a third category — biological deterioration — is often employed. While this category is not presented as a standalone in the diagram, it can most often be considered a subcategory of either chemical or physical weathering, depending on the predominant mechanism in place (i.e. chemical attack or pressure caused by shrinking and swelling of the biofilms). A quick glance at the aforementioned diagram suggests that even a mere shift in average temperature and/or availability of water, as is the case with climate change, can significantly alter the typical

weathering patterns of stones within a specific region.

A systematic approach, implemented to analyse deterioration of heritage assets in general, is given by the 10 agents of deterioration (Pedersoli, Antomarchi and Michalski 2016)¹. This concept typically forms the base for risk assessment analyses but can be alienated and serve as a framework for the analyses of changing risks resulting from climate change.

Changes in outdoor temperature and humidity due to shifts from climate change directly influence any decay caused by **inappropriate temperature (1)** and **humidity (2)** levels, both outdoors and indoors. At the same time, the redistribution of precipitation results in more frequent extremes in relative humidity, making it increasingly difficult to maintain constant humidity levels in museums and collections even where **Heating, Ventilation and Air-Conditioning (HVAC)** systems are employed.

Intensifying rain events will alter the availability of (liquid) **water (3)**, whether in the form of rising groundwater or water seeping through leaks in roofs and gutters. Many water-drains and gutters will become undersized in future, leading to more damage through water ingress. Flooding will become more frequent in many parts of the world (Sesana et al. 2021).

Wild fires (4) will become more probable due to rising temperatures especially in already arid regions (Sabbioni, Brimblecombe and Cassar 2012).

The intensity and the diversity of species involved in **pest infestation (5)** in collections and historic buildings are expected to increase and/or change. It will be of utmost importance in such cases to act fast and to adapt the existing **Integrated Pest Management (IPM)** concepts to the new challenges (Querner et al. 2022).

The change in **pollutant (6)** levels is directly interconnected with climate change, with pollutants being in part, the reason for climate change itself. Future levels of pollutants and their impact on heritage with focus on calcareous materials will be discussed in chapter 3 in more detail.

UV radiation and light (7) have, in general, no direct connection to or with climate change, but some indirect correlations might become apparent in future.

Mechanical forces (8) as agents of deterioration might become relevant in connection with earth slides, the melting of permafrost or in the case of floods etc. Mechanical forces resulting from armed conflicts (war) or criminal activities, as well as **theft (9)** and **displacement (10)**, are forms of deterioration that on first glance have no direct connection to climate change. However, many scholars are researching the impact that climate change will have on society, on peace, on migration, and on the well-being of people (Schorlemer and Maus 2015). With changing patterns in this sector, the last three agents of deterioration might also experience change.

Next to the 10 agents of deterioration, the so-called types of risk occurrence are also of utmost importance in traditional risk assessment in conservation, as originally proposed by Michalski (1994) and

¹ The 10 agents of deterioration are: inappropriate temperature, inappropriate humidity, water, fire, pests, pollutants, light, mechanical forces, theft and displacement.

adapted and revised by Pedersoli, Antomarchi and Michalski (2016). The occurrence is defined in three categories: **rare events** (once every 100 years), **common events** (many times per century) or **cumulative processes** (Pedersoli, Antomarchi and Michalski 2016).

In a similar manner, the scientific community differentiates between so-called **slow** and **fast or extreme events** when discussing climate change (Lefèvre 2010). The slow events tend to be cumulative and involve effects like rise of average temperature, redistribution of rain and snow, sea level rise, melting of permafrost etc. (Lefèvre 2010). The other group concerns so-called fast or extreme events that involve flash floods, storms, heat waves, earth slides and so on (Lefèvre 2010). Following this differentiating principle, impacts on cultural heritage and heritage materials can also be slow or fast (extreme). Changes in mean temperature or precipitation will bring changes to weathering and decay mechanisms, i.e. the corrosion of metals, damage due to freeze-thaw cycling, salt crystallisation, biomass accumulation and similar.

The increase in frequency of extreme events such as storms, wild fires, floods or earth slides can however cause enormous destruction in a short period of time due to the high intensity of these events. If we try to apply the types of risk occurrence from the aforementioned risk assessment system to the climate change scenario, it is evident that one of the most prominent changes for the preservation of cultural heritage is expected to be the shift in the type of risk occurrence for many of the risks involved. For example, devastating floods could increasingly occur and become **common events** in regions where they were once **rare**. The same applies to wild fires or earth slides and strong storms. In contrast to slow events, extreme events are harder to model and/or predict. Therefore, it has taken the scientific community much longer to establish a certain correlation between observed changes in extreme weather and climate change compared to, for example, the rise in average temperature. However, in the last IPCC report (AR6) it is stated that:

“Evidence of observed changes in extremes such as heatwaves, heavy precipitation, droughts, and tropical cyclones, and, in particular, their attribution to human influence, has further strengthened since AR5. Human influence has likely increased the chance of compound extreme events since the 1950s, including increases in the frequency of concurrent heatwaves and droughts (high confidence).” (Lee et al. 2023).

The challenge with these types of events is that they occur rapidly and often result in the total loss of the cultural asset involved. Dealing with extreme events requires a comprehensive risk management at all stages. The most frequently used risk analyses strategy in conservation is the so-called ‘ABC scales’ which enables the calculation of the magnitude of different risks in order to detect and prioritise the same for a certain asset (Pedersoli, Antomarchi and Michalski 2016). This strategy also encompasses various measures of risk control, including avoidance, mitigation, detection, response, recovery, monitoring, and review. In recent years, it has become increasingly evident that climate change is rapidly altering the risks associated with certain types of heritage. Consequently, new strategies have been developed, many based on the aforementioned approach. For example, in order to assess the vulnerability of world

heritage property (natural and cultural) the **C**limate **V**ulnerability Index (CVI) was proposed (Day, Heron and Markham 2020). In the frame of many projects founded by the European Union, focus was laid on risk assessment, preparedness, and reduction in respect to natural disasters and climate change impact on cultural heritage (e.g. STORM², HYPERION³ and ARCH⁴) with focus on extreme events.

Possible changes to so-called slow events and their impact to decay mechanisms of heritage materials have been rarely addressed in the course of such projects. Variations in temperature and humidity, along with the quantity and distribution of precipitation throughout the year are perhaps the most straightforward changes to consider when regarding slow events. The solubility of different substances can increase or decrease with rising temperature; freeze-thaw cycling, thermic dilatation, biocolonisation and salt damage are all influenced by the same. The changing availability of water also impacts the amount of substance dissolved, the intensity of biocolonisation, the corrosion of metals or the rotting of wood. In essence, even subtle changes in climatic parameters (can) have an impact on the decay and deterioration of cultural heritage. In this context, the term 'Heritage Climatology' should be mentioned. It was first defined within the NOAH's Ark⁵ Project (Brimblecombe 2010) and describes the relationship between climate and cultural heritage, looking at the effects that climate and weather⁶ have on heritage materials in terms of decay and deterioration.

Given that present changes are undeniable, it's imperative to consider the potential responses that conservation may offer to address this new reality. Even though slow events are easier to model than extreme events, knowledge about forthcoming changes does not necessarily bring about a suitable remedy, it only appoints the fields that are in need of further research. Therefore, the identification of possibilities for protection of cultural heritage has to be a key objective of practical conservation and conservation science, both at present and in the near future. Innovative approaches are needed but also existing concepts should be reassessed as they might offer the potential to deal with new situations. Some of these are evaluated and looked at in detail in the second part of this work.

Next to climate, air quality also plays an important role in the decay of heritage materials especially in the outdoor environment. Depending on the heritage material concerned, different pollutants play important roles. In the case of organic materials, for example, various photochemical oxidising agents such as ozone are of interest (Brimblecombe 2003).

In regard to stone as heritage material, specifically calcareous lithotypes, SO₂, NO_x and CO₂ play the most important roles in its decay. Pollution with SO₂ posed a significant problem in terms of decay in the 19th and 20th century (as early as the 18th century in England, due to the early industrialisation). However,

² <https://www.storm-project.eu/>

³ <https://www.hyperion-project.eu/>

⁴ <https://savingculturalheritage.eu/>

⁵ 2004-2007, Project ID: 501837, founded by the EU,

⁶ Climate refers to the long-term (typically 30 years) average of weather parameters of a specific region. Weather refers to much shorter time frames, usually being described like the state of our atmosphere in a certain region and time.

humanity has successfully reduced emissions over the past half-century, leading to a decrease in damage from sulphation. It is crucial to emphasise that lowering pollutant levels cannot reverse the damage already caused. Furthermore, damaging processes may persist to a certain degree because mineral materials retain a 'memory' of past conditions. For instance, if a stone block was exposed to a sulphur-rich atmosphere for an extended period, it will contain a reservoir of sulphates (Lefevre et al. 2007). These accumulated reserves will continue to migrate to the surface of monuments in the coming years and decades due to the processes of dissolution, capillary transport, and crystallisation. However, over time, it can be expected that the stored sulphur will be depleted. This prognosis is only valid if no new sources of SO₂ become significant in the future. As a matter of fact, a potential new source could emerge from geoengineering measures aimed at combating the present Climate Crisis. If cutting CO₂ and other GHG emissions to net zero takes too long, **Carbon Dioxide Removal (CDR)** methods will become essential (United Nations Environment Programme 2023, United Nations Economic Commission for Europe). Yet, current carbon capture technologies remain limited in effectiveness and scalability, making it unlikely that they alone will achieve the wanted results. Therefore, geoengineering - especially **Solar Radiation Modification (SRM)** - is discussed as a potential last resort. SRM aims to reduce incoming solar radiation or increase heat loss. The most prominent option is the so-called **Stratospheric Aerosol Injection (SAI)**, which would introduce SO₂ aerosols into the lower stratosphere to reflect sunlight and cool down the planet. This is similar to the natural process that is sometimes triggered by volcanic eruptions, in the course of which, different materials (solid particles like ashes but also SO₂-aerosol) are released in the atmosphere. As a result to this phenomenon, cold years often follow big volcanic eruptions. While this strategy would almost certainly lead to a fast cooling of the earth (1-2 years), it will not deal with all of the other problems that derive from climate change (CO₂ concentrations would stay high leading e.g. to further acidification of the oceans) (United Nations Environment Programme 2023). It is not entirely clear which additional consequences would result from the SAI process. Potential impacts to human, animal, and plant health, as well as to cultural heritage, particularly through increased stone deterioration, are possible. Persistently high CO₂ concentrations in the atmosphere, together with possible additional SO₂ introduced via gas exchange between the stratosphere and the troposphere, could create conditions similar to the most severe pollution episodes of the 19th and 20th centuries, characterised by acid rain and highly polluted air.

Taken that SO₂ levels continue to decrease and/or stay low (Vestreng et al. 2007) it can be expected that new pollutants are likely to become more dominant. For example, emissions of nitrogen oxides from some branches of economy have risen in the recent years (e.g. aviation). The expected change for mineral building materials, therefore, includes heightened microbiological activity on heritage surfaces due to the increased presence of nitrogen, which serves as a nutrient for many types of microorganisms. Also, a contamination of heritage surfaces with soluble nitrate salts may become more common in future, leading to further problems due to efflorescence and subflorescence.

Last but not least, CO₂ concentrations in the air are constantly rising. Since CO₂ is involved in the dissolution of carbonates, it can be expected that the rate of dissolution will change in the future, thus

increasing the impact of the so-called “karst effect”⁷ for the surface recession of carbonates. In the following chapters, the situation for heritage made of calcareous stones will be analysed. This includes their use and prevalence, typical deterioration in outdoor environments, as well as potential changes resulting from climate change and shifts in air quality.

⁷ The karst-effect is defined as the dissolution of soluble carbonate rocks such as limestone and dolomite in clean rain water.

2. Calcareous stones as heritage materials

Stone is not only a primary building material but also one of the most abundant heritage materials (Dimes and Ashurst 1998). It has been used for both architecture and sculpture throughout history, its use dating as early as the transition from nomadic society to permanent settlements (Dimes and Ashurst 1998). Starting with Egyptian pyramids, spanning through Greek temples, Roman aqueducts, Renaissance sculpture, and Baroque palaces, stone has consistently been the material of choice for structures and artworks intended to be enduring, imposing, and to serve as witness of civilisations and epochs.

Within the broad range of natural stones, calcareous ones have been frequently used due to their distinct properties. This group includes common building stones but also decorative stones, chosen for their aesthetic properties. Examples include marbles, valued for their noble appearance, compact limestones selected for their colour and unique patterns (i.e. veining) as well as “softer” porous limestones used mainly locally, for both building and sculptural purposes. While calcareous stones may not be the most abundant group of lithic materials geologically (Fig.4 blue colour marks the abundance of carbonate rocks in Europe), they are very extensively used in cultural assets, including architecture and sculpture. Consequently, they are of significant concern in the field of heritage preservation.

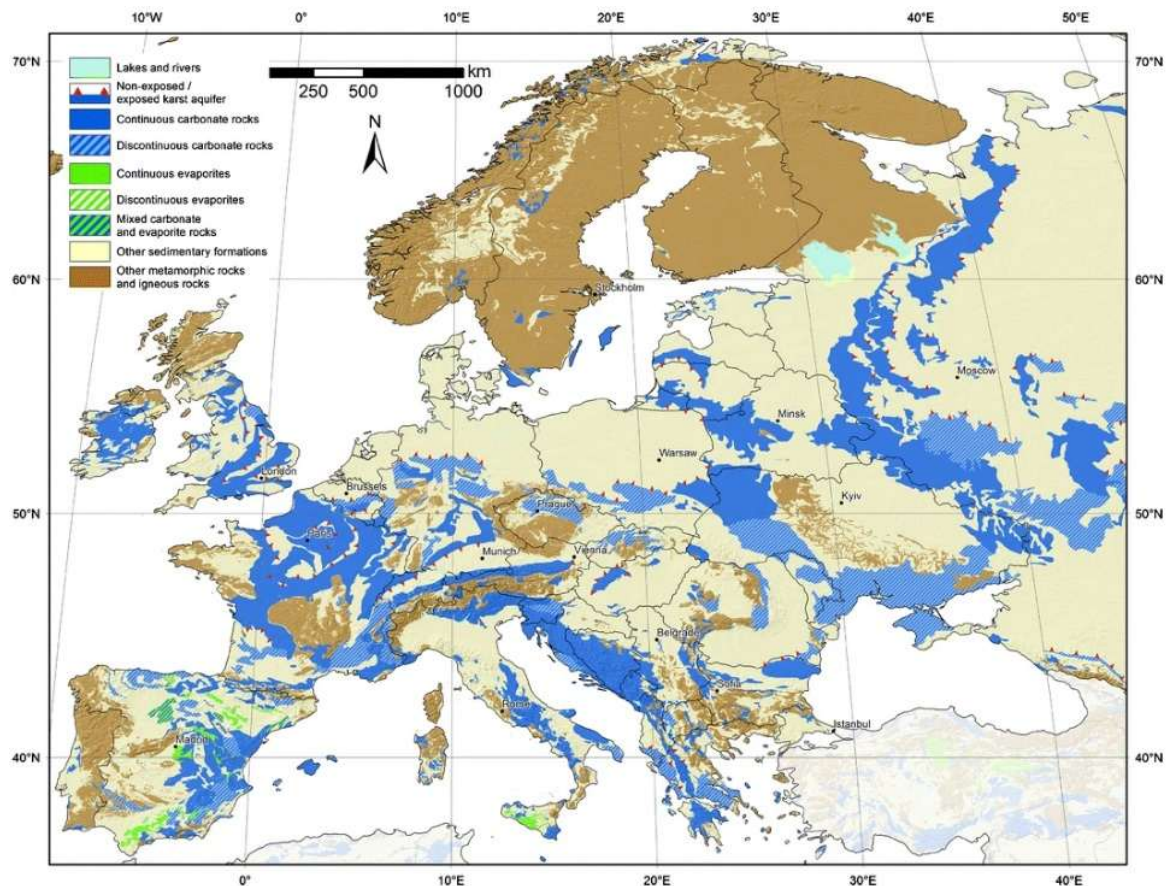


Fig.4: A map showing the abundance of carbonate rocks in Europe (blue) (Source:

<https://link.springer.com/article/10.1007/s10040-016-1519-3/figures/9>)

Some of the most renowned works of sculpture are hewn in white marble, i.e. numerous antique works of the ancient Greeks and Romans (e.g. Fig.5), works of the Italian Renaissance (e.g. Fig.6) and Baroque. But also outside of Europe, marble has been a highly respected material, used for iconic structures such as the Taj Mahal in Agra (India) and the Washington Monument in Washington D.C. (USA). The fact that marbles and compact limestones often have a very homogeneous structure and offer multiple possibilities for the surface finish (from roughly hewn to polished), combined with their relative “softness” has resulted in a very wide use through time and space.

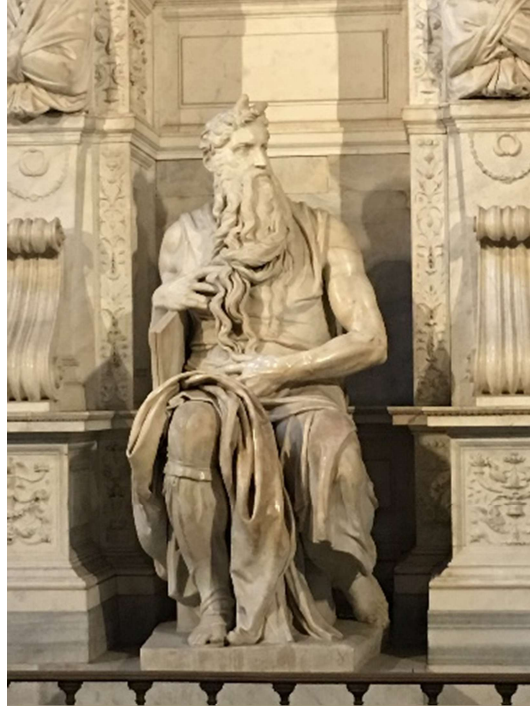
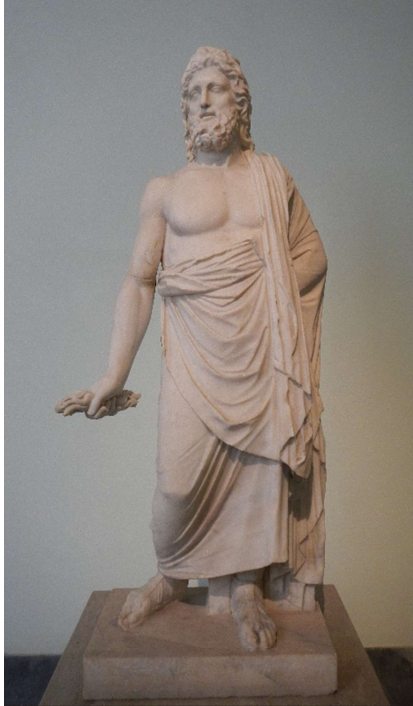


Fig. 5 and 6: White marbles used for sculptural purposes throughout history, Left: Roman copy after a Greek sculpture of Asclepius (Antiquity), right: Mosè by Michelangelo (Renaissance)

Until the time of the industrial revolution, most stones, especially in architecture, were typically only used locally⁸. The appearances of whole cities and regions have been defined by the appearances of the local building stones – for example the porous limestone Globigerina is responsible for the colour and the impression of cities and villages on Malta (Fig. 7 and 8).

⁸ Due to the weight of stone and the difficulties associated with transport—especially in the absence of waterborne transport—stone was generally not used far from its quarry of origin.



Fig.7 and 8: Valletta, Malta: a view from the sea (left) and a street in the city (right)

Transport on land was expensive until the development of railway networks and modern roads, which only became widespread in the 19th century. Only special decorative stones, often scarcer and required in smaller quantities, were transported over longer distances, particularly when water transport was available (Siegesmund and Snethlage 2011). Today known under the term *marmi antichi*, primarily marbles and compact limestones, but also some hard stones like porphyry, with distinct colours and/or patterns, were traded in antiquity (Fig.9) (Borghini 1998). These stones were often transported over long distances to adorn Roman villas and baths throughout the Roman Empire. The travel routes of different *marmi antichi* are well documented and presented in various publications of the Association for the Study of Marble & Other Stones in Antiquity – ASMOSIA (Poljak and Marasović 2018; Yavuz, Yolaçan and Bruno 2023) and elsewhere. Not only in Antiquity but also, in the Renaissance, the Baroque period (see Fig. 10) or the 19th century, these decorative stones were sent on long journeys.

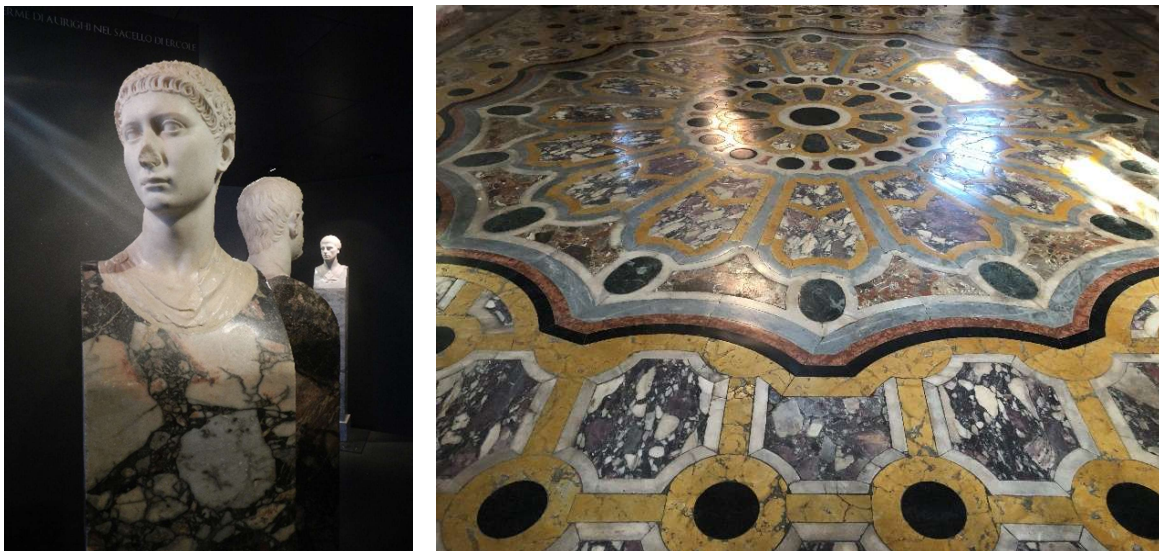


Fig. 9 and 10: The use of *marmi antichi* throughout history; left: antique Roman herms, white marble and the so-called *africano* stone (from Teos, Turkey), right: a baroque floor in the church "San Giovanni e Paolo" in Venice, consisting of different stones, some of them, *africano*, *breccia bruna* or *giallo antico* belong to the group of calcareous *marmi antichi*

However, with industrialisation and the availability of new and cheaper transport options, other (less precious) (lime-)stones — perhaps not renowned for their visual properties but valued for their dense and/or homogeneous structure or their resistance to decay — also gained significance. Consequently, such stones were used in locations distant from their primary sources, expanding their use and importance geographically. For example, Istrian limestones have been extensively used in Venice since medieval times, where they constitute the most abundant lithotype in the lagoon area, contributing significantly to the longevity of Venetian architecture (Fig.11) (M. Šimunić Buršić, D. Aljinović and S. Cancelliere 2007). This was only possible because of the very short and, in comparison, simple marine transportation. The same stones only gain importance for the massive construction site in Vienna (Fig.12) following 1857, when the "south railway" linking Vienna and Trieste was constructed, enabling economically viable transportation of materials (Milchin et al. 2022).



Fig.11 and 12: Istrian stone used on different façades; left: the façade of Palazzo Ducale in Venice (14th century), right: the sculptures on the façade of the Votivkirche in Vienna (19th century)

In many regions where marbles and compact limestones were either unavailable or only partially accessible, porous limestones were employed for sculptural and architectural works. While this group of stones facilitates easy and fast workmanship, they offer only very limited possibilities for surface finishes. Their high porosity and “softness” often prevent the achievement of polished surfaces. Moreover, their open porosity makes them more susceptible to deterioration, decay, and weathering. Often, these stones were therefore covered by either surface coatings (limewash, paint layer etc.) or plaster. In times of limited travel and/or trade possibilities, they were mostly used locally. Some important and better studied porous limestones are, for example, the Savonnières and Caen from France, Bath and Portland stone from England, or Globigerina from Malta. In the east of Austria, many different porous limestones have been used throughout history. Most of them come from the quarries in the so-called “Leithagebirge”.



Fig. 13: Roman quarry of the porous limestone of Stotzing, "Leithagebirge", Austria (©Andrea Hackel)

Some of these materials have been used since Roman times (Rohatsch et al. 2018). They vary in workability and resistance to deterioration processes, but they share the characteristic capillary porosity, which makes them generally susceptible to freeze-thaw and/or salt-induced damage (Fig. 15), as well as sulphation (Fig. 14) and surface recession due to the dissolution of calcium carbonate (Fig. 16).

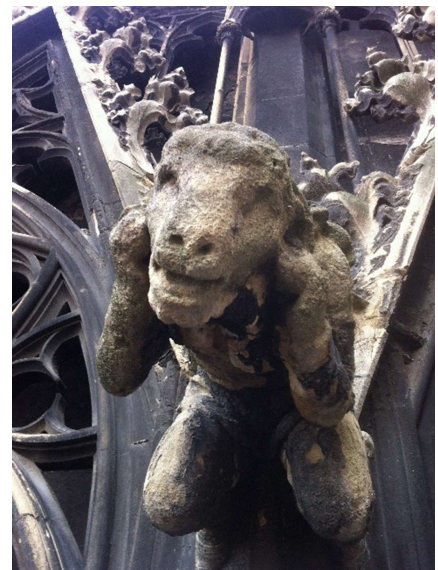


Fig. 14, 15 and 16: typical damage and decay patterns on porous limestones; f.l.t.r.: sulphation crust, salt-induced material loss and surface recession (rain exposed areas) with sulphation crust (rain protected areas)

It is evident that calcareous stones have been extensively used throughout history. While they may not always be the primary local building material, there are also regions in which entire cities and villages are constructed exclusively from local calcareous stones. Additionally, regions devoid of calcareous stone deposits, may still have heritage comprised of these. Distinct stones, used primarily for decorative and/or sculptural purposes, were frequently transported to distant locations. In more recent times (after the industrial revolution) the stone trade market globalised and the distances over which stones were/are transported became greater as transport became cheaper. Nowadays not only decorative stones are sent

on long journeys, but also less precious ones.

Hence, what the future brings for this group of lithic materials and their preservation is significant on a global scale. Before looking into potential changes, it is crucial to examine the current situation and understand the specifics of the deterioration of calcareous stones.

3. Deterioration mechanisms of outdoor calcareous stones

Most of the literature on stone deterioration and decay focusses on processes that are specific to the outdoor environment (Cartwright and Vergès-Belmin 2008; Dimes and Ashurst 1998; Henry and Pearce 2008; Siegesmund and Snethlage 2011). This should not imply that stone only deteriorates in outdoor environments; rather, that most deterioration processes are more common and/or occur more rapidly outdoors, thus making them more significant. Water plays a crucial role in most stone weathering mechanisms; it facilitates the transport of salts, causing freeze-thaw damage, inducing hygric and hydric dilatation, and facilitating the colonisation by microorganisms and growth of plants (Odgers and Henry 2012). In combination with variations in temperature and pollution, water accounts for almost all natural deterioration processes that are relevant to stone.

Calcareous stones follow this trend and deteriorate more rapidly when exposed to the outdoor environment. In addition to the already mentioned deterioration mechanisms relevant to all stones and porous building materials, calcareous stones exhibit patterns of chemical deterioration that are typical and specific to their chemical composition, the most important ones being the dissolution in clean rainwater (so-called “karst effect”) and sulphation (Sabbioni 2003). These mechanisms are interconnected, specific to carbonate materials, and result at least in part in surface recession. The same is described in most studies as a cumulative effect deriving from three different processes:

- 1) The dissolution of calcium carbonate in clean rain water (pH 5.6) or the so-called “karst effect”.
- 2) The wet deposition of pollutants or the dissolution in so-called “acid rain”.
- 3) The dry deposition of pollutants, and subsequent reaction with the stone surface (Cardell-Fernández et al. 2002; Siegesmund and Snethlage 2011; Torracca 2009).

Both sulphation (due to dry or wet deposition) of calcareous materials and the karst effect on the same start with the same process, the dissolution of calcium carbonate in water or weak acids. As one can see from the equation (1) below, the reaction is dependent on the availability on H^+ ions or the pH of the reaction milieu. The lower the pH (higher acidity), the more calcium carbonate is dissolved due to the shift in the equilibrium of the reaction.

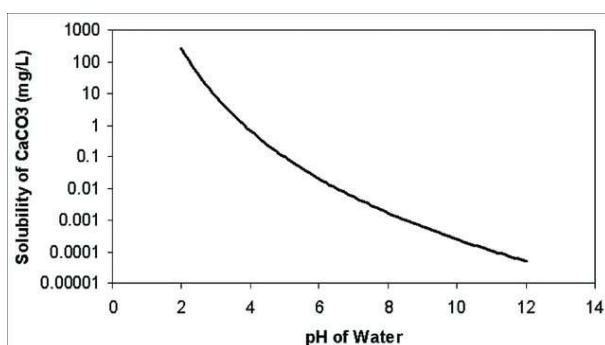
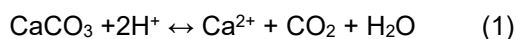
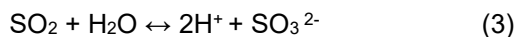


Fig. 17. Diagram showing the dependence of the solubility of calcium carbonate and the pH of the water (after Hart, Colson, and Burries 2012)

Weak acids can be formed by a dissolution of acidic airborne gases, like CO₂ (2) or SO₂⁹ (3) in rain or, less commonly, in fog or condensate (Odgers and Henry 2012).

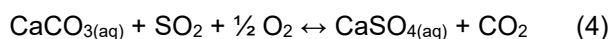


The solubility of calcium carbonate in pure water with pH 7 is very low (0,013 g/l at 25°C) but much higher in weak acids (Steiger, Charola and Sterflinger 2011). Rain in reality never consists of pure water but is always acidic to a certain degree. Due to the dissolution of CO₂ from the atmosphere, “clean” rainwater has a slightly acidic pH of 5.6. The same can dissolve up to four times more calcium carbonate than water with (neutral) pH 7. With polluting agents in the air, the so-called “acid rain” can occur, whose pH can fall as low as 4, with acid fog reaching pH values of 2 or even lower (Tilgner et al. 2021). To summarise, rain is always at least slightly acidic, therefore, calcareous surfaces, both in the landscape and on monuments, experience some dissolution with every rain fall.

After a dissolution has taken place, different paths are possible depending on the properties of the substrate, the exposition, the availability of pollutants, the amount, distribution and form of water involved, and the climatic conditions. In rain-exposed areas, the dissolved calcium carbonate is mostly washed away, resulting in surface recession (material is removed from the surface). In some situations, the dissolved material can re-precipitate on the surface of the monument, without undergoing a chemical change, recrystallising as calcium carbonate. This effect has been observed and described for the “white areas” of a monument as early as the beginning of the 1980s (Camuffo et al. 1982). More often, however, “black areas” can be found, especially in rain-sheltered surfaces. The same consist of precipitated material that had undergone a chemical reaction. In this case, it is mostly calcium sulphate, resulting from the reaction between calcium carbonate and SO₂ from the air (Camuffo et al. 1982).

3.1. Sulphation

As already mentioned, when a chemical reaction occurs between calcium carbonate from the substrate, and SO₂ from the air, with water serving as a reaction medium, gypsum is precipitated (4). This either builds up a crust on the surface of a monument or stays in the pore space of the subsurface, depending mainly on the exposition (Lefevre et al. 2007).



⁹ NO_x is an acidic gas that can be solved in rainwater and can cause the dissolution of calcium carbonate. The reaction of calcium carbonate and NO_x produces nitrate salts which are frequently washed away due to their good solubility in water. If nitrates can accumulate on the surface, they could lead to stronger biocolonisation because of their nutritious values for many microorganisms. This scenario might become more important in the future due to changes in air quality and climate change.

The availability of SO_2 necessary for this process is directly linked to the use of fossil fuels, particularly coal. Coal contains not only high concentrations of sulphur, but also generates significant amounts of soot and particulate matter when burned. The particulate pollutants can be embedded in the sulphation crusts and contribute to the well-known black colour of the same. The “black areas” (Camuffo et al. 1982) are only found on surfaces that are protected from direct rain but are wetted indirectly through capillary suction within the stone or condensation within the pores (Fig. 18-20).



Fig. 18-20: “Black areas” or sulphation crusts, on monument surfaces in different European cities f.l.t.r.: Brussels, Rome and Vienna

The particulate matter usually incorporates metallic cations that are known to serve as catalysts for the reaction of sulphation itself (Camuffo, Del Monte and Sabbioni 1983), thereby accelerating the formation of the crust through a positive feedback loop. The presence of the crusts only in rain-sheltered areas can be explained through the higher solubility of gypsum (2,6 g/l at 25°C) in comparison to calcium carbonate (0,013 g/l at 25°C), leading to the dissolution and washing away of the gypsum from the surfaces that are rain-exposed. Gypsum can, however, also accumulate in pores of the subsurface, causing a reduction of porosity, micro cracking due to volume increase and/or reduced drying rates which further result in secondary damage like scaling, peeling or other forms of material loss.

As stated above, the main source of sulphur dioxide has been the burning of fossil fuels, especially coal. Therefore, the rise in the concentration of SO_2 in the air is directly connected to the industrial revolution and has a different starting point in various countries. On the European mainland, the industrial revolution experienced a delayed start, around 1850, compared to Great Britain, where industrialisation already started in the 18th century. Therefore, some of the earliest literature focusing on air pollution originates from England. One of the most important early texts on this topic is the book “*Fumifugium; or, the Inconveniencie of the Aer and Smoak of London Dissipated*” by John Evelyn from 1772. The writer is

concerned about the quality of the air and its impact on human health and nature, but also on furnishings and buildings.

*“This is that pernicious Smoake which sullyes all her [London’s] Glory, superinducing a sooty Crust or Furr upon all that it lights, spoyling the moveables, tarnishing the Plate, Gildings and Furniture, and corroding the very Iron bars and **hardest Stones** with those piercing and acrimonious Spirits which accompany its Sulphure; and executing more in one year, than exposed to the pure Aer of the Country it could effect in some hundreds.”* (Evelyn 1772).

And he was right, as many scientific studies after his time have proven the negative impact that sulphur dioxide has on health, nature but also on monuments and cultural assets. Especially in the course of the 20th century, many scientists were working on understanding the mechanisms that are involved in the accumulation of pollutants and their interaction with different surfaces (Brimblecombe 2001; Camuffo et al. 2006; Camuffo and Bernardi 1996; Camuffo, Del Monte and Sabbioni 1983; Lefèvre and Sabbioni 2016; Moroni, Pitzurra and Poli 2004; Olaru et al. 2010; Russa et al. 2013; Saiz-Jimenez 2004). In the following chapter a short summary of the relevant information is given.

3.1.1. Wet deposition, dry deposition

There are, in general, two different ways of how gaseous pollutants, including SO₂, can accumulate on surfaces:

- 1) Wet deposition refers to the absorption of the hydrophilic gases in raindrops on their way through the atmosphere (Camuffo 2019). The pH of the water decreases due to the acidic gases dissolved in it, the same is subsequently delivered to the surface, where it can undergo further reactions¹⁰.
- 2) In dry deposition, particles or gases settle on a wet or dry surface. They dissolve upon contact with water that interacts with the surface (Camuffo 2019). It is important to note that the transport and accumulation of these particles do not occur in a liquid but in a dry phase.

Dry deposition is mostly relevant to surfaces in the direct vicinity of sources of pollution (short transport distances), whereas wet deposition can also be relevant hundreds and thousands of kilometres away from any possible pollutants. The relative relevance of the two mechanisms for a certain monument depends on the surrounding (urban or rural) and, therefore, distance to pollutant sources, the season (differences between summer and winter), but also on the geographical and climatic circumstances. For example, in Mediterranean climate, summers tend to be very dry, so pollutants accumulate in the dry phase on surfaces. If an intense “summer rain” follows a long period of drought where big amounts of

¹⁰ The peaks in wet deposition became better known under the name „acid rain“ in the 1970s and 1980s.

pollutants were deposited on the surfaces, some of these pollutants will be dissolved and will react with the surface, but most of them will just be washed away before they can cause a reaction (Camuffo 2019). On the other hand, if a long drizzle¹¹ follows the same dry season, much bigger amounts of the accumulated pollutants will be able to react. Hence, the intensity and abundance of rainfall also play a role, not only for the wet but also in the case of the dry deposition. Therefore, Camuffo (2019) proposes the use of precipitation intensity instead of the monthly totals of precipitation to better understand chemical deterioration. This underscores the magnitude of the changes in decay mechanisms that will occur as our climate changes and parameters such as precipitation distribution throughout the year shift.

3.1.2. The case of “acid rain”

The extreme wet deposition of sulphur dioxide on surfaces (not only cultural heritage) is arguably one of the most extensively studied effects of pollution altogether. The so-called “acid rain” was studied in depth in the last 30 years of the 20th century. Next to problems caused to soil, crops and woods (Singh and Agrawal 2008) and to the human well-being (Franklin et al. 1985) the impact on heritage was also discussed (Bernardi et al. 1985; Camuffo et al. 1982; Camuffo, Del Monte and Sabbioni 1983; Charola and Ware 2002). “Acid rain” was one of the most significant global issues, which was addressed through a collaborative effort involving science, politics, and society at large (Levy 1995). In the course of the late twentieth century, as international awareness was rising and first measures were taken, the concentrations of SO₂ in the air slowly but surely could be reduced in Europe. Nevertheless, as a consequence of historically high concentrations of SO₂ in the air, significant amounts of sulphates, particularly gypsum (CaSO₄ x 2H₂O), remain present on and within monuments, forming black surface crusts (Fig. 21-23) or deep sulphation. However, gypsum crusts are gradually disappearing from urban areas, largely due to cleaning efforts (Fig. 21) and the “self-cleaning”¹² of buildings (Milchin and Krist 2020)¹³.

¹¹ The situation is similar or even more intense with condensates such as dew or fog.

¹² The term “self-cleaning” refers to the cleaning of façades through weathering and without human intervention. For example, rainwater can clean stones and render façades free from soot particles over time.

¹³ The paper can be found in the appendix of this thesis.

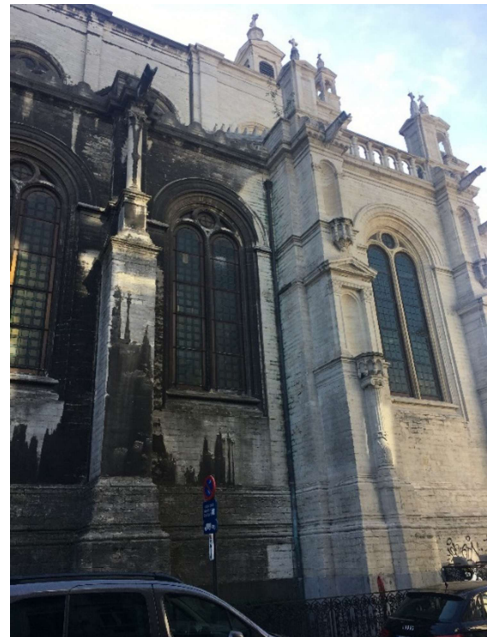


Fig. 21-23: St. Katherina church in Brussels: sulphation crusts (left up and down) and the half-cleaned façade (right)

From today's perspective, the sulphation and the black crusts are a problem of the past, and it is not very probable that the same will reappear in the close future. However, some uncertainty arises from recent discussions regarding the use of **Solar Radiation Modification (SRM)** with injections of SO_2 aerosol in the lower stratosphere in order to minimize the global warming effects (see chapter 1).

3.2. The “karst effect” and surface recession of calcareous stones

If we consider sulphation and gypsum crusts to be problems of the past, the dissolution of calcareous materials by the action of clean rain and with it the surface recession through the so called “karst effect” remains the singular most important chemical decay mechanism that is specific to calcareous materials in the outdoor environment.

The impact of pollutants was already discussed with the example of SO₂ (see chapter 3.1.), but may also occur with other gaseous pollutants. As already mentioned, the dissolution of calcium carbonate is strongly influenced by the pH of water. Therefore, in this case acidic pollutants like the already mentioned SO₂, but also NO_x and CO₂, are of relevance. Since the concentrations of SO₂ will probably further decrease in the future and the concentrations of NO_x will either slowly decrease or stay unchanged, the only gas whose concentration will almost certainly rise in the near and far future is CO₂. The solubility of CO₂ in water is, therefore, crucial for the future dissolution of calcite, as it facilitates the release of H⁺ ions necessary for the dissolution process. Indeed, with increased CO₂ in our atmosphere, not only does global warming intensify, but also the amount of CO₂¹⁴ and, as a result, calcite solved by rain water due to the karst effect increases. Consequently, this leads to higher surface recession of carbonate materials. Looking in detail, it seems crucial to understand the scale of the phenomenon analysed. In a geological timescale, the recession through the karst effect is a significant landscape-building phenomenon. But, monuments and the preservation of cultural assets typically operate in much shorter timescales, often measured in centuries rather than geological epochs. Nonetheless, this does not diminish the importance of the surface recession in heritage preservation, as the surface and the first millimetres underneath it often carry very (if not the most) valuable cultural information (e.g. fine bas-reliefs or inscriptions).

In order to make predictions for the future and to understand the present, modelling can be employed. For this purpose, functions can be established to describe the relationship between different parameters and their effects in a mathematical dependence. Many scholars have established so-called dose-response functions for the surface recession of calcareous materials (Kucera et al. 2007; Lipfert 1989). It is important to emphasise, however, that none of the available dose-response functions is a perfect match for real situations. This is due to the simplifications which have to be made in order to establish usable correlations. As already stated: the surface recession of calcareous stones is the result of at least three parallel mechanisms: the clean rain dissolution (karst effect), the recession due to acid rain and the recession due to dry deposition of pollutants (Bonazza et al. 2009). Frequently, other mechanisms, such as wind erosion, salt crystallisation etc. also play a role. Therefore, numerous parameters are of importance. These can be classified into material-inherent parameters, such as mineral composition, crystallinity, crystal size, shape and internal crystal structure, packing density, porosity, pore size distribution, etc. In addition, monument-related parameters, such as geometry, exposure, and location, as

¹⁴ Henry’s Law states that the amount of dissolved gas in a liquid is directly proportional at equilibrium to its partial pressure above the liquid.

well as environmental factors like temperature and humidity levels, wind, pollutant concentrations, precipitation amounts, intensity, and distribution, are also of great importance. Consequently, it is very hard to produce precise dose-response functions and models. However, general conclusions from the multiple studies can be drawn:

- 1) there is a difference between rural and urban areas, whereas the surface recession tends to be smaller in rural areas, likely due to lower levels of pollution; in these surroundings the karst effect is the only relevant chemical decay mechanism for calcareous stones.
- 2) a difference can be made between compact, low-porosity materials, which tend to lose less material, and porous calcareous materials. In the latter case, mechanical impacts from wind and/or rain appear to play a significant role by removing material that has already been weakened by the dissolution of calcium carbonate.

The impact of different textural features of the lithotypes involved was recently studied (Salvini et al. 2022) and a correction coefficient for different limestones in respect to Carrara marble established. It can be concluded that most limestones exhibit a faster recession through a higher porosity, a finer texture (e.g. micritic calcite) or through the presence of clay minerals.

In the course of the project Noah's Arch one of the addressed decay mechanisms and produced risk maps was dealing with surface recession of dense carbonate stones (Sabbioni, Brimblecombe and Cassar 2012). A study published in the frame of the project (Bonazza et al. 2009) looked into possible future surface recession for Europe. Different existing dose-response functions were compared and it was decided to use the dose-response function published by (Lipfert 1989) (5). It considers all three recession mechanisms and reads as follows:

$$L = 18,8 R + 0,016 [H^+] R + 0,18(VdS[SO_2] + VdN[HNO_3]) \quad (5)$$

where

L = surface recession per year ($\mu\text{m year}^{-1}$);
 18.8 = intercept term based on the solubility of CaCO_3 in equilibrium with 330 ppm CO_2 ($\mu\text{m m}^{-1}$);
 R = precipitation (m year^{-1});
 0.016 = constant valid for precipitation pH in the range 3–5;
 $[H^+]$ = hydrogen ion concentration ($\mu\text{mol l}^{-1}$) evaluated from rain yearly pH;
 0.18 = conversion factor from (cm s^{-1}) ($\mu\text{g m}^{-3}$) to μm ;
 VdS = deposition velocity of SO_2 (cm s^{-1});
 $[SO_2]$ = SO_2 concentration ($\mu\text{g m}^{-3}$);
 VdN = deposition velocity of HNO_3 (cm s^{-1});
 $[HNO_3]$ = HNO_3 concentration ($\mu\text{g m}^{-3}$).

However, in this dose-response function the concentration of CO_2 is assumed to be constant while the concentrations of nitrates and sulphates are represented through variables. Meanwhile, it is a proven fact,

shown in the so-called Keeling curve, that the CO₂ in our atmosphere is constantly rising. Since the 1980s, when the Lipfert dose-response function was proposed, CO₂ in the atmosphere rose from 330ppm to 440ppm, this fact being one of the reasons for the climate change in the first place. The same is shown in the so-called Keeling curve (Fig. 24).

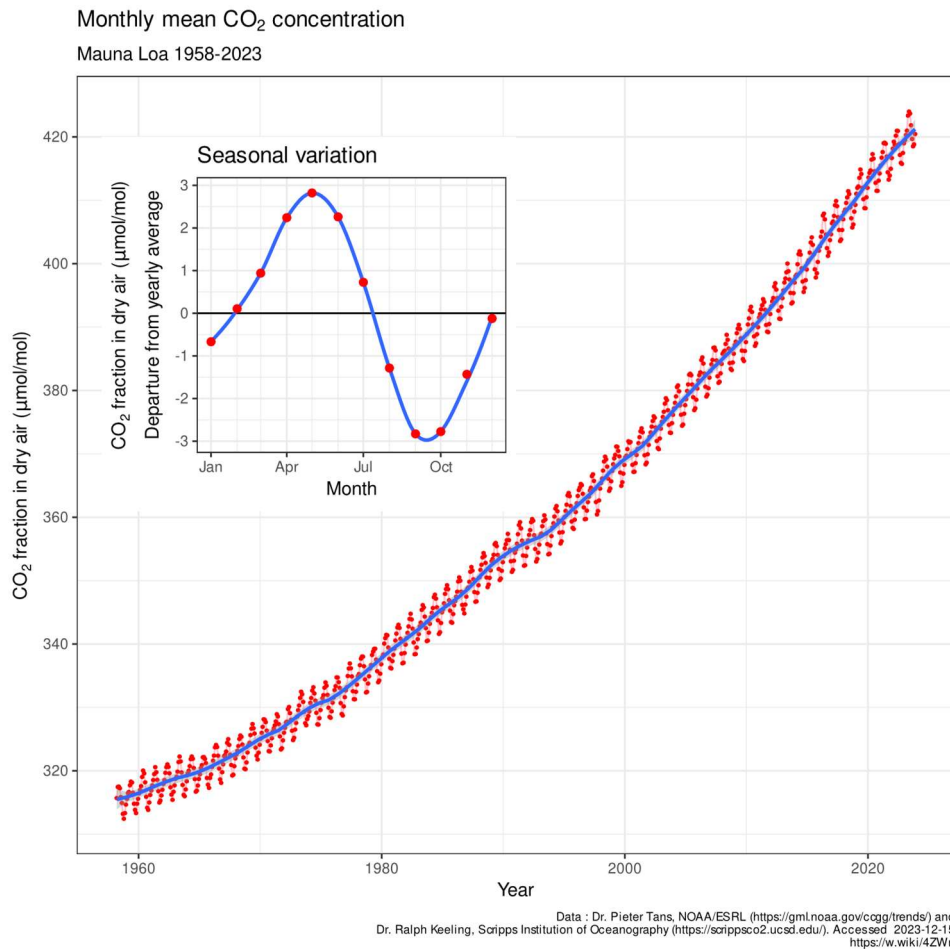


Fig. 24: The Keeling curve shows the rise in CO₂ concentrations, measured at Mauna Loa in the period 1958-2023 (By Oeneis - Own work. Data from Dr. Pieter Tans, NOAA/ESRL and Dr. Ralph Keeling, Scripps Institution of Oceanography., CC BY-SA 4.0, <https://commons.wikimedia.org/w/index.php?curid=40636957>)

There is another problem in Lipfert's dose response function and this is the effect of snow. Lipfert assumed that all precipitation comes in the liquid state only. Therefore, there was a source of error in the dose-response function due to this simplification. It was supposed that the effect of rain (when calculated per litre) is altogether smaller than it is in reality. This is relevant for the future since, due to the climate change and the shift in mean temperature, we should be experiencing more precipitation in form of rain and less in form of snow, therefore the source of error needs to be eliminated. Both of the needed corrections were applied on the Lipfert formula in the research paper mentioned above. After the corrections, the modelling of the surface recession for Europe was conducted for three periods: the baseline period (1961-1990), near future (2010-2039) and far future (2070-2099) (Bonazza et al. 2009).

Summarised as the significance of changes in the research paper one can read:

“The most marked change in recession rates across the period is the general increase throughout Europe, particularly noticeable in high rainfall areas, e.g. mountain areas of central Europe, Scandinavia and Scotland. The change can be of more than $6 \mu\text{m year}^{-1}$ in regions where the recession was around $20 \mu\text{m year}^{-1}$ in 1961-1990, which is a 30% increase.” (Bonazza et al. 2009).

So, it can be argued that through the rising concentrations of CO_2 in the air, the pH of rainwater will decrease¹⁵, allowing for higher solubility of calcium carbonate in the same. Therefore, the surface recession of calcareous materials is expected to increase mostly due to the karst effect. Additionally, the climate change and with it the change in temperature and the distribution of rain and snow throughout the year influence the rate of surface recession. The mean temperature has already risen more than one degree in average compared to pre-industrial levels; for Austria this value is even higher. Since calcium carbonate can only be dissolved in liquid water, the longer the periods above 0°C , the more exposure time at temperatures critical for surface recession due to the karst effect. Furthermore, it is important to note that the solubility of CO_2 in water is inversely proportional to temperature. This means that the highest solubility occurs just above 0°C , resulting in low water pH and, consequently, high solubility of calcareous materials. Coupled with the anticipated rise in atmospheric water during colder seasons, this will lead to an increase in surface recession in both the near and far future. These are, however, only predictions for the future that need to be verified through observation on actual monuments (see chapter 4).

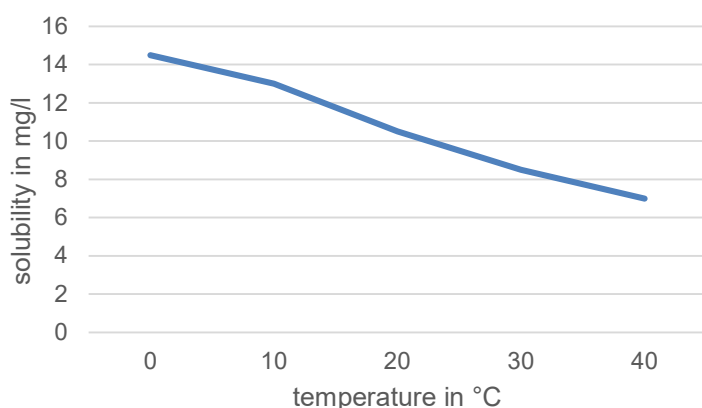


Fig. 25: Diagram showing the dependence of the solubility of calcite in clean water to temperature (after Plummer and Busenberg 1982; IUPAC-NIST Solubility Data Series, Volume 95)

¹⁵ According to Henry's law.

Another possibility is to try to directly measure the surface recession, either on monument surfaces or on exposed stone samples (material sensors). To achieve this, various methods have been employed in the past which will be explained in detail in chapter 4. However, all the methods used, pose different possibilities and challenges, and these will be discussed later on. It is important to note that most published results from both direct measurements and modelling indicate surface recession rates of approximately 0.010 mm/a to 0.030 mm/a for dense calcareous stones (mostly marbles, some dense limestones) (Bonazza et al. 2009). While this may seem like a relatively small value, it is important to consider the timescales typically associated with heritage preservation, which span over centuries. In that sense, calculated over a period of 100 years, surface recession adds up to 1-3 mm, which is significant for many monuments.

Taking the example of a marble sculpture from the Italian Renaissance further illustrates this point. If the sculpture had been continuously exposed to the outdoor environment since its production, it would have experienced a loss of between 5 – 15 mm in exposed surfaces by today. In areas with high pollution levels, or with monuments made of porous limestones, these numbers can even be significantly higher.

An extreme example of a surface recession is shown on figures 26-28. The building of the Austrian Parliament in Vienna, erected in 1883, was refurbished and historical parts conserved and restored in the last decade. For improved access of the crane to the construction site, an approach through the building's roof was employed. For this purpose, the sculptures from the attic were removed for the first time since the building was erected and transported to an atelier, where they could be examined at close range and where conservation work was carried out (Haralter-Tupi, Fuchs and Nimmrichter 2024). The sculptures are made of white marble (most probably different qualities of Carrara); some of the blocks are very impure, containing big quantities of less soluble minerals arranged along sub-parallel layers. These, less soluble components, showed no, or only very little, recession. When compared to the significantly recessed surrounding areas, the loss was striking. Recessions of almost 10 mm were observed. Unfortunately, no analysis of the nature of the less soluble components was conducted at the time. However, it is reasonable to assume that they most likely consist of either dolomite or coarser calcite, both of which have lower solubility. Theoretically, quartz impurities could also be responsible for similar patterns; however, they would not exhibit the previously mentioned layering. Due to the position (inner city) and the exposition of the sculptures (fully exposed on the roof of the building) the effect is surely not solely a result of the “karst effect”, but also “acid rain” and high wind velocities. At the same time, it seems important to add that the sculptures are “only” less than 150 years old.

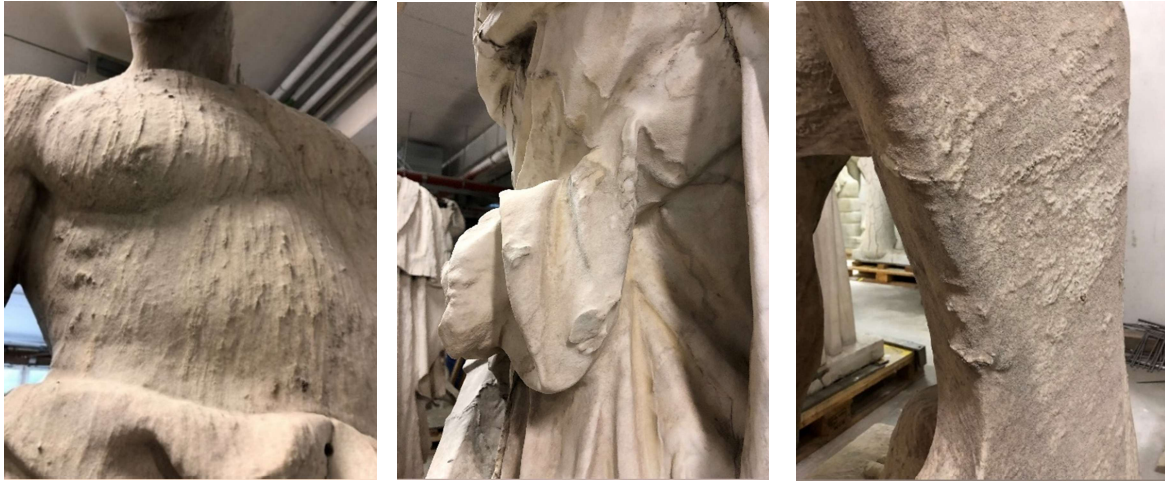


Fig.26-28: extreme surface recession visible due to the presence of less soluble components, marble sculptures from the attic of the building of the Austrian Parliament in Vienna

4. Assessing surface recession of calcareous stones

As indicated in the previous chapter, knowing the exact extent of surface recession, i.e. material loss on monuments, is a challenging task. However, it is essential for understanding the rate of decay and deterioration of heritage surfaces, especially of calcareous stones, and it plays a critical role in supporting preservation decision-making processes. In the context of climate change and evolving conditions affecting heritage, this information has become even more vital.

In the past, scholars employed various methods to assess the loss of material from heritage surfaces. Recession was directly measured on heritage assets by comparing recessed areas to less soluble components, such as the lead lettering on marble grave slabs (Inkpen, Mooers and Carlson 2017) or less soluble minerals in the stone (i.e. dolomite or quartz). Also, methods like micrometre measurements using reference points (Inkpen et al. 2012; Trudgill et al. 2001), comparison of the upper and lower thickness of marble slabs (e.g. gravestone) (Feddema and Meierding 1987) and the collection and analyses of runoff water from monument surfaces (Livingston 2016) were used.

Next to direct measurement on monument surfaces, frequently field exposures of material sensors (sometimes also called material samples, material probes, stone tableaux or dosimeters) are used (Bidner et al. 2002; Kucera et al. 2007; Simon and Snethlage 1996; Weber et al. 1984). Such material sensors are not a new idea in conservation science. The best-known sensors used in the field aim to assess the suitability of materials for the use in museum storages or showcases; these are known as Oddy tests (Green and Thickett 1995). For the test, a set of metal coupons (thin sheets) is exposed in an atmosphere alongside the material being evaluated. Any emerging corrosion indicates the presence of harmful gases. Also, “glass dosimeters”¹⁶ are used in indoor environments, particularly as an early warning system for heritage assets made of glass.

Similarly, in stone conservation, some studies have attempted to use lithic materials to estimate the harmfulness of a particular environment and/or exposure (Bidner et al. 2002) and the response of a certain stone to the same. However, most of these studies have focused on sulphation (Lefevre et al. 2007) or on the combined effects of weathering in general (Bidner et al. 2002). In German speaking countries, the so called “Mank’s carousel” has frequently been used for the exposure; a wind-spinning wheel with small stone slabs (material sensors) mounted on it, exposed in dry or wet conditions enabling more or less homogeneous weathering from all sides (Bidner et al. 2002; Brüggerhoff 2007).

In such cases, gravimetric measurements are frequently employed for the assessment. Sometimes, also runoff water is collected and analysed (Delalieux et al. 2002; Reddy 1988) along with ultrasonic pulse velocity measurements (Bidner et al. 2002) used for the estimation of some decay processes.

¹⁶ by the Fraunhofer Institute founded International Convention Centre for Cultural Heritage Preservation IZKK.

Additionally, tests in controlled environments, in so-called ageing chambers, have also been performed. Artificial weathering of stone specimens, in the 1980s and 1990s mainly focused on the impact of gaseous pollutants, such as SO₂ at elevated relative humidities (Weber et al. 1984).

Many of the existing studies were reviewed in the book “Stone in Architecture” (Siegesmund and Snethlage 2011), Chapter 4: “Weathering and deterioration” (Steiger, Charola and Sterflinger 2011). It is, however, a fact that studies with different methodologies and research designs produce(d) very scattered results for the surface recession of calcareous stones and the same vary from 2 µm/a up to 78 µm/a (Steiger, Charola and Sterflinger 2011). Most of the measurements on actual monuments and on material sensors in field exposures have been conducted on marbles, with fewer studies focusing on limestones. Marbles were predominantly chosen due to their chemical and structural homogeneity and lack of porosity, which simplifies experiments and measurements. However, some of the highest surface recession values have been observed in the few studies performed on porous limestones, such as the Portland limestone (49 µm/a for 1980-1990, London) (Inkpen et al. 2012) or various types of Leithakalk limestone (6,2 mm/100 years or 62 µm/a, Vienna) (Weber 1985).

To account for some of these differences resulting partly from stone morphology, texture, and composition, a study (Salvini et al. 2022) was conducted in a controlled environment where different heritage stones were artificially aged. The surface recession was then compared to a "standard" made of Carrara marble. A coefficient was calculated to determine the correlation between the surface recession of a specific calcareous stone and that of Carrara marble under the same exposure conditions. For example, Portland limestone has a coefficient (Φ) of 1.23 when compared to Carrara marble, meaning it loses almost 25% more material over the same exposure time in the same conditions (Salvini et al. 2022).

Theoretical assumptions, results from tests on heritage assets, field exposures, and measurements in controlled environments are used to develop dose-response functions which describe the process and its dependencies mathematically (e.g. Lipfert 1989). However, it is important to note that the same are always approximations and cannot involve all of the variables impacting the decay processes. It can be noted that the calculated recessions follow the trend of the measured ones, however they always yield much lower results (2,75 – 3,3 times lower) (Inkpen et al. 2012). For the future recession, modelling involving these dose-response functions needs to be employed. Such modelling was conducted in the work of Bonazza et al. (2009), Di Turo et al. (2016), Visone et al. (2025) and others; the results from Bonazza et al. (2009) seem to give the best match to the values gained in direct measurements on monuments and are therefore addressed in this work. However, the available measured recession data is highly heterogeneous. It consists of mean values gained using various measurement methods on diverse monuments, sometimes even obtained from idealised situations in laboratories due to challenges of field exposures. Therefore, these values should be regarded indicative rather than definitive when applied to a specific monument.

The situation of a particular monument, on the other hand, is influenced by various factors, including the specific properties of the material (Salvini et al. 2022), the monument's form and position, orientation, exposure, and the prevailing climatic conditions, including microclimatic effects. The need for conservation response depends on the specific circumstances of each monument. Therefore, for asset-focused decision-making regarding possible and/or necessary conservation measures, only the material response — or, in this case, the rate of surface recession — is relevant, rather than the dose (climatic parameters, pollution etc.), which can rarely be altered. Consequently, the approach presented in the following text focuses on understanding the material response, regardless of the manifold causes underlying it.

4.1. The development of a protocol for the use of material sensors

In this work, material sensors emerged as the most feasible method for gathering information on the rate of decay, in specific the material loss leading to surface recession for a specific monument or heritage asset. The aim is to use different lithic materials and/or surface morphologies to better understand the specifics of decay and deterioration of a particular exposure, through field exposure in the proximity of the asset.

For the exposure protocol, various existing protocols from past studies were consulted, most of which focused on the impact of different pollutants on heritage stones (e.g. Weber et al. 1984; Bidner et al. 2002; Lefevre et al. 2007; Moroni, Pitzurra and Poli 2004; Simon and Snethlage 1996). The development of the protocol involved several tests and trials, the results of which will be presented in a chronological order in the following sections.

4.2. Preliminary tests

In view of the above outlined need of sensors to monitor the recession rates of calcareous monument surfaces, a protocol was developed in several steps. The various stages of this study were published in a number of papers (see Appendix) and shall be synthesised and discussed below.

At the beginning of the research, preliminary tests were conducted in a controlled environment in the laboratory to better understand the possibilities given by the use of material sensors in field exposure. The idea was to use material sensors in field exposure and, by analysing the same pieces before and after a certain time of exposure to the atmosphere, to assess the dimension and rate of weathering, specifically with focus on the surface recession of calcareous stones.

For this reason, various stone materials, surface morphologies (surface preparation), and sensor designs were tested. Simultaneously, scientific investigation methods were evaluated for their potential in providing reliable results in both qualitative and quantitative analysis for surface recession. The focus was laid on simple and cost-effective analytical methods like gloss, colour and gravimetric measurements,

but more elaborate methods like light microscopy and digital 3D microscopy were also applied and used to gain a deeper understanding of the occurring processes.

The first set of tests was focusing on hand-polished sensors made of alabaster (Volterra, Italy), moderately porous limestone (Vratsa, Bulgaria), and marble (Carrara, Italy). The limestone and the marble were chosen as calcareous stones due to their relatively homogeneous composition, structure, and moderate-to-low porosity, as well as their availability (both were readily available). The decision for Carrara marble was also backed by the numerous studies conducted on this material in the past. This places the results from the recent research in context with already existing studies. Alabaster, which primarily consists of fine-grained gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, was included because of its higher solubility in water¹⁷. It was presumed that sensors made of alabaster could act as highly sensitive indicators in situations where the time frame for field exposure is limited or where a low dose of atmospheric impact is expected.

Table 1: Some properties of the stones used for the sensors

stone	origin	raw density	porosity	water absorption	composition calcite %	composition gypsum %
alabaster ¹⁸	Volterra, Italy	2300 kg/m ³	0.15%	0.20%	-	96-99%
limestone ¹⁹	Vratsa, Bulgaria	2370 kg/m ³	12.22%	3.15%	93%	-
marble ²⁰	Carrara, Italy	2700 kg/m ³	0.4%	0.11%	98%	-

A first set of samples was exposed to 100% relative humidity (rH) in a desiccator containing a vessel with water placed under the samples for a period of 28 days. A second set was submerged in water for defined periods of time (from 2 hours up to 4 days). The goal was to assess the general suitability of the chosen stones, evaluate possible surface preparations, and test different analytical methods in preparation for the planned field exposure. It can be concluded that the chosen lithotypes were suitable for an outdoor exposure and the use of a polished surface allows for easy tracking of surface changes through dissolution. In figures 29 and 30, changes in the surface of an alabaster sample after exposure to 100% relative humidity (rH) can be observed under an optical microscope²¹. After four weeks of exposure, grain boundaries became visible, and imperfections (such as scratches) from the hand-polishing that were not previously noticeable became more apparent²². These imperfections may interfere with further observations; therefore, better surface preparation could be beneficial for the future.

¹⁷ The solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is 2.6 g/L at 25 °C, whereas the solubility of CaCO_3 is 0.013 g/L at 25 °C which is a difference with a factor of 200

¹⁸ The information is extracted from <https://www.stonecontact.com/p/alabastro-di-volterra/>

¹⁹ The information is extracted from <https://lazarovmarble.com/products/vratsa-limestone/>

²⁰ The information is extracted from <https://acemarstone.com/marble/carrara-bianco-cd/> and <https://www.byblostone.com/uk/marble/carrara-white.asp>

²¹ Olympus BX 40

²² It is not entirely clear why the imperfections in the polish only become visible after the exposure to 100% rH, but it can be assumed that very thin micro scratches were present from the start, and the same grew through dissolution and became visible after the exposure.

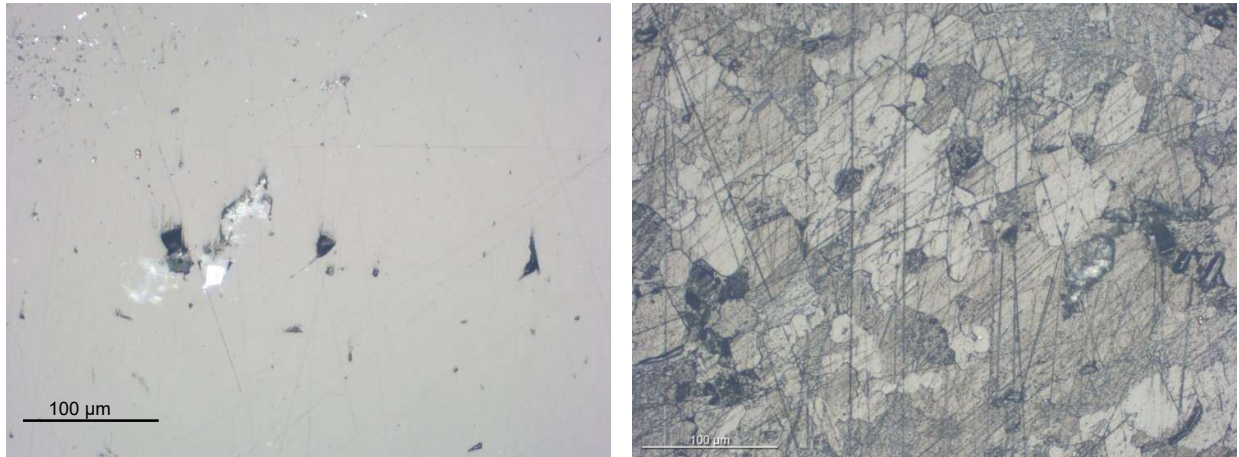


Fig. 29 and 30: alabaster sensor (hand polished) before (left) and after 4 weeks of exposure to 100% rH (right) in the lab (bright-field microscopy showing the same spot on the sensor). Grain boundaries and imperfections in the surface polish become visible.

4.2.1. First field exposure

In the first field exposure, the experience from the preliminary tests was used for the exposure design (Protocol A).

Exposure Protocol A:

- Limestone from Vratsa, Carrara marble and three different types of alabaster (in terms of transparency and colour) were used for the sensors.²³
- The size of the sensors was 4 x 4 x 1 cm.
- The sensors were hand-polished using different grained sand paper and lapping film, with the lateral sides and the back side coated with a silicone resin paint to confine any surface recession to the front.
- The prepared sensors were exposed on a rack with a reclining angle of 45°.
- Before exposure, the sensors were weighed by an analytical scale and the gloss was measured²⁴ at 20°, 60° and 85° (at least 3 measurements per sensor in different directions).
- After a period of 3 and 6 months, the sensors were removed from the rack.
- After a drying period (until constant weight was achieved) on room temperature (or in a drying cabinet at not more than 60°C to remove any rest humidity), the samples were weighed and the surface gloss measured as described above.

²³ The use of three different alabaster types is explained by concerns regarding the translucence of the alabaster and possible problems arising with the analyses in the digital microscope. Therefore, alabaster types with different optical properties were trailed.

²⁴ BYK®, micro-TRI-gloss

- In the 3D microscope²⁵ the surface topologies were analysed.
- To better understand the observed phenomena, analyses in the optical microscope²⁶ were used.

The samples were placed on an exposure rack, in a rural area in Sattelbach²⁷, Lower Austria, facing northwest (Fig.31), for defined periods of time (three and six months).



Fig. 31: first exposure of material sensors on a rack in Sattelbach, Lower Austria

The results of the first trials are described in Milchin, Weber and Krist (2023). Here, only a short overview will be given.

The gloss measurements revealed a significant drop in the gloss values for all stones and all angles of illumination (20°, 60° and 85°) even after the exposure period of only three months (26 – 97%), making the gloss measurement a promising testing method for the initial surface recession. However, the changes in surface gloss flattened with alabaster sensors with increasing exposure time, as the surface recession produced a matt surface and the gloss approached 0 GU (gloss units).

All sensors showed some weight reduction. Due to the higher solubility, the weight reduction was more relevant with the alabaster sensors than with the marble and the limestone sensors. However, it can be expected that gravimetrical analyses will become more relevant with longer exposures also for the carbonate lithotypes. 3D microscopy proved to be of interest, because the development of a relief on the surfaces can be quantitatively measured and graphically visualised (Fig. 32 and 33).

²⁵ Kayence, VHX-7000

²⁶ Olympus BX 40

²⁷ GPS: 48.031389°, 16.141944°

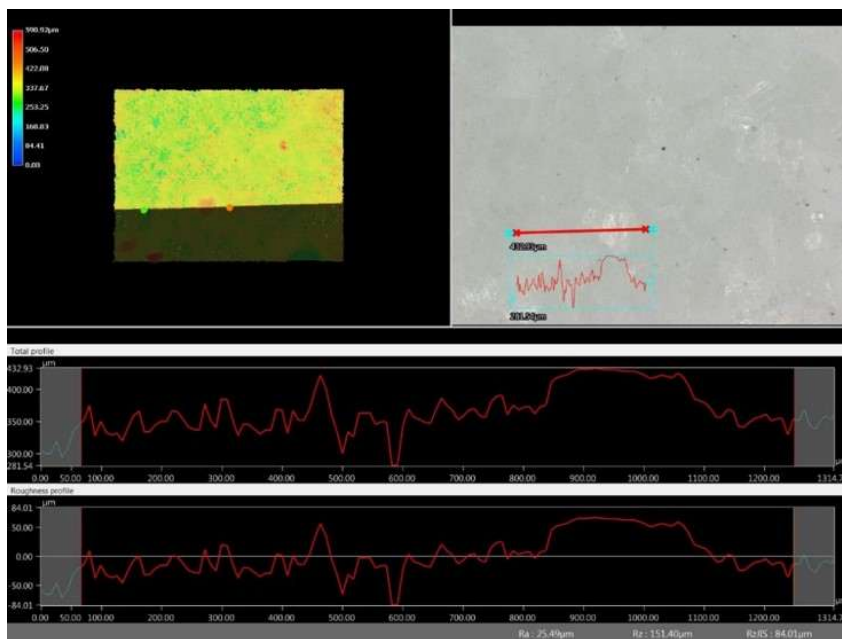
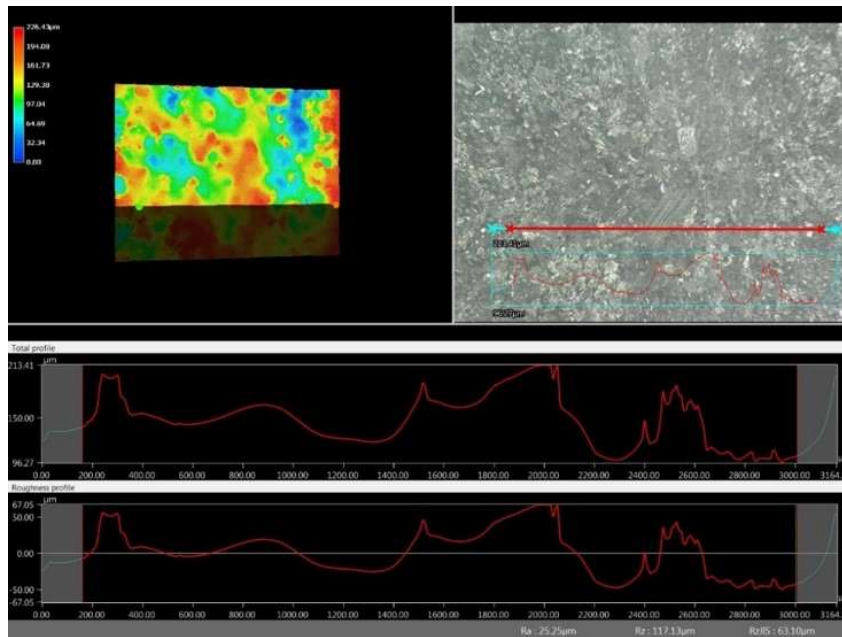


Fig. 32 and 33: In the digital 3D-microscope the surface roughness and therefore the recession can be assessed indirectly using the line roughness function; the alabaster (up) shows a much stronger surface profile than marble (down) in the same period of time (three months of exposure).

Based on this first exposure, the following conclusions regarding the exposure protocol were yielded: the paint used as a sealant for the lateral and back sides was not stable enough against weathering (peeling), indicating that a different isolation material needs to be found. The 45° exposure angle proved effective and should be maintained. The hand polish yielded acceptable results, a higher initial gloss level would likely be beneficial. Therefore, for the following exposures a high-quality polish as used for microscopic sections and produced by a machine should be used. All three types of alabaster showed comparable results, meaning they can be used for sensors regardless of their optical properties. Therefore, only one

type of alabaster (Alabastro Volterra Bianco) was used in subsequent exposure tests. The limestone exhibited similar surface recession rates as the marble. Gravimetric measurements are more relevant for alabaster than for calcareous stones, at least in combination with exposure times under one year. Gloss measurements were more pertinent for marble and limestone than for alabaster. Digital 3D microscopy proved valuable for all sensors, though it requires some experience in the operation to yield meaningful results. Because direct comparison of protected and weathered areas is expected to provide useful insights for the next set of sensors, a portion of the front surface should be covered to protect it from weathering. Optical microscopy proved helpful for better understanding of weathering phenomena in detail.

4.2.2. Second field exposure

Bearing the results from the first field exposure in mind, the protocol B was developed and used for the second field exposure:

Exposure Protocol B:

- | |
|--|
| <ul style="list-style-type: none"> - White alabaster from Volterra and Carrara marble were used for sensors. - The size of the sensors was 4 x 4 x 1 cm. - The surface of the sensors was polished uniformly by using a fully mechanical polishing device in a professional laboratory. The sensors were glued to a glass tile on their back side. All four lateral sides were sealed with an aluminium tape²⁸. The uppermost 1 cm of the sensor was also covered with the same aluminium tape (Fig.34). - The prepared sensors were exposed on a rack with a reclining angle of 45° facing the main wind and rain direction. - Before exposure, the sensors were weighed and the gloss measured at 20°, 60° and 85° (at least 3 measurements per sensor in different directions)²⁹. - After a defined amount of time (1, 2, 7, 9 and 10 months), the sensors were removed from the rack. - The aluminium tape was removed mechanically (peeled off), any glue residues removed with acetone; attention was paid not to harm the surface in the process. - After a drying period (until constant weight) on room temperature (or in the drying cabinet at a maximum of 60°C to remove any residual humidity) the samples were weighed and the surface gloss measured as described above. |
|--|

²⁸ tesa® Aluminium Tape, is a tape from aluminium foil (100 µm) with acrylate as glue, suitable for repairs indoors and outdoors (stable in temperature range of -40°C until +160°C).

²⁹ BYK®, micro-TRI-gloss

- In 3D microscope³⁰ the surface topology was analysed.
- To better understand the observed phenomena, analyses in the optical microscope³¹ were used. Reflective light at bright-field proved to be a useful mode of illumination. For further understanding of the decay mechanisms, thin sections from chosen sensors were produced and analysed in the case of this trial exposure.

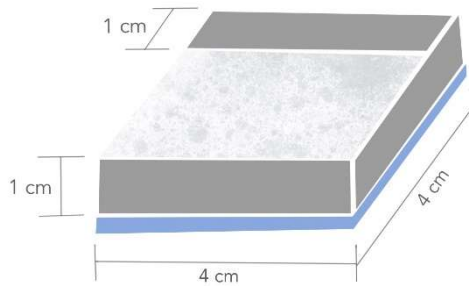


Fig 34: Design of the material sensors for the second field exposure (blue-glass, grey-aluminium tape, white/grey-polished stone surface), Protocol B (© Ilija Milchin)

The second set of sensors was exposed from April 2023 until February 2024 according to the aforementioned Protocol B. The majority of the relevant results are published and can be found in detail in the appendix of this thesis (Milchin, Weber and Krist 2024). Here, only a brief summary is given.

The results showed that the gravimetrical differences are, as expected, more relevant for the alabaster than for the marble samples. While the alabaster samples showed a loss of more than 1 g (max. of 1.14 g or 3.28 w%) over a surface of approx. 12 cm² in 10 months, for the marble samples a maximum loss of only 0.03 g (or 0.07w%) for the same surface and period of time could be measured. However, gravimetric measurements for the marble sensors are expected to become more relevant for longer exposure periods (i.e. several years). The gloss measurements yielded useful results within the first months of exposure for both alabaster and marble. After the full exposure period, all results from the gloss measurements were subjected to statistical analysis³² (Milchin, Weber and Krist 2024) to evaluate their significance individually and in relation to each other, considering different exposure times. The loss of gloss of alabaster samples occurred so rapidly that after two months only few gloss units remained, making any later measurement unreliable, and giving no further information on decay. However, alabaster may prove useful for rapid-sensors or for indoor or sheltered exposure, particularly for assessing the impact of condensate on stone surfaces. Due to the importance of processes caused by humidity and condensation this topic needs further investigation in the future. The statistical analysis of the results for marble, both as single sample (Table 2) and when paired with different exposure times, gave significant results. One of the least significant combinations was the gloss measured at 60° before (M=104.87;

³⁰ Kayence, VHX-7000

³¹ Olympus BX 40

³² Many thanks to Jana Korunovska who analysed the statistical data.

SD=1.55) and after one month of exposure (M=75.67; SD=1.76). However, even here, a high level of significance was achieved ($t(2)=12.34$; $p<0,01$; Cohen's $d=4.07$), thus demonstrating the compatibility of marble sensors with gloss measurements for the exposure.

Table 2: Gloss measurements (60°), marble sensors exposed in Sattelbach, Lower Austria

	N	Gloss in GU, Mean	Std. Deviation	Std. Error Mean
before exposure	15	104.67	1.55	0.40
1 month exposure	3	75.67	1.76	1.02
2 months exposure	3	58.17	1.74	1.00
7 months exposure	3	51.90	1.93	1.11
9 months exposure	3	35.60	5.39	3.11
10 months exposure	3	33.87	0.97	0.56

The results (Table 2) exhibit greater consistency and demonstrate greater potential with marble than with alabaster, revealing a gradual decrease in gloss values. The measurement of the gloss at 60° angle appears to be the best choice since the expected values cover a wide range of gloss units (0 - 120 GU). In addition, some gloss meters measure only at a 60° angle, making it a practical minimum requirement for all measurements to ensure better accessibility.

When plotted in a diagram (Fig. 35), the results suggest a seasonal dependence. The sensors were exposed from April (M0) to February (M10). The diagram clearly shows that the greatest reduction in gloss occurred in spring, late autumn, and winter, while there was almost no change during the summer months and early autumn. This trend correlates with the colder months and more intense rainfall events. While this observation appears logical, it warrants further investigation in the coming years.

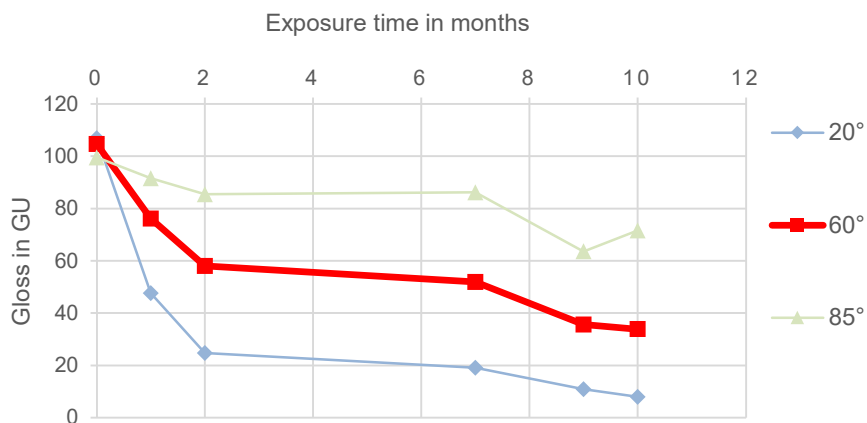


Fig. 35.: Gloss loss in GU, marble samples (20°, 60° and 85°)

The results suggest that similar measurements could also be beneficial for longer exposures (i.e. several years) and are both easy and cost-effective to employ. It can also be anticipated that the same measurements will be reliable for compact limestones. However, further exposures and measurements are necessary to establish a correlation between the decrease in gloss and the rate of surface recession.

Differences in the surface relief between the protected and exposed areas were examined by different methods of microscopy. Using a 3D microscope, line roughness was measured; i.e. for the 10-months exposed marble, the protected areas exhibited very low roughness values: $R_a=0.06\mu\text{m}$, $R_z=0.42\mu\text{m}$ (Fig. 36), whereas the exposed areas showed much higher roughness: $R_a=5.50\mu\text{m}$, $R_z=30.94\mu\text{m}$ (Fig. 37).

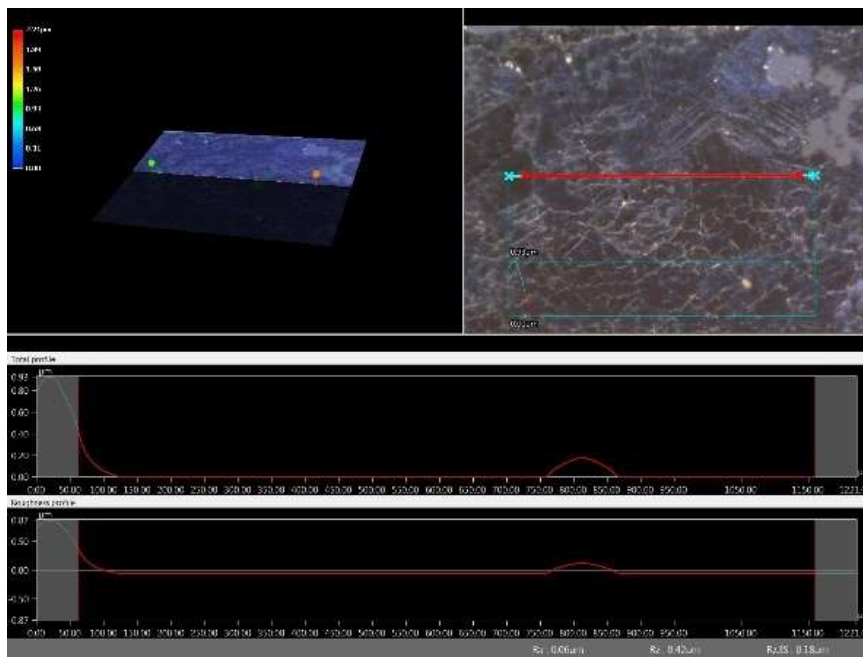


Fig. 36: roughness measurement, MV- 10-months exposed marble sensor, protected area (aluminium tape)

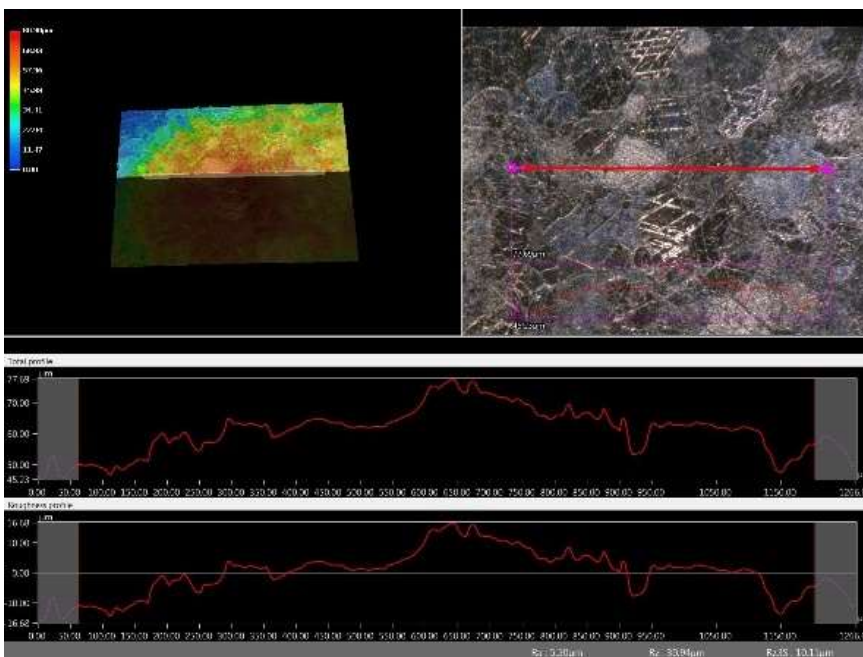


Fig. 37: roughness measurement, MV- 10-months exposed marble sensor: exposed area

In order to better understand how the roughness of the sample surface is developed, transversal thin sections were prepared from the weathered sensors and analysed under transmitted light. For the marble sample exposed for 10 months, it can be concluded that, as expected, initial dissolution patterns are observed along the crystal grain boundaries as well as on some cleavage surfaces (Fig.38 and 39).

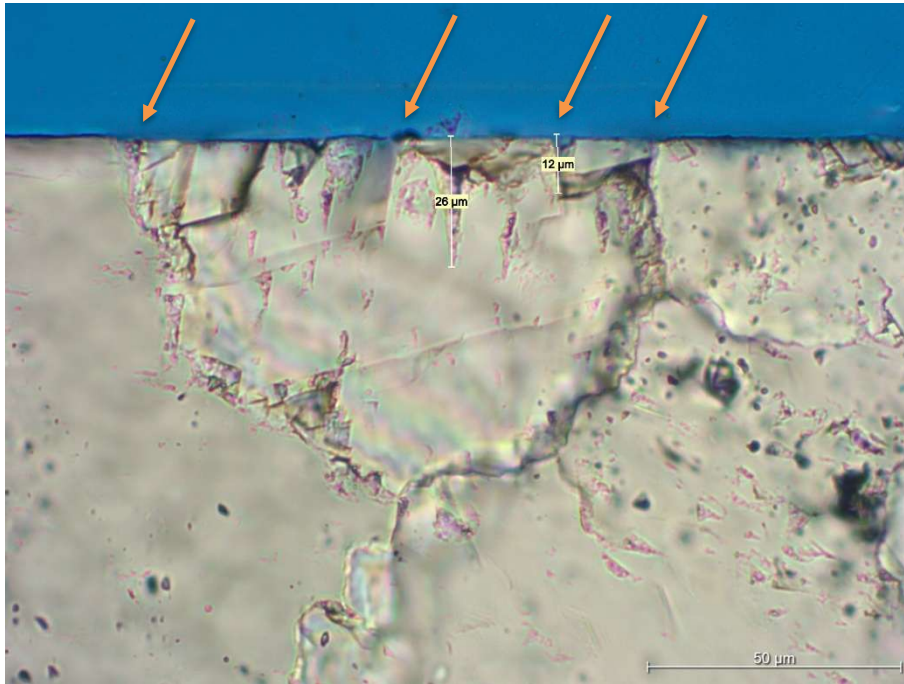


Fig. 38: orange arrows are showing beginning dissolution and therefore surface recession on grain boundaries and cleavage surfaces (transversal thin section from MV- 10-months exposed marble sensor, OlympusBX40, transmitted light, x50)

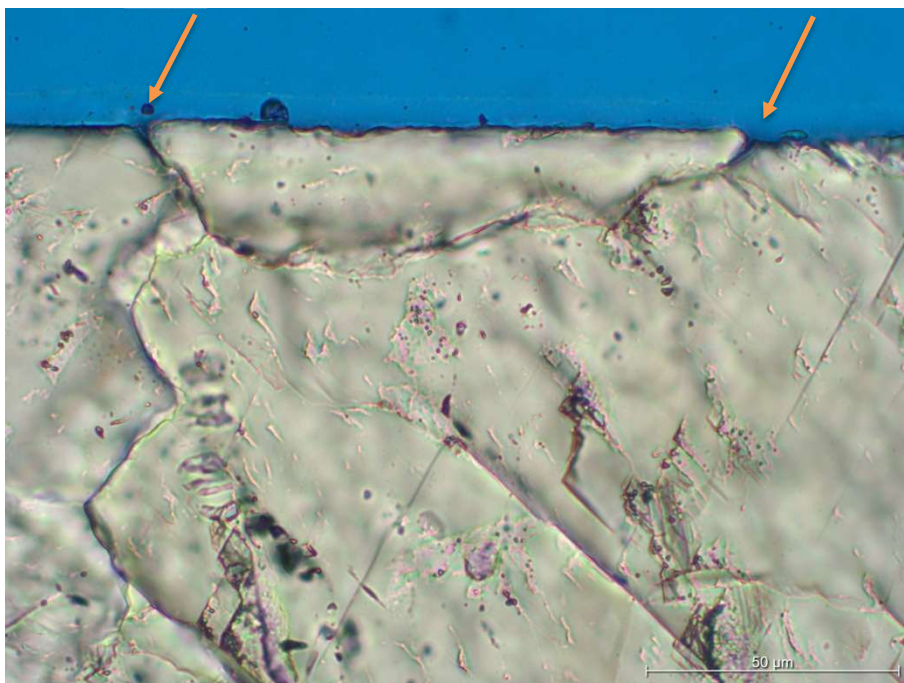


Fig 39: orange arrows are showing beginning dissolution and therefore surface recession on grain boundaries (transversal thin section from MV- 10-months exposed marble sensor, OlympusBX40, transmitted light, x50)

By directly comparing the protected and unprotected surfaces, surface recession can be assessed using the line roughness measurement mode of a digital microscope (Fig. 40). As expected, the alabaster samples exhibit a higher rate of surface recession compared to the marble samples. Fig. 40: surface profile, protected area, wash out and exposed area, AV (10-months exposed alabaster sensor)

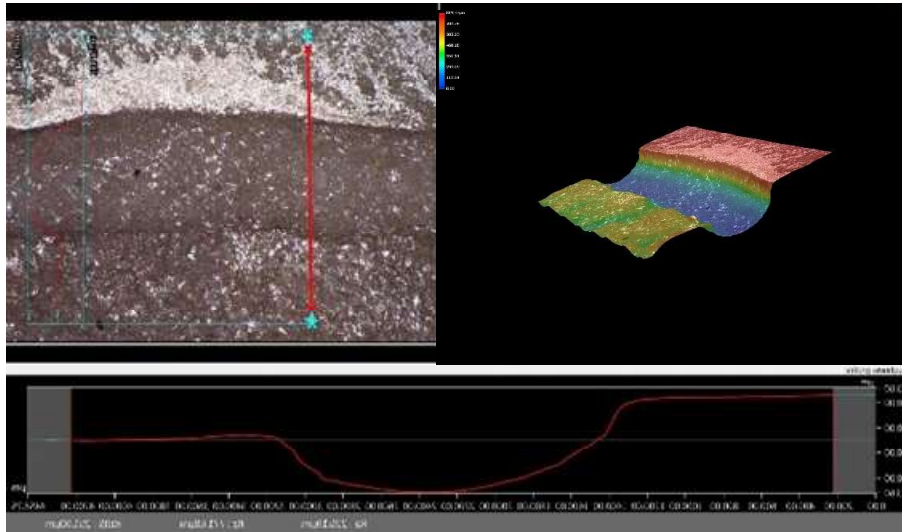


Fig. 40: 3D relief of the surface of AV (10-months exposed alabaster sensor), protected area, wash out (in blue colour), exposed area (yellow) and protected area (red)

Figure 40 depicts the analysis of the alabaster sensor after ten months of exposure. The washout along the border between the protected and exposed areas is noticeable in the blue region. As evident from the profile in Figure 40, subtracting this effect is relatively straightforward, facilitating the calculation of surface recession. In this case, the surface recession for the alabaster over ten months exposure amounts to approximately 360 μm .

The analysis of thin sections in transmitted light allows for a better understanding of the processes leading to surface recession. It is evident that, also in the case of alabaster, dissolution is the main mechanism causing material loss, as shown in Figures 41 and 42.

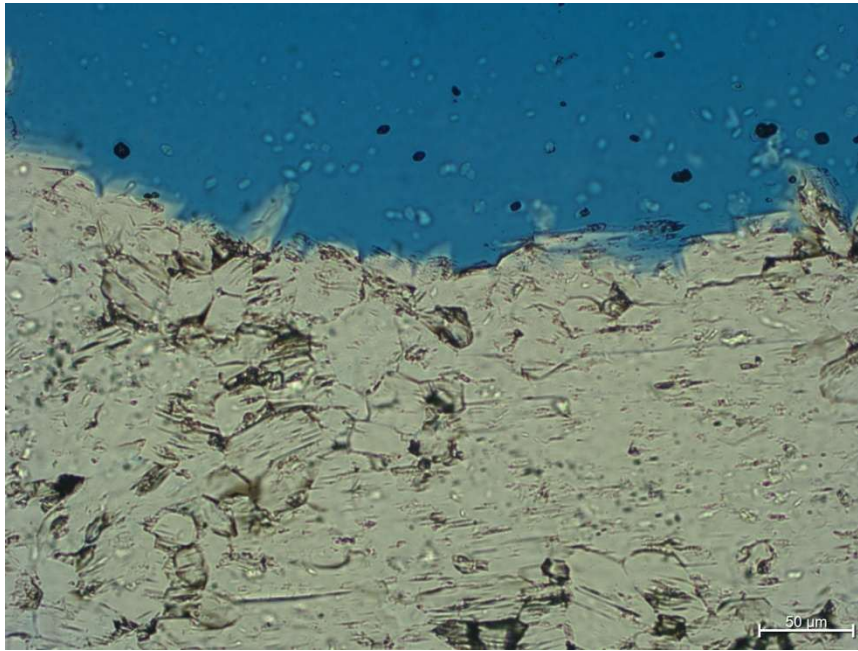


Fig. 41: uneven surface caused by the dissolution of alabaster (transversal thin section from AV- 10-months exposed alabaster sensor, OlympusBX40, transmitted light, x20)

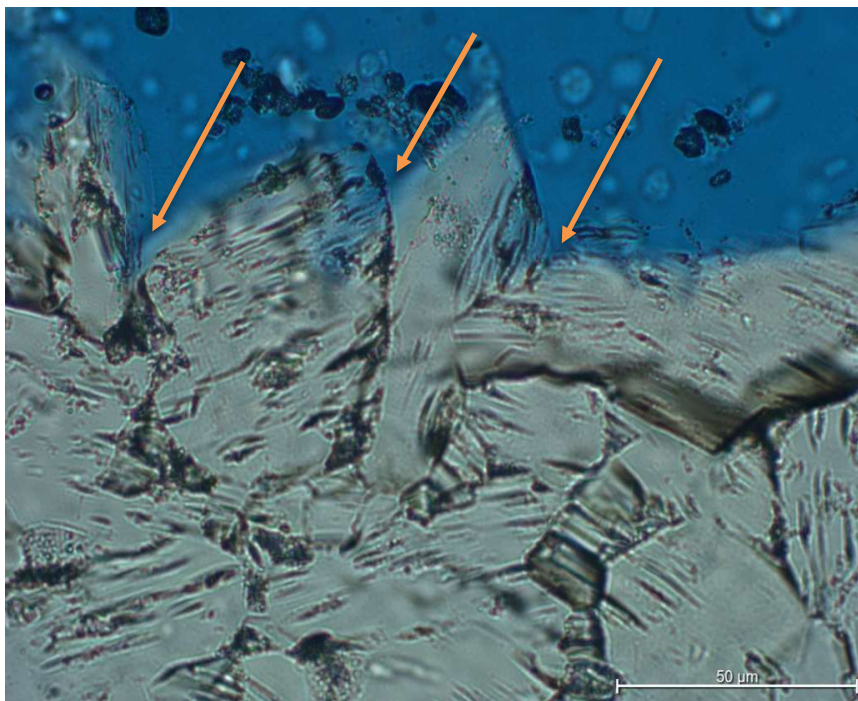


Fig. 42: orange arrows show the main dissolution / surface recession spots, on grain boundaries (transversal thin section from AV- 10-months exposed alabaster sensor, OlympusBX40, transmitted light, x40)

Based on the results of the exposure, it can be concluded that combining Carrara marble sensor with the original stone material of the monument is expected to yield the most favourable outcomes for calcareous stones. Alabaster can be excluded from the outdoor exposure tests due to the prompt loss of material, making it reliable only for the first few months of the exposure. However, it may be of interest in the future as a sensor for indoor or sheltered environments or for applications where exposure time is very limited, due to its higher solubility. This has to further be studied in the future. The use of highly polished surfaces for the sensors proved to be the best possibility for the measurement of surface recession. Additionally, using a sensor with a rougher surface preparation (e.g. bush-hammered) may be of interest when aiming

to detect soiling and/or biocolonisation simultaneously. However, in such cases, a different set of analytical methods must be employed, as gravimetric analysis, gloss measurements, and surface roughness are unlikely to produce meaningful results. Bush-hammered surfaces will likely require visual inspection, both at the macro and microscopic level. The exposure angle of 45° is to be kept, the rack should be facing the main wind and rain direction if there are no other indications (e.g. predominant direction of the monument itself). For the gloss measurements, it proved sufficient to use the 60° angle only. The gravimetrical measurements and digital microscopy remain important analytical methods for the assessment of the recession. For the analyses in the digital 3D microscope, it is useful to cover parts of the surface during the exposure (e.g., the uppermost centimetre) and in some cases additionally to coat a part of the sample with carbon before the analysis, as used for non-conductive materials when investigated in the scanning electron microscope (SEM). Especially for crystalline carbonate stones, such as marble, this helps avoid errors due to the suppression of the reflectance of partially transparent crystals in incident light. For best results, line surface roughness can be measured across both (formally) protected and unprotected areas. Here, the effect of the extreme wash-out on the border between protected and unprotected should be deduced from the results. Additionally, especially for coloured stones, colour measurements might be of interest for future investigations.

4.2.3. Third field exposure programme in the frame of the STECCI Project

Through the information gained from the first and the second trial, the design of the sensor, the exposure and the analytical methods employed could be further clarified and the protocol modified. These results led to the development of the Protocol C:

Exposure Protocol C:

- The stone of the monument concerned and Carrara marble as reference material are used for the sensors. If relevant, also further lithotypes can be used as reference materials (in the case of STECCI a reference limestone is also used³³).
- The size of the sensors is 5 x 4 x 1 cm (this leaves a 4 x 4 cm surface for the exposure while a 1 x 4 cm strip on the surface is sheltered for a direct comparison).
- The surfaces of the polished sensors are produced using standard microscopic polishing techniques. The sensors are glued to a glass plate on their backside. The surfaces of the “rough” sensors are bush-hammered using a small pneumatic bush hammer. All four lateral sides, as well

³³ In the STECCI Project, the impact of climate change on the so-called *stećci* (medieval tombstones in the Balkans) is being investigated. To better understand the varying conditions across different necropolises, material sensors are used. Since locally sourced stone is always employed for the sensors, it was also decided to include a common reference stone on all exposure racks in order to assess the differences in exposure under comparable conditions.

as the backside of the bush-hammered sensors, are sealed with aluminium tape³⁴. The top 1 cm of the sensor, is shielded with the same aluminium tape.

- The prepared sensors are exposed on a rack with a reclining angle of 45°, and facing the main wind and rain direction (unless there are other indications e.g., predominant direction of the monument itself).
- Before exposure, the sensors are weighed (with and without aluminium tape) and the gloss is measured at 60° (at least 3 measurements per sensor in different directions).
- Additionally, where necessary, colour measurements can be conducted (as is the case with STECCI).
- After a defined amount of time (e.g. 3, 6 or in this case 12 and 24 months) the sensors are removed from the rack.
- The aluminium tape is removed mechanically; any glue residues are removed with acetone; attention needs to be paid not to harm the surface in the process.
- After a drying period on room temperature (or in a drying cabinet at a maximum of 60°C until weight balance) the samples are weighed and the surface gloss (and colour) measured as described above.
- In 3D microscope³⁵ the surface topology is analysed. For best results, line surface roughness is measured across both (formally) protected and unprotected areas. For some stones (e.g. marble), it is useful to sputter a part of the sample with carbon, as used for SEM³⁶. The effect of an extreme wash-out on the border between protected and unprotected areas is deduced from the results.
- To better understand the observed phenomena, analyses in the optical microscope³⁷ and other analytical methods can be used.

Protocol C was implemented for the exposure racks which are used in the frame of the HORIZON Europe project STECCI - STone monument Ensembles and the Climate Change Impact (Project Nr.: 101094822)³⁸.

The project looks into the impact of climate change on limestone monuments across Europe with focus on so-called stećci³⁹. It combines approaches from heritage and life sciences, practical conservation, digitisation, and the humanities to provide a holistic understanding of the medieval tombstones (stećci) and the challenges associated with their preservation. As part of **Work Package 3, Task 3.4.**(WP3, T3.4)

³⁴ tesa® Aluminium Tape, is a tape from aluminium foil (100 µm) with acrylate as glue, suitable for repairs indoors and outdoors (stable in temperature range of -40°C until +160°C).

³⁵ Kayence, VHX-7000

³⁶ this helps avoid errors due to the suppression of the reflectance of partially transparent crystals in incident light.

³⁷ In this case Olympus BX 40

³⁸ <https://steccihorizoneu.com/>

³⁹ Medieval tombstones on the territory of Bosnia and Herzegovina, Croatia, Montenegro and Serbia.

exposure racks using the methodology and the protocol developed in this thesis are used on 11 sites⁴⁰ in 8 countries across the continent. The racks carry two sets of sensors which are exposed for 12 and 24 months respectively (Fig. 43). Every set carries five sensors made of three different lithotypes (local limestone, reference limestone and Carrara marble). Three sensors have polished surfaces and two have bush-hammered surfaces. As pointed out earlier, the idea is to use the polished sensors for the assessment of the surface recession and the bush-hammered surfaces for the assessment of soiling and micro-biological colonisation. In each set, two of the sensors are made from the local stone (the stone from which the monuments are made), one polished and one bush-hammered. Two sensors, a polished and a bush-hammered, are made of a reference limestone, a fairly pure and homogeneous reference limestone, coming from the island of Brač in Croatia (variety Veselje Unito). Finally, one polished sensor is made of white Carrara marble from Italy. The last sensor should help understand possible differences emerging between limestone and marble and to contextualise the results in the already existing literature on weathering of calcareous stones, often regarding Carrara marble (e.g. different publications from the EURO CARE-EUROMARBLE Project).

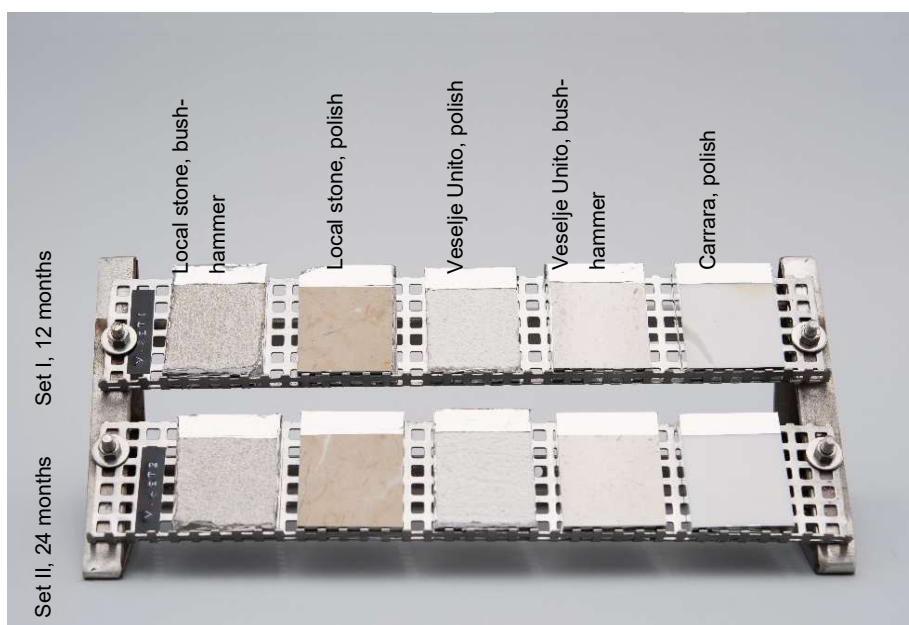


Fig. 43: Exposure rack configuration as used for the STECCI Project (© Christoff Schleßmann, modified by Marija Milchin)

⁴⁰ Hundskirche (AT), Unsleben (DE), Rabat (MT), Caen (FR), Perućac (SRB), Žabljak (MNE), Kopošići (B&H), Križevici (B&H), Dugo Polje (B&H), Split (HR) and Cista Velika (HR)



Fig. 44 and 45: The exposure racks for the STECCI project: four racks prepared for the installation (left) and the first installed rack (07.24) on the site of Kopošići in Bosnia and Herzegovina (right)

The use of the material sensors in the frame of the STECCI Project gives a chance to check their suitability on a larger scale and in different exposures and climatic conditions. It offers the possibility for exposure in eight different European countries⁴¹ and different climates (Temperate: Cfa, Cfb and Csa and Continental: Dfb) (Drešković et al. 2025). As previously noted, two sensor sets are exposed at each site within the framework of the project. The first set is collected and analysed after 12 months of exposure, the second after 24 months. Consequently, the final results and the comprehensive interpretation of the exposure campaign are expected in 2027. Publication of these findings is planned.

However, for this type of material sensor to become readily usable in the future, many more comparable exposures must be conducted. In this way, a large dataset can be accumulated and analysed. With each conservation decision and new piece of information, the data grid will become more comprehensive, providing a more contextualised understanding of the results obtained from future exposures. To achieve recognition similar to the Oddy tests, it is essential that many professionals use the sensors, publish their findings, and identify any possible issues with the proposed protocol.

The sensors provide information only on the rate of surface recession of an object during the exposure period. The underlying idea is that, when it is uncertain whether a monument requires conservation treatment or protective measures — or when the rate of decay cannot be inferred from existing archival documentation — a set of sensors exposed for a defined period (e.g. one year) can help clarify the need and urgency of the same.

Because the sensors are intended to provide information for a specific monument in a specific setting, they are not designed to assess the “dose”, be that pollutant or other environmental parameters, but rather to measure the material response of the stone from which the monument is made. Accordingly, the

⁴¹ Austria, Bosnia & Herzegovina, Croatia, Germany, France, Malta, Montenegro and Serbia

sensors can operate independently and do not necessarily require concurrent climatic or environmental monitoring. Nevertheless, when such data are available, they can and should be used to further contextualise the results.

The information obtained from the sensors must be considered alongside the monument's history, information from archives, past condition assessments, and any available environmental data. Resources and relevant stakeholders involved in the monument's care and preservation are fundamental and must be taken into account. These factors are essential for decision-making regarding potential conservation measures, whether preventive or interventive. The following chapter discusses and evaluates the existing options for conservation measures.

5. Conservation measures for the protection of outdoor stones

The future presents new challenges in the preservation of outdoor stone materials. Patterns of decay and mechanisms of deterioration are expected to change and diversify, particularly in outdoor environments. In the previous chapters, the evolving conditions affecting limestone monuments exposed outdoors were discussed. The difficulties in understanding the pace and frequency of these changes were addressed. One of the most significant issues — the challenge of determining the rate of surface recession — was examined, and a potential method for its assessment was proposed. However, the preservation of cultural heritage does not end with the identification of the problem; it must also be actively addressed and resolved. Conservation seeks to meet these challenges by implementing a variety of strategies aimed at preserving the regarded cultural assets. For the effective safeguarding of heritage, it is crucial to identify current conservation strategies that remain effective in the future, while also intensifying research into new and innovative approaches.

Before delving into a detailed discussion of existing conservation measures, it is important to first clarify the terminology used to define these.

Conservation is defined as a field that comprises “...*all measures and actions aimed at safeguarding tangible cultural heritage while ensuring its accessibility to present and future generations.*” (ICOM-CC 2008). This definition originates from the “Resolution on terminology to characterize the conservation of tangible cultural heritage” which was adopted at the ICOM-CC Conference in New Delhi, 2008. The document states further: “*Conservation embraces preventive conservation, remedial conservation and restoration*” (ICOM-CC 2008).

The document has helped establish a common understanding of the terms used within the conservation community. Due to the rapid development of the field in the second half of the 20th century and the beginning of the 21st, various terms emerged and were sometimes used interchangeably. Terms like remedial, curative, interventive, active, and direct conservation all referred to the same aspect of conservation, opposed by preventive, indirect, protective, passive, etc. In both groups, the terms were and in part still are used as synonyms, despite the slight differences that may be noted. The resolution aimed at simplifying the nomenclature, so it listed and defined the following three sub-categories of conservation:

*“Preventive conservation - all measures and actions aimed at avoiding and minimizing **future** deterioration or loss. They are carried out within the context or on the **surroundings** of an item, but more often a group of items, **whatever** their age and **condition**. These measures and actions are **indirect** – they do not interfere with the materials and structures of the items.*

...

*Remedial conservation - all actions **directly applied to an item** or a group of items aimed at arresting **current** damaging processes or reinforcing their structure. These actions are only*

carried out when the items are in such a **fragile condition** or deteriorating at such a rate, that they could be lost in a relatively short time.

...

Restoration - all actions **directly applied** to a single and **stable item** aimed at facilitating its appreciation, understanding and use. ...”

(ICOM-CC 2008)

According to these definitions, preventive and remedial conservation and restoration measures differ on three different levels. The first distinction lies in the **time** dimension: preventive measures aim to prevent future deterioration and loss, while remedial conservation and restoration address already existing damage. The second distinction involves the **location** of the measures: preventive conservation always modifies the surroundings and never the materials and structures of the items themselves, whereas remedial conservation and restoration are directly applied to the asset. The third level of differentiation arises from the **condition** of the item of relevance. While preventive treatments can be applied to all items regardless of their condition, remedial treatments are always applied to items in a fragile condition and aim at improvement of the same, while restoration measures are applied to items in stable condition (sometimes directly following remedial conservation treatment which stabilised the condition) that have lost part(s) of their significance.

These multiple layers of the definition present some challenges in practice, since some treatments may fall into more than one or no category at all; e.g. the classification of protective coatings, relevant to our case. These aim to prevent further decay (speaks for classification as preventive conservation!) but intervene with the asset itself since they are applied directly to the surface (disqualifies them as preventive conservation treatments). This problem was already acknowledged in the resolution itself, where one can further read: “*The application of protective coatings can be both restoration and preventive conservation.*” (ICOM-CC 2008). In the case of this thesis, it can be argued that protective coatings (e.g. lime shelter coats) especially in the given context, show elements of both preventive and remedial conservation. In any case, it becomes clear that occasionally it is not easy to attribute a certain conservation treatment to one of the three categories. While the definition provided by ICOM-CC is useful in most scenarios, the present work is in need of a terminology aligned with the specific context of the research topic. The same will be proposed in the next section.

As stated in the ICOM-CC document, remedial conservation treatments involve interventions aimed at dealing with existing damage; these “remedies” combat effects (symptoms) of decay and deterioration. The same are fairly ineffective in providing a solution for the surface recession of calcareous stones, given the irreversible and cumulative nature of this type of material loss. The situation can only be addressed with protective measures, irrespective of whether they affect the surrounding or the item itself. In this case the crucial factor is the timescale; it is important to address future decay rather than seek a remedy for already existing loss. The opposite term of remedial in the above stated document is preventive. To avoid misunderstandings (e.g. with the problematic case of protective coatings) I suggest

the use of the term “preventive” only for measures that fulfil both relevant criteria: preventing future damage and intervening with the surroundings only. All other treatments, whether they are remedial or aim at avoiding future decay, will be called “interventive” because of the intervention that engages directly with the asset. Therefore, in this thesis the two terms “preventive” and its antonym “interventive” will be used for conservation measures. The term “restoration” is not essential for this work and retains the same meaning as in the ICOM-CC resolution which are all actions applied directly to the object that go beyond remedial conservation. In Table 3, the relevant terms, as outlined in the “Resolution on terminology to characterize the conservation of tangible cultural heritage,” and used in this thesis are summarised for a clearer overview

Table 3.: terms definitions as stated in the ICOM-CC resolution and used in this thesis

Term	Time of decay	Localisation	Condition
Preventive Conservation (Thesis)	future	surrounding (only)	stable and fragile
Preventive Conservation (Resolution)	future	surrounding (predominantly)	stable and fragile
Interventive Conservation (Thesis)	past, present, future	Item	stable and fragile
Remedial Conservation (Resolution)	past and present	Item	fragile
Restoration (Thesis)	past and present	Item	stable
Restoration (Resolution)	past and present	Item	stable

5.1. Preventive Conservation

As stated above, preventive conservation deals by definition with the surrounding of objects and concerns topics like temperature, humidity, pollutants, pests and more recently legislation, risk management, community involvement etc. In indoor environments, climate control and air quality regulation can be achieved through various measures, such as climate-controlled display cases and HVAC systems, albeit often at considerable cost. However, in an outdoor environment (due to the open nature of the system) controlling climate and air quality becomes an almost impossible task. Therefore, there are fewer possibilities of how to implement aspects of preventive conservation in an outdoor environment, especially when focusing on stone as heritage material. Some of the existing possibilities should be discussed hereafter.

5.1.1. Relocation

One of the most straightforward approaches to preventive conservation for “movable” outdoor stones is aiming at utilising the better circumstances in indoor environments. For “smaller” items, like singular sculptures, the possibility for a relocation of the same from the outdoor to an indoor environment is sometimes given. Depending on the relocated asset and its context, a copy might be placed to substitute the missing item; e.g. the reliefs of “Goldenes Dachl” (the Golden Roof) in Innsbruck, Tyrol, were substituted by polychrome stone copies on the façade (Fig. 46), while the originals were placed in a museum (Fig. 47) in the 1950s and 1960s (Milchin, Fuchs and Krist 2020).



Fig. 46 and 47: The reliefs of the “Goldenes Dachl” in Innsbruck, Tyrol, left: the façade displaying the stone copies of the reliefs (2018); right: the original stone reliefs from “Goldenes Dachl” on display in the Tyrolean Museum “Ferdinandeum” (2018)

One of the best-known examples of relocating a cultural asset involves the famous marble sculpture David by Michelangelo. The sculpture was removed from the “Piazza della signoria” in Florence in 1873 and moved to the “Galleria dell’ Academia”, while a marble copy was produced and installed in the outdoor environment in 1910 (www.galleriaaccademiafirenze.it).

Many examples of relocations of various sculptures and smaller monuments can be found worldwide. While relocation offers clear benefits for the physical preservation of the asset, considerations regarding the loss of context and the erosion of aesthetic values must be taken into account when deciding upon this measure.

5.1.2. Permanent sheltering

Another possibility for a preventive conservation measure is the sheltering of assets in their original position with a permanent structure, to keep different decay agents (most often meteoric water, but also sunlight, wind etc.) away from the same. For statuary on façades, this mostly means the installation of projecting roofs and/or the extension of existing ones (Fig. 48 and 49).



Fig. 48 and 49: permanent roofs as protection: left: historic roofs over gravestones on a church façade in Eggenburg, Lower Austria; right: a contemporary roof over a stone portal, St. Pantaleon-Erla, Lower Austria

The introduction of permanent shelters such as roofs or sometimes entire protective buildings over free-standing sculptures in parks and gardens can be beneficial in conservation terms, but certainly interferes with the original intention of the artwork and the overall impression it conveys. Only very few such shelters for free standing sculpture and small monuments can be noted in public space, most of which were planned together with the monuments themselves and often date back to the 19th century (Fig. 50). Therefore, in the case of gardens and parks mostly temporary shelters are employed, the same will be discussed in the next chapter.



Fig. 50: historic permanent shelter over the monument to Nicola Demidoff (1870) in Florence, Italy

Permanent shelters are more commonly found in the context of archaeological sites (Schmidt 1995; Woolfitt 2007). More recent research on this topic was initiated with the implementation of the shelters for the megalithic sites of Ħaġar Qim, Mnajdra and Tarxien on Malta (Cassar et al. 2018) (Fig. 51). The shelter at Ħaġar Qim was evaluated in a thesis by Briones (2015).



Fig. 51 and 52: permanent shelter over archaeological sites: Ħaġar Qim, Malta (left) and Slope house II, Ephesus, Turkey

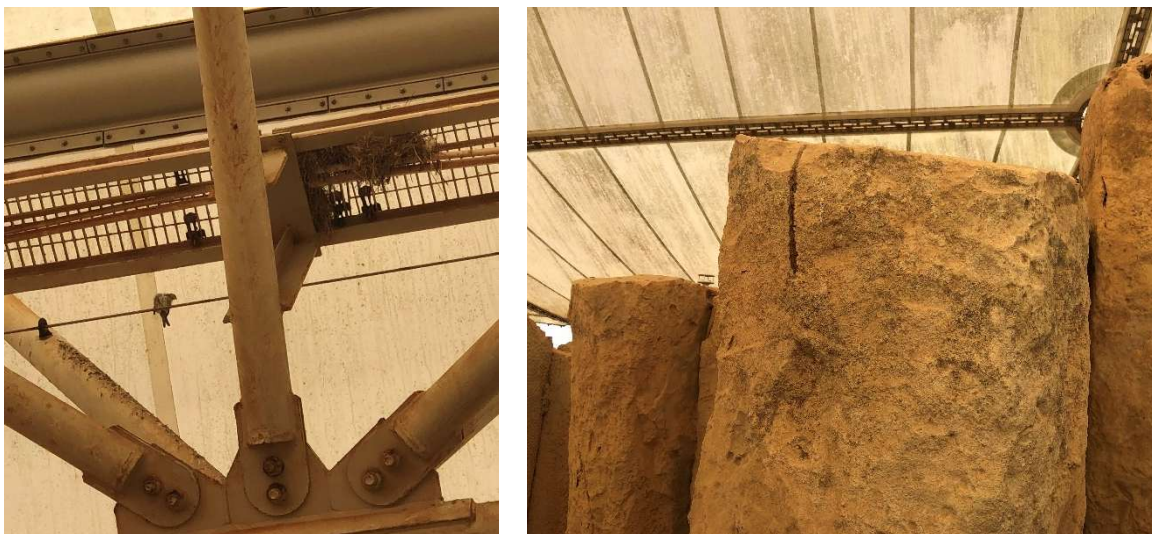


Fig. 53 and 54: Problems deriving from the installation of permanent shelters: nesting birds and accumulation of bird droppings on surfaces (Ħaġar Qim, Malta)

A conference organised by the MOSAIKON Initiative in Herculaneum, Italy (23. – 27.09.2013) focused on the issue of permanent shelters for archaeological sites (Aslan et al. 2018). At the conference, various case studies were presented, and both the benefits and challenges associated with the use of permanent shelters were discussed (Aslan et al. 2018).

The permanent shelter for Roman gravestones and sarcophagi in Leithaprodersdorf, Lower Austria, was examined in a study (Milchin, Haselberger and Krist 2020) that can be found in the Appendix of this thesis. While the shelter protects by keeping rain and snow away from the assets exhibited underneath, it also has hint sides. The accumulation of dust and bird droppings, which are not washed away by rain due to the presence of the shelter, as well as the accumulation of litter, are among the associated issues. These problems are similar to those published in literature and noted elsewhere, e.g. the aforementioned shelters over the megalithic temples on Malta (Fig. 53 and 54). The changes in perception of the surroundings and context also seem important, but addressing the issue of bird droppings is probably the most crucial one, as it is the potentially most damaging change to the system in terms of materiality, after a permanent shelter is installed. Bird droppings are very acidic, contain salts and can therefore etch the surfaces and cause the accumulation of salts (Rubén 2022). Shelters also provide favourable conditions for the prolonged presence of birds, as they offer protection and numerous nesting opportunities. Dust accumulation on monument surfaces can also pose problems if no maintenance is conducted, as it is not washed away by rain.



Fig. 55: Permanent shelter in Leithaprodersdorf, Lower Austria

Given the previously discussed chemical decay of calcareous stones, the significance of dry deposition of pollutants and the accumulation of bird droppings becomes evident. The pollutants are partly embedded in the particulate matter/dust on the surfaces and can react with the same in case of surface condensation, or when water in form of dew or fog becomes available.

Lack of care and maintenance of the shelter itself, which is often not planned upfront, can frequently cause further problems. However, the most significant concerns are regarding the potential impact of permanent shelters on aesthetics and the context of monuments. This explains the relatively high acceptance of permanent shelters in archaeological sites (Fig. 51, 52 and 55), as opposed to parks and gardens (e.g. Fig. 56). There is a notable difference in the perspective shift, brought about by a permanent shelter installation between non-archaeological and archaeological sites. At archaeological sites, structures often exist in a state and context that diverge significantly from their original intended state. Therefore, the installation of a shelter represents (only) yet another layer of alteration (Fuchs, Milchin and Krist 2024). Conversely, non-archaeological sites often retain a closer connection to the intentions of the

artist or architect who designed them; baroque gardens provide a clear example of this difference in impact.



Fig 56: The installation of permanent shelters over the freestanding sculptures in the Gardens of Schönbrunn is not a viable solution (©Christian Philipp, CC-by-sa 3.0)

While permanent shelters are more common, medium-term shelters are also used, though less frequently. These shelters are intended for extended use but are not meant to be permanent. Such was the case of the medium-term shelters (used for couple of years) in the Baroque Park in Kuks, Czech Republic. The purpose of these shelters was to facilitate the drying of the sculptures and serve as a temporary solution until sufficient information was gathered to develop a conservation concept for long-term solution. After two years, the shelters were evaluated, revealing many positive aspects along with some minor drawbacks (Kotlik and Heidingsfeld 2002).

5.1.3. Temporary shelters – winter shelters

The surface recession of calcareous materials was discussed earlier in this thesis. Due to the temperature dependence of the solubility of CO₂ in water, the karst effect is most pronounced when temperatures are just above 0°C. Therefore, in situations where permanent shelters are not an option, temporary shelters for the cold season can be of benefit for the preservation of outdoor monuments made of calcareous stones. As pointed out above, this measure is primarily employed with small monuments such as freestanding statuary, including sculptures, vases, and fountains in parks and gardens.

The use of such shelters is believed to have a long tradition, although it is challenging to find written sources documenting this. Koller (1995) mentions the use of winter shelter for the Josefssäule⁴² (Josef's column) in Vienna as early as 1755 but he does not state the source of this information.

In the archive of the building department of the Austrian court⁴³, recently, quotes were found by Mader-Kratky regarding the Schönbrunn Palace and its gardens, stating the use of different winter covers for statuary as early as 1780. The use of wood for sheltering is noted for vases (1780), stairways (1782) and the obelisk of the Obelisk Fountain (1800). Interestingly, in a documented discussion in 1787 and 1788, shelters were proposed for the 40 garden sculptures made of marble from Sterzing (Vipiteno), Italy and Tropaion groups of the Gloriette. However, due to the large number of sculptures and the resulting costs, the use of wooden shelters was rejected. The outcome was that only the sculptures on the Gloriette were sheltered, but instead of wooden shelters, the sculptures were covered with foliage and straw as a more cost-effective winter shelter (Mader-Kratky 6.5.2024).

Franzen (2018) was also looking into the history of winter sheltering with focus on Germany and other (neighbouring) European countries and could find some information about sheltering in the second half of the 19th century. The most interesting findings are photos from the King's Palace in Pillnitz, Germany, dating back to 1895, which depict winter shelters covering two sphinx sculptures (Franzen 2018). A drawing of a winter shelter over a sculpture with a pedestal from 1870 from Antwerpen, Belgium, could also be traced (Franzen 2018).

In summary, it is certain that winter shelters were used at least since the second half of the 18th century in central Europe, however, at some point in the 20th century, their use was abandoned in most places. This decline likely occurred in the time of the Second World War, but it is conceivable that even between the two world wars, there was relatively little interest in the maintenance and protection of monuments due to societal changes and social problems.

In the last decades of the 20th century and the beginning of the 21st century, this important measure of

⁴² Koller writes about a Josefssäule on Hoher Markt, but since there is no column (Säule) on Hoher Markt, he probably refers to the „Vermählungsbrunnen“ which is sometimes also called Josefsbrunnen or Josef's fountain.

⁴³ Akten des kaiserlichen Hofbauamtes (HBA), starting with December 1772 the meetings are documented in protocols which are kept in the „Hofarchiv“.

preventive conservation gained importance again. Nevertheless, it remains the case that only very few monuments are being sheltered during the winter months. According to the aforementioned study from 2018 (Franzen) the most winter shelters are used in Germany, but also some use is notified for Austria, France, Belgium, Holland and Sweden. It is however highly likely that the list is incomplete, since some research programs from England dedicated to winter shelters (Berry et al. 2005) are not mentioned in the study.

The use of winter shelters in Austria

In the Appendix of this thesis, a publication can be found (Milchin, Haselberger and Krist 2020) dedicated to the use of (traditional) wooden winter shelters in the garden of the Langenzersdorf Museum in Lower Austria. The soft winter shelters used in the past in the gardens of the Schönbrunn palace present another well-documented and evaluated case study from Austria (Haselberger and Milchin 2015; Milchin, Haselberger and Krist 2020). Also, other small monuments, i.e. sculptures and fountains in Austrian cities, but also singular assets in more rural surroundings, like small towns and villages, are regularly sheltered. However, there appears to be no systematic approach to winter sheltering, as various materials and designs are used for the shelters (Fig. 57 - 60). While some shelters employ traditional methods and materials (e.g. wood), others use materials and designs that are not always beneficial for the protected assets (e.g. glass or acrylic glass) sometimes leading to a greenhouse effect on the inside.



Fig. 57- 60: Different winter-shelter designs seen around Austria; f.l.t.r.: upper row: fountain in Monastery St. Peter, Salzburg, Bust of Leopold von Habsburg in the gardens of Laxenburg; lower row: Fountain in Monastery St. Paul in Lavantal, Fountain in Friesach (© Johann Nimmrichter and Marija Milchin)

In the city of Vienna various small monuments are sheltered in winter. However, the majority of the winter shelters are simple covers for fountains, which often aim to protect only the basin of a fountain (Fig. 61

and 62). The concept is to ensure that the emptied basin remains devoid of rainwater and/or snow, preventing damage due to freeze-thaw cycling and to a lesser extent protecting surfaces from surface recession. The covers also only protect the basin and not the statuary of the fountain, which often stays exposed.



Fig. 61 and 62: Viennese fountains with winter covers for the fountain basin: Palais Athenna Fountain in front of the Austrian Parliament (left), Albrecht Fountain in front of the "Albertina" (right)

Few fountains in Vienna have winter shelters that cover both, the basin and the statuary (Fig. 63 and 64). Since many fountains are already being (semi-)sheltered, it can be suggested to extend the shelters to include the statuary as well. In doing so, the protection potential would be extended to the statuary and the whole fountain would profit.



Fig. 63 and 64.: Winter-sheltered fountains in Vienna: Maria-Theresien Platz (left) and Austrian Academy of Sciences (right)

At the same time, free-standing statuary in Vienna is not, or rarely, sheltered in winter. A walk through the city in February 2024, passing through Stadtpark, Karlsplatz, Resselpark, the Belvedere Gardens, and Schweizergarten, revealed a single sheltered sculpture among more than 60 freestanding sculptures and small monuments⁴⁴. The one sheltered sculpture is a recent bronze work (1973) by Henry Moore, situated in front of St. Charles Church. The rationale behind the winter sheltering of this specific sculpture, as opposed to numerous 18th- and 19th-century marble and limestone sculptures that remain unsheltered, was clarified by the institution responsible for its preservation (MA 7). The sculpture is sheltered during the winter due to the proximity to the Christmas market. This shelter is therefore intended to mitigate mechanical damage potentially caused by visitors' interaction with the sculpture and not to protect the sculpture from weathering⁴⁵.

One of the very few examples of consequent use of winter shelters for a stone sculpture in Vienna is noted for the so-called "Lion of Aspern" by Anton Fernkorn (1858), a sculpture in the 22nd district of Vienna. The sculpture, made of porous limestone, has been protected for more than a decade by a wooden winter shelter bearing a photograph of the underlying sculpture during the winter months (Fig. 65).



Fig. 65: Winter shelter for the "Lion of Aspern" (2024)

Materials and designs of winter-shelters

In the long history of use, winter shelters have developed different forms and designs and have been made from different materials.

The "traditional" wooden shelters (a wooden "box" consisting of four sides and a roof) are still in use in many places (Fig. 57, 63, 65, 66 and 67). They offer several advantages such as durability, effective protection from snow, rain, and to some extent wind, as well as easy and low-cost production. Their

⁴⁴ Out of which more than two thirds were made of stone, mostly calcareous, and only one third consists of metal (mostly bronze) or a mix of stone and metal.

⁴⁵ Many thanks to Nina Linke from the City of Vienna for clarifying the situation.

drawbacks include the required storage space in summer and the labour-intensive process of mounting and dismantling. When deciding upon the “traditional” version, it is important to think about a stable and firm fixation of the shelter (the problem of wind will be discussed further on in this chapter) and the possibility of air circulation.



Fig 66 and 67: “Traditional” wooden winter-shelters in the museum garden of LEMU in Langenzersdorf, Lower Austria (left), one of the shelters during dismantling (right)

Another possibility for winter-sheltering is presented by the use of a rigid skeleton, e.g. from scaffolding bars, on top of which a soft (textile) cover is applied. In this case, it is important to use a non-transparent material in order to avoid a green-house effect and therefore condensation of water and the growth of microorganisms. Assuring there is enough air exchange, e.g. through ventilation holes, is essential. These types of shelters require less storage space during the summer; however, their use is labour-intensive. The rigid structural framework, often composed of scaffolding components, must be assembled and subsequently covered, resulting in a greater number of working hours than any of the other available options. Additionally, they can create problematic microclimates, as previously noted, due to the reduced permeability of the materials used and depending on the design details.

The last here presented possibility is given by the so-called soft wraps with or without spacers (Fig. 68 – 70). These require very little storage space during the summer but are not particularly durable, owing to wear and tear resulting from close contact with the stone and from folds in the sheltering material. Also, some major problems with wind were reported in the past and will be summarised in the following text.

The soft shelters used in the gardens of the Schönbrunn Palace in Vienna (Haselberger and Milchin 2015; Milchin, Haselberger and Krist 2020) were evaluated and a need for adaptation was noted. The defects primarily concerned the rapid deterioration of the sheltering material caused by the partial direct contact with the stone, as well as by folding during storage. This aspect is important in respect to the sustainability of the shelter itself, however not in respect to the protection they offer. Unfortunately, in

spite of the aforementioned evaluation, the old shelters were neither adapted nor replaced with a new system. Consequently, the principle of winter sheltering was abandoned altogether in the Schönbrunn Gardens.



Fig. 68 – 70: soft winter-shelters in the Schönbrunn Gardens (left), prominent problems and damage (middle and right)

However, the evaluation highlighted the importance of further research on this topic and underscored the complexity of winter shelters. In the following section the case of the winter shelters for the museum garden at LEMU in Langenzersdorf will be presented.

Case study: winter shelters for the museum garden of LEMU

The development of a winter sheltering concept for the garden of the Langenzersdorf Museum (LEMU)⁴⁶ began with an evaluation of two different sheltering systems: a rigid wooden shelter and a flexible Tyvek® wrap⁴⁷. During the first year of the project, prototypes of both shelter types were fabricated and installed in the museum garden. The microclimatic conditions inside and outside the shelters were monitored over one winter season. Air temperature, surface temperature, and relative humidity were recorded within both shelter types and on one unsheltered sculpture for comparison. In addition to climatic performance, factors such as durability, production costs, storage requirements, labour demands for installation and removal, and the sustainability of the sheltering systems were considered in the decision-making process. The following page presents exemplary diagrams from the climate recording in the same time interval of the two sheltered and one unsheltered sculpture are presented (Fig. 71).

⁴⁶ The collection of LEMU comprises to great extent of sculptures from different artists from the region. The sculpture garden presents sculptures made of bricks, concrete, metal, and different calcareous stones (compact and porous limestones).

⁴⁷ Tyvek is a brand of synthetic material consisting of high-density polyethylene (HDPE) fibres made by DuPont. It is known for being lightweight, durable, water-resistant, breathable (allows moisture vapour to pass through, but blocks liquid water and particles).

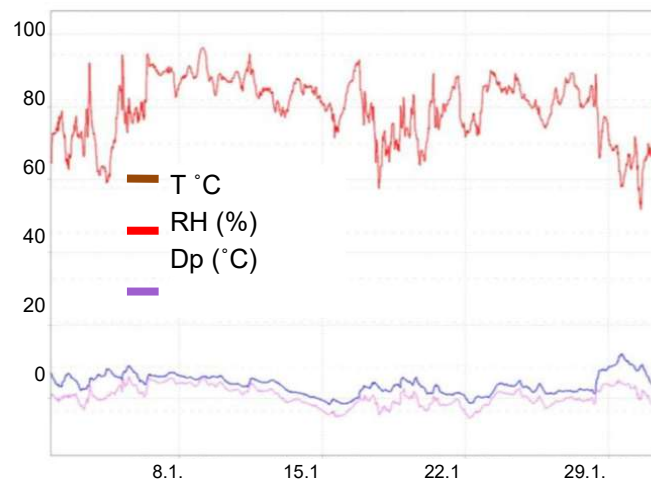
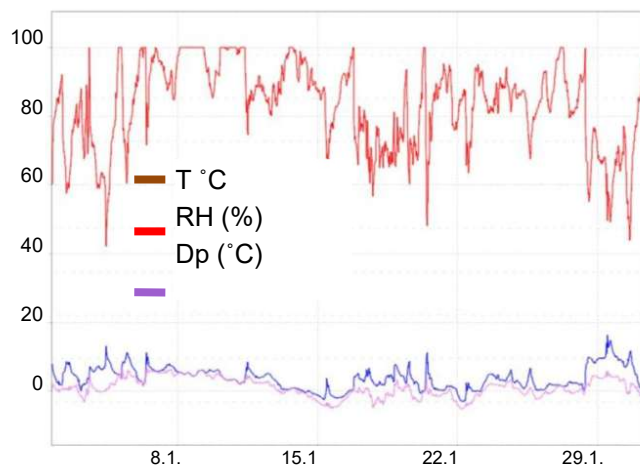


Fig. 71: climate diagrams for January 2018 for the two shelter prototypes and an unsheltered sculpture at LEMU

It is worth noting that both the wooden and the Tyvek® winter shelters help buffer extreme climatic conditions and fast changes in relative humidity. However, the wooden shelter is more effective in preventing condensation (in the presented period of time the relative humidity did not reach 100%) whereas the Tyvek® shelter permits longer condensation events (in regard to the sculpture surface) compared to an unsheltered sculpture. In both cases, environmental fluctuations occurred at a reduced rate, and both shelter types effectively prevented direct contact of rain water and snow with the surfaces, indicating that each system offers a measurable mitigating effect. Nevertheless, the wooden shelters appeared to perform more effectively (Milchin, Haselberger and Krist 2020). In the case of the Langenzersdorf Museum, the decision was made to use wooden shelters due to their enhanced protective qualities. Additionally, their durability and economic value as well as sustainability were key factors in this choice.

During the course of this project, it became evident that while sheltering may appear straightforward at first glance, closer examination reveals potential challenges. The selection of materials and designs for the shelter is crucial, as is determining the optimal timing for their installation and removal. Depending on the given circumstances, including the budget and workforce involved, different solutions might be suitable for different situations and/or institutions. In order to make a decision for the “right” winter shelter, following questions should be addressed and possible limiting factors discussed

How many single items (e.g. sculptures) should be sheltered?

How big are they? At what height are they mounted? Are they free-standing?

How harsh are the winters? How high is the risk of winter storms with strong winds?

How much storage space is available for the shelters in summer?

How much workforce is available for the mounting and dismantling in autumn and spring?

What is the available budget?

When a decision regarding the type of winter shelters is made, it is very important to choose the right time for the mounting of the winter shelters⁴⁸ and the right moment for the removal of the same⁴⁹. It is of utmost importance to monitor the process of sheltering in the first years of use. One sometimes has to adapt the system and/or design of the shelters or coach the personnel⁵⁰ in dealing with the shelters and the artefacts being sheltered. Therefore, the involvement of a conservator in the first years is necessary both when mounting and when dismantling the shelter. It is recommended to record and evaluate the

⁴⁸ The mounting of the shelters is recommended for the second half of October/November latest December for Austria, depending on the region and altitude.

⁴⁹ The dismantling of the shelters is recommended for March/April for Austria, depending on the region and altitude.

⁵⁰ Often, the personnel responsible for winter shelters are gardeners or general maintenance staff who are not necessarily accustomed to working with artefacts.

inside climate in the shelters especially in the first year(s) of use. This can help improve and adapt when needed. Annual monitoring and maintenance cycle by a conservator should be scheduled for spring, immediately after the shelters have been dismantled. This way, possible changes can be noted and when necessary, treatments can be applied. For example: artefacts with a certain salt load may show efflorescence in spring when the shelters are removed (Fig. 72 and 73); these should be brushed off (dry, with a soft brush), as soon as possible. The salt crystallising under a winter shelter should not be misunderstood as a drawback of the shelter. The reduced availability of water on sheltered surfaces frequently results in slow but steady drying which often leads to salt efflorescence on the surface. In contrast, without a shelter the salts would be solved in atmospheric water and partly transported back in the material where they could continue to cause damage due to crystallisation and dissolution cycles.



Fig. 72 and 73: Salt efflorescence visible after the dismantling of the winter shelters in spring, LEMU (© Katharina Breunhölter)

During the initial years of use, particular attention should be paid to monitoring microbiological colonisation. Changes can be expected here due to the use of a winter shelter⁵¹. In the case of mould formation this might be a sign for a too tight fit of the shelter; more air circulation might be needed. In this case some ventilation holes should be added.

⁵¹ no direct water and light, but also fewer temperature extremes and likely less frost time

The problem of wind

Experience shows that wind is a big and growing problem for winter shelters. Due to climate change, it is expected that extreme weather events will become more frequent. In Austria, not only are springs and summers becoming stormier, but also in winter months storms with high wind intensities are becoming more frequent. An extreme example of these changes occurred in February 2020 when a series of storm lows caused immense material damage in alpine regions and the north of the country (Stangl et al. 2021). Wind pressure can cause soft wraps and sometimes wooden shelters to lean and rub against monument surfaces causing wear off of both the sheltering material and the monument itself. In more extreme situations wind pressure can cause extreme damage up to total loss of the asset sheltered. Such problems were reported from Germany (Franzen 2008), where in the baroque gardens of Großsedlitz a sculpture of Zeus was damaged three years in a row although the shelter was adapted after every problem noted. Even more dramatic was the situation with the “Üppigkeitsvase” by Antonio Corradini from 1720 which was standing in Großer Garten, Dresden (Fig.74). The vase was sheltered in a textile soft wrap when a winter storm in 2005 brought it to fall and the vase broke in more than 150 pieces (Franzen 2008). It cannot be definitively determined whether this situation was directly caused by the winter shelter itself. However, it is likely that the textile cover used created larger surface areas, making it more susceptible to wind pressure.



Fig.74: Üppigkeitsvase, Antonio Corradini, Großer Garten, Dresden (© Ad Meskens / Wikimedia Commons)

Similarly, in Vienna and Lower Austria some problems connected to wind and winter storms have been reported. In the course of the evaluation of the textile covers for the Schönbrunn statuary many defects to the soft wraps could be brought in connection to the direct contact with the stone surface and the action of wind. Even though the textile shelters were strapped in order to limit the impact surface for wind, the

problem could still not be solved. Fortunately, in the case of Schönbrunn only damages to the shelters but not to the sculptures were recorded (Haselberger and Milchin 2015).

More severe issues were observed during the project at the LEMU. As previously discussed, two different types of shelters were installed and evaluated after the first sheltering season. One type of shelter was made of Tyvek®, a soft cover material, while the other was a “traditional” rigid wooden winter shelter. After only one winter (2017/18), the Tyvek® shelters exhibited significant damage; one of the soft wraps was lost, most likely displaced by wind. The most critical issue, however, concerned one sculpture that had not been secured to its pedestal and was subsequently blown off by the wind (Fig. 75 and 76). All of these problems resulted from winter storms in December 2017 and January 2018 with very high wind velocities.



Fig. 75 and 76: Damage to the sculpture “Kangaroo” after a storm in the winter 2017/18, Langenzersdorf, Lower Austria

The damaged sculpture was restored and moved back to the garden. At the same time the decision to use winter shelters made of wood (due to security, price and durability) was taken and winter shelters were produced for all sculptures. The winter 2019/2020 was also very stormy, with very strong winds and great amounts of rain. In spring, after the dismantling of the wooden shelters it became clear that the same sculpture had been damaged again. This time the damage was smaller and the mechanism different. The problem was caused to a bigger extent due to the very intense rain events, more than through the strong winds. Because of the big amounts of water, the ground (earth) around the sculpture softened and the winter shelter sunk asymmetrically. Since the sculpture is rather tall but narrow, this small movement made the heavy wooden shelter lean on the fragile brick sculpture causing breakage and cracks. The shelter was therefore modified with spacers that keep it at a distance to the base/pedestal. Also, tensioning paracord ropes, similar to the ones used with tents, were employed on all shelters (Fig. 77).



Fig. 77: Wooden shelters stabilised by tension ropes

It can be concluded that in future winter shelters can be of use especially for monuments made of calcareous stones in order to tackle the problem of surface recession, which will likely worsen as a result of the rise of CO₂ concentrations in the air and the redistribution of precipitation. However, the expected rise (frequency and strength) in extreme weather events and therefore also storms connected to climate change will need to be taken into account. Therefore, when deciding on winter shelters, significant effort must be made to ensure that they are securely fixed and do not pose any threat to the monuments that they are meant to protect. The example of the garden of LEMU illustrates one possible solution to this problem. For other gardens and parks, different solutions will need to be found, as the use of tensioning ropes⁵² may not be suitable in some cases due to the potential tripping hazard they can pose for visitors.

⁵² The same is only possible in LEMU because the garden of the museum is closed for visitors in winter.

5.2. Interventive Conservation

As already discussed, in this work the differentiation between preventive and interventive conservation is used. The following chapter deals with protective coatings which are referred to as interventive treatments due to the direct intervention with the surface of the heritage item itself. Such coatings can follow different protection mechanisms. They can be anti-graffiti or anti-fouling treatments, salt inhibitors, reactive inorganic coatings⁵³, water repellents or shelter coats (Gherardi 2022; Gherardi and Maravelaki 2022).

When regarding the surface recession of calcareous stones, the last three categories (inorganic coatings, water repellents and shelter coats) are of interest. Due to their manifold use in Austria in the last decades, the focus in this work will be laid on (lime) shelter coats and water repellents, followed by a short overview of less frequently used (inorganic) coatings and new developments with potential for future use.

5.2.1. (Lime) Shelter Coats

These protective coatings are frequently used in countries where significant amounts of porous limestones are used as heritage materials. The shelter coats are originally made of slaked lime, fine sand and/or crushed stone and water only, and aim at buffering different damaging potentials through “self-sacrifice”. The same have probably the longest history of use of all of the above-mentioned coatings in stone conservation. The idea behind these shelter coats is essentially to enhance the traditional lime wash⁵⁴ by adding fine sand and/or crushed stone to match the appearance of the stone surface⁵⁵ and to increase the protective potential through thicker layers. A shelter coat primarily aims at protecting the underlying surface, whereas the main goal of a lime wash is to modify the appearance of a monument. The sacrificial role of the shelter coat regards the chemical, physical and biological deterioration.

The use of lime shelter coats intensified in the second half of the 20th century, most probably due to the intense sulphation of limestone surfaces in this period (Caroe 1985; Fidler 1995; Nimmrichter et al. 2000; Odgers and Henry 2012). When acting as a sacrificial layer with respect to sulphation, the shelter coat is aimed at reacting with sulphur dioxide (and/or other pollutants) instead of the stone. Judging from different cases where this phenomenon could be studied under the microscope (e.g. Nimmrichter et al. 2000), this principle worked well in practice and lime shelter coats can be regarded as a suitable protection from deterioration through sulphation for monuments made of calcareous stone.

⁵³ Here the definition as used by Gherardi and Maravelaki is adopted. Coatings that undergo chemical reaction with the substrate are understood under the term reactive inorganic coatings i.e. ammonium oxalate or hydroxyapatite.

⁵⁴ “Lime wash” refers to diluted lime milk, commonly used for “lime washing,” a term applied to the white painting of walls with this material. Occasionally, pigments may be added to achieve other colours. However, the use of lime wash always remains that of a paint layer and not of a shelter coat. Additionally, lime might prevent biological colonisation through its high pH.

⁵⁵ Shelter coats are rarely designed to match a lost paint layer rather than the stone. Examples for this approach can be found in different conservation works from the 1990s and early 2000s, as lime shelter coats with marble dust were used to imitate a lost lead white in oil surface for different Baroque Park sculptures in Austria.

In England, shelter coats are used as part of the “Lime Method”⁵⁶ (Odgers and Cox 2020) and are often tempered with casein and biocide (Fidler 1995)⁵⁷. In Italy they are known as “strato di sacrificio” (Ban et al. 2018). In Austria the so-called “Kalkschlämme” is especially used in the east of the country rich in monuments made from porous limestones. Similar to the “Lime Method” in England, the shelter coat is part of the so-called “Kalktechnologie”⁵⁸ in Austria, which involves consolidation with lime water, injection of cracks and backfilling with a grout made of diluted slaked lime (“lime milk”), mortar repairs with lime-based mortars (usually without hydraulic components) and a finish with lime wash or shelter coat (Huber 2012).

A wide range of recipes and application details have been developed through the extensive use in the past decades in Austria. Starting from the basic coat of slaked lime and fine aggregate, various recipes incorporating the addition of acrylics, oil, cement, or casein have been developed (Ban et al. 2018). To extend the lifespan of a shelter coat, an additional water repellent treatment was proposed in the last quarter of the 20th century, applied on top of the already dried and carbonated lime coat (Fuchs and Pinter 2020; Nimmrichter et al. 2000; Paschinger and Richard 1982). The water repellent coat was particularly commonly applied on parts of monuments situated at higher elevations, such as attic sculptures, where regular maintenance could not be ensured (Koller 2001). This approach was especially propagated by Hubert Paschinger, the late chemist in the laboratory of the Department for Conservation and Restoration of the Federal Monuments Authority Austria (BDA)(e.g. Nimmrichter et al. 2000).

At the same time, some stakeholders in the field of monument protection in Austria already opposed this approach and were more sceptical to new materials and technologies; one of the strongest opponents to water repellents was the promoter of the above mentioned “Kalktechnologie”⁵⁹, Karl Neubarth⁶⁰ the late director of the Centre for Education of the Federal Monuments Authority Austria (BDA) in the Charthouse in Mauerbach, Lower Austria.

The impact of the additional water repellent on the lime shelter coat as a sacrificial layer is still raising questions regarding possible alterations to the protective mechanism and possible reversibility and/or retreatability. Some of these questions have been partially answered in the course of an evaluation study

⁵⁶ The “Lime Method” was originally developed for the conservation of the façades of Wells Cathedral. It is a set of conservation treatments that rely on lime-based materials. The method includes lime poultices for cleaning, limewater for consolidation, lime-based mortars for repairs, and a lime-based shelter coat as a protective layer.

⁵⁷ The use of biocide is common with materials containing casein, as it should counteract the fact that casein is nutritious for microorganisms.

⁵⁸ In the Charterhouse of Mauerbach, the Education Centre of the Federal Monuments Authority Austria teaches the use of “Kalktechnologie” to craftsmen working in the field of heritage preservation, such as stonemasons and masons. It consists similarly to the English “lime method” of different steps adding up to a full range of measures for a conservation treatment. Different to the English “lime method”, the original intention of the „Kalktechnologie“ was probably to create a range of steps for the conservation of plasters instead of limestones. However, through time these have also been applied to porous limestones and other natural stones.

⁵⁹ Translates to “lime technology” and is a concept similar to the English “lime method”.

⁶⁰ Friendly remark by Karl Stingl, 22.03.2024 in Mauerbach.

of past treatments on the façades of the Natural History Museum (NHM)⁶¹ in Vienna (Fuchs and Pinter 2020), but more work has to be done in this direction in the future. The most important result from the mentioned study was that the additional water-repellent treatment penetrated through the shelter coat and into the underlying stone in most of the analysed samples, thereby failing to meet the criterion of reversibility. At the same time, substantial differences were observed not only in visual parameters but also in resistance to weathering, which could be attributed to variations in application. Consequently, the importance of high-quality application of both the shelter coat and the water repellent became increasingly evident (Fuchs and Pinter 2020).

The combination of the above mentioned two distinct layers (lime-based shelter coat and a hydro-repellent), each with unique properties, led to further developments by conservator-restorers in Vienna and elsewhere in Austria. A single-layer silicon resin shelter coat was supposed to unite the properties of both, in a single, more convenient coating. Essentially, it comprises commercial silicon resin façade colour with addition of fine sand and/or crushed stone to increase the layer thickness, enabling it to bridge small cracks and fill pores. It is important to note that this type of shelter coat does not provide a chemical buffer against sulphation. Instead, it protects the stone by preventing water — and the dissolved pollutants and airborne dust particles it carries — from penetrating the surface, thereby keeping contaminants away from the stone. After these developments, numerous combinations and varied binders for shelter coats emerged, the result was an unclear terminology and formulation coupled with varying application protocols and a very flexible understanding of the term shelter coat (“Schlämme”). Consequently, in 2011, a working group was established to focus on shelter coats, delving into their diverse formulations and applications. This group comprised conservator-restorers, material experts, and heritage officials, including the author of this work⁶². The outcome was a guideline for their application which was published on the website of the Federal Monuments Authority Austria (BDA) in 2018 (Ban et al. 2018). The guideline clarified the terminology of shelter coats. It also analysed aspects of materiality, protective mechanisms, and recommended applications, with particular focus on the “original” lime shelter coat, both with and without additives. In the frame of this work, a set of ten slabs of porous limestone from St. Margarethen in Burgenland were coated with different shelter coats⁶³, additionally partially coated with water repellent, and exposed in 2017 on a rack at the Charterhouse in Mauerbach, Lower Austria. The aim of the exposure was to study the deterioration and decay of the coatings and the underlying stone, as well as the developing soiling. For this reason, the slabs were documented in detail before exposure. A

⁶¹ The façades were treated 2001-2009. For the finish of the surfaces a lime-based shelter coat was applied and the same additionally coated with a water repellent.

⁶² The working group was initiated by Johann Nimmrichter from the Federal Monuments Authority Austria and involved Matea Ban, Susanne Beseler, Marija Milchin, Johann Nimmrichter, Andreas Rohatsch and Johannes Weber. Contributions on single aspects were also made by Katharina Fuchs, Christian Gurtner, Georg Hilbert, Farkas Pinter and Daniela Trauninger. The publication was edited by: Bernd Euler-Rolle and Robert Linke.

⁶³ The slabs were prepared, coated and documented by students of stone conservation from the Institute of Conservation (Head: Prof. Gabriela Krist), University of Applied Arts Vienna. The 10 slabs were coated with: pure lime (1) and lime with addition of acrylics (2), lime with white cement (3), lime with linseed oil (4) lime with casein (5), dispersed lime hydrate – Calxnova (6), nano lime – CaloSil E50 (7), Roman cement (8), water glass (9), and silicon resin (10). The slabs 1-9 were additionally treated, half of their surface was covered with a water repellent.

first evaluation of the exposed slabs and the different shelter coats used was conducted after one year of exposure (2018), the published results can be found in the Appendix of this work (Milchin et al. 2020). The most recent evaluation was conducted in spring 2025, eight years after the installation of the slabs. It is planned to continue the evaluation cycles and to collect more data on how the different recipes of shelter coat, with or without additional water repellent, weather and change visually and functionally over time.

Even after only one year of exposure in 2018, some of the shelter coats already showed some deterioration and decay (e.g., the nano-lime shelter coat was almost fully worn off) and/or heavily soiled surfaces (e.g., lime-based shelter coats tempered with casein and linseed oil) (Fig. 78). The halves treated with an additional hydrophobic coating exhibited no visible signs of weathering apart of minimal soiling (Fig. 79).



Fig. 78 and 79: Exposure of stone slabs with different shelter coats in Mauerbach, Lower Austria (left) and slab I (lime shelter coat) after 12 months of exposure, the right side of the slab is additionally treated with hydro repellent



Fig. 80 and 81: after 8 years of exposure: stone slabs with different shelter coats (left) and slab III - lime shelter coat with white cement addition (right) (© Katharina Fuchs)

After eight years (2025), all slabs showed much higher degree of soiling, many of them with very intense biocolonisation. As expected, some slabs showed a marked difference in the intensity of biocolonisation between the surfaces with and without hydrophobic treatment (see Fig. 81, slab III), whereas on other slabs both halves looked very similar (e.g., slab I). It can be concluded that the initial trends from the previous assessments still remain relevant. However, some of the applied shelter coats were completely decayed. In addition, initial material loss through detachment — affecting both the shelter coat and the underlying stone — could be observed, as is the case with slab II (lime-based shelter coat with addition of acrylic dispersion, without hydrophobic treatment) (see Fig. 82).

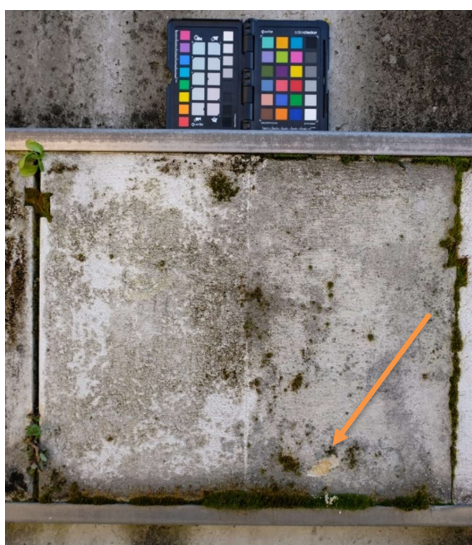


Fig. 82: Slab II (lime shelter coat with addition of acrylic dispersion) first surface detachments after 8 years of exposure (© Katharina Fuchs)

It can be concluded that all tested shelter coats — both with and without hydrophobic treatment — function as protective layers for the surfaces. The hydrophobic effect achieved through the use of water-repellent product remains effective, although it diminishes slightly over time. In contrast, many of the shelter coats without water-repellent treatment are becoming less wettable over time, and their water uptake is decreasing. This effect is likely related to soiling and biological colonisation of the surfaces.

To sum up, shelter coats have historically been an effective means of protecting monuments from the impact of SO_2 , and they still hold potential for reducing surface recession in the future. Taking into account the predicted surface recession for Central Europe in the far future, exceeding $30 \mu\text{m/a}$ for dense limestones and marbles (Bonazza et al. 2009), a simple mathematical extrapolation shows that a layer (of dense limestone and/or marble) with a thickness of 1 mm would be recessed in approximately 33 years. It is possible to find values for the surface recession of porous limestones (some of them in Vienna), the available data shows values of about $70\text{--}80 \mu\text{m/a}$ (Steiger, Charola and Sterflinger 2011). These values can also be expected to increase by 30% (or more) for the far future in parallel to the modelling of surface recession for dense calcareous stones (Bonazza et al. 2009) resulting in values of about $100 \mu\text{m/a}$ or the recession of a layer of 1 mm in 10 years. If we assume that shelter coats have a porosity much higher

than compact calcareous stones but smaller or equal to porous limestones, it can be concluded that a well-executed lime shelter coat with a layer thickness of 1 mm could serve as a sacrificial and therefore protective layer for a period of up to 10-30 years in future. This calculation is supported by the decay rates identified on the shelter coated slabs in Mauerbach. The microscopical analyses of samples taken from the slabs before the exposure show different layer thicknesses depending on the material used⁶⁴. The thickest layers were built up with lime-based coats with or without additives (white cement and/or acrylic dispersion), the layers were on average 0,5 mm reaching up to 1 mm on the thickest spots (Fig.83 and 85). The thinnest layers were produced by the use of dispersed lime hydrate – Calxnova (VI) and nano lime – CaloSil E50 (VII), mostly 0,3 mm, in some spots the measured thickness was as low as 0,1 mm (Fig. 84 and 86). This was also reflected in the weathering behaviour of the films, with the thinnest layer (nano lime) being the first to be completely weathered off.

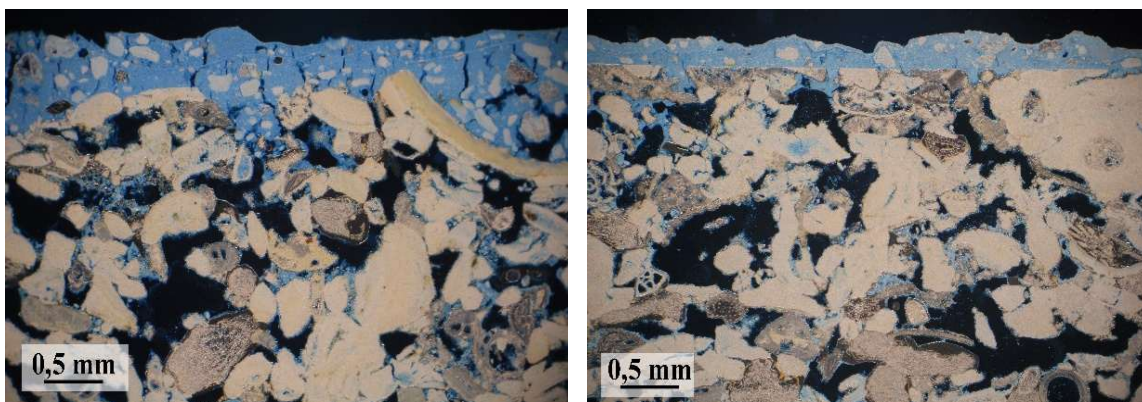


Fig. 83 and 84: Thin section microscopy in incident light, samples taken before exposure: lime shelter coat (slab I, left) and nano lime shelter coat (slab VI, right)

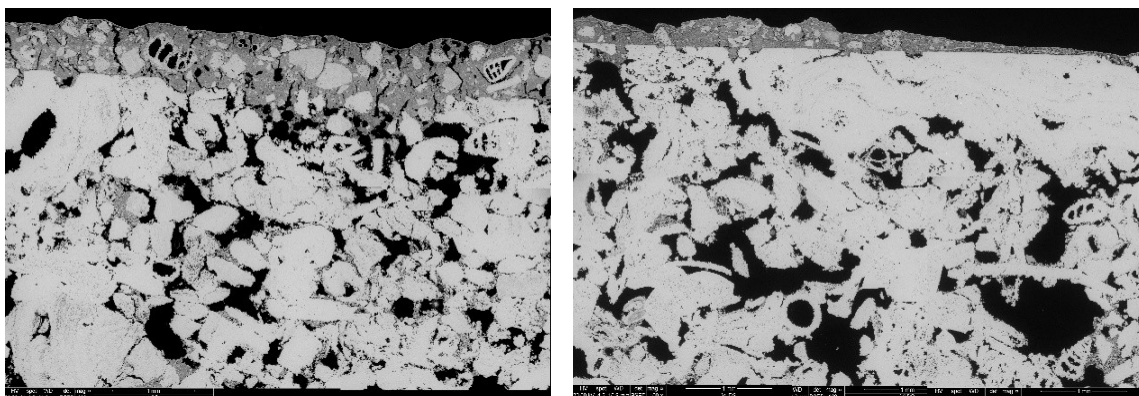


Fig. 85 and 86: SEM-BSE analyses of polished thin sections, samples taken before exposure: lime shelter coat (slab I, left) and nano lime shelter coat (slab VI, right)

⁶⁴ The application of the shelter coats was carried out in the same manner as it would be on a monument. Each surface was covered with three layers. Between layers, the surface was brushed with a dry brush to remove any excess material or foam build-up. Depending on the viscosity of the slurry, different layer thicknesses resulted.

In addition to their protective and self-sacrificing properties, lime shelter coats offer other positive aspects, including low material costs and good compatibility with the underlying substrate when applied to calcareous stones.

However, it is important to stress that the use of lime shelter coat is limited to application on calcareous stones. The use of the same on silicate stones or concrete does not yield successful results. On concrete, adhesion can be problematic (Odgers and Henry 2012). Additionally, the lime in the shelter coat reacts to calcium sulphate if SO_2 is present⁶⁵, thus introducing a soluble salt to the system which can be damaging to cementing matrices of different sandstones (Fidler 1995). There are often discussions about the aesthetics of monuments where shelter coats are applied. The critics argue that the coated surfaces look too homogeneous, that the stone character (texture and shade) is lost or that façades or smaller monuments look uniform and blunt. However, if used in the right manner, the shelter coat will not intervene with the shape of a monument. The shelter coat is applied with a brush and rubbed in the surface so that the pores, cracks and small defects of the surface are filled. After the initial setting, the excess material should be softly removed from the surface with a dry brush. This procedure is repeated two to three times until the wanted layer thickness is reached⁶⁶. A skilled conservator who pays attention to details is important in this phase. The colour and the roughness of the coated surfaces are of utmost importance for the result. If the shelter coat is produced to match the underlying stone, it can be very hard to differentiate between the stone and the shelter coat itself. The third and last argument is the uniformity of whole façades, due to the use of the same shelter coat in contrast to possible chromatic differences between single blocks of the same lithotype when uncoated. This can be solved with variations of the formulation matching the various underlying stone colours (Fidler 1995). The same principle was used as a guiding principle for the conservation works on the façades of the Museums of Natural and Art History in Vienna (NHM and KHM) at the end of the 1990s and the beginning of the 2000s (Rohatsch, Hodits and Nimmrichter 2015) and resulted in an aesthetically satisfactory result (Fig.87).

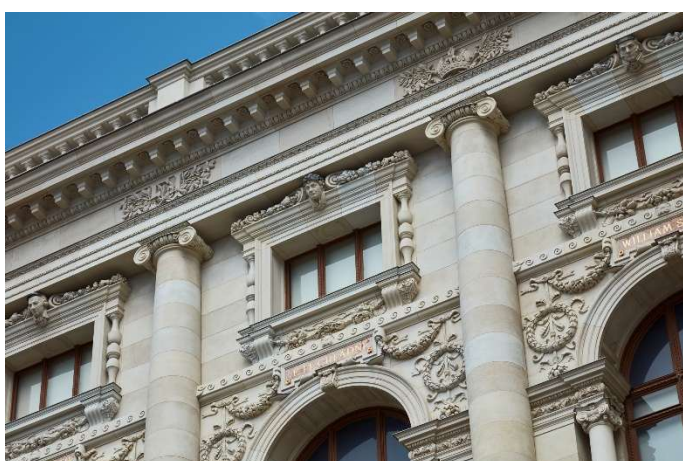


Fig.87: Natural History Museum Vienna, during the most recent conservation the façades were coated with shelter coats in different shades to match the underlying stone colours (© Helmut Neumayer)

⁶⁵ Even though the SO_2 levels in Europe are very low in comparison to the last third of the 20th century, some SO_2 will always be present. Also, in other regions, this might still pose a problem.

⁶⁶ In the case of the trial slabs in Mauerbach the procedure was repeated 3 times in the case of the lime-based shelter coats.

To summarise, lime-based shelter coats have a sacrificial function, as they are designed to decay in order to protect the underlying surfaces. In the past, they were primarily used as protection against sulphation, but they also hold potential for future use in mitigating enhanced surface recession caused by rising CO₂ levels and the effects of climate change. This mechanism explains the need for regular maintenance and repair, or complete renewal, of lime shelter coats at regular intervals (Durnan 2006; Fidler 1995).

Depending on the monument and the climatic circumstances as well as the exposure, a lime shelter coat, if executed correctly, has a life span of 5-10 years on rain exposed surfaces. On extremely exposed surfaces the layer might be weathered-off in 1-2 years, whereas in very protected areas it can stay up to 15 years and more. However, the sacrificial role is the very function of the coat itself. Therefore, it is recommended to plan a maintenance campaign every year where possible, but at least every 5 years, for surfaces that are coated with a lime-based shelter coat. During this maintenance periods, the situation should be evaluated, and where needed remedial treatments conducted (mortar repairs, joints, cracks etc.). The shelter coat can be partly or completely renewed. The surfaces should be cleaned and pre-wetted before the application of new shelter coat. For the repair of a shelter coat, it is always advisable to store some shelter coat mixture in a container⁶⁷ in order to skip the long process of matching the correct colour for small repairs. The new layer can be applied on top of the old one, however one has to be careful not to build layers so thick that they deform the details of sculptural work unreadable.

5.2.2. Water repellents

Alongside shelter coats, water repellents have been extensively used as a surface protection treatment in stone conservation in Austria and other European countries, especially since the 1970s, with a peak in their use in the late 1990s and the early 2000s. The primary objective of the use of water repellents in stone conservation is to mitigate deterioration and decay by limiting surface wettability (Rodrigues 2025) and water ingress (Snethlage and Sterflinger 2011). Limiting the amount of water in contact with stone materials helps mitigate various deterioration mechanisms, including material dissolution, salt formation, freeze-thaw cycling, microbiological colonization, and stress induced by hygric and hydric expansion. Water serves as a primary agent in decay mechanisms affecting stones in outdoor environments, therefore water repellents initially appear to give a straightforward solution. However, upon closer analyses, the complexities of the matter become evident (Snethlage and Sterflinger 2011).

Water repellent coatings have been known and used at least since antiquity. Materials based on organic substances with hydrophobic properties, such as oils and waxes, have been used throughout history (Gherardi 2022). However, these can be problematic because they also seal surfaces, may attract dirt

⁶⁷ The lime shelter coat can be kept wet in a bucket over years. Only if the recipe includes cement or other hydraulic binders or aggregates this is not an option and freshly mixed shelter coat has to be mixed for every application.

and promote biocolonisation. Therefore, since the era of industrialisation and with the advancement of the chemical industry, especially in the second half of the 20th century, new products have been developed and introduced to the market. Most of these products, particularly those significant for the field of stone conservation, belong to the group of silicone-organic compounds. Silanes and siloxanes are among the most frequently used water repellents (Rodrigues 2025; Snethlage and Sterflinger 2011).

The goal is not to seal surfaces completely, but rather to make them hydrophobic through the formation of a continuous thin non-polar layer on the pore walls of the substrates, thereby hindering the transport of liquid water while vapour is supposed to pass through more or less unhindered. The total sealing of surfaces, including the inhibition of water vapour transport, as often is the case in connection to the use of film-forming acrylic resins, waxes, oils, etc., can accelerate decay mechanisms by trapping moisture beneath these layers. It is crucial for porous materials to have the possibility to dry, especially considering the possibility of cracks and minor defects in the layer that allow for water penetration. Such small defects can be present since application or develop over time due to the weathering of the coating. Consequently, the stone must retain the ability to facilitate the movement of water out of the material. This presents the first challenge associated with water repellents that requires attention.

The most effective and fastest drying for capillary-active stones occurs when water is transported to the surface in its liquid state and transitions to vapour only upon reaching the same (Camuffo 2019). Depending on the penetration depth of the water repellent, the water entrapped in the substrate may need to transition from the liquid to the gas phase millimetres to centimetres before reaching the surface. This leads to a slower transport in the gas phase; the water molecules (vapour) migrate through the pores of the material, only pushed by concentration gradients (Camuffo 2019). This highlights a downside of water-repellent coatings, especially after water has entered the monuments. Water ingress can occur through rising capillarity, cracks, defects in joints, or in the coating itself. The more porous and capillary-active the stone is, the more challenging it becomes to control potential water uptake. Therefore, even though such porous stones were initially considered the prime example materials benefiting from hydrophobic treatments, recent conservation efforts are moving away from deep-penetrating hydrophobic treatments for porous limestones.

Another issue arises with salt-loaded monuments. As previously described, the drying mechanism changes when a hydrophobic coating is applied. The deeper the coating material penetrates, the further into the substrate the phase transition of water must occur during the drying process. Salt crystallisation would occur exactly in the place where this phase transition from liquid to vapour takes place, as salts can only dissolve in liquid water. Therefore, salts will crystallise on the very spot, leading to subflorescence and causing damage due to crystallisation pressure. Therefore, hydrophobic treatments should not be applied to monuments contaminated with salts.

The swelling of clay minerals in certain stones also involves water. Studies on hydrophobic coatings suggest that hygric and hydric expansion might be exacerbated by these types of treatments (Snethlage

and Sterflinger 2011). Therefore, hydrophobic treatments do not always solve the problems associated with these decay mechanisms. When addressing hydric or hygric dilatation issues in stone, a decision to apply a hydrophobic treatment should only be made after thorough preliminary investigations. These investigations must assess the specific stone type and the water repellent product being considered. The hydrophobic treatment should be used only if these studies demonstrate a clear benefit for the preservation of the asset in question.

It was also anticipated that hydrophobic surfaces would have a lesser tendency to soiling and be less frequently colonised by microorganisms. This is only partly true. Indeed, the tendency towards soiling is reduced on freshly treated surfaces (Fig. 79). The same appears to be true for primary and secondary biocolonisation (Snethlage and Sterflinger 2011). However, water behaves differently on hydrophobic surfaces compared to how it does on hydrophilic ones. Due to surface tension, water running down surfaces concentrates into thin streaks that depend on the form of the asset but tend to follow the same paths consistently. This leads to accelerated degradation of the uppermost layers of the hydrophobic coating in these areas. Combined with the availability of water, these areas are more frequently and intensively colonised by cyanobacteria and algae (Snethlage and Sterflinger 2011). Hence, water repellents cannot be recommended as a prevention against biocolonisation (Rodrigues 2025).



Fig. 88 and 89: Extreme soiling patterns due to a water repellent treatment documented on monuments in Austria: Klagenfurt (left) and Greillenstein (right)

Therefore, a holistic evaluation is required, extending beyond the field of natural sciences, delving into aesthetics and psychology. The patterns produced by differential soiling and biocolonisation of surfaces can significantly alter our perception of a monument. In one of the few studies conducted in this area, participants were asked to select the least and most disturbing soiling patterns from various computer-simulated patterns of a simple architectural element (a pedimented window) (Brimblecombe and Grossi

2007). The results indicated a preference for uniform patterns and those exhibiting shadowing effects. The study also revealed that vertical features were less acceptable, and low contrasts with high homogeneity were crucial for acceptance. Taking this information into account, one can anticipate that even if soiling and biocolonisation are generally reduced when compared to untreated surfaces, the extreme contrast and intense patterns produced (Fig. 88 and 89) may disrupt the appreciation of the monument more than it would be the case with untreated surfaces.

In terms of mitigating the dissolution of calcareous surfaces, particularly with compact limestones and marbles, the application of water repellents appears initially very promising. These stones have minimal pore space, reducing the risk of water ingress from capillary rise or through defects in the coating. Minimising water contact with the surface by reducing wettability leads to decreased rates of dissolution, subsequently reducing surface recession. However, the challenge lies in the decay of the water repellents themselves. These coatings exhibit sensitivity to UV radiation and degrade rapidly on exposed surfaces (Rodrigues 2025). Still, this does not necessarily compromise their overall effectiveness, as the hydrophobicity in the deeper layers persists for extended periods, ranging between 5 and 30 years, depending on the substrate, the product used and the specific environmental conditions. Nonetheless, the properties of the surface can change within months after application. Since the recession of dense calcareous stones primarily affects the surface, the protection offered by such a water repellent⁶⁸ is timely very limited (Snethlage and Sterflinger 2011), questioning the sustainability of the treatment.

Another aspect still mostly overlooked in conservation science, yet crucial for practical conservation, is the compatibility and retreatability of such treatments. Several specific issues need to be addressed here. The first, which has already been partially discussed, concerns the decay and deterioration of the hydrophobic coating itself. Due to this process and the varied shapes and therefore exposures of the monument in question, the differential decay of the water repellent layer itself can lead to inconsistent behaviour across different surfaces. For instance, more exposed surfaces (e.g., horizontal ones) may already lose all hydrophobic properties and absorb water through capillary action, while other, more sheltered surfaces (e.g., recessed vertical surfaces) may remain fully hydrophobic. These differences in the condition can contribute to different decay mechanisms if left untreated. One possible solution to this problem might be the partial application of water repellents on exposed surfaces only, from which water enters the monument, as suggested by (Rodrigues 2025). However, regardless of the application details, monuments treated with water repellents require ongoing evaluation and monitoring. Without regular maintenance, rapid decay and deterioration can occur in some cases.

As a comparison, when other protective coatings—such as lime-based shelter coats—show differential weathering, it is also advisable to repair or reapply them. However, if left untreated or without maintenance, they might give unsightly surfaces but typically do not lead to increased deterioration of the

⁶⁸ In order to understand the efficacy of the water repellent on the surface Contact sponge and/or the Droplet method measurements can be used as part of a monitoring plan.

substrate.

Here, the case of the coat of arms from Greillenstein Castle in Lower Austria should be mentioned. The monolithic Baroque object (Fig. 91) was mounted above the castle's main entrance (Fig. 90), tilted toward the ground to provide better visibility for anyone passing through the portal. The piece is made of *Zogelsdorfer Stein*, a porous limestone from northern Austria that was frequently used for sculptural work in Baroque times (Breunhölder et al. 2018).



Fig. 90 and 91: The position of the coat of arms on the south façade of the Greillenstein castle, Lower Austria (left) and an overview of the dismantled coat of arms before the conservation treatment in 2016 (right) (©Katharina Breunhölder)

By the 1980s, the coat of arms was in very poor condition and therefore treated by a stone conservation company under the supervision of the Federal Monuments Authority Austria. The asset was cleaned, the effects of sulphation were treated, and the stone was consolidated using ethyl silicate (Wacker OH) and acrylates (Paraloid B72, 7%). At the end of the treatment, the coat of arms was painted with a silicon resin paint and a water repellent (Wacker 190) was applied on top (Breunhölder et al. 2018).

Approximately three decades later, the coat of arms was showing severe damage and decay, particularly due to freeze-thaw action affecting the front of the object (Breunhölder et al. 2018). After careful analysis, it was concluded that a combination of factors was responsible for the recent deterioration. These included the south-facing exposure of the façade, the climatic conditions of northeastern Austria, with very wet autumns and winters (fog, drizzle, and snow), the tilted mounting on the façade for visibility, the legacy of the 1980s treatment, and, importantly, the application of the water repellent.

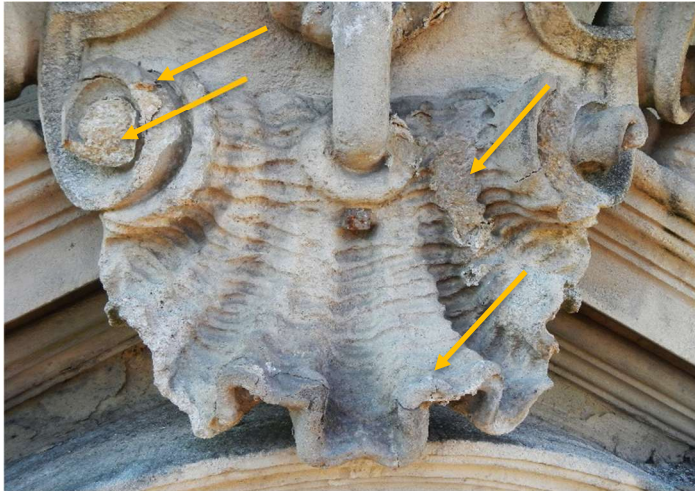


Fig. 92: Damage due to freeze-thaw cycling (orange arrows) on the front of the coat of arms

The water-repellent layer deteriorated more rapidly on the back and, in general, on upward-facing surfaces, whereas the front remained hydrophobic. As a result, water from rain, fog, and snow was able to penetrate the stone but could not dry out sufficiently quickly. The south-facing orientation further accelerated this problem: snow melted during the day, moisture entered the pores, and then refroze at night. This extreme combination of conditions led to the severe deterioration observed in 2016 (Fig. 92). The asset was removed from the façade and brought into the studio of the IoC for an extensive conservation treatment, which included consolidation with ethyl silicate under “vacuum”, cleaning, re-adhesion of loose pieces, and the reconstruction of missing parts. At the end of the treatment, a modified lime-based shelter coat was applied to the whole surface. The object's back and upper side, from where water most easily enters the stone, was additionally treated with a water repellent paint layer. The front was not treated with water repellent (Breunhölder et al. 2018). In this case the partial application of a water repellent was regarded the only promising possibility. After seven years, the object still presents itself in a stable condition; however, it will be more instructive to assess its condition after 15 to 20 years following conservation, particularly given that no maintenance can be carried out due to its inaccessible position on the façade.

Another aspect that is crucial for the conservation practice is the compatibility of water repellents with other materials. Most materials used in stone conservation are polar and hence hydrophilic (at least during application). This is true for all lime-based materials, such as shelter coats and mortars, as well as for most of the currently applied consolidants and paints. Hydrophobicity can interfere with the ability of hydrophilic materials to adhere to the surface and/or to absorb CO₂. This is particularly problematic for mortar repairs and joint pointing (Sandner, Linke and Nimmrichter 2017) and presents significant challenges for conservators, particularly during major conservations, regarding the potential use of mortars and other hydrophilic or water-based materials.

In summary, the use of water repellents is far more complex than initially stated. In many cases in stone conservation, water repellents are not an ideal solution. Monuments with a certain salt load or those experiencing issues with hygric and hydric expansion should not be treated with hydrophobic coatings

without further investigation, as these treatments may exacerbate existing problems. While water repellents may theoretically offer a solution for assets made of porous and highly capillary-active stones, in practice, their use has often led to new challenges. Achieving a flawless application of water repellent to prevent water ingress from joints, cracks, or capillary rise is difficult. Over time, water inevitably finds its way into the stone, where the reduced drying rates keep it trapped, sometimes leading to more severe problems.

Treating dense calcareous stones to limit surface recession due to dissolution may seem promising. However, the rapid decay of surface treatments means that protection is effective for only a very brief period. Similarly, using water repellents to minimise soiling and biocolonisation has its limitations. Beyond a certain point, the development of unsightly patterns can obscure the appearance of the monument more than would be the case with an untreated surface or a surface treated with other coatings (such that do not result in hydrophobic surfaces).

So, under what circumstances can and should water repellents be used? Most potential applications are rather specialised. Monuments previously treated with water repellents will often require partial or complete re-treatment. As previously mentioned, the application of water repellents as a secondary layer over a lime shelter coat may have some relevance. Additionally, for assets made of artificial stone, like concrete, this still presents a significant option⁶⁹. However, for the use on calcareous stones, water repellents are not generally recommended due to their incompatibility with water-based conservation materials and their potential to inhibit future treatments.

5.2.3. Reactive inorganic coatings

There are other coatings that can be used to prevent or minimise the decay and surface recession of calcareous stones. These treatments primarily aim at reacting with the surface of a monument, chemically modifying it to create a layer that is less soluble and more stable. Probably the best studied surface treatment aiming at chemical alteration of calcareous surfaces was developed in the 1980s, inspired by observations of the “natural” patina on monuments (Fig. 93 and 94). In the Mediterranean region, a very stable patina was observed on monuments made from calcareous stones like marbles, dense lime stones and travertine (Antonelli et al. 2016; Galanos and Doganis 2003). This patina, primarily composed of calcium oxalate (mainly weddellite), is less soluble in water and weak acids, and mechanically more stable than the underlying stone. The exact origin of the patina remains partially unresolved, although various potential mechanisms for its formation have been identified and studied in the past (Cariati et al. 2000; Del Monte and Sabbioni 1987; Lazzarini and Salvadori 1989). They include the metabolic activities

⁶⁹ Cement-based artificial stones and concrete can benefit from water repellents, as these reduce the rate of carbonation, which is one of the primary decay mechanisms in these materials, particularly in connection with reinforcement.

of lichens and historic protective layers comprised of organic compounds such as caseinates, oils, etc., or a combination of both.



Fig. 93 and 94: Visible orange layers of natural oxalate patina on façade elements on the Cathedral of Pisa

Different procedures were used to artificially imitate this layer leading to diverse results. The most commonly employed approach involves the use of ammonium oxalate in concentrations of approximately 5%, typically applied in poultices to the surface. Oxalic acid has also been used. Both marble and limestones were treated in the past and in both cases the results were promising (Aragoni et al. 2021; Dreyfuss and Cassar 2017; IJCS; Matteini et al. 2020; Mudronja et al. 2013).

However, there are two negative aspects for the use of ammonium oxalate. The first regards the nature of the treatment. The reaction of ammonium oxalate with the calcium carbonate in the stone produces a new mineral compound, practically insoluble calcium oxalate, resulting in a permanent chemical change that renders the treatment fully irreversible. The second concerns potential alterations of the aesthetic appearance of the surfaces, as observed in numerous cases. Changes in colour and gloss can occur with this treatment. The newly formed calcium oxalate crystals on the surface exhibit a pale-yellow colour. Depending on the colour of the underlying stone, this may result in an unwanted or even unacceptable visual change.

One other uncertainty is also connected to this treatment: ammonium oxalate has primarily been tested on dense stones such as marble and compact limestones. Whether this treatment can also be applied to monuments made of porous limestones, and whether it might cause issues — such as differential behaviour between the treated surface and the underlying material, potentially leading to accelerated decay, i.e. in the form of contour scaling — requires further study.

Therefore, the use of ammonium oxalate may be considered when surface recession represents the most significant deterioration risk for monuments made of dense calcareous stones. However, its application must be carefully evaluated due to its irreversible nature.

Similar to the use of oxalates, products based on phosphates are recently used to chemically react with calcareous stones in order to produce a layer of calcium phosphate (hydroxyapatite) on the surface. The principle is similar to the already described treatment with oxalate. Hydroxyapatite is chemically and mechanically more stable than calcium carbonate and even less soluble than calcium oxalate, theoretically offering an even better protection towards acid attack. Due to the similar properties of hydroxyapatite to calcite, the risk of stress and drawbacks in the sense of new decay mechanisms is limited. The treatment is still relatively new and shows considerable potential, but it also presents certain application-related challenges (i.e. homogeneity of the layer) that require further attention. However, this treatment is also fully irreversible and should be used as a last resource and possibility of conservation (Pesce et al.).

5.3. Case study: The Sculpture of St. Johannes von Nepomuk, Königstetten, Lower Austria

Following, the presentation of a case study should provide a practical illustration of the possible decision-making process regarding the use of protective treatments on small monuments made of calcareous stones in the outdoor surrounding.

The sculpture of St. Johannes von Nepomuk, 18th century, from Königstetten in Lower Austria was in very bad condition in 2018. The stone from which the sculpture is made is a highly porous limestone from the tertiary Leithakalk formation in the east of Austria (Loretto), unfortunately not very resistant to weathering. The sculpture was showing a multitude of damage patterns like cracks, scales, sanding and powdering, missing parts, sulphation crusts and surface recession (Fig. 95, 96 and 97).



Fig. 95 and 96: Condition of the sculpture of St. Johannes von Nepomuk, before conservation (2018)

The sculpture was dismantled (Fig. 98) and transported to the IoC studio (Fig. 99) for a remedial conservation treatment⁷⁰. In the course of the treatment the sculpture was consolidated with TEOS through full immersion, cracks were filled, missing parts reconstructed in a matching mortar, the surface cleaned and crusts removed (Weninger 2019). At the conclusion of an extensive conservation effort, the issue of protection against future decay arose. It was anticipated that without additional protection and by exposing the sculpture in the same location as before, the benefits of the conservation would only endure

⁷⁰ The work was conducted as part of the conservation study program, (Prof. Gabriela Krist) by the student Georg Weninger at the Institute of Conservation, University of applied Arts Vienna. The dismantling and reinstallation of the sculpture was conducted by Johannes Falkeis, Georg Weninger and the author. The conservation works in the atelier were supervised by the author.

for a brief period. Hence, the need for a protective treatment was acknowledged, prompting the initiation of a discussion of given possibilities.

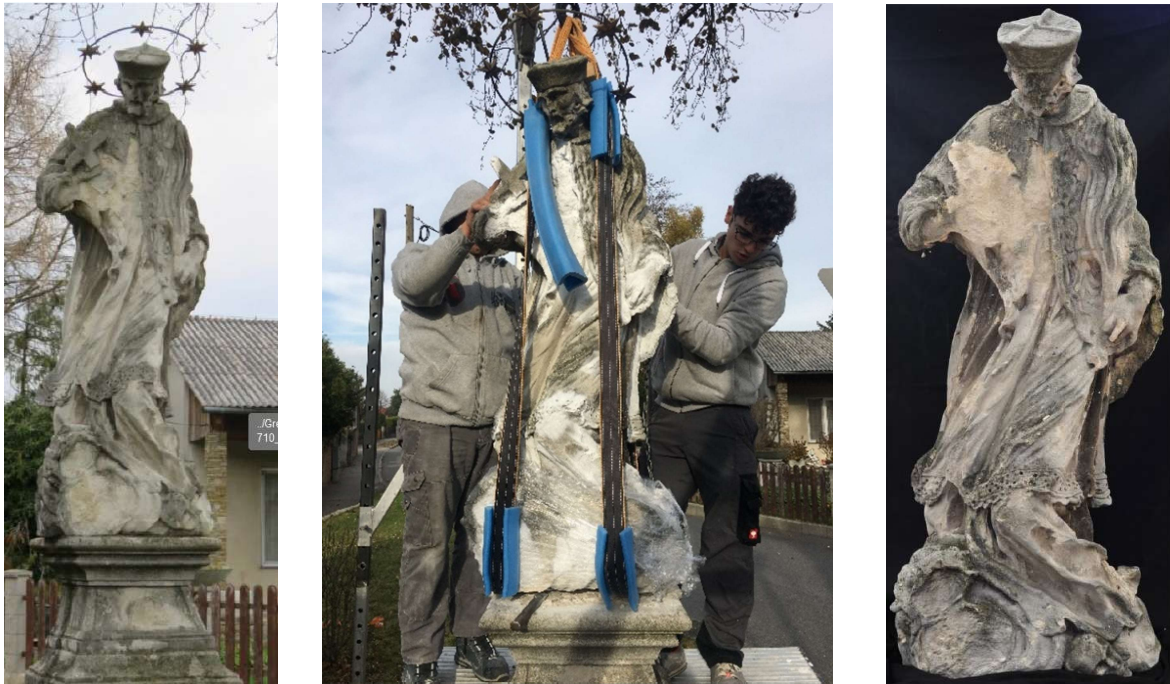


Fig. 97, 98 and 99: The sculpture of St. Johannes von Nepomuk, Königstetten, Lower Austria: before (left), while dismantling (middle) and after the transport to the studio (right) (all 2018)

Königstetten, a small rural municipality in Lower Austria with approximately 2500 inhabitants, lacks a museum. Moreover, the sculpture remained in its original location until 2018, therefore, relocation was not a viable option. Due to the nature of the stone material used for the sculpture (porous limestone), it was decided to apply a lime-based shelter coat in order to tackle issues such as biocolonisation, soiling, crust formation, and surface recession. The shelter coat consisted of lime putty and crushed limestone (Fig. 100). Additionally, it was decided that a winter shelter should be employed in order to reduce the impact of freeze thaw cycling as well as surface recession (of the stone but also of the shelter coat). Given that the municipality has storage space available during summer and sufficient workforce for mounting in autumn and dismantling in spring, a decision was made to opt for a “traditional” wooden shelter (Fig. 101). The production of the winter shelter was carried out by craftspeople from the municipality.



Fig. 100, 101 and 102: The sculpture of St. Johannes von Nepomuk, Königstetten, Lower Austria: after conservation 2019 (left), winter sheltered February 2024 (middle) and six years after the conservation treatment in 2025 (right)

In February 2024 while winter sheltered (Fig. 101), and July 2025 without winter shelter (Fig. 102), the situation was evaluated. The temporary shelter is still employed and the sculpture presents itself in a well-preserved state. Only some initial staining (mostly where black crusts were present before conservation) and some starting soiling can be noted (Fig. 103).



Fig. 103: Initial soiling visible on the sculpture after more than 5 years of exposure after treatment (2025)

The conservation treatment (consolidation, cleaning, filling of cracks, mortar repair, etc.) combined with the subsequent protective intervention (shelter coat) and preventive measures (winter shelter) proved effective and contribute to the preservation of the sculpture. After a period of more than 5 years, only initial signs of weathering are becoming evident. Therefore, it can be advised to monitor the situation further, with estimation that a first maintenance phase will be needed in 2-3 years. The previously proposed maintenance cycle frequency for shelter-coated assets of 5 years proves to be beneficial, allowing for the repair of small damages before they escalate into larger, costly issues.

Conclusions

This thesis examined potential challenges faced by outdoor monuments constructed from calcareous stones, arising from climate change and shifts in air quality. It is highly probable that surface recession of calcareous materials in Central Europe will intensify in both the near and distant future, rendering the preservation of outdoor assets — particularly the information conveyed by their surfaces — a progressively complex task. Depending on the path humanity chooses to combat climate change, the outlook for this group of materials may become increasingly challenging to potentially critical. Stone conservators will require a range of protective measures — encompassing both preventive and interventive strategies — to effectively address these challenges and preserve stone heritage for future generations. Hence, it seems important to explore new, but also evaluate old, existing measures that might have a potential in the future.

It is crucial to emphasise that any decision-making process, whether in favour of or against a protection measure, should be grounded in comprehensive information on the asset involved and its surrounding. To determine the suitability of a protection measure, it is essential to have a thorough understanding of the monument itself, including the materials used, construction techniques, and the prevailing conditions leading to its deterioration. Additionally, having insights into the rate of decay and deterioration is highly beneficial. To understand this better, material sensors as proposed and discussed in Chapter 4 of the thesis and in the paper “Material Sensors for the Surface Recession of Calcareous Stones” (Milchin, Weber and Krist 2024) which can be found in the Appendix of this thesis, can be used. The sensors focus on the specific decay rate — primarily surface recession — of a given monument, with the aim of providing information that can support decision-making regarding the need for conservation measures. These sensors measure the material’s response, irrespective of the underlying causes; their strength lies in informing conservators and other stakeholders about the rate of decay of a specific monument, thereby bridging scientific research with practical conservation and heritage preservation. If decay rates appear high and action is deemed necessary for the monument’s preservation, it becomes crucial to consider additional factors such as budgetary constraints, available workforce, storage capacity, and potential maintenance requirements. By combining this data with existing information about the asset, an informed decision can be made regarding the implementation of suitable measures.

Preventive conservation measures, including dislocation, permanent and temporary sheltering, with a specific focus on winter shelters, were analysed more closely. Additionally, existing intervention measures were investigated, particularly lime shelter coats and water repellents. Further, less commonly employed treatments for protecting calcareous stones, already existing but not widely used in Austria, were also discussed.

When considering preventive treatments, it is important to emphasise that all potential measures can significantly affect the aesthetics and context of a monument. However, the impact of winter shelters is limited to only one part of the year. Dislocation, by contrast, can offer a greater positive effect in terms of

preservation, but it often entails a more substantial alteration of the monument's context. This impact can sometimes be mitigated to some extent by replacing the original with a replica. Permanent shelters typically result in the most significant aesthetic change, but they also provide considerable benefits for material preservation.

Although preventive measures often have a substantial impact on the context and aesthetics of an asset, they generally have the smallest effect on the monument's materiality, leaving it unchanged. All preventive measures are applicable and relevant for both dense (marble and compact limestone) and porous (porous limestone) calcareous stones.

When preventive measures are not feasible due to various constraints, interventive measures can be employed. The limitations for the use of preventive measures may include: lack of workforce for the mounting and dismantling, and/or space for storage of the winter shelters; inability to dislocate or provide permanent shelter due to aesthetic or content-related reasons; and challenges related to the size, shape, location, or exposure of the asset, making the implementation of preventive measures generally impractical. In such scenarios, intervention becomes a viable option.

Lime shelter coats have been successfully used on monuments made from porous limestones in the east of Austria. This likely remains one of the most significant methods available to protect these types of stones. Shelter coats operate on the principle of self-sacrifice, making them reversible to some extent. They are compatible with the underlying material as well as any future potential conservation materials. Additionally, they leave the surface retreatable. Some of the few drawbacks may include certain aesthetic considerations, although these are largely dependent on the experience and skills of the conservator applying the layer. Proficient professionals are able to produce coatings that match the colour and texture of the stone surface, preserving its formal details. On the other hand, if applied without care, the shelter coat layer may obscure details in the form, appear too uniform or potentially exhibit decreased resistance to weathering. Assets treated with shelter coats normally require maintenance carried out at least every five years, during which the shelter coat may need partial or complete renewal based on its condition. The use of an additional water repellent layer on top of the shelter coat requires further study and cannot be generally recommended at present.

A further measure discussed in the thesis is the use of water-repellents for the protection of calcareous stones. In this case there are some important limitations to their use. The use is not recommended on assets with salt load. Also, the use for the protection of monuments that show damage due to hygric and hydric dilatation cannot be recommended without further investigation of the stone involved and the possible water-repellent product. Moreover, the use of water repellents cannot be recommended for porous calcareous stones due to practical issues observed on various monuments that have undergone such treatments in the past. It appears entirely implausible to treat a monument in a manner that completely prevents water penetration. With all monuments, some degree of water ingress is inevitable. However, in porous stones treated with hydro-repellents, water that enters the material cannot easily

evaporate or does so very slowly, leading to potential issues such as damage from freeze-thaw cycling, as well as hygric and hydric expansion. Consequently, water repellents cannot be recommended for porous limestone. The use of hydro-repellent coatings might seem more suitable for compact limestones and marbles at first glance. The same can reduce initial soiling and biocolonisation after a conservation treatment. However, after some time this effect diminishes and a rather disturbing soiling pattern might develop. By decreasing the surface's wettability, water repellents halt or at least minimise surface recession of such stones for a certain period of time. The challenge arises from the fact that these stones only lose material from their surface, and water repellents degrade rapidly on the surface, losing their protective potential precisely where they are needed most in a rather short period of time. Therefore, it can be concluded that water repellents are not a universally applicable protective coating in conservation, as they do not effectively address a wide range of situations. Nevertheless, for specific situations, water repellents will continue to hold importance. For instance, many monuments have been treated with water repellents in the past. As the superficial layers decay, differential surface wettability and water transport occurs, resulting in a patchy surface. In such cases, partial or total reapplication of a water repellent may be the most suitable solution.

Furthermore, other inorganic protective coatings that react chemically with the surface of calcareous stones — transforming it into a substance more resistant to weathering — may become increasingly relevant in the future. Oxalates and hydroxyapatite appear to be promising treatment options for compact calcareous stones, and potentially also for porous types; however, current knowledge in this area remains limited, and further research is necessary. Given the irreversible nature of these treatments, their application should be considered a last resort. This is particularly true for hydroxyapatite, a relatively new material in the field, for which comprehensive data is still lacking. In Austria, such coatings have not been widely used so far. Therefore, dedicated research on their compatibility with local stone types and climatic conditions is essential before any general recommendations can be made.

In certain cases, employing more than one protective measure can prove beneficial and feasible, although this always depends on the specific situation. Such was the case of the sculpture of St. Johannes von Nepomuk presented at the end of the last chapter.

Therefore, it can be concluded that the future presents new and evolving risks for monuments constructed of calcareous stones. Nonetheless, by consistently employing established conservation tools such as condition assessment, analysis of damage and decay patterns, and the use of analytical methods to support these efforts, a thorough understanding of the situation can be achieved. This provides a solid foundation for developing a comprehensive conservation treatment and or management plan. The consistent application of both interventive and preventive conservation treatments, coupled with ongoing evaluation and regular monitoring, establishes a robust framework for the care and preservation of monuments constructed of calcareous stones. Some minor gaps in the process have been identified, and suggestions for solutions have been proposed. The use of material sensors, as described in Chapter 4, could assist in estimating the rate of decay for certain monuments in their specific environments.

Additionally, inorganic coatings such as oxalates and hydroxyapatite may hold promise for future applications and thus deserve further attention.

Last but certainly not least, I am confident that both practical conservation and conservation science will continue to evolve and find solutions for the new and upcoming challenges, just as previous generations of conservators-restorers and conservation scientists found solutions for the challenges of their time!

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Appendix

Consent forms for the use of co-authored publications for a cumulative doctoral dissertation:

Marta Anghelone

Martina Haselberger

Gabriela Krist

Cecilia Pesce

Matea Urbanek (formally Ban)

Johannes Weber

Publications:

- 1) Milchin, M., Krist G. (2020), Herausforderung Steinrestaurierung. Vergangenheit, Gegenwart, Zukunft / *Challenges in Stone Conservation: Past, Present, and Future* (in German)
- 2) Milchin, M., Haselberger M. & Krist, G. (2023), Maßnahmen zur Erhaltung des baukulturellen Erbes – Monitoring, Schutz und Pflege als Behandlungsstrategien / *Measures for the Preservation of our Built Cultural Heritage – Monitoring, protection, and care as treatment strategies* (in German and English)
- 3) Milchin, M., Weber, J. & Krist G. (2023), Sensor Materials for the Deterioration of Carbonates in a Changing Outdoor Environment
- 4) Milchin, M., Weber, J., & Krist, G. (2023). Material Sensors for the Surface Recession of Calcareous Stones: Understanding Present and Future Decay
- 5) Milchin, M., Haselberger, M. & Krist, G. (2020), Preventive Conservation Measures for Stone Statuary in the Outdoor Environment: Three Case Studies from Austria
- 6) Milchin, M., Pesce, C., Weber, J., Krist, G., Ban, M. & Anghelone, M. (2020), An evaluation of shelter coats for the protection of outdoor stones

Consent Form for the Use of Co-authored Publications in a Cumulative Doctoral Dissertation

I, the undersigned, hereby confirm that I am a co-author of one or more of the scientific publications listed below, which were jointly authored with **Marija Milchin**.

I acknowledge that **Marija Milchin** intends to include these publication(s), in whole or in part, in her cumulative doctoral dissertation submitted to the University of Applied Arts Vienna.

By signing this document, I confirm the following:

1. I am aware of and agree to the use of the above-mentioned co-authored publication(s) as part of the cumulative dissertation of Marija Milchin.
2. I confirm that the scientific contributions of all co-authors are appropriately acknowledged and that authorship remains unchanged.

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Full Name: Marta Anghelone

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Signature: 

Place, Date: Vienna, 20/01/2026

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2) Milchin, M., Haselberger, M. & Krist, G. (2020), Preventive Conservation Measures for Stone Statuary in the Outdoor Environment: Three Case Studies from Austria, Studies in Conservation 65/Issue sup1: Special issue: IIC 2020 Edinburgh Congress preprints/2020, DOI:10.1080/00393630.2020.1757879, <https://doi.org/10.1080/00393630.2020.1757879>

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A handwritten signature in black ink, appearing to read 'Haselberger', with a stylized, flowing script.

Place, Date: Vienna, 19.01.2026

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- 2) Milchin, M., Haselberger M. & Krist, G. (2023), Maßnahmen zur Erhaltung des baukulturellen Erbes – Monitoring, Schutz und Pflege als Behandlungsstrategien, in: Luger K./Würfl A. (Ed.), Welterbe Salzburg in Zeiten des Klimawandels/ World Heritage in Times of Climate Change, Müry Salzmann Verlag, p. 211-225.
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A handwritten signature in blue ink, appearing to be 'G. Krist', with a long horizontal stroke extending to the right.

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Consent Form for the Use of Co-authored Publications in a Cumulative Doctoral Dissertation

I, the undersigned, hereby confirm that I am a co-author of one or more of the scientific publications listed below, which were jointly authored with **Marija Milchin**.

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Place, Date: Hannover, January 30, 2026

Consent Form for the Use of Co-authored Publications in a Cumulative Doctoral Dissertation

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Place, Date: Vienna, 16.01.2026

- 1) Milchin, M., Krist G. (2020). Herausforderung Steinrestaurierung. Vergangenheit, Gegenwart, Zukunft / *Challenges in Stone Conservation: Past, Present, and Future* (in German). *Beiträge zur 26. Tagung des Österreichischen Restauratorenverbandes „Gestern, Heute, Morgen in der Konservierung und Restaurierung“*, p. 76 - 83

Herausforderung Steinrestaurierung Vergangenheit – Gegenwart – Zukunft

MARIJA MILCHIN / GABRIELA KRIST

Einleitung

Die Konservierung und Restaurierung, auch die Steinrestaurierung, sind junge wissenschaftliche Disziplinen, die sich verstärkt mit Alterungsverhalten von Materialien und Objekten beschäftigen. Dadurch ergeben sich lange Zyklen von Handeln, Feedback, Evaluierung und Anpassung von Erkenntnissen und Maßnahmen. Nicht nur deswegen muss in der Konservierungswissenschaft in großen Zeiträumen gedacht werden. Diese „langsame“ und überlegte Vorgehensweise bringt im Falle der Konservierung aber auch Vorteile mit sich; sie schont Objekte und schützt die Gesundheit von RestauratorInnen. Ein Beispiel für diese positive Wirkung ist der Einsatz von Materialien und Methoden, die lange erprobt und deren Auswirkungen untersucht und somit bekannt sind. Besonderes Augenmerk wird hier auf die Langzeiterfahrungen bzw. die Kenntnisse der Alterung der eingebrachten Materialien gelegt.

Die langsame Entwicklung unserer Disziplin hat aber auch ihre Nachteile. Diese werden immer dann deutlich, wenn sich die (Umwelt-)Bedingungen schnell ändern. Einer der größten Veränderungen unserer Zeit ist sicherlich der Klimawandel. Dieser schreitet so schnell voran, dass sogar schnelllebige Branchen Probleme mit der rechtzeitigen Anpassung haben. Die Auswirkung auf das Kulturgut ist mittlerweile unbestritten. Hand in Hand mit dem Klimawandel geht die Veränderung der Luftqualität; zusammen beeinflussen sie die Erhaltung des Kulturguts und verändern Schadensmechanismen. Am direktesten betroffen sind ungeschützte Objekte im Außenbereich. Um diesen Veränderungen entgegenzusteuern, müssen wir, entgegen unserer Gewohnheiten, proaktiv agieren, anstatt zu reagieren. In diesem Beitrag soll die Veränderung der Problemstellungen in der Steinrestaurierung, vor allem für karbonatische Materialien im Außenbereich, analysiert und die Auswirkungen für die Konservierungspraxis diskutiert werden. Von „Vergangenheit“ über „Gegenwart“ soll ein Blick in die „Zukunft“ gewagt werden. Neue Probleme, sich ändernde Fragestellungen sowie vorgeschlagene Lösungsansätze sollen aufgezeigt werden.

Die Zeit vor 1969

Man könnte natürlich noch viel weiter in die Vergangenheit zurückgehen, in diesem Beitrag wird aber als Beginn der Betrachtungen die Zeit der Industrialisierung gewählt. Diese Epoche ist besonders wichtig für die am Naturstein im Außenbereich wirksamen Schadensmechanismen. Begonnen hat die Industrialisierung in England im 17. Jh. und damit viel früher als in anderen europäischen Ländern.¹ Englands große Kohlevorkommen und der Mangel an Brennholz² waren ausschlaggebend für diese Entwicklung. Die Kohle war die Energiequelle für die Industrialisierung. Bei der Verbrennung von v. a. minderwertiger Kohle werden Schwefeldioxid (SO₂), Ruß, Feinstaub sowie andere Luftschadstoffe freigesetzt. Die Auswirkungen dieser exzessiven Kohleverwendung auf die Luftqualität und die Gesundheit der Menschen, sowie die Schädigung von verschiedenen Materialien waren nicht von Anfang an bekannt. Wie die Industrialisierung selbst, hat auch die Auseinandersetzung mit den Auswirkungen in England ihren Anfang genommen. Bereits im 17. Jh. schreibt John Evelyn in seiner 1661 erschienenen Publikation „Fumifugium“ über die mögliche Verbindung zwischen Luftverschmutzung und der Nutzung von Kohle und weist darauf hin, dass die Luftverschmutzung Ursache für die schnellere Alterung von Gebäuden und der Giltung von Gemälden sei.³ 1683 werden die ersten Schäden an der Westminster Abbey durch Rauch von verbrannter Steinkohle beobachtet und dokumentiert.⁴

1 Brimblecombe/Camuffo (2003) 14–15.

2 Grossi/Brimblecombe (2007) 117.

3 Evelyn (1661).

4 Lethaby (1906) 67, 92; Kieslinger (1932) 83.

In der ersten Hälfte des 20. Jh. widmet sich R. J. Schaffner in seinem 1932 erschienen „The Weathering of Natural Building Stones“ in zwei Kapiteln – „Atmospheric Pollution in Relation to Weathering“ und „Chemical Phenomena Associated with Weathering“ – diesem Problem.⁵ Zeitgleich erscheint in Wien das Standardwerk „Zerstörungen an Steinbauten“ (1932) von Alois Kieslinger. Dieser ist scheinbar noch nicht ganz überzeugt von dem direkten Zusammenhang, widmet dem Thema aber dennoch zwei Kapitel – III. „Die Krustenbildung“ und IV. „Die Wirkung von Rauch und Ruß“. Dort ist Folgendes nachzulesen: „Seit man der Verwitterung von Bausteinen Beachtung geschenkt hat, ist man auf die wirkliche oder vermeintliche schädliche Wirkung der Rauchgase als Sündenbock gekommen.“⁶ Dieses Zitat bringt noch Kieslingers Skepsis zum Ausdruck, doch in den kommenden Jahrzehnten wird sich der Autor der Zusammenhänge zwischen Luftverschmutzung und „Steinzerfall“ immer gewisser.

Bis zum letzten Drittel des 20. Jahrhunderts dominierten Untersuchungen des „Steinzerfalls“, die hauptsächlich von Geowissenschaftlern und Chemikern durchgeführt wurden. Die praktischen Restaurierungsarbeiten führten dagegen Handwerker und Künstler aus, die meist ohne Verständnis für Schadensphänomene und -mechanismen agierten. Die erste große Veränderung und somit der Anfang der interdisziplinären Arbeit in der Steinrestaurierung erfolgt dann, wie so oft, in Reaktion auf ein scheinbar unlösbares Problem.

Die Zeit nach 1969

Als Startpunkt für die moderne Steinrestaurierung wird oft auf das Jahr 1969⁷ verwiesen. Der Anlass war eine bevorstehende schwierige Restaurierung – die des Tympanons der Kathedrale in Ferrara. Diese stellte die RestauratorInnen vor so komplexe Probleme, dass man zum ersten Mal eine interdisziplinäre Vorgehensweise erwog, um Antworten auf die Vielzahl an Fragestellungen zu finden. Im gleichen Jahr und als direkte Folge dieser Restaurierung wurde die erste „International Conference on Stone Conservation“ in Bologna abgehalten. Drei Jahre später (1972) fand bereits der erste „International Congress on the Deterioration and Conservation of Stone“ in La Rochelle statt. Diese Konferenzen werden im Rhythmus von drei bis vier Jahren bis heute veranstaltet und bilden die Basis der internationalen und interdisziplinären Forschung und Zusammenarbeit in der Steinrestaurierung. Im Rahmen dieser wurde auch die Auseinandersetzung über den Zusammenhang von Luftverschmutzung und Steinzerfall fortgesetzt. In den darauffolgenden Jahren und Jahrzehnten werden der genaue Chemismus und die Dynamik der Schädigung durch Schwefeldioxid auf den Punkt gebracht. Es konnte geklärt werden, dass karbonatische Stoffe, die in Kontakt mit schwefelhaltigen Gasen oder Flüssigkeiten kommen, je nach Exposition eine Gipskruste oder Vergipsung bilden können. Die Gipskruste ist meist durch dunkle Staub- und Rußpartikel, die in der Kruste gebunden werden, schwarz gefärbt (Abb. 1 und 2). Es wurde bewiesen, dass der Schwefelanteil in einer Vergipsung auf Luftschadstoffe zurückgeführt werden kann und dass dieser durch zwei unterschiedliche Prozesse von karbonatischen Oberflächen aufgenommen wird. Die trockene (dry deposition) und feuchte Ablagerung (wet deposition) wurden genau untersucht und beschrieben.⁸ Die Morphologie, die genaue Zusammensetzung, die einzelnen Komponenten und ihr Habitat wurden geklärt.⁹ Genauso wurden die mit der Vergipsung bzw. den Gipskrusten verbundenen potentiellen Folgeschäden durch Feuchtestau, thermische und hygrische Dilatationen etc. erforscht und geklärt.¹⁰

Darauf basierend konnten konservatorisch-restauratorische Maßnahmen erprobt und weitgehend untersucht werden. Man hat früh erkannt, dass im Falle einer Gipskruste eine Reinigung sinnvoll ist. So schreibt Kieslinger bereits vor dieser Zeit (1932): „An den Gebäuden selbst kann die Reinigung jener Teile die nicht ohnedies von Regen bespült werden, die Schädigung wesentlich verzögern.“¹¹ Über die Zeit, vor allem nach 1969, werden in verschiedenen Ländern diverse Methoden für die Entfernung von Gipskrusten und für die Umwandlung von tiefliegenden Vergipsungen entwickelt. Diese wurden im Rahmen interdisziplinärer Forschungsarbeit untersucht und weiterentwickelt. Es handelt sich dabei oft um abrasive Methoden, wie z. B. verschiedene Arten des Partikelstrahlens (mit und

5 Schaffner (1932) 25–32.

6 Kieslinger (1932) 83.

7 Schmid (1990) 34.

8 Sabbioni (2003) 63–65.

9 Bonazza/Brimblecombe (2016) 30.

10 Vgl. Odgers/Henry (2012) 68–71.

11 Kieslinger (1932) 103.



1



2

ohne Wasser, Wirbelstrahl, verschiedene Partikel etc.), chemische Methoden (Ammoniumkarbonat, EDTA, Ionenaustauscherharz), aber auch die Verwendung von Laser wird vor allem für die Entfernung von dunklen Krusten weiterentwickelt. All diese Methoden haben ihre Vor- und Nachteile und offerieren eine breite Palette an Möglichkeiten, die eine differenzierte Vorgehensweise im Umgang mit Vergipsungen und Gipskrusten erlaubt. All dies kann als eine Art Best Practice in der Steinrestaurierung für die lösungsorientierte Arbeitsweise bei neuen Herausforderungen gesehen werden. Durch internationale und interdisziplinäre Bemühungen ist es gelungen, ein komplexes restauratorisches und konservierungswissenschaftliches Problem zu lösen.

Die Vergipsung war für über 100 Jahre eine der Hauptzerstörungsmechanismen von karbonatischen Gesteinen¹², seit den 1970er und 1980er Jahren spielt sie aber eine immer geringere Rolle. Die stark reduzierten Konzentrationen von Schwefelabgasen sind dafür verantwortlich. Durch die Senkung des Schwefelanteils in Mineralölprodukten und Treibstoffen und den Einbau von Entschwefelungsanlagen in Kraftwerken sanken die SO_2 -Konzentrationen in den letzten 120 Jahren drastisch. Gleichzeitig werden immer schwefelärmerer Brennstoffe, wie Erdgas, genutzt. Das führte u. a. dazu, dass in der Zeit zwischen 1970 und 2005 der Schwefeldioxidanteil der Luft in Wien um mehr als 95 % reduziert worden ist.¹³

Obwohl es keine genauen Datensätze für die SO_2 -Konzentrationen in der Zeit um 1900¹⁴ gibt, kann man angesichts der angegebenen Hausbrandmengen in Wien davon ausgehen, dass die Menge an Rußpartikeln und die SO_2 -Konzentration in der Wiener Luft in der Zeit um 1900 am höchsten waren. Demnach müsste, zumindest theoretisch, auch das Wachstum von Gipskrusten in dieser Zeit am schnellsten gewesen sein. Man kann davon ausgehen, dass die Fassaden der Stadt, genauso wie in anderen europäischen Metropolen, einheitlich dunkelgrau waren (Abb. 3). Diese Annahme lässt sich durch fotografische und schriftliche Dokumente bestätigen.

12 Siehe z. B. Brimblecombe (2011) 328.

13 Wiener Umweltbericht (2005) 44.

14 Kieslinger (1932) 92.

Abb. 1: Gipskrusten am Wiener Stephansdom, © Marija Milchin.

Abb. 2: Gipskrusten, St. Katharina, Brüssel, © Marija Milchin.

Da sowohl Kalziumkarbonat als auch Gips wasserlöslich sind, können Fassaden an für Regen zugänglichen Stellen „sauber gewaschen“ werden. Voraussetzung dafür ist, dass

die aktuelle Gipsbildungs- bzw. Verschmutzungsrate langsamer als das „Sauberwaschen“ der Fassade ist. Auch können nur solche Bereiche auf diese Art gereinigt werden, die für Regenwasser zugänglich sind. Um nachzuprüfen, ob diese Überlegungen auch an Wiener Fassaden festgemacht werden können, wurden Fotos der Ostfassade der Votivkirche in Wien aus verschiedenen Jahren zwischen 1880 und 1994 miteinander verglichen. Die Fotografien wurden im Ausschnitt, Kontrast und Farbwert bearbeitet, um einen Vergleich zu ermöglichen. Dabei wurde immer die gesamte Bilddatei und keine Teilbereiche dieser bearbeitet, um eine Verfälschung der Ergebnisse zu vermeiden (Abb. 4a–e).

Die Votivkirche in Wien wurde von Heinrich Ferstel geplant und erbaut. 1879 wurde sie fertiggestellt und eingeweiht. Sie ist eine der wichtigsten historistischen Sakralbauten Österreichs. Ausschlaggebend für die hier getätigte Untersuchung ist der Fakt, dass die Votivkirche seit ihrer Erbauung nie gereinigt bzw. restauriert worden ist. Die gegenwärtig noch laufende Restaurierungskampagne, die im Jahr 2001 begonnen wurde, ist der erste große Eingriff. Bereits 1929 wurden erste Untersuchungen zu den durch Ruß und Rauch bedingten Schäden und ihrer Verteilung an der Fassade durchgeführt. Danach sind aber keine restauratorischen Maßnahmen erfolgt.¹⁵

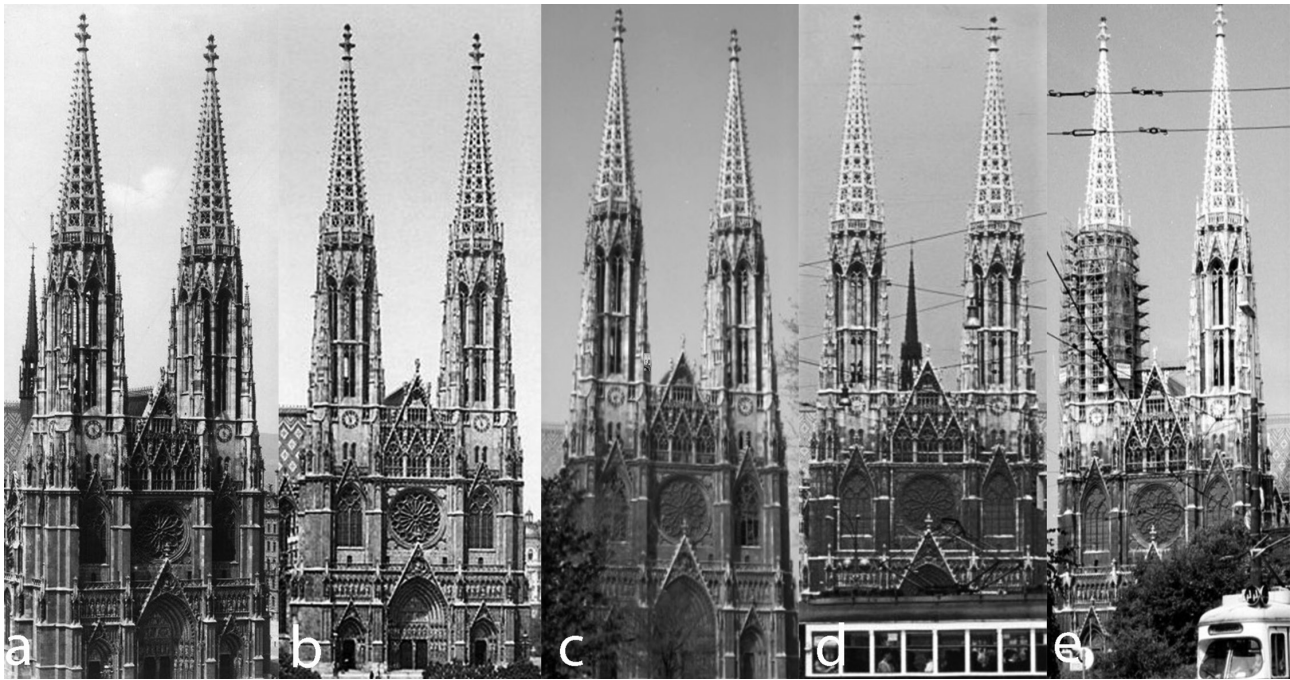
Es werden hier fünf Photographien aus den Jahren 1880, 1900, 1946, 1972 und 1994 (Abb. 4a–e) miteinander verglichen. Ganz deutlich können Unterschiede in der Verteilung und Intensität der Verschmutzung der Fassade ausgemacht werden. Die Veränderungen der Luftqualität in Wien zeigen sich, wie erwartet, mit einer gewissen Verspätung an der Fassade der Kirche. So kann man vor allem in den Jahrzehnten nach der Fertigstellung (Abb. 4a und 4b) eine sehr schnelle und einheitliche Verschmutzung ausmachen, die sich in einem durchgehenden Grauton präsentiert. Diese betrifft sowohl regengeschützte als auch regenexponierte Bereiche. Das spricht für eine schnelle und intensive Verschmutzung aller Oberflächen, die vermutlich durch eine ebenso rasche Vergipsung bzw. Gipskrustenbildung begleitet war. In einer zweiten Phase differenzieren sich die regenexponierten Bereiche zunehmend; sie werden immer heller. Das spricht für das Einsetzen der sogenannten „Selbstreinigung“, also der Lösung von Gips und Kalziumkarbonat im Regenwasser und dem „Herunterwaschen“ zusammen mit vorhandenen Ruß- und Staubpartikeln. Durch diese Prozesse werden die regenexponierten Flächen immer „sauberer“ und „blitzen“ aufgrund der hellen Farbe des Bausteins deutlich hervor. Gleichzeitig werden die regengeschützten Flächen immer dunkler. Zwar verlangsamt sich die Ablagerungsrate durch die immer besser werdende Luftqualität; weil die regengeschützten Flächen aber nicht gereinigt werden, nimmt die Verdunkelung stetig zu. Der Kontrast zwischen den regenexponierten Flächen und jenen im Regenschatten wächst weiter, bis in den 1990ern eine

3



¹⁵ Vgl. https://www.votivkirche.at/_restaurierung.htm [11.06.2020] und Kieslinger (1932) 93–97.

Abb. 3. Postkarte, Graben, 1010 Wien, um 1905; https://commons.wikimedia.org/wiki/File:19060208_wien_graben.jpg; Unknown author / Public domain [20.08.2020].



4a-e

regelrechte Zweiteilung in der Vertikalen auszumachen ist. Also kann hier eine „Selbstreinigung“, zumindest anhand von Fotos, auch für Wien im 20. Jh. bestätigt werden.

Ausblick

Der Klimawandel ist heute keine Prognose für die Zukunft mehr, sondern eine Tatsache. Wie sich diese klimatischen Veränderungen auf das Kulturerbe auswirken, wird in den letzten Jahren verstärkt untersucht. Das wohl wichtigste Projekt, das sich diesem Thema gewidmet hat, ist das NOAH's ARK¹⁶, das einen weitreichenden Einfluss auf „Policy Makers“ wie das Temporary Committee on Climate Change (CLIM) der EU oder die UNESCO ausübte.¹⁷ Im Rahmen dieses Forschungsvorhabens wurde versucht, Prognosen für die neuen bzw. sich verändernden Risiken für das Kulturerbe zu erstellen. Während KlimatologInnen mit Zukunftsprognosen beschäftigt sind, konzentriert sich die Diskussion in der Steinrestaurierung immer noch auf invasive Behandlungsstrategien für Symptome aus der Vergangenheit. So werden beispielsweise Diskussionen über die Entfernung oder Nicht-Entfernung von Gipskrusten geführt. Die Vorhersagen aus dem Projekt NOAH's ARK und anderen Studien beziehen sich unter anderem auf verschiedene Parameter, die die Löslichkeit von Karbonaten im Außenbereich verändern können bzw. werden. In diesem Zusammenhang sind vor allem die Veränderung der Temperatur, der Niederschlagsmengen und deren Verteilung im Jahr, aber auch die CO₂-Konzentration in der Luft von Interesse. Naturstein im Außenbereich, vor allem karbonatische Gesteine wie Marmor und Kalkstein, stellen die Konservierungswissenschaft vor eine sehr spannende Herausforderung. Die „klassischen“ Außenbereich-Schadensmechanismen wie Frost-Tau-Wechsel, Salzkristallisation und mikrobiogene Besiedelung, werden um die Löslichkeit von Karbonat erweitert und ergeben eine äußerst komplexe Situation. Diese wird durch den Klimawandel verändert und möglicherweise verstärkt; die Notwendigkeit einer Auseinandersetzung drängt sich geradezu auf. Die Löslichkeit von Kalziumkarbonat in Wasser und ihre Abhängigkeit von Temperatur und pH-Wert des Wassers sind bereits lange bekannt.¹⁸ Somit ist auch die Schädigung von karbonatischen Gesteinen vor allem in der kalten Jahreszeit ein gut untersuchter Parameter. Die immer milder werdenden Temperaturen im Winter bedeuten für Zentral-Europa und vor allem für Österreich eine längere Zeit im Temperaturbereich über der Nullgradgrenze. Kombiniert man diese mit den längeren Feuchteperioden, kann dies gerade für karbonatische Baustoffe einen größeren Materialabtrag bedeuten. Der

16 European Project (2004–2007).

17 Cassar (2009) 6.

18 Siehe z. B. Steiger et al. (2011) Seite 259.

Abb. 4a–e: Die Ostfassade der Votivkirche in Wien 1880, 1900, 1946, 1972, 1994; bearbeitet durch Marija Milchin; Bildmontage aus: Abb. 4a–c: Autorenschaft unbekannt, Wikimedia Commons; Abb. 4 d–e: © Kurt Rasmussen, Wikimedia Commons.

Anstieg von CO_2 in der Luft wird sich so auf karbonatische Materialien auswirken und eine Erhöhung ihrer Löslichkeit bewirken.¹⁹ Der Abtrag von Kalziumcarbonat wurde von verschiedenen Wissenschaftlern in der Vergangenheit untersucht und beschrieben. Die Dosis-Wirkungs-Funktion nach Lipfert²⁰ ist wohl die am meisten genutzte mathematische Beschreibung für den Abtrag von Kalziumkarbonat. Leider wurde bei dieser Funktion eine konstante CO_2 -Konzentration in der Luft von 330 ppm angenommen. Heute wissen wir, dass die CO_2 -Konzentration in der Luft deutlich ansteigt und voraussichtlich weiter ansteigen wird. Momentan befinden wir uns bei 440 ppm; für das Ende des Jahrhunderts werden 800 ppm erwartet. Der Anstieg der CO_2 -Konzentration in der Luft wurde von Charles David Keeling beschrieben und in der sogenannten Keeling-Kurve dargestellt. Im Jahr 2009 wurde dann die Lipfert Funktion mit den Erkenntnissen und Voraussagen der Keeling-Kurve korrigiert²¹ und Prognosen für die Zukunft getroffen. Dadurch wird ersichtlich, dass eine viel schnellere, intensivere Lösung von Kalziumkarbonat und somit ein stärkerer Materialabtrag von karbonatischen Oberflächen zu erwarten ist.

Da Prognosen für Naturstein im Außenbereich bereits mit einer gewissen Sicherheit getroffen werden können, ist es an der Zeit zu überlegen, welche Maßnahmen angewandt werden können, um dem entgegenwirken zu können. Da Kalkstein und Marmor immer schon beliebte Materialien für künstlerisch hochwertige Arbeiten waren, kann mit einem Blick in die Vergangenheit versucht werden, mögliche Lösungsansätze zu identifizieren. Die historischen Schutzmaßnahmen sollen evaluiert und für die zukünftige Anwendung optimiert werden; z. B. Überdachung, Einhausung bzw. Aufstellen im Innenraum auf der Seite der präventiven Konservierung. Beispiele für solche Maßnahmen finden sich in allen Zeiten und Kulturen. Der „David“ von Michelangelo wurde im Jahre 1873 in der Academia in Florenz aufgestellt; die Skulptur wird im Außenbereich seit 1910 durch eine Kopie ersetzt.²² Auch die Reliefs vom Goldenen Dachl²³ in Innsbruck wurden, nachdem ein „schlechter Zustand...“ 1937 (Kieslinger) bzw. 1938 (Bayerisches Landesamt für Denkmalpflege) festgestellt wurde²⁴, in den 50er und 60er Jahren des 20. Jahrhunderts in den Innenraum gebracht und an ihrer Stelle Kopien aus Naturstein präsentiert. Aber auch Wintereinhausungen sind bereits historisch belegbar und erleben in den letzten Jahren eine Renaissance.²⁵

5



19 Bonazza et al. (2009) 2044.

20 Bonazza et al. (2009) 2040.

21 Bonazza et al. (2009) 2044–2048.

22 Coonin (2014).

23 1500 bzw. 1508.

24 Hörman (1938).

25 Bspw. Winterschutzeinhausungen von Natursteinskulpturen in national bedeutenden Gartenanlagen, modellhafte Bewahrung von Kulturressourcen und Qualitätssicherung (DBU 2012–2017) oder die Entwicklung von ArtCoat durch die TU Dresden und die Firma Empacher (<http://www.artcoat.at>).

Abb. 5: Wintereinhausung von Wandbrunnen, Akademie der Wissenschaften, 1010 Wien; © Marija Milchin.

In Rahmen einer Konservierung-Restaurierung kann mit verschiedenen Oberflächenbehandlungen im Sinne von Beschichtungen und Imprägnierungen versucht werden, die Oberflächen zu schützen und den Substanzabtrag zu minimieren. Traditionelle Maßnahmen wie Tünchen und (Öl-)Farbfassungen bzw. Wachsimprägnierungen sollten neu überdacht werden; aber auch modernere, teils aus der Tradition kommende Methoden wie (Kalk-)Schlämmen und Hydrophobierungen zeigen viel Potenzial hinsichtlich ihrer Schutzfunktion. Angesichts der sich verändernden Umweltbedingungen wird eine ganze Palette neuer und bewährter, jedoch adaptierter Lösungen gebraucht. Wie so oft in der Restaurierung, wird es auch hier keine allgemeingültige Lösung geben. Deswegen ist es so wichtig – wie am Beispiel der Vergipsungsproblematik gezeigt – den Problemstellungen interdisziplinär zu begegnen, um diese im Detail zu verstehen. Eine Auswahl an möglichen restauratorischen Maßnahmen wird benötigt, um für jedes Objekt das optimale Konzept entwickeln zu können.

Zusammenfassung / Summary

Die Gesteinsverwitterung im Außenbereich, an Denkmälern wie auch in der Natur, ist von der Luftqualität und den klimatischen Bedingungen abhängig. Diese sind nicht konstant, sondern ändern sich kontinuierlich. Im 19. Jh. hat die Industrialisierung eine Veränderung der Produktionsweise und eine allgemeine Beschleunigung der gesellschaftlichen Entwicklung hervorgerufen, die eine Veränderung der Luftqualität und folglich des Klimas bedingt haben. Während die Vergipsung im 19. Jh. und den ersten zwei Dritteln des 20. Jh. die wichtigste Schadensursache für Naturstein im Außenbereich darstellte, verlor diese im letzten Drittel des Jahrhunderts an Wichtigkeit und wurde somit ein „Problem der Vergangenheit“. Der Beitrag zeigt den Weg, den die Konservierungswissenschaft und der Steinrestaurierung gegangen sind, um dieses Problem zu lösen. Die Veränderung des Klimas und der Luftzusammensetzung, vor allem der Anstieg der CO₂-Konzentration in der Luft, bringt v. a. für karbonatische Stoffe im Außenbereich eine neue Problemstellung mit sich. Dem Beispiel der Vergipsung folgend, sollte sich auch hier durch interdisziplinäre und internationale Zusammenarbeit eine Lösung finden lassen. Durch die Veränderung der Löslichkeit verändern sich auch der Materialabtrag von Fassaden und somit der ästhetische Eindruck, den sie hinterlassen. Am Beispiel der Wiener Votivkirche wird dieser Wandel gezeigt. Von einem durchgehenden Grau kurz nach ihrer Fertigstellung, veränderte sich die Ostfassade immer mehr Richtung eines kontrastreichen schwarz-weißen Bildes im 20. Jh. Alle Prognosen legen nahe, dass die Steinrestaurierung auch in der nahen und fernen Zukunft vom Klimawandel und seinen Folgen geprägt sein wird. Neben dem Anstieg der Temperatur und der Neuverteilung der Feuchteperioden, kann vor allem in Kombination mit einem starken Anstieg der CO₂-Konzentration in der Luft eine intensivere Lösung von Karbonaten im Außenbereich erwartet werden. Die mögliche Verstärkung des Karsteffekts erfordert Schutzmaßnahmen im Außenbereich. Alte/bewährte und neue/innovative Maßnahmen sind gefragt, um der zukünftigen Situation zu begegnen.

Stone decay, on outdoor monuments as well as in the landscape, depends on air quality and the prevailing climatic conditions. These are not constant but change continuously. In the 19th cent., industrialization caused a change in the way of production and a general acceleration. A rapid change in air quality, subsequently leading to climate change, was the result. While sulphation was the main damage mechanism for outdoor stone in the 19th and the first two thirds of the 20th cent., this phenomenon became less and less important in the last third of the century, thus becoming a „problem of the past“. The article shows the road gone by conservation science and stone conservation in order to solve the problem of sulphation and how this became a best practice model. The change in climate and air composition, especially the increase in CO₂ concentration in the air, brings a new problem for carbonate materials. Following the example of sulphation, interdisciplinary and international work can lead to a solution in this case as well. The increase in solubility causes an increase in the rate of surface recession, thus changing the appearance of monuments. The article shows this using the example of the Votive Church in Vienna. For this purpose, the facade is analyzed with the help of photographs from different eras.

Starting with a homogeneous gray shortly after completion, the facade increasingly shows a contrasting black and white image in the second half of the 20th century. Taking into account all available forecasts, the near and distant future for stone conservation will be shaped by the consequences of climate change. In addition to the increase in temperature and the redistribution of moisture around the year, a more intensive dissolution of carbonates outdoors is to be expected. The possible intensification of the karst effect necessitates protective measures. Old/reliable and new/innovative measures are required to meet the future situation.

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Beiträge zur 26. Tagung des Österreichischen
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Denkmalpflege.

Mitteilungen des Österreichischen Restauratorenverbandes, Band 17/2020

ISBN: 978-3-9504618-3-1

IMPRESSUM

HERAUSGEBER

ÖRV – Österreichischer Restauratorenverband
Postfach 576, 1011 Wien, www.orv.at

REDAKTION

Anke Schäning
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LEKTORAT

Anke Schäning / Andreas Hartl / Beate Murr / Catherine Bouvier

FOTOS

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GRAFIK-DESIGN

Sibylle Gieselmann, www.null7.at

DRUCK

Medienfabrik Wien, www.mfg.at

Wien, 2020

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Maßnahmen zur Erhaltung des baukulturellen Erbes

Monitoring, Schutz und Pflege als
Behandlungsstrategien

Marija Milchin/Martina Haselberger/Gabriela Krist

Einleitung

Alterung, Abbau und Verwitterung sind Prozesse, die auch vor Kunst- und Kulturgut nicht Halt machen. Vor allem im Außenbereich sind Denkmäler, Fassaden oder Skulpturen der Witterung und Luftschadstoffen teils ungeschützt ausgesetzt. Bei Verwitterungsmechanismen spielen Energie in Form von Wärme und die Verfügbarkeit von Wasser eine wichtige Rolle: Wärme beschleunigt in der Regel Abbau- und Degradationsprozesse; Feuchtigkeit, Temperatur und Schadstoffe beeinflussen das Wachstum von Mikroorganismen und höheren Pflanzen bzw. bestimmen die An- oder Abwesenheit von Salzen, ihren Transport und Kristallisation. Daneben beeinflussen auch die Eigenschaften des Materials, aus welchem ein Objekt gefertigt wurde, die Herstellungstechnik, sowie eventuelle Oberflächenbearbeitungen und -behandlungen, in welchem Ausmaß und in welcher Geschwindigkeit dieses beschädigt, abgewittert oder zerstört wird.

Die Konservierungswissenschaft ist eine relativ junge Disziplin, die sich unter anderem mit dem Alterungsverhalten unseres kulturellen Erbes beschäftigt. Diese intensive Auseinandersetzung bedarf üblicherweise längerer Betrachtungs- und Evaluierungszyklen. Auf Grundlage der daraus gewonnenen Erkenntnisse können konservatorische und restauratorische Maßnahmen entwickelt und bei Bedarf angepasst werden. Deswegen muss in der Konservierungswissenschaft in größeren Zeiträumen gedacht werden. Diese „langsame“ bzw. vorsichtige Vorgehensweise bringt im Falle der Konservierung Vorteile mit sich: sie schont Objekte und schützt Restaurator*innen. So werden beispielsweise nur Materialien und Methoden ein-

Measures for the Preservation of our Built Cultural Heritage

Monitoring, protection and care as treatment
strategies

Marija Milchin, Martina Haselberger & Gabriela Krist

Introduction

Ageing, deterioration and weathering are all processes that affect art and cultural heritage. Especially outdoors, monuments, façades and sculptures are exposed to the weather and to air pollutants. Energy in the form of heat and the availability of water play important roles: heat usually accelerates deterioration processes; humidity, temperature and pollutants influence the growth of microorganisms and higher plants, as well as the presence or absence of salts, their transport and crystallisation. In addition, the properties of the material from which an object was made, the manufacturing technique, as well as any surface treatments and finishes also influence to what extent and at what rate it is damaged, weathered or destroyed.

Conservation science is a relatively young discipline that deals, among other things, with the ageing behaviour of our cultural heritage. Intensive examination here usually requires longer observation and evaluation cycles. On the basis of the knowledge gained, conservation and restoration measures can be developed and adapted as necessary. For this reason, conservation science must think in terms of longer time-periods. This 'slow' or cautious approach has advantages, as it protects objects and conservators as well. For one thing, only materials and methods that have stood the test of time and whose ageing and effects have been studied in detail are used. However, the slow development of the discipline also has its disadvantages. These become particularly apparent when environmental conditions change rapidly. Climate change and the climate crisis are no longer speculations

gesetzt, die lange erprobt und deren Alterung und Auswirkungen eingehend untersucht und somit bekannt sind. Die langsame Entwicklung der Disziplin hat aber auch ihre Nachteile. Diese werden besonders dann deutlich, wenn sich die (Umwelt-)Bedingungen schnell ändern. Eine der größten Veränderungen unserer Zeit ist der Klimawandel bzw. die Klimakrise. Diese ist heute keine Spekulation mehr für die Zukunft, sondern eine Tatsache. Ebenso sind die Auswirkungen der klimatischen Veränderungen auf das Kulturgut, das Restaurator*innen zu schützen versuchen, mittlerweile unbestritten und wurden in den letzten Jahren verstärkt untersucht. Das wohl wichtigste Projekt, das sich diesem Thema gewidmet hat, ist das von der EU geförderte NOAH's ARK¹, welches einen weitreichenden Einfluss auf „Policy Makers“ wie das Temporary Committee on Climate Change (CLIM) der EU oder die UNESCO ausübt (vgl. Cassar 2009). Im Rahmen dieses Forschungsvorhabens wurde versucht, Prognosen für die neuen bzw. sich verändernden Risiken für das Kulturerbe zu erstellen.

Hand in Hand mit der Klimakrise geht die Veränderung der Luftqualität. Zusammen verändern sie Schadensmechanismen und beeinflussen so die Erhaltung des Kulturguts. Am direktesten betroffen sind ungeschützte Objekte im Außenbereich. Um hier entgegenzusteuern, muss man proaktiv agieren, anstatt zu reagieren. In diesem Beitrag sollen einige ausgewählte Problemstellungen, die mit dem Klimawandel einhergehen, und einige vielversprechende Lösungsansätze dargelegt werden.

Die Herausforderung

Verschiedene globale und regionale Klimamodelle lassen uns heute in etwa erahnen, mit welchen Rahmenbedingungen wir in Zukunft² rechnen müssen: wie sich das Klima bei verschiedenen Treibhausgas-Konzentrationen

for the future, but a much-tested fact. Moreover, there is undisputed evidence of the effects of climatic changes on the cultural assets that conservators seek to protect. Probably the most important project here is the EU-funded NOAH's ARK,¹ which has had a far-reaching influence on policy makers such as the EU's Temporary Committee on Climate Change (CLIM), and UNESCO (Cassar 2009). The aim of the NOAH's ARK research project was to forecast the new or changing risks to cultural heritage.

The climate crisis is accompanied by changes in air quality; together they affect damage mechanisms and thus affect the conservation of cultural heritage. Unprotected outdoor properties are the most directly affected. To counteract this, it is necessary to be proactive rather than reactive. This article presents some of the problems associated with climate change, noting several promising approaches to solving them.

The challenge

Various global and regional climate models² give a rough idea of the general conditions to be expected in the future: how the climate will develop with different concentrations of greenhouse gases, and how parameters such as temperature, precipitation, wind and sunshine are likely to change at various latitudes. It is already known that global warming and changes in precipitation patterns will vary greatly, regionally and seasonally. The extent to which extreme weather events, such as heavy precipitation, heat waves or winter storms, will increase in intensity and number, however, is subject to uncertainty, although it is becoming increasingly clear that they will increase.³ These climatic changes do not necessarily mean that the ageing, weathering or damage processes of cultural pro-

¹ NOAH's ARK Project – Global Climate Change Impact on Built Heritage and Cultural Landscapes, Project ID: 501837, Funded under: FP6-POLICIES, 2004–2007.

² Modelle sind in der Regel für die nahe (2021–2050) und ferne Zukunft (2071–2100) verfügbar.

¹ NOAH's ARK Project – Global Climate Change Impact on Built Heritage and Cultural Landscapes, Project ID: 501837, Funded under: FP6-POLICIES, 2004–2007.

² Models are available for the near (2021–2050) and long term (2071–2100).

³ <https://www.zamg.ac.at/cms/de/klima/informationsportal-klimawandel/klimazukunft/europa/extremereignisse>, 23.3.2023

entwickeln und wie sich damit einhergehend auch Parameter wie Temperatur, Niederschlag, Wind und Sonnenschein in verschiedenen Breitengraden voraussichtlich ändern werden. Bekannt sind die zu erwartende globale Erwärmung und Änderungen im Niederschlagsverhalten, welche sowohl regional als auch saisonal sehr unterschiedlich ausfallen werden. Inwieweit Extremwetterereignisse, wie Starkniederschläge, Hitzeperioden oder Winterstürme, in Intensität und Anzahl zunehmen, ist hingegen mit Unsicherheiten behaftet obwohl immer sicherer wird, dass diese prinzipiell zunehmen werden.³

Diese klimatischen Veränderungen bedeuten nicht zwangsläufig, dass sich die Alterungs-, Verwitterungs- oder Schädigungsprozesse von Kulturgut in ihrem Ablauf verändern. In den Konservierungswissenschaften beschäftigen sich Restaurator*innen gemeinsam mit Naturwissenschaftler*innen eingehend mit der Erforschung dieser Prozesse und der Frage, wie Schäden durch geeignete präventive, konservatorische und restauratorische Maßnahmen entgegengewirkt werden kann. Heute wissen wir daher über eine Vielzahl an Schadensmechanismen Bescheid und können die Empfindlichkeit verschiedener Materialien in unterschiedlichen Umgebungen und Expositionen gut einschätzen.

Wie bereits erwähnt, werden sich mit dem Klimawandel die Rahmenbedingungen ändern und damit die Geschwindigkeit, in der die zuvor genannten Prozesse ablaufen, sowie die Intensität, in der sie auftreten. Auch das Spektrum an potentiellen Schadensursachen wird sich von Region zu Region verändern. So könnten beispielsweise in höher gelegenen Regionen zuvor eher seltene Schadensmechanismen, wie Frost-Tau-Wechsel, mit Betonung auf „Wechsel“, vermehrt zu Problemen führen, da der Gefrierpunkt durch die generelle Erwärmung häufiger überschritten wird. Auch die Menge an Kulturgut, welches von gewissen Schadens- und Verwitterungsphänomenen betroffen ist, kann sich regional schlagartig ändern: bei-

perty will change, however. Conservators, together with natural scientists, are engaged in detailed research into these processes, asking how damage can be counteracted by suitable preventive, conservation and restoration measures. Today, we know about a range of damage mechanisms and are able to assess the sensitivity of different materials in different environments and exposures. Climate change will alter the general conditions and thus the speed at which the above-mentioned processes take place and the intensity with which they occur. The range of likely causes of damage will also vary from region to region. For example, in higher regions, previously rather rare damage mechanisms, such as freeze-thaw cycles (with the emphasis on 'cycles'), could lead to more problems as the freezing point is exceeded more frequently due to general warming. Moreover, the amount of cultural property affected by damage and weathering phenomena can vary from region to region: for example, when previously 'protected' cultural property, such as (archaeological) objects still in the ground, which are usually protected by the surrounding soil, are exposed to different environmental conditions. Especially conservators of archaeological findings must be prepared, due to the thawing of permafrost soils and/or the drying out of wetlands and marshes.

It is important to combine findings from conservation science with data from climate research – as has been done in NOAA's ARK project. In this way, a better understanding and more precise forecasts can be obtained, enabling conservators to be better prepared for the future and to deal with changes in a more targeted manner.

Examples from stone conservation

In eastern Austria, quarrying sites in the Vienna Basin have supplied 'porous limestone' (calcarenite) for use as building and sculptural stone. This is a sedimentary rock consisting mainly of calcium carbonate, whose pore space is filled only to a limited extent, resulting in relatively high porosity. Depending on the size distribution of

³ <https://www.zamg.ac.at/cms/de/klima/informationsportal-klimawandel/klimazukunft/europa/extremereignisse>

spielsweise, wenn bisher „geschütztes“ Kulturgut, wie noch im Boden befindliche (archäologische) Objekte, welche in der Regel durch das sie umgebende Erdreich geschützt sind, anderen Umgebungsbedingungen ausgesetzt werden. Besonders Restaurator*innen von Bodenfunden müssen sich für diese große Anzahl an Objekten, die durch das Auftauen von Permafrostböden oder die Austrocknung von Feucht- und Sumpfgebieten anfallen, wappnen.

Angesichts dessen ist es wichtig, Erkenntnisse der Konservierungswissenschaften mit Daten der Klimaforschung zu kombinieren, wie es unter anderem in dem Projekt NOAH's ARK geschehen ist. So können ein besseres Verständnis und präzisere Prognosen gewonnen werden, womit Restaurator*innen besser für die Zukunft gerüstet sind und Veränderungen gezielter begegnen können.

Beispiele aus der Steinrestaurierung

Im Osten Österreichs wurde aufgrund der nahegelegenen Abbaustätten im Wiener Becken vor allem "Kalksandstein" (Kalkarenit) als Bau- und Bildhauerstein verwendet. Bei diesem handelt es sich um ein vorwiegend aus Kalziumkarbonat bestehendes Sedimentgestein, dessen Porenraum nur begrenzt gefüllt ist, wodurch insgesamt eine relativ hohe Porosität existiert. Bei den verschiedenen Varietäten ist die Wasseraufnahme je nach Größenverteilung der Poren relativ hoch (teilweise bis 25 %).

Zu den gängigen Schadensmechanismen, die bei diesen Gesteinen zu Rissen, Brüchen oder Abplatzungen führen können, zählt unter anderem der Frost-Tau-Wechsel: Wasser nimmt beim Gefrieren an Volumen zu; geschieht dies im Porenraum des Gesteins, können die Eiskristalle Druck auf die Porenwände ausüben und so zu einem Frostscha den führen. Besonders gravierend können Frost-Tau-Wechsel bedingte Schäden ausfallen, wenn ein Objekt durchfeuchtet oder durchnässt ist und das Über- bzw. Unterschreiten des Gefrierpunktes mehrmals hintereinander geschieht. Zu derartigen Situationen kommt es üblicherweise im Herbst oder Winter, wenn

the pores, the water absorption of the different varieties can be as much as 25 %.

Common damage mechanisms that can lead to cracks, fractures or spalling in these rocks include *freeze-thaw*: water increases in volume when it freezes. If this happens in the pore space of the rock, the ice crystals can exert pressure on the pore walls, leading to freeze-thaw damage. Damage caused by freeze-thaw cycles can be particularly serious if an object has become soaked and the freezing point is exceeded or undershot several times in succession. Such situations usually occur in autumn or winter, when temperatures fall below freezing at night after days of heavy precipitation and the air or object surface is heated up again during the day by solar radiation. Although there will be fewer freeze-thaw events in Europe, the higher temperatures in northern latitudes or at high altitudes are expected to increase the number of freeze-thaw events (Sabbioni, Brimblecombe & Cassar 2010). A look at the climate model discussed in the publication shows that these 'high altitudes' include the Alpine region, which makes up large parts of Austria. Thus, although fewer freeze-thaw cycles and the resultant damage are to be expected in the Vienna area in the future, they will bring completely new problems for stone objects in the south and west of the country, expanding the range of relevant damage mechanisms for some types of objects.

Another damage mechanism that will become increasingly relevant for carbonate rocks is *surface recession*. This is caused by the solubility of lime (calcium carbonate) in water, which is heavily dependent on the temperature and pH value of the water. The solubility of calcium carbonate decreases with increasing temperature, but increases disproportionately with decreasing pH values. In the past, sulphur-containing air pollutants were primarily responsible for surface erosion. Dissolved in rainwater, they lower the pH value, resulting in 'acid rain'. The pollutants enter the atmosphere through the combustion of sulphur-containing fossil fuels such as coal and coke.

nach niederschlagsreichen Tagen die Temperaturen nachts unter 0°C fallen und die Luft oder Objektoberfläche untertags durch Sonneneinstrahlung wieder aufgeheizt wird. Man geht davon aus, dass, obwohl es in Europa weniger Frostereignisse geben wird, durch die höheren Temperaturen in den nördlichen Breiten oder in Höhenlagen die Zahl der Frost-Tau-Ereignisse erhöht wird (vgl. Sabbioni/Brimblecombe/Cassar 2010). Ein Blick auf das in dieser Publikation diskutierte Klimamodell zeigt, dass die „Höhenlagen“ auch den Alpenraum miteinschließen, der große Teile Österreichs ausmacht. So sind zwar im Wiener Raum in Zukunft weniger Frost-Tau-Wechsel und somit auch dadurch bedingte Schäden zu erwarten, jedoch werden sie für Steinobjekte im Süden und Westen des Landes ganz neue Probleme mit sich bringen und somit die Palette der relevanten Schadensmechanismen bei manchen Objektgruppen erweitern.

Ein weiterer Schadensmechanismus, der bei karbonatischen Gesteinen relevanter werden wird, ist der Oberflächenabtrag (engl.: surface recession). Verantwortlich für diesen ist die Löslichkeit von Kalk (Kalziumkarbonat) in Wasser, die stark von Temperatur und pH-Wert des Wassers abhängig ist. Mit steigender Temperatur sinkt die Löslichkeit von Kalziumkarbonat, mit sinkendem pH-Wert steigt sie dagegen überproportional. In der Vergangenheit waren für den Oberflächenabtrag in erster Linie schwefelhaltige Luftschadstoffe verantwortlich. In Regenwasser gelöst, senken sie den pH-Wert stark herab und führen zum landläufig bekannten „sauren Regen“. Die Schadstoffe gelangen durch die Verbrennung schwefelhaltiger fossiler Brennstoffe wie Kohle und Koks in die Atmosphäre. Mit der Zeit ist die Konzentration an Schwefeldioxid in der Luft zwar stark zurückgegangen, jedoch haben heute Kohlendioxid und Stickoxide ihren Platz eingenommen.

Bei näherer Betrachtung der Löslichkeit von Kohlendioxid in Wasser zeigt sich, dass anders als bei vielen anderen chemischen Prozessen mit zunehmender Temperatur weniger CO₂ gelöst wird. Stellt man dem die Prognose der globalen Erwärmung mit wahrscheinlich „wärmerem“ Nie-

Over time, the concentration of sulphur dioxide in the air has greatly decreased – only to be replaced by carbon dioxide and nitrogen oxides.

Closer examination of the solubility of carbon dioxide in water shows that, unlike many other chemical processes, less CO₂ is dissolved as the temperature increases. Contrast this with the prediction of global warming with likely ‘warmer’ precipitation, and one might assume that acid rain (at least, that which is due to CO₂) will be less of a problem in the future.

But this is mainly true of rain in the warm months. In the winter, rainwater stays cold – and it may become increasingly so. A study undertaken by Blöschl et al. in 2011 concluded that, especially in the central region of Austria (Lower Austria, Upper Austria, Styria, Carinthia) an increase in winter precipitation and a higher snowline are to be expected. Both imply a higher amount of precipitation in the form of rain – and the concentration of carbon dioxide in the air is constantly increasing.

So we will face winters with increasingly milder temperatures and longer periods of humidity with precipitation in the form of cold (‘acid’) rain. For carbonate building materials in particular, this can mean an increase in their solubility, and greater and more rapid removal from the original surface (Bonazza et al. 2009).

Possible approaches: Determine, document, monitor, evaluate

It is one thing to anticipate possible changes and try to model them as accurately as possible: it is something else to measure and verify them on the actual object, to check whether and to what extent the assumed changes have indeed occurred.

Various sensors are suitable for such measurements, including what are known as ‘material sensors’, like the ‘Oddy Tests’. These metal plates are used in museums, especially in display cases, to examine or test the environmental conditions for the conservation of metal objects. The sensors are sensitive to various air contami-

derschlag gegenüber, könnte man vermuten, dass saurer Regen (zumindest durch CO_2 bedingt) in Zukunft ein geringeres Problem darstellt.

Doch dies trifft vornehmlich auf den Regen in der warmen Jahreshälfte zu. In den Wintermonaten bleibt das Niederschlagswasser kalt – und es wird unter Umständen mehr. Die Studie von Blöschl et al. kam 2011 zu dem Schluss, dass vor allem im Zentralraum Österreichs (Niederösterreich, Oberösterreich, Steiermark, Kärnten) einerseits mit einer Zunahme der saisonalen Niederschläge (Winterniederschläge) und andererseits mit einer höheren Schneefallgrenze zu rechnen ist. Beides impliziert eine höhere Niederschlagsmenge in Form von Regen. Gleichzeitig steigt die Konzentration an Kohlendioxid in der Luft konstant an.

Wir sehen uns also im Winter mit immer milder werdenden Temperaturen über der Nullgradgrenze und längeren Feuchteperioden mit Niederschlag in Form von kaltem („saurer“) Regen konfrontiert. Dies kann gerade für karbonatische Baustoffe eine Erhöhung ihrer Löslichkeit und einen größeren und rascheren Abtrag von originaler Oberfläche bedeuten (vgl. Bonazza et al. 2009).

Mögliche Lösungsansätze: Ermitteln, Dokumentieren, Monitoren, Evaluieren

Es ist eine Sache, mögliche Veränderung zu antizipieren und zu versuchen, diese möglichst genau zu modellieren, etwas anderes aber, diese dann am Objekt zu messen und zu verifizieren, um so zu überprüfen, ob und inwieweit die vermuteten Veränderungen eingetreten sind.

Für solche Messungen eignen sich verschiedene Sensoren, unter ande-

nants and can indicate the presence of corrosive gases by forming various corrosion products.

Similar concepts can be developed for specific changes expected due to climate change. One possibility would be to use polished material sensors made of various mineral materials, including marble and/or limestone (chemical composition: calcium carbonate) or alabaster (calcium sulphate), to measure the surface erosion of calcium carbonate.

The water-solubility of calcium carbonate and its dependence on temperature and pH value of the water have been known for a long time (Steiger et al. 2011), and scientists have investigated and described the removal of calcium carbonate (Bonazza et al. 2009). The dose-response function according to Lipfert is probably the most common mathematical description in this context: how-



Abb. 1: Testreihe, exponierte mineralische Material-Sensoren (Marmor, Kalkstein und Alabaster)
Fig. 1: Test series, exposed mineral material sensors (marble, limestone and alabaster)

rem die sogenannten „Material-Sensoren“ (engl.: material sensors). Die wohl bekanntesten in der Restaurierung sind die sogenannten „Oddy Tests“. Diese Metallplättchen werden in Museen, vor allem in Vitrinen eingesetzt, um die Umgebungsbedingungen für die Erhaltung von Metallobjekten zu untersuchen bzw. prüfen. Die Sensoren sind gegenüber verschiedenen Luftverunreinigungen empfindlich und können durch das Bilden von verschiedenen Korrosionsprodukten die Anwesenheit von korrosiven Gasen aufzeigen.

In Anlehnung an diese Sensoren können für spezifische Veränderungen, die durch den Klimawandel zu erwarten sind, ähnliche Konzepte entwickelt werden. Eine Möglichkeit wäre, mit polierten Material-Sensoren aus verschiedenen mineralischen Materialien, unter anderem Marmor und/oder Kalkstein (chemisch: Kalziumkarbonat) bzw. Alabaster (chemisch: Kalziumsulfat), den Oberflächenabtrag von Kalziumkarbonat zu messen (Abb. 1).

Die zuvor bereits erläuterte Löslichkeit von Kalziumkarbonat in Wasser und ihre Abhängigkeit von Temperatur und pH-Wert des Wassers sind lange bekannt (vgl. Steiger et al. 2011). Verschiedene Wissenschaftler*innen untersuchten und beschrieben den Abtrag von Kalziumkarbonat (vgl. Bonazza et al. 2009). Die Dosis-Wirkungs-Funktion nach Lipfert ist in diesem Zusammenhang wohl die gängigste mathematische Beschreibung. Einziges Manko dieser Funktion ist, dass eine konstante CO_2 -Konzentration in der Luft von 330 ppm angenommen wurde. Heute wissen wir aber, dass diese deutlich ansteigt und voraussichtlich weiter ansteigen wird. Momentan befinden wir uns bereits bei 420 ppm; für das Ende des Jahrhunderts werden bei manchen Emissionsszenarien 800 ppm prognostiziert. Der Anstieg der CO_2 -Konzentration in der Luft wurde von Charles David Keeling beschrieben und in der sogenannten Keeling-Kurve dargestellt. Im Jahr 2009 korrigierte man die Lipfert Funktion mit den Erkenntnissen und Voraussagen der Keeling-Kurve, um präzisere Prognosen für die Zukunft machen zu können. Dadurch wird ersichtlich, dass eine viel schnellere und intensivere Lösung von Kal-

ever, it assumed a constant CO_2 concentration in the air of 330 ppm. Today we know that this is increasing significantly and will probably continue to do so. We have already reached 420 ppm; for the end of the century 800 ppm are predicted in some emission scenarios. The increase in CO_2 concentration in the air was described by Charles David Keeling and depicted in the so-called Keeling curve. In 2009, the Lipfert function was corrected with the findings and predictions of the Keeling curve in order to make more precise forecasts for the future. This indicates that much faster, more intensive dissolution of calcium carbonate and increasing material removal from carbonate surfaces is to be expected. This hypothesis must now be tested, not least with material sensors.

Another important tool is *monitoring* of objects and surfaces. This can enable better, more precise determination of changes in the speed and intensity of weathering mechanisms caused by climate change. In conservation work, monitoring involves repeated survey of condition, with the basic aim of assessing the speed or dynamics of any changes or weathering and deterioration. Monitoring can help us to better assess the cycles in which maintenance and/or conservation measures need to be planned. It also makes possible early detection of new damage.

In *preventive conservation*, monitoring is already widely used as a long-term strategy, both indoors and outdoors. Indoors, it is mainly the monitoring of temperature and humidity, but also pest monitoring, which are essential for long-term conservation. In outdoor areas, parameters such as material properties, changes in the state of preservation and the effects of measures taken are recorded via monitoring, in addition to the climate. Simple *in situ* test procedures and analyses are often suitable for this.

Renaissance of the tried and tested?

In addition to identifying, documenting and evaluating, it is essential to consider what measures can be applied to respond to forecasts for the preservation and weathering of natural stone in outdoor areas from the perspective of

ziumkarbonat und somit ein stärkerer Materialabtrag von karbonatischen Oberflächen zu erwarten ist. Diese Hypothese gilt es nun unter anderem mit Material-Sensoren zu überprüfen.

Ein zweites und wichtiges Tool ist das restauratorische Monitoring von Objekten und Oberflächen. Dieses wird immer wichtiger, um durch den Klimawandel bedingte Veränderungen in der Geschwindigkeit und Intensität von Verwitterungsmechanismen besser und genauer festmachen zu können.

Unter Monitoring versteht man in der Konservierung eine wiederholte Zustandserhebung mit dem Hauptziel, die Geschwindigkeit bzw. Dynamik von eventuellen Veränderungen bzw. Verwitterung und Zerstörung abzuschätzen. Monitoring kann dabei helfen, besser einzuschätzen, in welchen Zyklen Pflege und/oder konservatorische Maßnahmen geplant werden müssen. Außerdem ermöglicht es eine frühe Detektion von neuen Schäden.

In der präventiven Konservierung hat das Monitoring als langfristige Strategie sowohl im Innen- als auch Außenbereich bereits eine breite Anwendung. Im Innenraum sind es vor allem die Überwachung von Temperatur und Luftfeuchtigkeit, aber auch das Schädlings-Monitoring, welche für die langfristige Erhaltung unerlässlich sind. Im Außenbereich werden neben dem Klima auch Parameter wie Materialeigenschaften, Veränderungen des Erhaltungszustandes sowie die Effekte von gesetzten Maßnahmen über das Monitoring erfasst. Hierfür eignen sich oft einfache In situ-Testverfahren und Analysen.

Renaissance von Altbewährtem?

Neben dem Ermitteln, Dokumentieren und Evaluieren ist es auch dringend an der Zeit zu überlegen, welche Maßnahmen angewandt werden können, um auf die Prognosen zum Erhalt und der Verwitterung von Naturstein im Außenbereich unter dem Gesichtspunkt des Klimawandels zu reagieren. Da Kalkstein und Marmor immer schon beliebte Materialien für künstlerisch hochwertige Arbeiten waren, kann mit einem Blick in die Vergangenheit versucht

climate change. As limestone and marble have always been popular materials for high quality artistic works, a look into the past can help to identify possible solutions. It makes sense to evaluate historical protective measures, subjecting them to new, critical assessment and investigating their potential for optimised future application. The possibilities include canopies, shelters and indoor placement on the preventive conservation side, as well as various surface treatments (coatings and impregnations) in the case of conservation and restoration.

Examples of such measures can be found in all times and cultures. Michelangelo's famous 'David', for example, was placed (indoors) in the Galleria dell'Accademia in Florence as early as 1873. An outdoor copy was created in 1910 (Coonin 2014). To take another example: The reliefs from the Golden Roof in Innsbruck⁴ were moved indoors in the 1950s and 1960s, after their 'poor condition ...' had been confirmed in 1937 (Kieslinger) and 1938 (Bayerisches Landesamt für Denkmalpflege; Hörmann 1938). Copies made of natural stone have stood in their place ever since. This transferring particularly valuable objects has long been a possible option. However, it must be recognised that not all objects affected by climate change can or should be replaced by copies and/or removed from their original surroundings. They were usually designed for a specific place or context, so this quite effective protective measure ought to remain an exception.

Particularly in view of the possible increase in precipitation in winter (surface recession, freeze-thaw cycles), winter shelters, known in Europe since the Baroque period, and canopies are again coming into focus (Franzen 2008). Various materials are used for shelters: from traditional wood to the semi-permeable textiles available today (Figs. 2 and 3). Such structures are erected before the onset of winter to protect the objects from direct contact with water, in the form of rain or snow, in the following months. The shelters also serve as a kind of buffer

⁴ 1500 and 1508

werden, mögliche Lösungsansätze zu identifizieren. Es ist sinnvoll, historische Schutzmaßnahmen zu evaluieren, einer neuen kritischen Bewertung zu unterziehen und ihr Potential für eine optimierte Anwendung in der Zukunft zu untersuchen: Überdachungen, Einhausungen und das Aufstellen im Innenraum auf Seite der präventiven Konservierung sowie verschiedenen Oberflächenbehandlungen, im Sinne von Beschichtungen und Imprägnierungen, im Falle der Konservierung und Restaurierung, gehören zu den Möglichkeiten. Beispiele für solche Maßnahmen finden sich in allen Zeiten und Kulturen.

Der berühmte „David“ von Michelangelo zum Beispiel wurde bereits im Jahre 1873 in der Galleria dell'Accademia in Florenz, also im Innenbereich, aufgestellt; die Skulptur wird im Außenbereich seit 1910 durch eine Kopie ersetzt (Coonin 2014). Auch die Reliefs vom Goldenen Dachl⁴ in Innsbruck wurden in den 50er und 60er Jahren des 20. Jahrhunderts in den Innenraum gebracht, nachdem 1937 (Kieslinger) bzw. 1938 (Bayerisches Landesamt für Denkmalpflege) ein „schlechter Zustand ...“ konstatiert wurde (Hörmann 1938); an ihrer Stelle werden seither Kopien aus Naturstein präsentiert. Das Verbringen in den Innenbereich war also besonders für sehr hochwertige bzw. wichtige Objekte immer schon eine mögliche Option und wird es auch weiterhin bleiben. Gleichzeitig muss klargestellt werden, dass nicht alle vom Klimawandel betroffenen Objekte einfach durch Kopien ersetzt und/oder aus ihrer Umgebung entfernt werden können und sollen, da diese meistens für einen bestimmten Platz bzw. Kontext konzipiert sind/waren. Deswegen sollte diese durchaus wirksame Schutzmaßnahme eher eine Ausnahme bleiben.

Besonders in Hinblick auf die mögliche Zunahme des Niederschlags im Winter (Oberflächenabtrag, Frost-Tau-Wechsel) rücken (Winter-)Einhausungen, wie sie seit dem Barock in Europa verwendet werden, und Überdachungen in den Fokus (Franzen 2008). Verschiedene Materialien

between the object and the outside, intended to cushion fluctuations in temperature and humidity.

In recent decades, their use has declined considerably – for reasons of cost, but also because of the personnel effort required for assembly and dismantling. In Vienna's Schönbrunn Palace Garden, for example, where the garden sculptures made of white Sterzing marble had been provided with wintertime wooden shelters since the Baroque period, shelters have dropped completely after a brief trial phase with textile wraps in the early 2000s (Hasselberger 2011).

In many cases, negative experiences with new types of shelter materials such as Plexiglas (e.g. condensation water and biological colonisation) or damage caused by shelters falling over during winter storms (expected to occur more often and with great force in the future) have led to a general withdrawal from this practice. However, with the correct application and choice of materials, this well-tried method has considerable potential. This is also reflected in recent research which has shown the renaissance of this measure.⁵ The choice of materials used is important; depending on the object and size, wood, but also various semi-permeable textiles, have proven suitable: these can 'breathe' and in some cases have good buffering properties. Further important criteria are a suitable construction without direct contact to the surface of the object and adequate stability and stability (storm resistance). Correctly dimensioned and positioned, canopies can protect objects and façades from direct precipitation all year round (Fig. 4). However, for reasons of conservation (interference with the original substance) as well as monument preservation and aesthetics, it is not possible to install such constructions (retrospectively) everywhere. Among the various surface treatments used for protecting objects and minimising substance erosion, traditional

⁵ For instance, winter shelters for natural stone sculptures in nationally significant gardens, model conservation of cultural resources and quality assurance (DBU 2012–2017) or ArtCoat, as developed by the University of Dresden and the Empacher company (<http://www.artcoat.at>).

⁴ 1500 bzw. 1508

kommen für Einhausungen zum Einsatz: von traditionell verwendetem Holz bis hin zu verschiedenen semipermeablen Textilien, die heute erhältlich sind (Abb. 2 und 3). Die Konstruktionen werden vor Beginn des Winters errichtet, um die Objekte in den Folgemonaten vor direktem Kontakt mit Wasser, in Form von Regen oder Schnee, zu schützen. Auch dienen die Einhausungen als eine Art Puffer zwischen Objekt und Außenbereich, welcher Schwankungen in Temperatur und Luftfeuchtigkeit abfedern soll.

In den letzten Jahrzehnten des 20. Jahrhunderts ist ihre Verwendung aus Kostengründen, aber auch aufgrund des personellen Aufwandes beim Auf- und Abbau stark zurückgegangen. Im Schönbrunner Schlosspark in Wien beispielsweise, wo die Gartenskulpturen aus Sterzinger Marmor seit dem Barock im Winter Holzeinhausungen erhielten, wird seit einer kurzen Probephase mit textilen Einhausungen Anfang der 2000er Jahre komplett auf Einhausungen verzichtet (Haselberger 2011).

In vielen Fällen führten auch negative Erfahrungen mit neuartigen Einhausungsmaterialien, wie Plexiglas (u.a. Kondenswasser und biogene Besiedelung), oder Schäden, die durch umstürzende Einhausungen beispielsweise bei Winterstürmen (welche in Zukunft vermutlich öfter und stärker vorkommen werden) bei meist unsachgemäßer oder unterdimensionierter Montage entstanden sind, zu einer generellen Abkehr von dieser Praxis.

Bei richtiger Anwendung und Materialwahl birgt diese altbewährte Methode jedoch viel Potential. Dies spiegelt sich auch in den Forschungen der letzten Jahre wider, die eine Renaissance dieser Maßnahme untermauern.⁵ Wich-



Abb. 2: Holz-Wintereinhausungen von Skulpturen und Plastiken, Langenzersdorf Museum, Niederösterreich

Fig. 2: Wooden winter shelters for sculptures, Langenzersdorf Museum, Lower Austria

measures such as whitewashing and (oil) paint or wax impregnation should be reconsidered. Also more modern measures, some of which are based on traditional approaches, such as (lime) sacrificial layers or industrially produced hydrophobic coatings also have considerable protective potential.

Simply put, (lime) sacrificial layers are coatings based on lime, modified with a filler or additive of mostly carbonate sand. This additive gives the coating more 'body' and thus enables a better buffering effect against chemical and physical (weathering) processes. In Austria, the use of these sacrificial layers became popular the last two decades of the 20th century; mainly as a chemical buffer against acid rain and the associated gypsification of surfaces. However, once this problem was more or less under control, the use of sacrificial layers in stone conservation decreased significantly. This led to a 'sacrificial layer con-

⁵ z.B.: Winterschutzeinhausungen von Natursteinskulpturen in national bedeutenden Gartenanlagen, modellhafte Bewahrung von Kulturressourcen und Qualitätssicherung (DBU 2012 – 2017) oder die Entwicklung von ArtCoat durch die Uni Dresden und die Firma Empacher (<http://www.artcoat.at>)

tig ist die Wahl der eingesetzten Materialien; hier haben sich je nach Objekt und Größe Holz, aber auch verschiedene semi-permeable Textilien bewährt, da diese "atmungsaktiv" sind und teils gute Puffereigenschaften haben. Eine geeignete Konstruktion ohne direkten Kontakt zur Objektoberfläche und die adäquate Stabilität und Standfestigkeit (Sturmsicherheit) sind weitere wichtige Kriterien, damit eine Einhausung ihre Schutzfunktion erfüllen kann.

Überdachungen können, sofern sie richtig dimensioniert und positioniert sind, Objekte und Fassaden ganzjährig vor direktem Niederschlag schützen (Abb. 4). Jedoch ist es aus konservatorischen (Eingriff in Originalsubstanz) aber auch denkmalpflegerischen und ästhetischen Gründen nicht überall möglich, derartige Konstruktionen (im Nachhinein) anzubringen.

Bei den verschiedenen Oberflächenbehandlungen, mit denen versucht wird, Objekte zu schützen und den Substanzabtrag zu minimieren, sollen traditionelle Maßnahmen wie Tünchen und (Öl-)Farbfassungen bzw. Wachsimprägnierungen neu überdacht werden; aber auch modernere, teils aus der Tradition kommende Maßnahmen wie (Kalk-)Schlämmen bzw. industriell hergestellte Hydrophobierungen zeigen viel Potenzial hinsichtlich ihrer Schutzfunktion.

Die sogenannten (Kalk-)Schlämmen sind, vereinfacht gesagt, Anstriche auf Basis von Kalk, die mit einem Füllstoff oder Zuschlag aus meist karbonatischem Sand modifiziert sind. Dieser Zuschlag gibt dem Anstrich „mehr Körper“ und ermöglicht somit eine bessere Pufferwirkung gegenüber chemischen und zum Teil physikalischen (Verwitterungs-)Prozessen. In Österreich sind diese Schlämmen in den letzten zwei Jahrzehnten des 20. Jahrhunderts in Mode gekommen; hauptsächlich als chemischer Puffer gegenüber dem sauren Regen und der damit verbundenen Vergipsung der Oberflächen. Nachdem wir dieses Problem aber mehr oder weniger in den Griff bekommen haben, hat auch die Verwendung von Schlämmen in der Steinrestaurierung deutlich nachgelassen. Dies führte zu einer

troversy' in monument conservation in Austria, in turn resulting in closer examination of sacrificial layers within the framework of a working group set up by the Federal Monuments Office. After seven years of intensive work, guidelines on sacrificial layers were published and an outdoor weathering facility for stone slabs with sacrificial layers was installed in Mauerbach (Lower Austria), and is regularly evaluated (Fig. 5).

Application of sacrificial layers is expected to be used increasingly in the future, especially for porous carbonate



Abb. 3: Textile Wintereinhausung von Wandbrunnen, Akademie der Wissenschaften, Wien

Fig. 3: Textile winter shelter of wall fountains, Academy of Sciences, Vienna

„Schlamm-Kontroverse“ in der Denkmalpflege in Österreich, die wiederum in einer näheren Auseinandersetzung mit Schlämmen im Rahmen einer vom Bundesdenkmalamt ins Leben gerufenen Arbeitsgruppe mündete. Nach sieben Jahren intensiver Beschäftigung mit der Thematik wurde der „Leitfaden Schlämmen“ publiziert und eine Freibewitterungsanlage von geschlammten Steinplatten in Mauerbach (NÖ) installiert, welche regelmäßig evaluiert wird (Abb. 5). Es ist durchaus zu erwarten, dass Schlämmen künftig wieder verstärkt, vor allem für poröse karbonatische Gesteine im Außenbereich, angewendet werden wird. Diesmal jedoch nicht in der Funktion einer Pufferschicht gegen die schwefelhaltigen Stoffe in der Luft, sondern gegen den Abtrag der „originalen Oberflächen“ durch Lösungsprozesse. So kann eine altbewährte Maßnahme durch Modifikationen eine neue Aufgabe und somit eine neue Chance bekommen.



Abb. 4: Dachkonstruktion über römischen Grabsteinen und Sarkophagen, Leithaprodersdorf, Burgenland
Fig. 4: Roof construction over Roman gravestones and sarcophagi, Leithaprodersdorf, Burgenland, Austria

Zusammenfassung

Die Gesteinsverwitterung im Außenbereich, an Denkmälern wie auch in der Natur, ist von der Luftqualität und den vorherrschenden klimatischen Bedingungen abhängig. Diese sind nicht konstant, sondern ändern sich kontinuierlich. Die Veränderung des Klimas und der Luftzusammensetzung, wie der Anstieg der CO_2 -Konzentration, bringt vor allem für karbonatische Stoffe im Außenbereich eine neue Problemstellung mit sich. Alle Prognosen legen nahe, dass die Steinrestaurierung auch in der nahen und fernen Zukunft vom Klimawandel

stones in outdoor areas – however, as a buffer layer against the sulphurous substances in the air, but against the erosion of the original surfaces by solution processes. In this way, a tested-and-true measure can be given new tasks and thus new chances.

Summary

Rock weathering in outdoor areas, on monuments as well as in nature, depends on the air quality and the prevailing climatic conditions. These are not constant, but change continuously. The change in climate and air composition, as with the increase in CO_2 -concentration, poses new

und seinen Folgen geprägt sein wird. Mit dem Anstieg der Temperatur und der Neuverteilung der Feuchteperioden ist in Kombination mit einem starken Anstieg der CO₂-Konzentration in der Luft von einer intensiveren Lösung von Karbonaten im Außenbereich auszugehen. Die „klassischen“ Außenbereich-Schadensmechanismen wie Frost-Tau-Wechsel, Salzkristallisation und mikrobiogene Be-

problems, especially for carbonate materials in outdoor areas.

All forecasts indicate that stone conservation will continue to be affected by climate change and its consequences, in the near and distant future. With the increase in temperature and the redistribution of humid periods, in combination with a considerable increase in CO₂-concentration,



Abb. 5: Evaluierung der Freiluftbewitterungsanlage von Schlammplatten, Mauerbach, NÖ

Fig. 5: Evaluation of the outdoor weathering system of slabs with sacrificial layers, Mauerbach, Lower Austria

siedelung werden erweitert und ergeben eine äußerst komplexe Situation. Diese wird durch den Klimawandel verändert und möglicherweise verstärkt. Die Notwendigkeit einer Auseinandersetzung drängt sich geradezu auf, denn die mögliche Verstärkung des Karsteffekts⁶ erfordert Schutzmaßnahmen. Objekte im Außenbereich, vor allem solche, die aus karbonatischen Gesteinen wie Marmor und Kalkstein bestehen, stellen die Konservierungswissenschaft vor eine sehr spannende Herausforderung, die nur interdisziplinär analysiert werden kann, um Prozesse im Detail zu verstehen und Lösungsansätze formulieren zu können. Alte/bewährte und neue/innovative Maßnahmen sind gefragt, um der zukünftigen Situation zu begegnen. Wie so oft in der Restaurierung wird es auch hier kein allgemeingültiges Rezept geben. Eine Kombination aus Monitoring, Evaluierung, präventiven und invasiven Schutzmaßnahmen wird notwendig sein, um den neuen Herausforderungen zu begegnen. Eine Auswahl an verschiedenen Maßnahmen wird benötigt, um für jedes Objekt ein optimales Konzept zu entwickeln.

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⁶ In der Geologie beschreibt der Begriff Karst Gesteine/Gesteinsformen (Karbonatgesteine), die vorwiegend durch Lösungsprozesse bzw. Kohlensäureverwitterung entstanden sind. Sie erhalten durch diese Form der Lösung/Auslaugung ihre charakteristische Erscheinung. Der durch den Klimawandel zu erwartende Oberflächenabtrag (surface recession) durch das "saure kalte Wasser" ist diesem natürlichen Prozess ähnlich.

trations in the air, more intensive dissolution of carbonates in outdoor areas can be expected. 'Classic' outdoor damage mechanisms such as freeze-thaw cycles, salt crystallisation and microbiological colonisation will be extended, resulting in an extremely complex situation. This will be affected and possibly intensified by climate change: dealing with this is indeed a matter of urgency. The possible amplification of the karst effect⁶ requires protective measures. Outdoor objects, especially those made of carbonate rocks like marble and limestone, present conservation science with major challenge. Interdisciplinary analysis is required to understand these processes in detail and formulate solutions. Tried and true as well as new and innovative measures are needed. As is so often the case in conservation, there can be no universal recipe. A combination of monitoring, evaluation, preventive and invasive conservation measures will be necessary to meet the new challenges, requiring a range of measures to develop an optimal concept in each case.

Bildnachweis/Picture credits:

Abb./Figs. 1 – 5: © Marija Milchin, Institut für Konservierung und Restaurierung, Universität für angewandte Kunst Wien

⁶ In geology, the term karst describes rocks/rock forms (carbonate rocks) that have predominantly been formed by solution processes or carbonic acid weathering. This form of dissolution/leaching gives them their characteristic appearance. The surface recession to be expected as a result of climate change due to the "acidic cold water" is similar to this natural process.

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Schutz vor Witterung und Luftschadstoffen Protection from weathering and air pollutants

Kurt Luger/Alexander Würfl (Hrsg.)

Welterbe Salzburg in Zeiten des Klimawandels

World Heritage in Times of Climate Change

- 3) Milchin, M., Weber, J. & Krist G. (2023). Sensor Materials for the Deterioration of Carbonates in a Changing Outdoor Environment. *News in Conservation 97, Wellington Congress Posters – Conservation and Change: Response, Adaption and Leadership*, p.92 - 95

SENSOR MATERIALS FOR THE DETERIORATION OF CARBONATES IN A CHANGING OUTDOOR ENVIRONMENT

By Marija Milchin, Johannes Weber and Gabriela Krist

In this time of climate change and changing air quality, efforts must be made to increase our knowledge of the processes and rates at which materials deteriorate. In order to understand how the changes in climate and air quality influence the decay of materials, sensor materials as well as on-site monitoring can be implemented. In this poster, possible sensor materials for the surface recession of carbonate stones are proposed, tested and discussed.

It is expected that the recession rate of carbonate materials will increase in the near and far future in Europe, as suggested by Bonnaza, et al. (2009). In order to measure this phenomenon on site, sensor materials are proposed and evaluated in the following work. Polished samples of natural stones consisting of calcium carbonate and calcium sulphate (marble, limestone and different alabaster types) were compared and evaluated regarding their possible use as sensor materials for the wettability and surface recession of carbonate stones. For the evaluation, different methods of analysis including 3D microscopy, gloss and gravimetric measurements were used.

As a result the pros and cons of each of the sensor materials can be stated and typical situations and expositions defined in which one or the other sensor is indicated. Alabaster sensors seem to be very promising for the wetting of the surfaces while surface recession is best estimated with help from the sensors consisting of calcium carbonate. In order to monitor the sensors, gloss and weight measurements provide a simple but promising possibility; the measurement of the surface relief using a 3D digital microscope gives more insight to the morphology and development of the decay patterns.

Sensors can contribute to the decision-making process regarding possible conservation strategies and methods. Depending on the exposure and the rate of decay, traditional conservation measures like protective coatings and/or shelters (permanent or temporary) can be recommended. Similar to the Oddy tests for metals, standardized sensor materials for evaluating the decay rate of outdoor stone monuments can help towards sustainable conservation solutions and case specific interventions in the future. Sensors can become part of wider monitoring strategies offering a sustainable approach to the preservation of outdoor monuments or ensembles in times of frequent resource shortage.



Marija Milchin is a stone conservator who gained her degree in conservation at the University of Applied Arts Vienna in 2006. After two years at a private conservation company (Atelier Gurtner Wien), she started working at the Institute of Conservation in 2008 in the position of university assistant, teaching the theory and practice of stone conservation. At the Institute she is frequently involved in projects concerning cultural heritage in Austria and abroad (Nepal, India, Mongolia, Albania, Croatia, etc.). Since 2019 her research has focused on the possibilities for protection of outdoor stone monuments with regards to climate change in the frame of her doctoral thesis.



Johannes Weber, a petrologist who graduated from the University of Vienna, has been employed since the 1980s at the University of Applied Arts Vienna where he has been lecturing on mineral material sciences in respect to the characterization, decay diagnosis and principles of conservation to students of heritage conservation. His national and international research activities have focused on issues of stone deterioration and conservation as well as on ancient and historic mortar characterization. Retired from his position as professor in 2020, Johannes Weber is currently active as an honorary professor and lecturer and continues working in his fields of expertise.



Gabriela Krist has been university professor at the University of Applied Arts Vienna since 1999 and is head of the Institute of Conservation. Since 2019 she has been chair holder of the UNESCO Chair on Conservation and Preservation of Tangible Cultural Heritage. She studied conservation at the Academy of Fine Arts Vienna as well as art history and archaeology in Vienna and Salzburg. For many years she worked for ICCROM in Rome and at the Austrian Federal Office for the Care of Monuments (Bundesdenkmalamt). She leads education co-operation programmes, conservation campaigns and workshops in India, Nepal, Mongolia and Thailand.

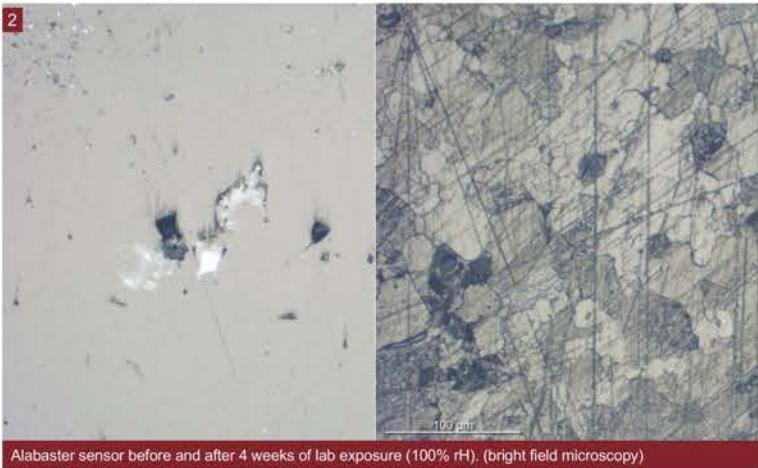
SENSOR MATERIALS FOR THE DETERIORATION OF IN A CHANGING OUTDOOR ENVIRONMENT

Marija Milchin, Johannes Weber and Gabriela Krist

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1. Introduction

In the time of climate change and changing air quality, efforts must be made to increase our knowledge of the processes and rate at which materials deteriorate. In order to understand how these factors affect the decay of heritage materials, the exposure of sensors as well as on-site monitoring can be implemented. It is expected that the recession rate of carbonate materials will increase in the near and far future in Europe, as suggested by Bonnaza et al. (2009). In order to ensure this phenomenon on site, sensor materials are proposed and evaluated in this study. Different compact natural stone materials consisting of calcium carbonate (compact limestone from Vraca, Bulgaria and Carrara marble from Italy) and calcium sulphate (different types of alabaster) were tested for their potential as materials for sensors for the recession of carbonate surfaces. Preliminary testing in the lab was followed by field exposure (Fig.1). Varying types of surface polish were assessed for their suitability to monitor surface erosion under different environmental impact found on sites. Three different analytical approaches were used for the assessment of surface alterations, namely gravimetry, gloss measurements and microscopy (3D digital and optical microscopy).



1
Sensor material
Alabaster
Alabaster
Alabaster
Vraca compact limestone
Carrara marble
3
The relative drop in gloss

3. Methodology and Results: Field exposure tests

In the first field exposure test series, three alabaster types differing in transparency and colour and two carbonate stones (Carrara marble and Vraca compact limestone) were tested. The samples (4x4x1cm) were mounted facing NW in Lower Austria, placed on an exposure rack at an angle of approx. 45° (Fig.1). The surfaces before exposure were hand polished; back and sides of the sensors sealed. Gloss and weight were measured before as well as after exposure; microscopy was used for the detailed examination of the surface. After 3 months the first set of sensors was removed from the exposure rack and tested.

Results: Gloss and gravimetry

The results from the gloss measurements (20°, 60° and 85°) reveal a significant drop in the gloss value (drop of value between 26 and 97%) for all stones and all angles after three months, making the gloss measurement a promising testing method for the initial surface recession (Fig.3). However, it is expected that changes in surface gloss will flatten with increasing exposure time, as the surface recession produces a matt surface and the gloss approaches 0 GU. Although all sensors show weight reduction after 3 months, the loss is still under 1%; the alabaster samples have lost between 0,3 and 0,5%, the carbonate stones (Vraca and Carrara) under 0,1%.

Results: Microscopy

The use of incident light microscopy before and after the exposure enables a better understanding of microstructural effects of the weathering process as well as the assessment of initial changes in the surface morphology of the sensor materials. While the 3D microscopy before exposure could not trace any relief on the (polished) surfaces, it did reveal a partly strong surface relief after 3 months exposure (Fig. 4), especially with the alabaster samples. To which extent this can be used for the quantification of roughness as a measure of the recession, especially when applied in combination with the other two methods, has yet to be studied.

4. Conclusions and Outlook

The differences found between the sensors in the loss of gloss in this case, might be due to the prolonged periods of exposure, especially under high humidity. Additional data is expected to become more reliable over 1 year, especially under high humidity.

In order to understand the impact of the sensors can be useful. The use of the sensors during prolonged periods of exposure, especially under high humidity, of the sensors. Additional data in the preparation of polished materials may prove useful if financial resources have different starting points and help in the process of conservation.

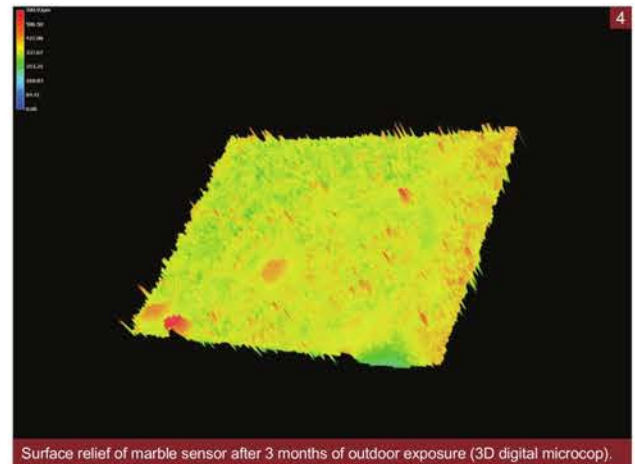
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2. Methodology and results: Laboratory tests

The tests in the lab were focussing on the optimal surface preparation of the sensors in view of standardized impact of moisture under lab conditions (water condensation and short-term contact of the surface with liquid water). The effects achieved in terms of surface etching were measured before and after the ageing tests, using the same analytical methods as for the field exposed samples (gravimetry, gloss measurements, microscopy). As expected, mechanical high gloss polish of the sensor materials showed the best results as it provides highly sensitive sensors which can be used both for outdoor and indoor exposure conditions. Thus, minute surface alterations as e.g. obtained due to indoor condensation or under sheltered outdoor conditions can be monitored. Alabaster proved to be very moisture sensitive material (Fig. 2) as compared to carbonate sensors. The latter ones are more useful for monitoring unprotected outdoor exposure conditions, where even hand polishing of sensor surfaces may yield satisfactory results achieved by decline in gloss and increase of microscopic roughness.

Material	Drop in gloss value after 3 months of exposure (%)		
	for 20°	for 60°	for 85°
Alabaster I	78,6	63,64	92,1
Alabaster II	38,24	40,57	90,51
Alabaster III	26,32	50,51	97,06
Impact limestone	90,8	85,76	42,37
Marble	91,33	89,21	55,9

Drop in gloss value for hand polished material sensors after 3 months of unsheltered outdoor exposure.



the stone types were as expected. Alabaster revealed more soluble, therefore showing higher rates of weight loss as well as decline of gloss. However, the results prove too fast for mid and long term sensing. The carbonates on the contrary are expected to give good sensors for medium- and long-term monitoring under unprotected exposure conditions outdoors. To verify this, an additional set of sensors is further exposed and will be evaluated in future. The gravimetrical set of results is more relevant with longer exposure. The correlation of microscopy with the other two methods has to be studied more in depth.

Impact of the immediate surrounding at given conditions of exposure, including specific microclimatic situations under the effect of climate change, material sensors on alabaster sensors for the indirect study of the surface recession of carbonate stones is a possibility, especially in situations where time is the limiting factor. For carbonate stones provide better sensors. The measurement of the surface gloss and the sensor's weight give a good methodical combination for the evaluation. Microscopic analyses, help better understand the deterioration processes on a micro scale. Sensors with initial high gloss polish (machine preparation, as used in microscopic sections), should be preferred over manual polishing due to their higher sensitivity in the initial phase. But also, sensors that are polished by hand and there is no standardized protocol for the use and the evaluation of such material sensors. Nevertheless, results from such material sensors can be of great value for the monitoring and/or preservation of cultural assets made of stone, and provide a tool for informed decision-making.

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News in Conservation is published by
The International Institute for Conservation of
Historic and Artistic Works,
3 Birdcage Walk, London SW1H 3JJ
Website: iiconservation.org
Email: iic@iiconservation.org
ISSN (online) 1995-2635

Cover Image

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- 4) Milchin, M., Weber, J., & Krist, G. (2023). Material Sensors for the Surface Recession of Calcareous Stones: Understanding Present and Future Decay. *Zbornik Umjetničke akademije u Splitu*, 2(2), p. 97-105

Material Sensors for the Surface Recession of Calcareous Stones: Understanding Present and Future Decay

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UDK 7.025.3/.4:691.2
Pregledni rad / Review Paper
Priljeno / Received: 12.4.2024.
Prihvaćeno / Accepted: 2.12.2024.



Summary

The study proposes material sensors to assess the rate of the surface recession of calcareous stones through atmospheric weathering. The sensors, made of highly polished alabaster and Carrara marble, were exposed outdoors for up to 10 months. The analytical methods employed involve gravimetry, gloss measurements, and microscopy. For alabaster sensors, the results show a good reliability for gravimetry, but lesser for gloss; this sensor material might prove more relevant for sheltered exposure. In turn, the marble sensors yield very promising results for gloss measurements, but less with gravimetry; longer exposure times might change this. Microscopy proves suitable for both types of sensors, with emphasis on the surface profile and roughness obtained by digital microscopy. The trial exposure confirms that material sensors can help understand exposure and microclimatic conditions affecting the preservation of heritage assets.

Keywords: *calcareous stone, surface recession, material sensor, gloss measurement, digital microscopy, field exposure*

Introduction

Calcareous stones, including porous and compact lime-stones and marbles, are common and significant heritage materials. They have been extensively used in sculpture and architecture across various regions and historical periods. Certain calcareous stones were primarily used regionally, while others journeyed vast distances, as early as antiquity. Important heritage landmarks such as the Parthenon in Athens, Michelangelo's David, the Taj Mahal in Agra, and gothic churches such as St. Stephen's Cathedral in Vienna are constructed from stones belonging to this material group.

These are chemically vulnerable materials due to the solubility of calcium carbonate in water and acids. Consequently, monuments constructed from these stones have always been subject to intensive maintenance and repair, a practice continuing to present times. As part of preventive conservation strategies, some heritage assets are sheltered or relocated to indoor environments. Various types of coatings have been developed to protect calcareous surfaces against material loss. However, within the framework of minimal intervention, determining which monuments require protective treatment and which not poses a significant challenge for conservators.

To support the decision-making process regarding conservation measures, it is essential to assess the rate of material decay. Various methods have been developed to measure or calculate surface recession for specific stones or monuments. These methods vary in approach, ranging from theoretical mathematical calculations and dose-response functions to gravimetric measurements or analyses of runoff water. However, the actual situation with a particular monument may differ from the values derived from these methods. In this paper, we present one potential approach to address this challenge.

The Surface Recession of Calcareous Stones

The surface recession of calcareous stones is mostly explained by three different but interconnected mechanisms.

The so-called "karst effect" explains the dissolution of calcite in unpolluted rain. Calcium carbonate is slightly soluble in water (0,014 g/l) but much more in weak acids. In reality, rainwater is never pure but rather slightly acidic due to the absorption of carbon dioxide from the atmosphere. As a result, clean rainwater typically has a pH of 5.6 and

can dissolve up to four times more calcium carbonate than water with pH 7.¹ Hence, calcareous surfaces, whether in the landscape or on monuments, undergo dissolution with each rain event. In rain exposed areas on monuments the dissolved calcium carbonate is mostly washed away; this results in surface recession – material is removed from the surface.

With polluting agents in the air, different deterioration mechanisms become more important. The so-called 'acid rain' (wet deposition) is produced by the dissolution of different acidic pollutants in rainwater on its way through the atmosphere, the pH falls as low as 4 (acid fog reaching sometimes a pH of 2).² A different mechanism, known as dry deposition, involves pollutants accumulating first on and within the surface of a material, only to be dissolved later by precipitation. This mechanism is mostly relevant in dry phases and in direct vicinity of pollution sources.³ With both deposition scenarios, if the pollutant is SO₂, as was commonly the case in the past, sulphation occurs. Depending on the exposure and the substrate involved, a crust forms (only in rain-protected areas), and/or deep sulphation of the stone material occurs.⁴

Due to the decreasing levels of SO₂ in the air (at least in Europe), the future recession of calcareous stone can mainly be attributed to the so-called "karst effect." The increasing amount of CO₂ in the air, coupled with shifts in climate due to climate change, is expected to further exacerbate material loss due to the "karst effect," especially in northern and central Europe. This and other shifts in heritage climatology were addressed in the NOAH's ARK Project (2004 – 2007).⁵ The findings regarding surface recession of compact calcareous stones were published in 2009:

The most marked change in recession rates across the period is the general increase throughout Europe, particularly noticeable in high rainfall areas, e.g. mountain areas of central Europe, Scandinavia and Scotland. The change can be of

1 Michael STEIGER, Elena A. CAROLA, and Katja STERFLINGER, "Weathering and Deterioration," in *Stone in Architecture: Properties, Durability*, ed. Siegfried Siegesmund and Rolf Snethlage, 4. ed. (Berlin, Heidelberg: Springer Berlin Heidelberg; Springer, 2011), 258–59.

2 *Ibid.*, 259.

3 Dario CAMUFFO, *Microclimate for Cultural Heritage: Conservation, Restoration, and Maintenance of Indoor and Outdoor Monuments*, 3rd ed. (San Diego: Elsevier Science & Technology, 2019), <https://ebookcentral.proquest.com/lib/kxp/detail.action?docID=5799303>, 125–30.

4 *Ibid.*, 129.

5 NOAH'S ARK, Funded by the EU, FP6-2002-SSP-1, Grant agreement ID: 501837,

more than 6 $\mu\text{m year}^{-1}$ in regions where the recession was around 20 $\mu\text{m year}^{-1}$ in 1961–1990, which is a 30% increase.⁶

So, it can be argued that with the increasing concentrations of CO_2 in the air, the surface recession of calcareous materials due to the “karst effect” will rise. This is attributed to higher levels of CO_2 dissolved in rainwater, resulting in lower pH levels and in rising solubility of calcium carbonate in rainwater. Additionally, climate change and with it the change in temperature and distribution of precipitation through the year influence the surface recession. Longer exposure periods above 0°C result in increased time spent at temperatures critical for surface recession due to the “karst effect,” as calcium carbonate can only dissolve in liquid water.

However, in reality, surface recession is highly dependent on the specific calcareous substrate involved and its physical properties, such as porosity, capillarity, microstructure, and relevant mineral impurities. Additionally, factors such as the exposure and/or the relevant microclimatic effects also significantly influence the rate of surface recession. To better understand these for a particular monument, this paper suggests the use of material sensors.

Material Sensors

Material sensors are not a new idea in conservation. The best-known sensors used in the field aim to assess the suitability of materials for the use in museum storages or showcases; these are known as Oddy tests.⁷ Many materials release gaseous compounds when they degrade, which can harm or endanger museum objects. In the Oddy test, a set of metal coupons (thin sheets) is exposed in an atmosphere alongside the material being evaluated. Any emerging corrosion indicates the presence of harmful gases.

Similarly, in stone conservation, some studies have attempted to use lithic materials to estimate the harmfulness of a particular environment and/or exposure. However, most of these studies are focused on sulphation⁸ or on the

combined effects of weathering in general.⁹

The present study aims to systematize the use of material sensors to enhance the understanding of surface recession of calcareous stones, within a dynamic outdoor environment. This approach aims at examining particular monuments always in their specific position and exposure conditions in contrast to the phenomenon of surface recession in general.

Methodology

In preliminary tests and studies, various stones were evaluated for their potential as material sensors to measure surface recession in calcareous stones. These included compact limestone from Vratsa, Bulgaria, marble from Carrara, Italy, and three different types of alabaster.¹⁰ Different surface finishes, such as hand-polished and machine-polished, were examined, along with various analytical methods for assessing material loss, including gloss measurements, gravimetry, and optical and 3D digital microscopy.

The preliminary studies began with laboratory tests, followed by a short-term outdoor exposure period of 3¹¹ and 6 months in a rural area of Lower Austria (a reclining angle of 45° facing NNW). Insights gained from analyses of the sensors (using gloss measurements, gravimetry, and microscopy) were utilized to further refine and develop the methodology.

As a result, the exposure protocol implemented in this study and discussed here was designed. Samples of Carrara marble and a white homogeneous alabaster with a size of $4 \times 4 \times 1$ cm were produced; the front was polished to the highest degree possible. The rear-side was protected by a thin glass plate glued to the sample, the four lateral sides

6 Alessandra BONAZZA et al., “Mapping the Impact of Climate Change on Surface Recession of Carbonate Buildings in Europe,” *The Science of the Total Environment* 407, no. 6 (2009): 2047, doi:10.1016/j.scitotenv.2008.10.067.

7 L. R. GREEN and D. THICKETT, “Testing Materials for Use in the Storage and Display of Antiquities: A Revised Methodology,” *Studies in Conservation* 40, no. 3 (1995): 145, doi:10.2307/1506472.

8 R. A. LEFEVRE et al., “Modelling of the Calcareous Stone Sulphation in Polluted Atmosphere After Exposure in the Field,” *Geological Society, London, Special Publications*, 2007.

9 Thomas BIDNER et al., “Stone as Sensor Material for Weathering,” in *Understanding and Managing of Stone Decay: SWAPNET 2001*, ed. Richard Prikryl, Heather A. Viles (The Karolinum Press, 2002).

10 The inclusion of alabaster, despite its chemical differences to calcareous stones, aimed to explore the potential for a rapid sensor. Such a sensor would be valuable in scenarios where time is limited and quick decision-making assistance is needed. A typical case would be the conservation of a single sculpture, where a decision is required regarding whether to apply a protective coating at the end of the conservation treatment. The sensors could be installed at the beginning of the project and analysed towards the end. Alabaster’s higher solubility could ideally aid the decision-making process even after exposure for a couple of months.

11 Marija MILCHIN, Johannes WEBER, and Gabriela KRIST, “Sensor Materials for the Deterioration of Carbonates in a Changing Outdoor Environment,” *IIC News in Conservation*, no. 97 (2023).

by an aluminium tape.¹² The same tape also covered the upper 10 millimetres of the front in order to create a sheltered surface that can be directly compared to the unsheltered and therefore weathered surface (Fig.1).

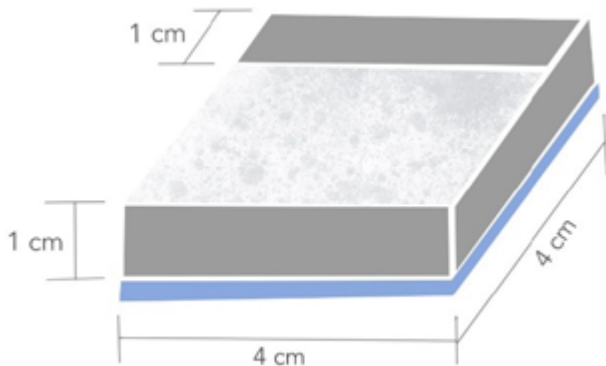


Fig. 1: The design of the material sensors (blue: glassplate; grey: aluminium tape)

The samples were weighed before exposure (with and without aluminium tape). The gloss before exposure was measured with a multi gloss meter¹³ on all samples in three angles (20°, 60°, and 85°) at at least three positions. Prior to measurement, the potential dependence of gloss values on measurement direction was assessed. No differences were detected for Carrara and alabaster. The samples were then exposed (start of the exposure 01.04.2023) on a rack with a reclining angle of 45° facing NNW in a rural area in Lower Austria¹⁴ at a height of approximately 4m, unsheltered by roof or trees.

After time periods of 1, 2, 7, 9, and 10 months, samples were collected and analysed. The gravimetric measurements were repeated both with and without aluminium tape. The tape was removed mechanically; any adhesive residues were removed with acetone. The gloss was measured as previously described. Microscopic analyses were conducted using both a 3D digital microscope¹⁵ and an optical microscope¹⁶ with incident light. The 3D digital microscope employed in this study has the capability to detect surface relief via a light beam, allowing for the indirect measurement of surface roughness. This feature

was implemented with the exposed samples. The previously mentioned sheltered upper portion of the sample was compared to the exposed and weathered portion. To ensure precise measurement, one sample section was carbon-sputtered, which is typically used in SEM analysis, resulting in an opaque surface and improved accuracy.¹⁷ Line roughness measurements were conducted on weathered and sheltered areas of the sensors, allowing for surface recession assessment from the profile. The extreme washout on the border between sheltered and unsheltered regions was disregarded in the analysis.¹⁸

Results

Gravimetry

The differences in weight measured before and after exposure were, as expected, much more relevant for the alabaster than for the marble samples. This discrepancy is explained by the higher solubility of calcium sulphate in comparison with calcium carbonate.¹⁹ While the alabaster samples showed a loss of more than 1 g (1.14 g) over a surface of approx. 12 cm² in 10 months,²⁰ for the marble samples a maximum loss of only 0.03 g for the same surface and period of time could be measured. The gradual loss noted for the alabaster samples shows that gravimetric measurements are reliable for this kind of sensor. Over longer exposure periods, it is anticipated that the loss of material for alabaster will continue at a similar rate.

12 Tesa® Aluminium Tape, is a tape from aluminium foil (100 µm) with acrylate as glue, suitable for repairs indoors and outdoors (stable in temperature range of -40°C until +160°C).

13 BYK®, micro-TRI-gloss

14 Sattelbach in Lower Austria (48.0297938, 16.13777273).

15 Kayence, VHX-7000.

16 Olympus BX 40.

17 In preliminary studies, it was observed that surface roughness measurements, which are conducted with a light beam in the 3D digital microscope, encountered issues with semi-transparent crystals, a common occurrence with marble and alabaster. Consequently, a solution was required to cover the surface and render it opaque, while minimizing interference with the surface relief.

18 It is hypothesized that the significant washout observed in this area was triggered by the prolonged presence of water drops due to their adhesion to the sticky tape. Therefore, this effect was considered atypical of the actual exposure conditions but rather typical of the design of the exposure setup.

19 Calcium sulphate has approx. 20 times higher solubility in pure water than calcium carbonate.

20 Calculated with a density for alabaster of about 2.3 g/cm³ this results in an average surface recession of about 0.5 mm/year.

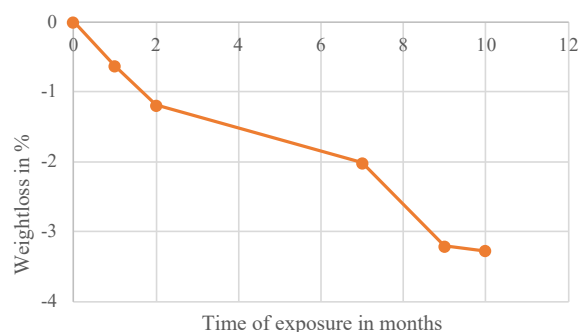


Diagram 1. Weight loss in % of total weight, alabaster samples

The values obtained for the marble samples on the other hand are so low that the results are not significant or reliable, in part due to the error range of the scale used.²¹ Gravimetric measurements for the marble sensors might become more relevant for longer exposure periods (several years).

Gloss Measurements

The gloss measurements showed very promising results within the first months of exposure for both alabaster and marble. After the full exposure period, all results from gloss measurements were subjected to statistical analysis to evaluate their significance individually and in relation to each other, considering different exposure times.²²

The weathered alabaster samples show significant differences compared to both the initial experiment's baseline and the values observed after one month. However, after two months of exposure the comparison with values from longer exposures becomes insignificant e.g. the gloss at 60° after two months of exposure ($M=1.77$; $SD=0.06$) is not significantly different to the gloss at 60° after nine months of exposure ($M=1.96$; $SD=0.11$; $t(2)=-3.46$; $p=ns$; Cohen's $d=0.10$). The loss of gloss occurs so rapidly that after two months only few gloss units remain, making any later measurement unreliable, and providing no further information on decay. However, alabaster may prove useful for rapid-sensors or for indoor or sheltered exposure, particularly for assessing the impact of condensate on stone surfaces. This topic needs further investigation in the future.

	N	Gloss in GU, Mean	Std. Deviation	Std. Error Mean
before exposure	15	90.4800	1.32568	0.34229
1 month exposure	3	1.2333	0.05774	0.03333
2 months exposure	3	1.7667	0.05774	0.03333
7 months exposure	3	1.8333	0.05774	0.03333
9 months exposure	3	1.9667	0.11547	0.06667
10 months exposure	3	2.1000	0.00000a	0.00000

a. t cannot be computed because the standard deviation is 0.

Table 1. Gloss measurements 60°, alabaster sensors

The statistical analysis of the results for marble, both as a single sample and when paired with different exposure times, gave significant results. One of the least significant combinations was the gloss measured at 60° before ($M=104.87$; $SD=1.55$) and after one month of exposure at 60° ($M=75.667$; $SD=1.76$). Even here a high level of significance was achieved ($t(2)=12.34$; $p<0.01$; Cohen's $d=4.07$), thus demonstrating the compatibility of marble sensors with gloss measurements.

	N	Gloss in GU, Mean	Std. Deviation	Std. Error Mean
before exposure	15	104.87	1.552	0.401
1 month exposure	3	75.6667	1.76163	1.01708
2 months exposure	3	33.8667	0.97125	0.56075
7 months exposure	3	58.1667	1.73877	1.00388
9 months exposure	3	51.9000	1.93132	1.11505
10 months exposure	3	35.6000	5.38609	3.10966

Table 2. Gloss measurements (60°), marble sensors

The results exhibit greater consistency and demonstrate greater potential with marble than with alabaster, revealing a gradual decrease in gloss values across all three angles. However, the 60° angle appears to be the best choice since the expected values cover a wide range of gloss units (0–120 GU). Additionally, some gloss meters only measure at a 60° angle. Therefore, maintaining a 60° angle as a minimum requirement for all measurements allows for better accessibility of the method for users, especially for conservator-restorers.

²¹ Sartorius®, BP 2100S, $d=0.01g$.

²² The statistical analyses were conducted by Jana Korunovska.

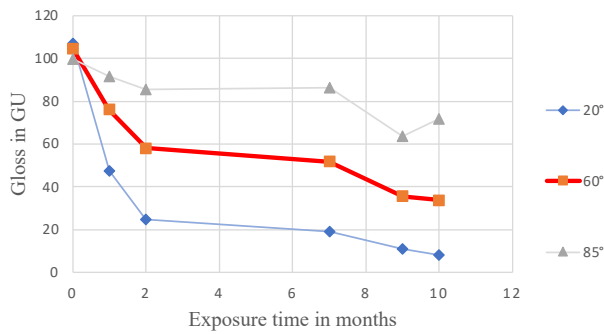


Diagram 2. Gloss loss in GU, marble samples (20°, 60°, and 85°)

The results suggest that similar measurements could also be beneficial for longer exposures (i.e., several years) and are both easy and cost-effective to employ. It can also be anticipated that the same measurements will be reliable for compact polishable limestones. However, further exposures and measurements are necessary to establish a correlation between the decrease in gloss and the rate of surface recession.

Microscopy

Microscopically, differences in the surface relief between the protected and exposed areas were examined. Using a 3D microscope, line roughness was measured; i.e. for the 10-month exposed marble, the protected areas exhibited very low roughness values: $R_a=0.06\mu\text{m}$, $R_z=0.42\mu\text{m}$ (Fig. 2), whereas the exposed areas showed much higher roughness: $R_a=5.50\mu\text{m}$, $R_z=30.94\mu\text{m}$ (Fig. 3).

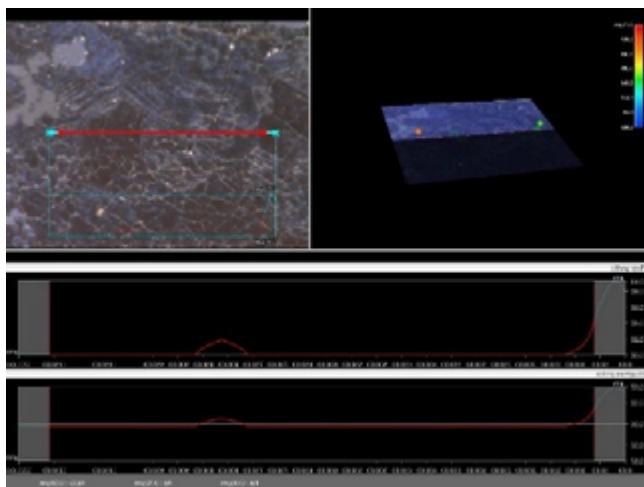


Fig. 2. Roughness measurement, protected area, MV- 10-months exposed marble sensor

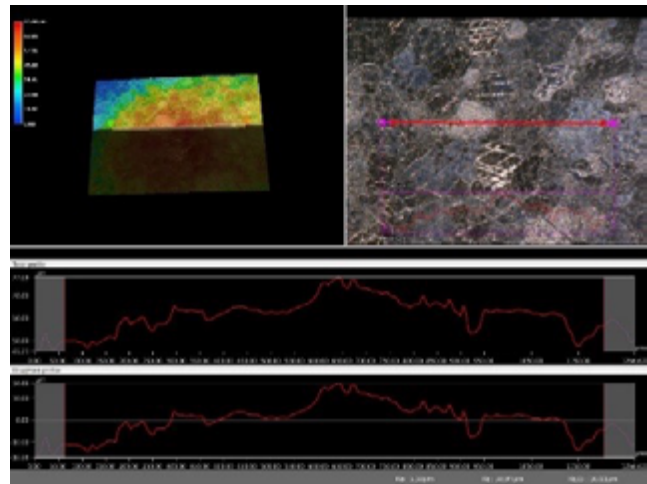


Fig. 3. Roughness measurement, exposed area, MV- 10-months exposed marble sensor

Additionally, the structure and morphology of the surface were analysed using the 3D microscope. By direct comparison of the protected and unprotected surfaces, surface recession could be directly measured using line measurements. As anticipated, the alabaster samples exhibited a higher rate of surface recession compared to the marble samples.

Figures 4 and 5 depict the analyses of the alabaster sensor after 10 months of exposure. The washout along the border between the protected and exposed areas is noticeable in the blue region. As evident from the profile in Figure 5, subtracting this effect is relatively straightforward, facilitating the calculation of surface recession. In this case, the surface recession for the alabaster over 10 months amounts to approximately $360\mu\text{m}$.

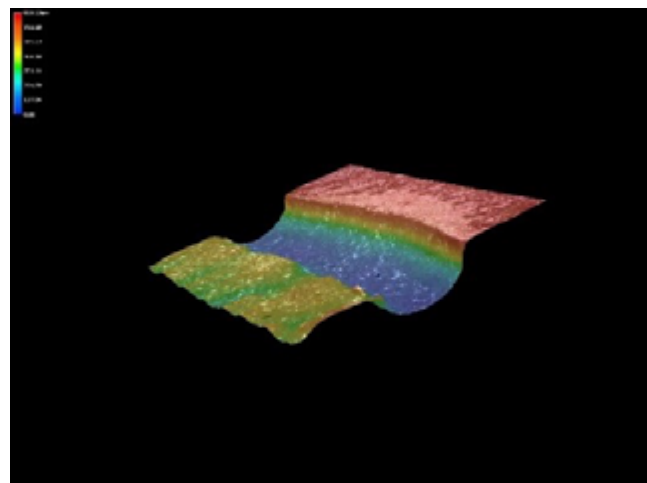


Fig. 4. 3D relief of the surface of AV (10-months exposed alabaster sensor), protected area, wash out and exposed area

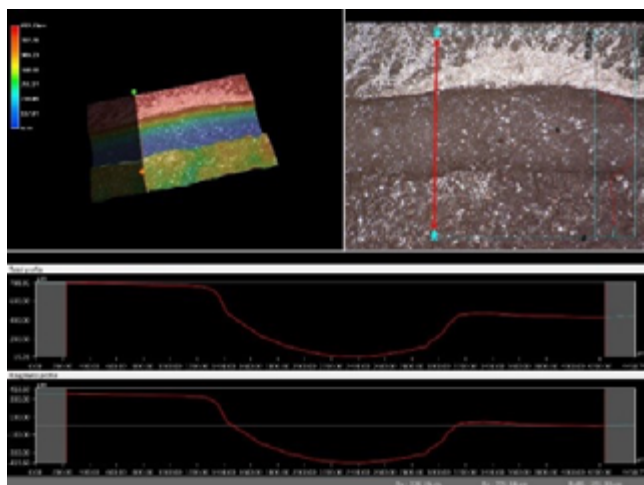


Fig. 5. Surface profile, protected area, wash out and exposed area, AV (10-months exposed alabaster sensor)

The microscopy results indicate that sheltering an area in close proximity to the exposed surface is highly beneficial, particularly when combined with analyses with the digital 3D microscope.

Discussion

The results show that material sensors have the potential to help understand the rate of deterioration for a specific position and exposure of a monument with focus on the surface recession of calcareous stones.

For the exposure of alabaster sensors, gravimetry proved to give usable results, whereas gloss measurements are of relevance only for the first couple of months in the exposed outdoor environment. Microscopy provides very clear and accessible results both in terms of surface roughness and surface recession. However, it is recommended wherever possible to use sensors with the same or similar composition as the monument asset. Therefore, alabaster sensors should rather not be the first choice for monitoring monuments made of calcareous stones in outdoor environments, unless as a rapid sensor for very short (accelerated) exposure times or under indoor or sheltered conditions. The same could aid in understanding the effect of potential condensation events on surface decay. Nevertheless, this area requires further research and should be explored in future studies.

The marble sensors show a very useful pattern of surface recession which can be best analysed with a combination of gloss measurements and 3D digital microscopy. Especially, the inexpensive and straightforward gloss

measurements offer promising prospects for future use. They are easily implemented and appear to provide a high level of confidence in understanding the rate of surface recession. The gravimetric measurements may hold greater interest with longer exposures. However, it is advisable to track weight changes at every exposure duration to ensure comprehensive monitoring. To establish a robust correlation between the loss of gloss and the amount of material loss, further measurements are required in future studies. For improved correlation, it is recommended to retain the Carrara sensor throughout all exposures. Additionally, it is advisable to expose the calcareous material from which the assessed monument is made. If the original material is not available or accessible, lithic material very similar to the original should be exposed instead. Combining the Carrara sensor with one made from a lithotype of the monument's heritage material can facilitate relevant results for the monument asset and at the same time allow for comparability between different sites.

Conclusions

This trial confirms that using material sensors can help us better understand the decay rate of monuments or heritage assets. Gravimetry, gloss measurements, and surface microscopy prove valuable in comprehending the real conditions on-site. However, there are currently no standardized values available to aid decision-making regarding protection or preventive conservation measures. The establishment of such a protocol is imperative and will require numerous future measurements. The investigation of the influence of seasonal variations and climatic parameters on individual results has not yet been studied. This aspect constitutes an area of future research.

Outlook

This study will enter the next phase in the framework of the EU founded Project STECCI,²³ in which material sensors will be exposed on 10 different sites²⁴ and analysed after 1 and 2 years. In order to establish a correlation with the already existing data, each sensor set will include a polished sample of Carrara marble. More importantly, each set will accommodate two samples from the stone from which the monument involved is made (a polished one and one

23 STECCI - Stone monument ensembles and the climate change impact (Project number: 101094822, HORIZON-CL2-2022-HERITAGE-01), Funded by the EU, <https://steccihorizoneu.com/>.

24 The locations are in six different countries: Austria, Bosnia and Herzegovina, Croatia, Germany, France and Malta.

with a rough surface for analyses of bio colonisation and possible soiling), and last but not least, as a connecting reference stone, a compact lime stone from the island of Brač, the so-called Veselje Unit, with two samples pro set, analogue to the local stone, will be exposed. The samples will be exposed on a rack with a reclining angle of 45°. The polished samples will be analysed following the methodology already stated in this paper. The two samples with rough surfaces will mostly be analysed microscopically. The precise methodology is in the development phase and will be published elsewhere in future.

The project consortium hopes that this set-up will allow for comparable information on surface recession, bio-colonization, and soiling between different sites and monuments. All sites consist of calcareous materials and are placed in different geographical and climatical regions of Europe. Together with data from weather stations and climate modelling, this should help make decisions about conservation concepts (preventive and interventive), maintenance, and care in the future.

Acknowledgements

The authors would like to thank Jana Korunovska for conducting the statistical analyses of the gloss measurement data.

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Sažetak

Materijalni senzori za površinsko udubljivanje vapnenačkog kamena: razumijevanje sadašnjeg i budućeg propadanja

U radu se predlažu materijalni senzori za utvrđivanje udubljivanja površina na vapnenačkim vrstama kamena i metodologija njihova korištenja. Senzori koji su korišteni u radu načinjeni su od homogenog alabastera i kararskog mramora. Lica senzora polirana su, a sve ostale strane i gornjih deset milimetara lica izolirani su kako bi se ograničilo propadanje njihove nezaštićene, prednje strane. Priređeni senzori izloženi su na otvorenom, u Donjoj Austriji, u različitim vremenskim razdobljima (od jednog do deset mjeseci), na nosačima okrenutim u smjeru sjever-sjeverozapad i postavljenim pod kutom od 45°.

Promjene nastale zbog propadanja analizirane su nakon izlaganja pomoću gravimetrije, mjerenjem sjaja i pod mikroskopom (digitalna 3D i optička mikroskopija), a napravljena je i usporedba s početnim izmjerama.

Rezultati su pokazali zadovoljavajuću pouzdanost kada je riječ o senzorima od alabastera i gravimetrijskim mjerenjima, a nešto manju pouzdanost pri mjerenju sjaja. To senzore od alabastera čini zanimljivijim u kratkoročnim izlaganjima (brzi senzori) ili u zaklonjenim položajima i izlaganjima u zatvorenom, za što će biti potrebna daljnja istraživanja.

Mramorni senzori daju vrlo pouzdane i relevantne rezultate pri mjerenju sjaja, a manje pouzdane kada je riječ o gravimetrijskim mjerenjima. Za bolje je rezultate gravimetrije za mramorne senzore potrebno dulje vrijeme izlaganja. To se posebno odnosi na razdoblja dulja od dviju godina, što bi moglo biti područje istraživanja u budućnosti.

Mikroskopija je podobna i za alabaster i za mramor. Tu su posebno relevantni profil površine i izmjere njezine hrapavosti, a to je moguće postići digitalnim mikroskopom.

Ovo testno izlaganje potvrđuje da materijalni senzori mogu značajno poboljšati razumijevanje izloženosti i mikroklimatskih uvjeta koji pogađaju spomenike i druga baštinska kulturna dobra. Gravimetrija, mjerenje sjaja i mikroskopija pokazali su se vrijednim za razumijevanje stvarnog stanja *in situ*. Ipak, trenutno se ne raspolaže standardiziranim vrijednostima koje bi pomagale u donošenju odluka, a

odnose se na zaštitne ili preventivne konzervacijske mjere. U tom je smislu imperativ ustanovljavanje protokola za brojna buduća mjerenja. Za poboljšanje korelacije preporučuje se zadržati senzore od kararskog mramora pri svim izlaganjima. Usto, savjetuje se izlagati materijal od kojega je određen spomenik sačinjen. Ako izvorni materijal nije dostupan, umjesto njega treba izložiti kameni materijal koji je vrlo sličan originalu. Kombiniranjem senzora od kararskog kamena sa senzorom načinjenim od litotipa povijesnog materijala spomenika može se olakšati dobivanje relevantnih rezultata za spomenike kojima se pristupilo i istovremeno omogućiti usporedivost različitih lokacija.

Ključne riječi: vapnenački kamen, udubljivanje površine, materijalni senzor, mjerenje, digitalna mikroskopija, terenska izloženost

- 5) Milchin, M., Haselberger, M., & Krist, G. (2020). Preventive Conservation Measures for Stone Statuary in the Outdoor Environment: Three Case Studies from Austria. *Studies in Conservation*, 65(sup1), p. 233 - 236.

Preventive Conservation Measures for Stone Statuary in the Outdoor Environment: Three Case Studies from Austria

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ARTICLE HISTORY Received April 2019; Accepted April 2020

KEYWORDS Stone; preventive conservation; outdoor environment; winter shelters; temporary; permanent

Introduction

In the time of budgetary cuts to all aspects of arts and culture, heritage and its preservation have to rely on simple and inexpensive solutions. Climate is an essential parameter affecting preservation of cultural heritage in an outdoor environment; hence climate change has a big impact on developing strategies for preservation of built heritage. Together with changing air quality, it influences the way and rate at which materials decay and deteriorate. The rate and intensity of biological colonisation is also subject to change. At the same time, sustainability becomes more important in all fields of preservation and imposes itself on the concepts and strategies developed. Green, sustainable and inexpensive solutions, which can be implemented on whole collections rather than single artefacts, have to be developed. Existing preventive measures for outdoor stone statuary are considered. Three case studies, with different restrictions and restraints, are presented and evaluated with respect to the protection they offer, costs, the workload involved and sustainability, as well as possible risks.

Sculptures in the gardens of Schönbrunn Palace

Over 40 marble sculptures from the eighteenth century are part of the statuary of the Schönbrunn Gardens in Vienna, Austria. The search for suitable protection for the statues over the winter period included different approaches; hydrophobic coatings have been tested as well as different temporary shelters: wood in 1995–1996; Plexiglas (poly(methyl methacrylate)) sheet (PMMA) from 1993 to 1996; the geotextile 'ART/COAT' in 2001–2002. The latest approach has involved soft wrap shelters made from a coated woven textile acting as a semi-permeable membrane employed in the period 2005–2012, when it was decided to evaluate the system. In 2012 the Institute of Conservation,

University of Applied Arts Vienna, conducted an evaluation within the framework of a pre-diploma thesis (Haselberger 2011). The climate inside and outside the soft wraps was monitored over one season (October until April) for three sculptures (Figure 1). Additionally, the material used for the shelter was investigated. This proved that the shelters achieved their primary goal, to buffer the climatic extremes and to keep rain and snow away from the surfaces during the first year of their use. This effect dropped radically once the shelters were reused for the second or third time. Holes and wear allowed water to penetrate the shelter. The experiment showed that the geotextile performed as a semi-permeable membrane as long as it was new and sound. As soon as the material was folded in order to store it in the summertime, the surface was damaged, which resulted in water penetrating the shelter. As result of the evaluation the use of the soft wrap shelters was abandoned.

Sculptures in the garden of Langenzersdorf Museum

The small Museum of Langenzersdorf in Lower Austria specialises in sculpture from the twentieth century. Stone, brick and concrete sculptures as well as some metal artefacts are presented in the museum garden. The University of Applied Arts Vienna has been active in the museum and its garden since 2017, when an inventory was made and a plan for the conservation of the different material groups was developed (Milchin and Sandner 2017). In order to be able to keep the sculptures in position in the garden, shelters have been planned from the beginning. A permanent shelter in the form of a roof was not considered because of the aesthetic impact it would have on the garden and the surrounding landscape. Instead, low-budget winter shelters that can be produced by the museum staff or the craftsmen of the municipality were chosen. Two different systems were tested. The first was a soft wrap with spacers made out of Tyvek



Figure 1. Soft wrap with spacers, Schönbrunn gardens.



Figure 2. Front: damaged Tyvek® soft wrap after one season of exposure; back, on the left, the prototype for a wooden shelter.



Figure 3. The permanent shelter in Leithaprodersdorf protects Roman sarcophagi and gravestones.

(DuPont, a breathable but water-resistant polyethylene material) (Franzen 2018, 25). The second system was a traditional wooden shelter, made of uncoated wood, with big gaps for air circulation. The climate was monitored over a year in both systems and compared to climate data from an unsheltered sculpture. The measurements consisted of air and surface temperatures accompanied by relative humidity. The stability of the shelters and their estimated life time were also taken into consideration. This, together with the workload for the mounting and demounting and the space needed to store the shelters in the summer months, helped the decision-making. Both systems could buffer weather extremes. After one winter the wooden shelters showed no signs of decay, but the Tyvek wraps were worn out and could not be used for a second season. The harsh winter climate is responsible for this phenomenon. Most of the Tyvek covers showed serious damage, with the development of large holes as quickly as a month after they had been installed (Figure 2). The risk of the soft wraps in connection with strong winds and their sail-like form should not be underestimated. The close contact to the surface of the sculpture adds to the damage to the cover, also making surface abrasion of the sculpture a plausible risk. The wooden shelters are initially more expensive than the soft wrap. Taking the expected life span – wood, 10 years, Tyvek, 1 year – into consideration, the Tyvek covers prove more expensive in the long run and are less environmentally sustainable. Considering the workload involved, the production of new Tyvek covers adds up to more working hours than the mounting and demounting of the wooden shelters. The only disadvantage of the wooden shelters is that they require more storage space in summer. As a result, all of the artefacts in the garden of Langenzersdorf Museum were sheltered in the winter 2019–20 for the first time, following the trial periods in 2017–18 and 2018–19.

Permanent shelter in the archaeological park of Leithaprodersdorf

In the archaeological park of Leithaprodersdorf a permanent shelter (roof) was designed to protect Roman gravestones and sarcophagi on display (Figure 3). The roof offers protection from rain, snow and direct sun for the stone artefacts. Unfortunately, birds and the local youths also appreciate the sheltering effects. At present the stone artefacts are soiled and covered with bird droppings. Rubbish (mainly food and drink containers as well as cigarettes) can also be found around and inside the artefacts. Youngsters are using the artefacts to sit on while meeting in the evenings; as a result recent mechanical damage can be seen on most surfaces. Therefore it can be argued that the well-intended structure that was supposed to protect the objects from the slow but steady decay due to weathering caused more aggressive mechanical damage due to anthropogenic factors, as well as a new problem with bird droppings. This should not mean that permanent roofs are problematic altogether, but rather that one should evaluate and modify all conservation measures, including those that seem as simple and straightforward as roofs (Curteis 2018, 47). In the case of Leithaprodersdorf, different approaches could be used to deal with the anthropogenic part of the problem, such as the installation of benches and/or fencing the area. At present two Plexiglas covers and one dome are planned for three artefacts as a trial solution. However, the concentration of birds and therefore bird droppings under the roof is a problem often encountered with permanent shelters. Similar situations have been reported from the shelters in Caesarea, Israel (Alef 2018, 95), Um er-Rasas, Jordan (Ha'obsh 2018, 118) and Terrace House 2 in Ephesus, Turkey (Bellibas 2018, 141). There is no satisfactory solution for this problem as yet.

Conclusion

There is no perfect solution for sheltering stone statuary in an outdoor environment. For the eastern part of Austria, temporary shelters made of wood prove to be a good and simple option. Given there is available space for the storage in summer, this also proves to be the best solution regarding the financial and sustainability aspect.

Soft wraps made of different geomaterials are not suitable for the outdoor environmental conditions in Austria.

Roofs offer a good protection from the elements and the costs involved can be low if looked at over the life span of the protection itself. The installation of a permanent roof can considerably reduce the yearly workload involved, although maintenance and security have to be planned up front (Pesaresi and Stewart 2018, 70). The side effects include aesthetic changes to the site as well as unexpected shifts in the circumstances and decay patterns.

The evaluation and possible repair and/or modification of all of these measures, permanent and temporary, are essential for their success.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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Preventive Conservation Measures for Stone Statuary in the Outdoor Environment: Three Case Studies from Austria

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To cite this article: Marija Milchin, Martina Haselberger & Gabriela Krist (2020): Preventive Conservation Measures for Stone Statuary in the Outdoor Environment: Three Case Studies from Austria, *Studies in Conservation*, DOI: [10.1080/00393630.2020.1757879](https://doi.org/10.1080/00393630.2020.1757879)

To link to this article: <https://doi.org/10.1080/00393630.2020.1757879>



Published online: 04 May 2020.



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6) Milchin, M., Pesce, C., Weber, J., Krist, G., Ban, M., & Anghelone, M. (2020). An evaluation of shelter coats for the protection of outdoor stones. In *Monument future: Decay and conservation of stone-Proceedings of the 14th International Congress on the Deterioration and Conservation of Stone, Volume I & II* pp. 645-650. Mitteldeutscher Verlag.

AN EVALUATION OF SHELTER COATS FOR THE PROTECTION OF OUTDOOR STONES

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Abstract

Climate change and air quality are impacting the way carbonate stones deteriorate in outdoor environment. The development of new materials and techniques to protect stones outdoors is a vivid part of research. However, the evaluation of existing measures to protect cultural heritage made of stone is lacking systematic research. This study aims to understand the efficiency and compatibility of different shelter coat systems applied on monuments made of carbonate stones in Austria. For this purpose slabs of a calcarenite were covered with 10 different coatings, one half of each subsequently treated with a water-repellent, and then exposed outdoors. The alterations in the course of weathering are monitored and documented annually by photography, tests of water absorption, material loss and gloss measurements. Cross sections were analysed before exposure and repeated on regular basis to further evaluate changes, with a focus on micro-structure and the interface between stone and coating: Polarized Light Microscopy (PLM), Scanning Electron Microscopy (SEM) as well as Fourier-transform infrared (FTIR) spectroscopy for chemical alterations. The visual and photographic inspections record microbiological colonization, tendency to soiling and specific patterns produced, as well as the weathering of the coat-

ing itself. While changes in water absorption may indicate a partial loss of effectiveness, FTIR and SEM analyses show possible chemical and physical degradation of the coatings. This combination of analytical methods proved useful to understand the functionality through the key physical parameters of the coatings and determine their condition and durability. This research assesses the different protection approaches from the past and identifies materials and maintenance strategies that can be recommended for the future.

Introduction

Carbonates have always been prone to chemical and physical weathering, but as climate and air quality change, especially in relation to the rising CO₂ concentration in the air, the solubility of calcium carbonate increases (Bonazza et al. 2008) and the need for protection of outdoor stone objects becomes increasingly important. There are various possibilities to address the problem, and a great deal of research has been concentrating on newly engineered coating materials for protection, primarily in form of water repellents with functionalized surfaces (Gherardi et al. 2018). More traditional approaches to the problem can be identified in Austria, namely, the use of shelter coats which

seem to be most promising for outdoor sculpture. The early uses of shelter coats, primarily related to lime-based systems with an addition of aggregate, can be found in England as part of the "lime method" (Durnan 2006, Fidler 1995). In Austria the understanding of shelter coats further broadened to include any kind of coating that contains a certain amount of aggregate (mostly sand) but, unlike mortar, can be applied by brush (Ban et al. 2018). The principal idea behind the use of shelter coats is to shift the weathering horizon, both in chemical and physical terms, from the stone surface to the surface of the coat. While the theory of material compatibility states similar petrophysical properties to the substrate as imperative (Snethlage 2011), another, often contradictory aspect regards the prevention of water uptake from the atmosphere. Above all, the durability of a coating treatment including its esthetic appearance upon weathering are additional factors of relevance.

The use of lime based shelter coats was promoted by the Federal Monuments Authority Austria (BDA) in the eighties and nineties of the last century, involving the use of silanes and/or siloxanes to further impregnate the shelter coat itself, in order to make it water-repellent and therefore longer lasting. This "Austrian approach" was introduced by H. Paschinger, the late chief chemist at the laboratories of BDA (Koller et al. 1996). Particularly, in the east of Austria such shelter coats are frequently used since then. Over time different recipes evolved; some even containing cement, silicate and/or silicon resin as primary binder. This resulted in a confusing terminology and a guideline was needed. Therefore, a working group of experts from the field was established in 2010 to produce guidelines for the use of shelter coats (Ban et al. 2018). While working on the document, many questions arose, and the need for a comparable long-term evaluation of shelter coats crystallized (Pintér et al. 2020). Thus, a field exposure program was established using 10 different recipes which were applied on slabs of calcarenite (St. Margarethen, Austria) and exposed outdoors (Tupi 2017). The evaluation of the slabs is done by students and staff of the Univer-

sity of applied Arts Vienna on annual basis. The field exposure site is additionally used as a test ground by other interested scientists and practitioners in the field.

Preparation and field exposure

A total of 10 slabs (40 × 40 × 4 cm) were coated each with different formulations of shelter coats. Besides the use in the practical stone conservation, important criteria were the expected material compatibility with the stone and/or the prevention of water uptake. A complete description of the coatings and details of the recipes used are listed in Table 1. All coats were applied in three successive layers using a brush. After one month of curing, half of each slab 1–9 was additionally treated with a water-repellent (Funcosil SNL, Remmers, Germany). After another month, the slabs were exposed to the outdoor environment. They were mounted by two aluminum rails on a west facing outer wall in the chartreuse of Mauerbach in Lower Austria. The exposure enables rainwater to wash down the slabs and it facilitates strong soiling, typical for rural surroundings, consisting of organic matter and earth as well as biological colonization.

Test results before exposure

Prior to exposure, tests and analyses were performed in order to characterize the unweathered coatings. Four measurement methods were used to assess the water absorption and the wettability of the surfaces: capillary water uptake (BS EN 15801:2009), contact angle (BS EN 15802:2009), contact sponge (Vandevoorde et al. 2013) and the droplet method (Bläuer et al. 2014). The brush method (Kirchner, Zallmanzig 2010) was used to assess the loss of material, the gloss was measured with a gloss meter. Thin-section (PLM) and scanning electron microscopy (SEM) was used to assess the microstructure of the coating itself and its interface to the stone. Water absorption tests showed that, compared to the uncoated stone, all shelter coats reduced the water absorption coefficient of the surface to some extent. The additional treat-

ment with water-repellent strongly reduced the absorption further. The highest absorption is shown by the pure lime and the Roman cement coatings. As expected, the lowest water absorption was measured for the silicone-based shelter coat and the water-repellent treated surfaces of slabs 1–9. The results of contact angle tests, measured for the coated surfaces without additional water-repellent application, supported those obtained by contact sponge and droplet method. According to these results, the pure lime (1) and the Roman cement (8) proved to be highly hydrophilic, precluding the measurement of the contact angle. The lime-based coats with addition of acrylic dispersion (2), or white cement (3), as well as the dispersed lime hydrate (6) and the nanolime (7) produced slightly hydrophilic coatings (contact angle 30–60°), while the addition of casein to lime (5), as well as the sil-

icate/waterglass (9) revealed slightly hydrophobic coatings (100/105°). The addition of linseed oil to lime (4), the silicone-based coating (10) and all of water-repellent treated surfaces resulted in strongly hydrophobic layers (120–135°). Gloss measurements showed that all coatings were rather matt (gloss value 0.22 GU) due to their relative roughness; they were also resistant to abrasion by brush in unweathered state (Kirchner, Zallmanzig 2010). PLM and SEM investigations of the samples taken from the slabs before exposure allowed for the following observations: the coating with lime-casein (5) showed numerous spherical air voids on the interface between the coat and the stone slab (Fig. 1a). These are so frequent that they seem to be interconnected and, upon weathering, may result in detachment or rapid wear-off. All lime-based coatings (1–7) show different amounts of

Table 1: Recipes of the applied shelter coats, results of the contact angle measurements on the fresh and not additionally treated surfaces as well as observations after one year of exposure.

No.	Short reference	Shelter coat recipe	Contact angle, before weathering	Observations after one year of exposure
01	Pure lime	1 Vol. Part Lime Putty 1 Vol. Part St. Margarethner 0–1mm	Completely hydrophilic	Very strong homogeneous soiling, some decay.
02	Lime with acrylic dispersion	1 Vol. Part Lime Putty 5 wt% (binder) Primal SF016 (Rohm & Haas, Germany) 1 Vol. Part St. Margarethner 0–1mm	Hydrophilic (60 °)	Homogeneous, moderate soiling. No defects.
03	Lime with white cement	1 Vol. Part Lime Putty 5 wt% (binder) white cement (Dyckerhoff, Germany) 1 Vol. Part St. Margarethner 0–1mm	Hydrophilic (30 °)	Homogeneous, moderate soiling. No defects.
04	Lime with linseed oil	1 Vol. Part Lime Putty 5 wt% (binder) cold pressed linseed oil, (Schmincke, Germany) 1 Vol. Part St. Margarethner 0–1mm	Hydrophobic (120 °)	Patchy discoloration of the surface, defects in the shelter coat.
05	Lime with casein	1 Vol. Part Lime Putty 5 wt% (binder) casein, (deffner & Johann, Germany) 1 Vol. Part St. Margarethner 0–1mm	Slightly hydrophobic (100 °)	Extremely strong soiling, strong biological colonization and decay.
06	Dispersed lime hydrate	1 Vol. Part CalXnova (dispersed lime hydrate, deffner & Johann, Germany) 1 Vol. Part St. Margarethner 0–1mm	Hydrophilic (50 °)	Homogeneous moderate, soiling. No defects.
07	Nanolime	1 Vol. Part CaLoSil E50 (IBZ-Salzchemie, Germany) 1 Vol. Part St. Margarethner 0–1mm	Hydrophilic (50 °)	Strong decay of the shelter coat.
08	Roman Cement	1 Vol. Part Roman cement (Rapido, Cemento Natural Tigre, Spain) 1 Vol. Part St. Margarethner 0–1mm	Completely hydrophilic	Strong soiling, no defects due to weathering.
09	Silicate	1 Vol. Part Silin AZ Fixativ (Silin, Germany) 1 Vol. Part St. Margarethner 0–1mm	Slightly hydrophobic (105 °)	Very light soiling, no decay.
10	Silicone	1 Vol. Part color LA colorless, (Remmers, Germany) 1 Vol. Part St. Margarethner 0–1mm	Hydrophobic (135 °)	No soiling, no decay.

cracks perpendicular to the surface, typically attributed to shrinkage (Fig. 1b).

The frequency of this kind of cracks seems to be the lowest in the samples from the slabs with acrylic dispersion (2) and linseed oil (4), in the lime coating. The latter additionally shows long thin cracks running parallel to the surface (Fig. 2a) which would possibly result in accelerated decay (Fig. 2b). The dispersed lime hydrate coating (6) shows few and small cracks, while the one with nanolime (7) is thin and highly porous with few micro cracks. The Roman cement coating (8), though highly absorbant, has no cracks at all.

Test results after one year of exposure

For the periodic evaluation of the performance of the coats, a combination of non-destructive and micro destructive methods was employed. While documentation and in-situ tests will be repeated each year (photographic documentation, water absorption using contact sponge and droplet method, gloss measurements etc.), laboratory tests will be carried out less frequently, depending on the expected relevance. They include analyses of polished thin-sections by PLM as well as SEM, and FTIR. Tests of the capillary water uptake in the laboratory and measurements of the contact angle will be repeated every two to three years.

After one year of exposure, there are already some results that deserve to be published at present. Most of them are related to the visual examination of the slabs and are confirmed by PLM and SEM. The visual inspection of the slabs yields the following observation: soiling of the surfaces is generally intense. The surfaces without water-repellent (halves of slabs 1-9) are in general soiled to a much higher degree as compared to the water-repellent treated and the silicone based coats (10). The latter can be explained by the hydrophobic properties even though the roughness seems to be the highest of all coatings. Amongst the lime-based coats, the one with casein additive (5) shows by far the strongest soiling and microbiological colonization; in this case both the half with and without water-repellent are concerned (Fig. 3b).

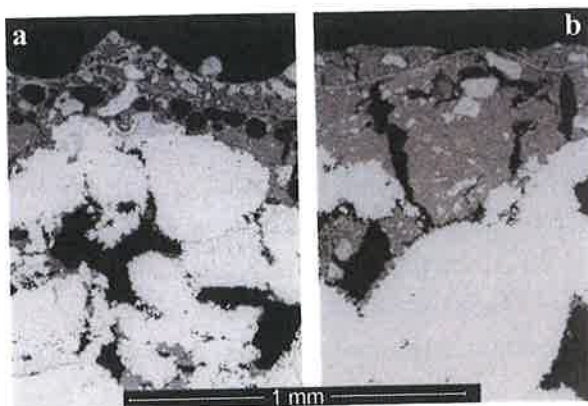


Figure 1a + b: SEM-BSE images of cross-sections from surfaces coated with (a) lime-casein and (b) pure lime.

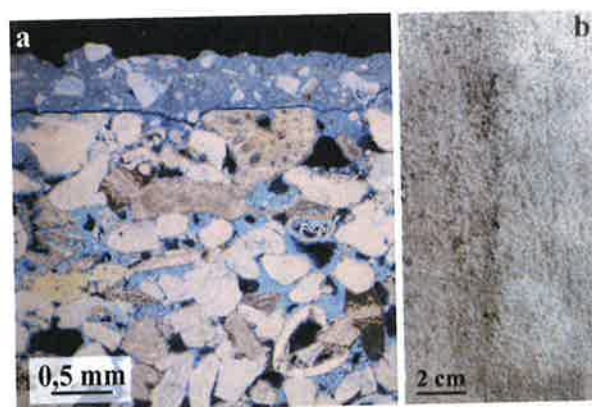


Figure 2a + b: Lime-linseed oil coating with tendency to detach; visible by PLM before exposure (a), resulting in surface flaking after one year of exposure (b).

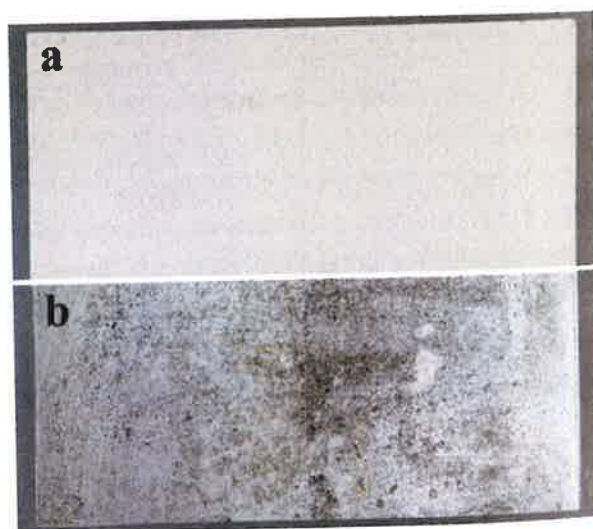


Figure 3a + b: Slab with lime-casein coating (left half with hydrorepellent) before (a) and after one year of exposure (b).

It can be argued that the microbiological activity is facilitated by the protein available in the coating. Also the lime coat with linseed oil (4) shows

patchy and unaesthetic discoloration after one year of exposure. The pure lime has a strong but evenly distributed soiling. Both additions of acrylic dispersion (2) as well as of white cement (3) prove to exert a positive effect by lowering the soiling tendency of lime-based coatings. The modern lime-based shelter coats performed very differently from each other. While the nanolime-based coat (7) was almost completely weathered off, the coat based on dispersed lime hydrate (6) performed very well in terms of both weathering resistance and the tendency to soiling. The Roman cement-based coat (8) shows a strong soiling similar to the one of the pure lime; this might be due to its high porosity, roughness and hydrophilicity. Both silicate- (9) and silicone- (10) based coats reveal almost no soiling and no weathering at all. In these cases, results from the coming years might be of greater interest, especially regarding their weathering patterns.

The micro-analyses on cross sections of samples taken after one year of exposure confirm the macroscopical observations, and allow a preliminary evaluation of the durability of the lime-based coatings and predictions for the coming years. The results show that early weathering of the pure lime coat (1) is visible in SEM: the carbonate skin starts to show signs of degradation. The recipes with acrylic dispersion and cement seem to be more durable and show fewer changes in the surface texture after the first year of exposure.

Discussion

When evaluating the pros and cons of a shelter coat system by its properties, one must get back to the question of the expected role of such a coating, i.e. a protective, a sacrificial or rather an aesthetic function. We believe that there is no universal answer to this question, though the principles of conservation must always be granted, e.g. the primacy of the original against the service life of a later surface coat. Thus, both the sacrificial and the protective role of a shelter coat may contribute to prolonging the life span of the object. However, whilst the latter aspect favors the physico-me-

chanical similarity between a coat and its substrate, e.g. in terms of porosity and absorptivity, the former rather supports the idea of the coating to be water repellent in contrast to the substrate. The question which approach is better can only be answered in view of the conditions of exposure and the properties of a given stone monument without neglecting the coating's durability and appearance. In addition to these general considerations, the exposure site presented, yields important insights which will become more significant in the course of further monitoring.

For the lime-based shelter coatings, the addition of acrylic dispersion or white cement (5wt% of the binder) showed a reduced soiling tendency and good durability. The dispersed lime hydrate coat also performed very promising. The addition of casein and linseed oil increased the tendency to soiling and microbiological colonization and seem to lower durability. The nanolime coat has a very low durability due to the low lime content in the product used, and the low thickness of the layer. Other nanolime formulations might be more suitable for this kind of task and should be tested in future. The Roman cement is strongly soiled presumably due to its rough surface along with the high porosity in favor of water absorption; this coat can thus be considered compatible to porous stone substrates but does not protect against precipitation or soiling. The silicate and silicone resin coats show almost no changes after a year of exposure, neither soiling nor signs of weathering. They can be considered least compatible in respect to the porous limestone because of their silicate nature and the water repellency, respectively, possibly resulting in a risk for the stone on a long-term perspective. Similar considerations apply to the halves of slabs 1-9 treated with hydrorepellent. With the exception of the lime coat with casein addition, they show drastically less soiling and weathering effects.

This small scale study reveals different trends and answers some of the questions posed. In order to fill the knowledge gaps regarding shelter coats, more research has to be conducted including laboratory tests and artificial ageing.

Summary

Shelter coats have been successfully used in different countries for some decades. Despite mostly positive experiences, little research has been done in this field. Since 2010, shelter coats have been the focus for conservators and heritage scientists in Austria (eg. Ban et al. 2018). A field exposure series was triggered by this debate and installed in Mauerbach, Lower Austria. Tests and analyses before and after one year of exposure were made and are presented in this paper. Some trends can already be observed. All shelter coats reduce the water absorption of the surface in case of the porous limestone of St. Margarethen. The additional water-repellent treatment reduces the water absorption further, as expected. Among the lime-based coats, the ones with addition of acrylic dispersion and white cement as well as the coats with dispersed lime hydrate show the lowest tendency to soiling, highest durability and esthetically acceptable soiling pattern. The Roman cement coat is subject to strong soiling, probably due to its rough and, absorbent surface. The silicate and silicone coats show almost no change after one year; results from the coming years will provide further insights. Finally, the hydrophobic treatment of the coats as proposed by H. Paschinger seems to increase the durability and delay soiling, however results of prolonged monitoring will be of great interest.

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Siegfried Siegesmund/Bernhard Middendorf (Eds.)

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**Decay and Conservation
of Stone**

**Proceedings of the 14th International
Congress on the Deterioration and
Conservation of Stone**

mitteldeutscher verlag