THE EFFECT OF ANTHROPOGENIC ACTIONS ON THE WEATHERING OF POROUS BUILDING STONES – EXAMPLES FROM THE AUSTRIAN CONSERVATION PRACTICE•

EMBERI TÉNYEZŐK PORÓZUS ÉPÍTŐKÖVEKRE GYAKOROLT HATÁSA – PÉLDÁK AZ OSZTRÁK RESTAURÁTORI GYAKORLATBÓL

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Abstract

Constantly changing environmental conditions, along with anthropogenic impacts result in new problems regarding the conservation of building stones. Based on examples from Austria, the present paper introduces the influence of mineral composition and microstructure, as well as the effect of environmental and anthropogenic parameters on the alteration of porous building stones. Although the weathering behaviour of stones is primarily determined by natural factors, the results showed that the effect of not properly conducted maintenance and conservation activities may also accelerate or even induce weathering. Examples concerning inadequate stone consolidation methods, inaccurate application of cement-based building materials, the removal of sacrificial layers and the ill-considered use of water repellent treatments are discussed. The results based on different methods of microscopy showed that the above-mentioned interventions may increase the damaging potential of freeze-thaw cycles, hygric and thermal dilatation and salt-induced corrosion. Consequently, instead of general, long-term solutions regular monitoring and fast interventions are key parameters to preserve cultural heritage in the future.

Kivonat

A folyamatosan változó környezeti paraméterek és antropogén tényezők hatásának együttes következményeként új problémák jelentek meg az építőkövek állagmegőrzésében. Jelen tanulmány az ásványos összetétel, mikroszerkezet, valamint a környezeti és emberi tényezők porózus építőkövek károsodására gyakorolt hatását mutatja be ausztriai példák alapján. Habár a kőzetek mállását elsősorban természetes tényezők irányítják, a tapasztalatok azt mutatják, hogy a nem megfelelően kivitelezett restaurálási és karbantartási munkálatok szintén felgyorsíthatják, vagy akár maguk is előidézhetik a károsodásokat. A károsodási jelenségeket a nem megfelelően kivitelezett kőszilárdítás, a cementes építőanyagok helytelen használata, az áldozati rétegek eltávolítása és a hibásan alkalmazott hidrofób kezelés témaköreiből vett példák segítségével mutatjuk be. Mikroszkópos vizsgálatok alapján megállapítható, hogy a fenti tevékenységek növelhetik a fagyáskár, a hőmérséklet vagy nedvesség hatására fellépő dilatáció, valamint a sókiválások okozta korrózió károsító hatásait. Következésképpen, az általános és hosszútávú megoldások helyett a folyamatos monitorozás és a gyors beavatkozás elengedhetetlen feltételei kulturális örökségünk jövőbeni eredményes megóvásának.

KEYWORDS: STONE WEATHERING, MICROSTRUCTURE, FLAKING, DAMAGING SALT, MICROSCOPY

KULCSSZAVAK: KŐZETMÁLLÁS, MIKROSZERKEZET, LEVELES ELVÁLÁS, KÁROSÍTÓ SÓ, MIKROSZKÓPIA

Introduction

Natural stone has been one of the oldest and most frequently used building materials of mankind. The large variety of stones allowed numerous architectural applications and sculptural works all over the world forming a significant part of our cultural heritage.

After quarrying, an exposed stone surface comes to imbalance with its environment; chemo-physical processes start up and the stone slowly begins to weather. As a consequence, secondary products may form, the stone disintegrates on a micro- and later also on a macroscopic level, or its surface gets stained.

• How to cite this paper: PINTÉR, F., (2020): The effect of anthropogenic actions on the weathering of porous building stones – examples from the Austrian conservation practice, *Archeometriai Műhely* **XVII/3** 303-316.

HU ISSN 1786-271X; urn: nbn: hu-4106

The rate and way of weathering is first and foremost related to the mineralogical composition, micro- and macrostructure of the stone and external factors (e.g. climatic parameters, air quality, exposure, etc. ICOMOS-ISCS 2008). In this relation, urban areas have a significantly higher impact on the rate of weathering, compared to the less inhabited regions. Therefore, the anthropogenic impact on building stones became one of the most significant damaging factors in the last century and was extensively discussed by several authors (e.g. Weber et al. 1984, Siegesmund & Ruedrich 2011). On the other hand, due to strict environmental regulations the emission of exhaust gases (mainly SO_2) has also significantly decreased in the last decades (EEA 2016). Consequently, the formation of some secondary products such as gypsum crusts, being one of the most frequently observed stone decay phenomena in the 20th century, almost entirely disappeared in the last decades. Nevertheless, secondary sulphates, originating from other sources (e.g. construction materials, soil solutions, etc.) are still meaningful factors in stone deterioration even if the damaging role of sulphur oxides in the air was partly taken over by NO_x (EEA 2016), favouring the formation of nitrate salts in mineral building materials.

Additionally, our built cultural heritage is also facing new challenges worldwide. Impacts of the global climate change (Adams 2008) on monuments are already traceable and their effects will, in the future, increasingly influence the condition and state of preservation of historical buildings and sculptures. Therefore, in order to obtain reliable and sustainable solutions for problems and processes related to stone alteration, consistent research and interdisciplinary co-operation are of outmost importance.

In Austria approx. 200 different types of rocks, predominantly of sedimentary and metamorphic origin, were used as building stones in the last two millennia. Some of the raw materials have been quarried since Roman times and many were used in the 19th and early 20th centuries in the former Austro-Hungarian Empire, or shipped abroad (Huber & Stingl 2014). A large number of these stones is thus characteristic for different regions and shapes the appearance of the so-called architectural landscapes (Huber & Stingl 2014).

Due to the rich Austrian cultural heritage (i.e. more than 35.000 listed monuments) investigation of building stone decay has a long tradition in the country (e.g. Kieslinger 1932, Weber et al. 1984, Rohatsch 2005a). Additionally, the know-how resulting from the scientific investigation and restoration of a large number of monuments since the post-war period allows for a better understanding of the advantages and disadvantages of different conservation techniques. Based on this experience the research of the weathering of building stones in Austria started to focus in the past 15 years on types of damage resulting from the application of incompatible building materials, coatings, or the inadequate use of conservations techniques (Nimmrichter 2007). This paper aims to present some characteristic examples of various porous building stones of sedimentary origin, sampled from historical monuments in East Austria and to demonstrate how mineral composition, microstructure and environmental impacts, along with the anthropogenic factors, contribute to their degradation.

Sampling and methods

The presented samples (**Table 1.**) were selected from six sacral objects situating in East Austria (**Fig. 1.**) and investigated in the frame of interdisciplinary conservation projects under the supervision of the Federal Monuments Authority Austria between 2013 and 2019. After sampling, all samples were dried and embedded in epoxy resin. Depending on the size of the samples thin or polished sections were prepared and analyzed by polarized light (Zeiss AXIOScope A1) and/or scanning electron microscopy (SEM, Zeiss EVO15, acceleration voltage 20 kV). Spot analyses and element mappings in the SEM were executed with an energy dispersive X-ray spectrometer (EDS, Bruker Quantax XFlash, Bruker Esprit software). Observations regarding the water repellent property were performed after Wendler (2011); micrographs were taken by a Leica DFC420 stereo microscope.

Results and discussion

Weathering processes of flysch and molasse sandstone

Most sandstone types of great historical importance, used at construction works in the north-eastern part of Austria, belong to the Rhenodanubian Flysch Zone (RFZ). The zone is situated in the northern foreland of the Northern Calcareous Alps (**Fig. 1.**) and composed mainly of siliciclastic sediments (i.e. claystone, sandstone, conglomerate) produced by subaquatic sediment gravity flows, the so-called turbidites (Tollmann 1980, Schwaighofer 2003).

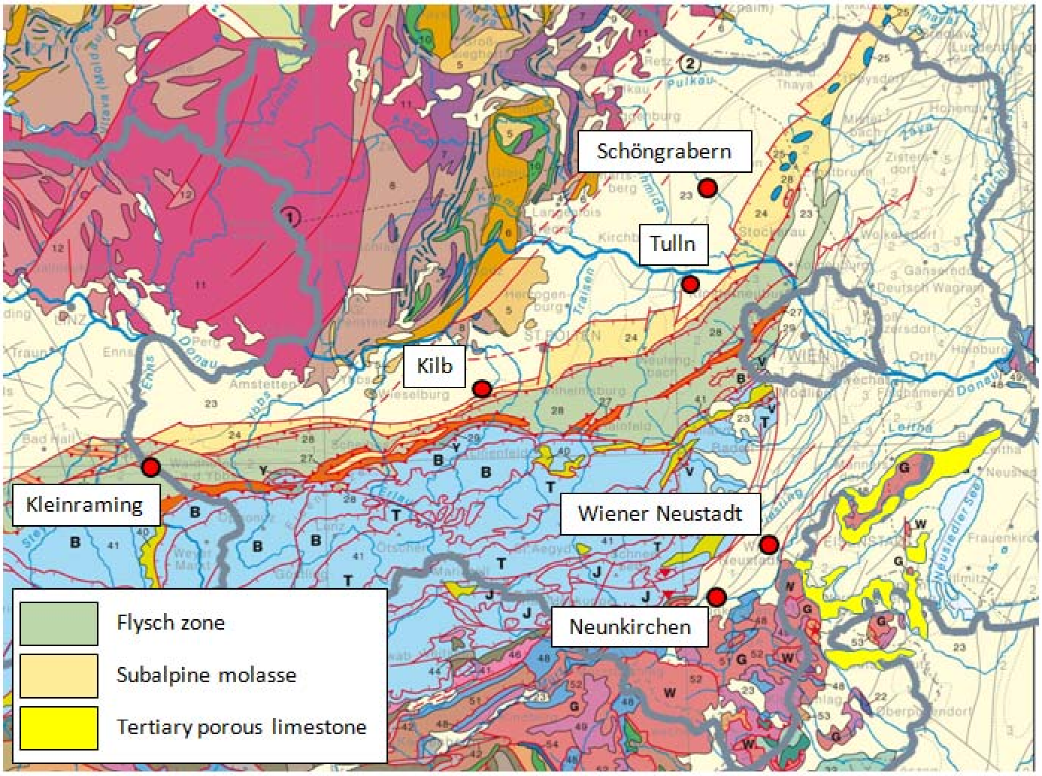

Fig. 1.: The geological setting of Northeast Austria and the sampling sites of this study (modified after Egger et al. 1999)
1. ábra: Északkelet-Ausztria geológiai felépítése a mintavételi helyek megjelölésével (Egger et al. 1999 után módosítva)

Table 1.: Sampling sites and petrographic characteristics of the samples (q: quartz, fsp: feldspars)
1. táblázat: Mintavételi helyek és a minták kőzettani jellemzői (q: kvarz, fsp: földpátok)

Sample	Origin	Object / Position / Sample	Stone type
KR	Kleinraming, Upper Austria	Parish church / belfry, buttress / stone slab	*grain supported subarkose* (q>>fsp>mica + rock fragments in traces; coarse secondary calcite cement >5%)
TU	Tulln, Lower Austria	Ossuary / north façade / stone ashlar	*grain supported subarkose* (q>>fsp>mica + rock fragments in traces, opaque minerals [pyrite, limonite]; coarse secondary calcite cement in traces)
SG	Schöngrabern, Lower Austria	Parish church / south façade, footing / stone ashlar	*grain to matrix supported subarkose* (q>>fsp>mica; coarse secondary dolomite cement >10%)
KB	Kilb, Lower Austria	Parish church / spire / stone ashlar	*grain supported subarkose* (q>>fsp>mica + rock fragments in traces; coarse secondary calcite cement ~5%)
WN	Wiener Neustadt, Lower Austria	Sacral column / pinnacle / stone slab	well-sorted *biocalcarenite*, grainstone with low amount (<2%) of siliciclastic detritus. Fossil content: mainly calcareous algae and foraminifers
NK	Neunkirchen, Lower Austria	Holy Trinity column / stone figure	

Different types of sandstone have been excavated for centuries in this region, especially in Land Salzburg, Upper and Lower Austria, but some of the most important former quarries are situated in the Wienerwald (Vienna Woods) near the capital. Archaeological excavations revealed that the so-called "Wienerwald Sandstone" was already used by the Romans nevertheless the opening of the large sandstone quarries was related to the extensive construction activities in Vienna in the late 19th century (Huber & Stingl 2014). Other historically relevant types of sandstone can be found in the Molasse Zone north of the RFZ (**Fig. 1.**). While molasse sandstone was also used at the construction of several historical buildings in the northern and central part of Austria, due to its limited surface occurrences and often poorer quality, it only had an ancillary importance compared to the flysch type (Huber & Stingl 2014, Rohatsch 2005b). Molasse sandstone was predominantly quarried in Vorarlberg (the so-called Bregenzerwald glauconite sandstone) and in a few places in the foreland of the Northern Calcareous Alps in Land Salzburg, as well as in Upper and Lower Austria (Rohatsch 2005b, Huber & Stingl 2014).

The flysch and molasse sandstone types in this study are medium to coarse-grained, moderately to well-sorted and mostly grain supported subarkose (**Fig. 2.**), in the case of some molasse types they have partly matrix supported microstructure (**Fig. 3., Table 1.**). Besides the main components (quartz, alkali feldspars and a few siliceous rock fragments), muscovite/biotite mica and opaque minerals (pyrite, iron-oxide, etc.) are minor but characteristics constituents. Except for the Wienerwald Sandstone (sample TU), where non-swelling clay minerals were also observed in minor amounts, all investigated types are free of fine-grained matrix components. Sparitic calcite or dolomite cement of secondary origin was found in each sample in variable quantities (~1 to 10%). The total porosity of the different types varies between 5 and 14%. Weathering phenomena mostly occur as flaking and scaling, parallel or sub-parallel to the surface. In some cases a granular surface disintegration was also observed.

The effect of freeze-thaw disintegration along mica flakes - sample KR, Kleinraming

In the sample KR a disintegrated zone was observed in a depth of 2 to 4 mm characterized by a crack system running sub-parallel to the outer surface. This crack pattern can indicate various degradation processes such as freeze-thaw cycles, salt degradation, or hygric/thermal dilatation.

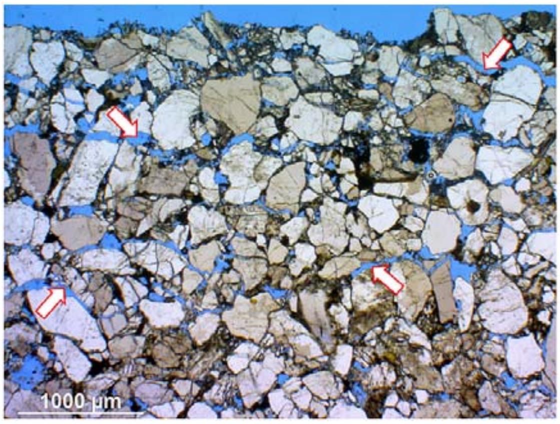

Fig. 2.: Characteristic textural appearance of flysch sandstone (subarkose) from Lower Austria (sample TU, 1N). Arrows show microcracks formed due to weathering processes.

2. ábra: Alsó-ausztriai flis homokkő (szubarkóza) jellegzetes szöveti képe (minta TU, 1N). A nyilak a mállás során kialakult mikrorepedéseket jelölik.

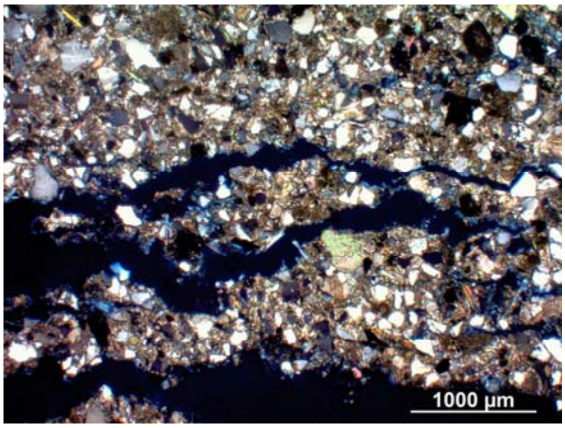

Fig. 3.: Characteristic textural appearance of molasse sandstone (subarkose) with large amount of secondary sparitic dolomite cement (sample SG, Lower Austria, +N).

3. ábra: Alsó-ausztriai molassz homokkő (szubarkóza) jellegzetes szöveti képe nagy mennyiségű másodlagos dolomitcementtel (minta SG, +N).

While the existence of damaging salts in the cracks could be excluded as a reason for the damage (Pintér 2018), sheet silicates (i.e. muscovite mica) exhibiting flaking lamellae were frequently observed in or in the vicinity of microcracks (**Fig. 4.**).

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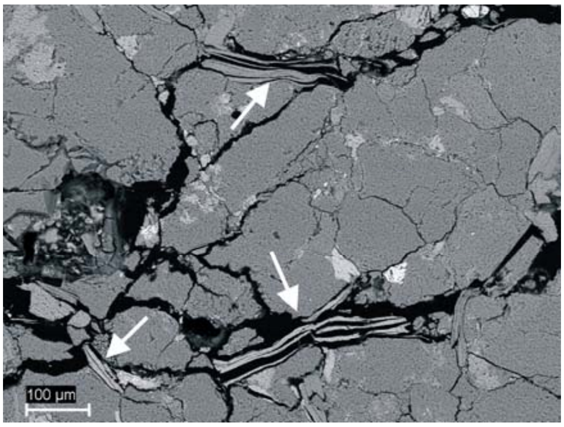

Fig. 4.: Formation of microcracks in the vicinity of mica lamellae (arrows) due to freeze-thaw damage (sample KR, SEM-BSD).

4. ábra: Csillámok (nyilak) környezetében fagyási károsodás hatására kialakult mikrorepedések (KR minta, SEM-BSD)

Consequently, the observed degradation pattern was clearly ascribed to physical processes, where no salt crystallization took place. Fine-grained flysch sandstones frequently show high affinity for hygric dilatation, a result of a certain amount of swelling clay minerals (Rohatsch 2003, Ban 2014), but in the present sample only mica was observed, thus the role of swelling clay minerals could also be excluded.

Based on the combined investigation of damaged samples and a local inspection at the object, it can be stated that the reason for the damage was a consequence of incorrect water draining on the façade and subsequent freeze-thaw cycles. The role of infiltrating water was also suggested by a thin calcium carbonate precipitation layer on the surface of the investigated stone slab. $Ca(OH)_2$ leached from cement-based joint mortars in the vicinity of the investigated slab and precipitated and carbonated on the stone´s surface also suggests the intensive impact of moisture on the façade where the damage was observed. Finally, intergranular microcracks indicate the relatively weak bounds between the sandstone grains, where mica grains acted as additional weak zones in the stone texture in two different ways. First, the weak bounds between the mica lamellae may favour the formation of cracks due to higher capillary suction compared to their vicinity and, secondly, highly acute mica wedges can be effective nucleation sites for ice crystallization (Campbell et al. 2017). Therefore, microporosity conducted the moisture from the surface into the stone´s interior, where, predominantly in the vicinity of mica crystals, due to freeze-thaw attack crystallization pressure provoked the formation of microcracks and thus the loosening of the stone´s structure.

Fig. 5.: Characteristic weathering pattern, granular surface disintegration and back weathering of the Wienerwald (flysch) Sandstone on the north façade of the Ossuary in Tulln, Lower Austria (picture courtesy J. Nimmrichter).

5. ábra: A Wienerwald (flis) Homokkő jellegzetes mállási képe (felületi szemcsekipergés és anyagveszteség) a tullni Csontház északi homlokzatán (kép: J. Nimmrichter)

Effects of permanent moisture and repeated consolidation treatments – sample TU, Tulln

Macroscopic appearance of the stone ashlars of the Romanesque ossuary in Tulln, Lower Austria, one of the most significant objects made from the Wienerwald Sandstone, showed granular disintegration and back weathering (**Fig. 5.**). Although this sandstone type (**Table 1.**) is characterized by high porosity and a more variable mineralogical composition, the microscopic degradation pattern is very similar to that of the sample KR and is characterized by cracks running sub-parallel to the outer surface (**Fig 2.**).

Although the pores and cracks are partly filled with gypsum up to a depth of 1.5 to 2.0 mm (**Figs. 6 and 7.**), a characteristic salt crust could not be detected on the surface. Careful investigation of the sample revealed that the pores and cracks in the sub-surface zones contain silica gel, indicating a stone consolidation treatment using an ethyl silicate consolidant (**Fig. 8.**). The first application of ethyl silicate at the object - and simultaneously in Austria - was performed during the 1970s (Nimmrichter 2007). Since then the consolidation has been repeated on different parts of the object in five different conservation campaigns (Ban 2014). In the analyzed sample at least two generations of silica gel with different water content could be observed, due to their different grey values in the backscattered electron images.

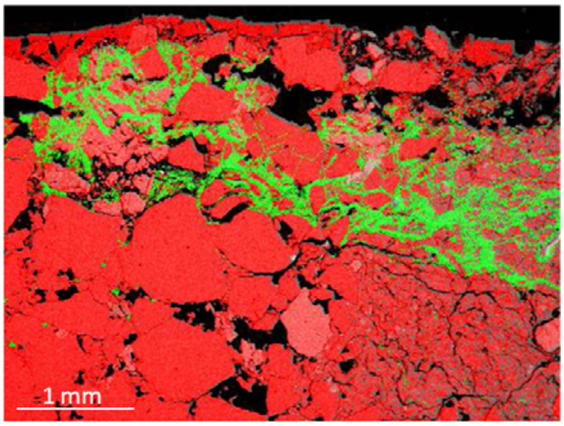

Fig. 6.: Cracked subsurface zone (red: Si = quartz, feldspar, etc.) filled with gypsum (S: green) in the sandstone sample TU. SEM element mapping

6. ábra: A TU homokkő minta (piros: Si = kvarc, földpát, stb.) repedezett felszín alatti zónája gipszkitöltéssel (S: zöld). SEM elemtérkép

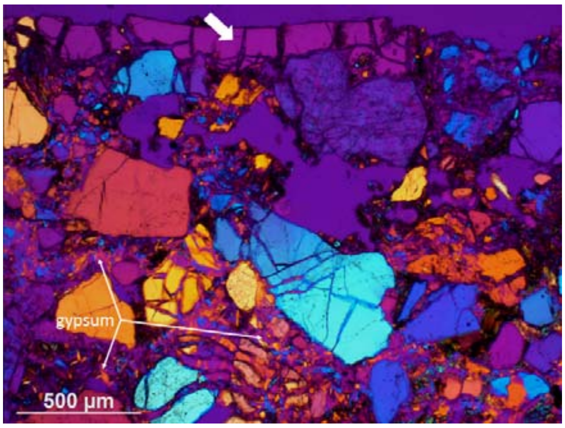

Fig. 7.: Cracked subsurface zone covered with a thick layer of silica gel (thick arrow) on the surface indicating a former consolidation. Partly cracked grains are filled with gypsum (sample TU, +N, λ plate)

7. ábra: Egy korábbi kőszilárdításra utaló vastag kovagél-réteg a repedezett kőzetszövet felszínén. A részben repedezett ásványszemcsékben gipsz figyelhető meg. (TU minta, +N, λ segédlemez)

The spatial distribution of gypsum and silica gel showed that in some areas gypsum crystals are covered by the silica gel (**Fig. 8a**) and in other, mostly deeper zones hypidiomorphic calcium sulphate grew on the surface of the consolidant (**Fig. 8b**).

Regarding the degradation processes the following explanation can be offered. The size, shape and distribution of mineral grains result in a fine capillary network of pores with fairly uniform pore openings. In this system the moisture penetrates the sandstone by precipitation, condensation in the pore space, seasonal dew point shift, etc., causing that the stone can never completely dry out. On the one hand, this leads to an increasing sensitivity to freeze-thaw-cycles. Furthermore, soluble mineral components can diffuse over a long period either from the stone itself, or from masonry mortars, but also from airborne dust settling on the stone surface. Due to dissolution and precipitation cycles, secondary mineral phases (e.g. gypsum) appear in the sub-surface zones and form a barrier layer. Consequently, micro- to millimetre thick layers detach parallel to the surface (Ban 2014) or cause granular disintegration. Additionally, consolidation activities have also contributed to the formation of new damages in the observed sample. Figure 7 shows a thick, cracked layer of silica gel on the surface; different consolidant generations can be traced up to a depth of several millimetres, but their frequency drastically decreases below 2 mm. This phenomenon suggests the so-called over-consolidation of the outer zones of the stone that occurs when the consolidant migrates back to the surface due to evaporation of the solvent (i.e. ethanol) and also poorly executed post-treatment of the surface (Nimmrichter 2007). While some of the microcracks in the sub-surface zones filled with the consolidant, massive joints in the deeper zones free of any silica gel suggest that they formed after the consolidation (Pintér 2016). Although silica gel does not completely fill the pores in the consolidated parts of the stone, it notably altered the microporosity properties in the sub-surface zones.

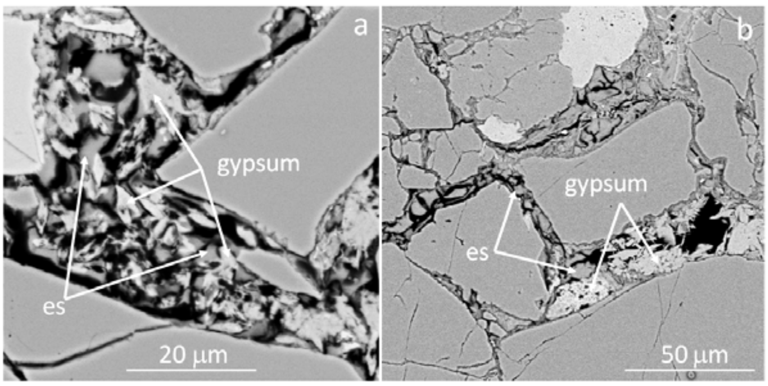

Fig. 8.: Silica gel (es = ethyl silicate) situating between gypsum crystals (a) and calcium sulphate growing on the surface of the silica gel precipitations (b) indicating the formation of gypsum before and after consolidation, respectively (sample TU, SEM-BSD image)

8. ábra: Szilikagél (es) kiválások között (a) és felületein (b) található kalcium-szulfát kristályok, amelyek a gipszesedés kőszilárdítás előtti, ill. utáni létrejöttére utalnak (TU minta, SEM-BSD kép)

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Fig. 9.: Flaking of molasse sandstone due to thermal/hygric dilatation and/or freeze-thaw cycles on the footing of the Parish church in Schöngrabern, Lower Austria (image courtesy J. Nimmrichter)

9. ábra: Molassz homokkő lemezes elválása hőmérséklet vagy nedvesség hatására fellépő dilatáció és/vagy fagyási kár következtében (Schöngrabern, Alsó-Ausztria, kép: J. Nimmrichter)

The measurement of the dynamic modulus of elasticity and water uptake also indicated large differences between sub-surface and deeper zones (Ban 2014) confirming the microscopic observations. The role of gypsum is, however, not completely clear in provoking the damages. Since it was found both coated with silica gel and growing on top of the consolidant (Fig**. 7a-b**), it is assumed that its formation took place prior and after the ethyl silicate treatment, respectively. In this special case the precipitation of gypsum and multiple application of stone consolidant resulted in a dense outer zone, where the altered capillary porosity favoured the subsequent accumulation of gypsum. The existence of cracks free of any sulphate corrosion products and consolidant formed below this dense zone (**Fig. 6.**) suggest that the last stage of the stone decay was provoked by freeze-thawing. Additionally, the dissolution-precipitation and subsequent crystallization of gypsum could provoke elevated degradation on the micro level.

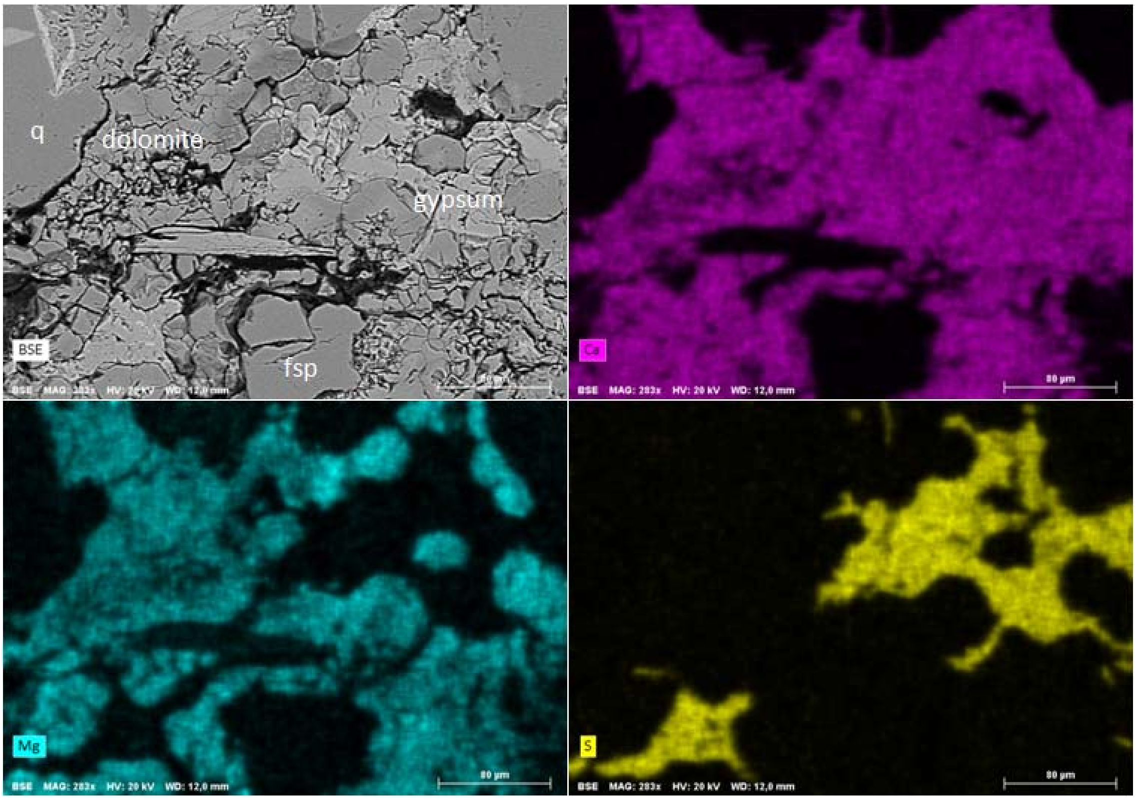

Fig. 10.: SEM-BSD image shows the main mineral components, while EDS mapping proves the correlation between the elements Ca (magenta) and S (yellow) indicating the presence of gypsum in the microcracks. Mg (cyan) only correlates with Ca showing the presence of dolomite cement in the stone (sample SG)

10. ábra: SEM-BSD kép alapján látható fő ásványi alkotók az SG mintában. Az EDS elemtérképezés, a Ca (magenta) és S (sárga) közötti korrelációt bizonyítva, gipsz jelenlétére utal, míg a Mg (világos kék) csak a kalciummal korrelál, ami a dolomitcementet mutatja (SG minta)

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Effects of the removal of sacrificial layers – sample SG, Schöngrabern

Another typical sandstone degradation phenomenon was observed in the Romanesque parish church in Schöngrabern, Lower Austria. Flaking of stone ashlars, especially on exposed edges (**Fig. 9.**) up to a depth of 1.0 cm, indicated prolonged weathering processes. Salt analyses based on ion chromatography, IC (Pintér 2019a) indicated the presence of calcium and magnesium sulphate salts. Detailed microscopic analyses confirmed that in the damaged sample a crack system sub-parallel to the outer surface existed. SEM-EDS also proved the presence of sulphates up to a depth of approx. 2.5 mm, where only gypsum was detected. Although microcracks and joints are completely filled with calcium sulphate, the dolomite cement seemed to be completely intact (**Fig. 10.**), suggesting that the sulphate salts were not directly formed by the reaction of $CaMg(CO_3)_2$ and SO_4 ions, otherwise magnesium sulphate would also have crystallized in the cracks. Thus, magnesium measured in the sample by IC originated from the sparitic dolomite binder of the stone leached out from the bulk sample during the elution in the laboratory.

The formation of cracks seems not to be connected directly with the crystallization of gypsum, which is also suggested by joints free of any secondary salts. The most probable explanation for the primary damages was thermal- and/or hygric dilatation induced stresses and subsequent loss of cohesion and not the formation of calcium sulphate. This theory is also supported by previous observations and research on the conservation history of the object (Nimmrichter 2007). Thus, the first damages have already been observed in the 19th century, when lime-based renders and coatings, the so-called protective sacrificial layers, were completely removed from the walls. Consequently, the yellowish-brown sandstone surface, especially on the east and south façades, could absorb more heat that provoked an increased thermal dilatation. Furthermore, the removal of the lime coating that acted as a buffer zone, created a direct contact between the stone surface and its surroundings, allowing a higher moisture uptake through capillary suction. Additionally, the crystallization of crack-filling gypsum caused a denser outer layer of several millimetres thickness (**Fig. 9.**). The lower porosity and stiffness of this crust increased the effect of thermal and hygric dilatation as well as freeze-thaw cycles and thus a more intense degradation of the stone, especially in exposed zones (**Fig. 9.**). In the 1990s and 2000s successful applications of lime-based coatings proved that even porous building stones of low weathering resistance can be protected by simple solutions (Ban et al 2018).

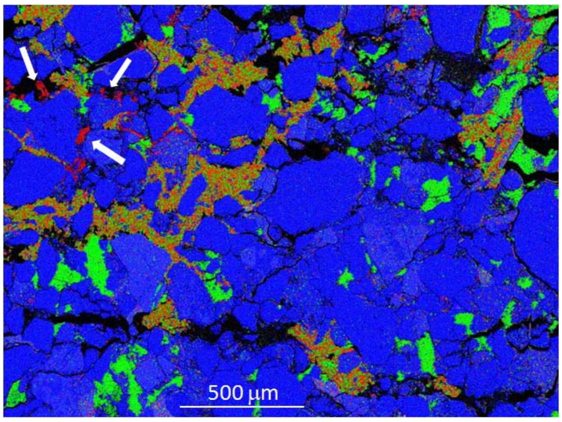

Fig. 11.: SEM-EDS element mapping of sample KB (Kilb, Upper Austria). Between the silicate mineral grains (Si: blue), calcite cement (Ca: green) and gypsum (green [Ca] and red [S]) are visible. Red areas (arrows) suggest the presence of sulphate phases free of Ca (i.e. alkali sulphates).

11. ábra: A KB (Kilb, Felső-Ausztria) minta SEM-EDS elemtérképe. A szilikát ásványok (Si: kék) között kalcit cement (Ca: zöld) és gipsz (Ca: zöld + S: piros) figyelhető meg. A piros részek (nyilakkal jelölve) kalciummentes szulfátfázisok (alkáli-szulfátok) jelenlétét valószínűsítik.

Nevertheless, continuous maintenance and repair of damages are the prerequisites of a long-term protection of sensible stone surfaces (Nimmrichter 2007).

Degradation due to contact with cementitious materials – sample KB, Kilb

Contrary to the previous examples, the flysch sandstone from Kilb (sample KB) shows the effect of salt corrosion on a porous building stone. The rock type that was used at the construction of the spire of the parish church in Kilb has very similar composition and microstructure to that of Kleinraming (**Table 1.**).

Similarly to the previous examples, this sandstone exhibits the common degradation pattern; microcracks run sub-parallel to the outer surface, their way of propagation mostly follows the silica grain boundaries and coarse calcite cement also clearly distinguishable from the detrital grains (**Fig. 11.**). SEM-EDS spot analyses and element mapping indicated the presence of sulphate salts (**Fig. 11.**), where besides gypsum alkali sulphates were also detected (**Fig. 11.**). Furthermore, the distribution pattern of sulphates is different from that of the samples TU and SG. In the sample KB the microcracks are not completely filled with the newly formed sulphate products, but rather form isolated clusters (**Fig. 11.**). This distribution pattern is similar to that of the calcite cement, indicating the direct formation of gypsum from calcite with subsequent degradation of the stone. The large amount of alkalis, also proved by IC (Pintér 2013), suggests the impact of Portland cement-based materials. Due to static considerations the spire was reinforced with a concrete ring beam in the mid-20th century, being in direct contact with the sandstone ashlars. The massive concrete structure affected the weathering of the stone in two different ways. First, the movement of moisture in the masonry is blocked and redirected by the less porous concrete, leading to an increased water load in the building stone. Secondly, water mobilizes and transports soluble components (i.e. alkalis, sulphates) from the cementitious construction material. Consequently, mineral solutions penetrate the stone substrate where dissolved sulphate and alkali ions react with the calcite of the sandstone, as well as directly crystallize from the solution. Subsequent crystallization pressure causes flaking and granular disintegration, followed by a massive material loss on the surface. Although the sample originates from the inner side of the belfry, damaged openings allowed for moisture (i.e. rain and snow) to directly enter the tower. Additionally, low temperatures in the winter months may have contributed to damages due to freeze-thaw cycles.

Weathering processes of porous limestone and calcarenite

In the vicinity of Vienna and the eastern part of Austria the most important building stones are Neogene calcarenite and porous, soft limestone types of diverse geological formations. The most significant historical quarries are situated southeast of the capital in the Leitha Mountains between Lower Austria and Burgenland. In this region excavated stones predominantly belong to the Middle Miocene (Badenium) Leithakalk Formation and to occurrences containing Sarmatian detrital limestone and calcarenite types (Rohatsch 2005b). Some of the quarries (e.g. St. Margarethen in Burgenland) were already operated in Roman times in the 1st century AD, but the reactivation of their use in construction dated back to the 11th-12th centuries, whereby monasteries, churches and castles were primarily built from this stone material (Rohatsch 2005b). From the late Middle Ages until the beginning of the 20th century, a large number of significant objects, such as the St. Stephen cathedral in Vienna, the Castle of Schönbrunn or the cathedral of Wiener Neustadt have been erected, using this type of stone. Especially in the late 19th century, during the so-called Vienna Ringstrasse period with its profane and sacred presentation buildings, numerous stone quarries experienced a renewed and final bloom (Seemann & Summesberger 1998).

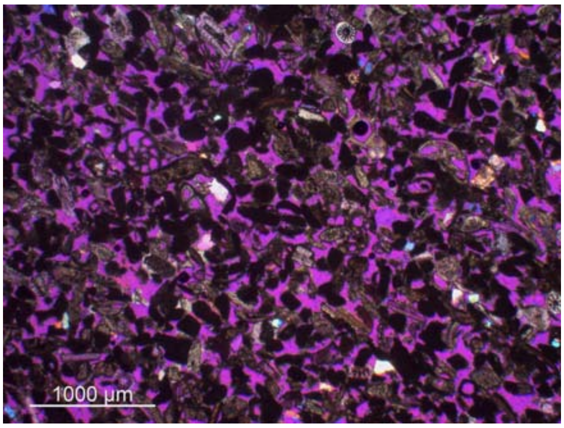

Fig. 12.: Characteristic textural appearance of Tertiary biocalcarenite from the Leitha Mts., Lower Austria/Burgenland. The components are predominantly made up of calcareous algae and foraminifera fragments and a few detrital quartz grains. The high porosity is highlighted by the magenta colour (+N, λ plate)

12. ábra: Lajta-hegységi harmadidőszaki mészhomokkő jellegzetes szöveti képe. Fő komponensek: mészvázú alga és foraminifera, illetve kevés detritális kvarc. Magenta: pórusok (+N, λ segédlemez)

In general, most of the Neogene calcarenite types exhibit high (i.e. 10 to 20%) porosity, and depending on the geological facies and subsequent lithification, they have low to moderate strength. Consequently, many lithotypes exhibit a low resistance against freeze-thaw cycles and salt damage (Rohatsch 2005b).

The most characteristic and intensively researched (Rohatsch 2005a) degradation pattern of porous limestone is the formation of dark, massive gypsum crusts on the surface and subsequent weakening as well as disintegration of the microtexture below the crust (Farkas et al 2018).

Since the air pollution-induced formation of gypsum became almost negligible in the last decades, the following selected examples show partly unexpected problems caused by conservation interventions at the objects.

Degradation due to over-consolidation – sample WN, Wiener Neustadt

The 21 meters high Gothic stone column, the so-called “Spinnerin am Kreuz”, in Wiener Neustadt was built using at least six different sedimentary and magmatic rocks, where the porous limestone and calcarenite variations from Burgenland and Lower Austria dominate the monument (Pliessnig & Mozdoniewicz 2019).

HU ISSN 1786-271X; urn: nbn: hu-4106

Fig. 13.: Weathering of porous biocalcarenite at the Spinnerin am Kreuz, Wiener Neustadt, Lower Austria (sample WN; picture: Pliessnig & Mozdyniewicz 2019).

13. ábra: Porózus biokalkarenit mállása. Spinnerin am Kreuz, Bécsújhely, Alsó-Ausztria (WN minta, kép forrása: Pliessnig & Mozdyniewicz 2019)

The zone where the sample was taken from is connected to the 19th century renovation activities. The stone is a porous calcarenite made predominantly up of the fragments of calcareaous algae (**Figs. 12. and 14.**) and foraminifera originating from one of the historical quarries on the northwestern slopes of the Leitha Mts. Although these fine-grained sedimentary rocks were used as significant sculptor stones, their low resistance against weathering has been known for centuries.

The damaged stone surface of the 19th century renovation was first treated in the 1990s with ethyl silicate consolidants. After approx. 20 years of service life scaling of the already treated surface was observed (**Fig. 13.**). Although the influence of damaging salts has been excluded by laboratory analysis (Pintér 2019b), detailed microscopic analysis revealed a very heterogenous distribution of the consolidant (**Fig. 14a**). While in the sub-surface areas (up to a depth of 1 to 1.5 mm) large amount of precipitated silica gel was detected, deeper zones contained the consolidant only sporadically (**Fig. 14a**). Surprisingly, and also very atypically for ethyl silicate consolidants, many pores were completely filled with silica gel (**Fig. 14b**). Furthermore, microcracks in a depth of 2 to 2.5 mm indicated a weak zone between the outer and inner parts of the stone. The above described phenomenon is a clear evidence for the over-consolidation of a surface; a common problem in case of not properly executed treatments.

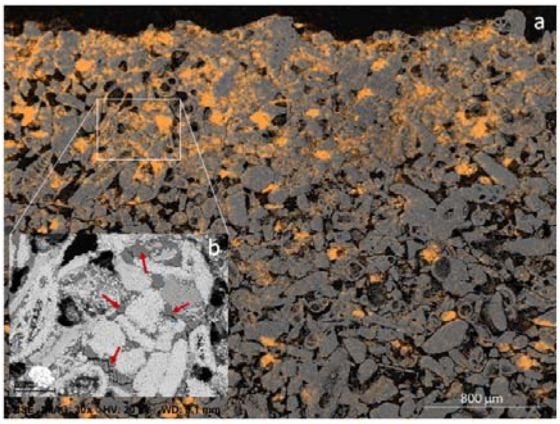

Fig. 14.: SEM-BSD image and element mapping of sample WN. Ochre areas (a) show the distribution of Si (i.e. mostly silica gel and some quartz). Si enrichment in the subsurface zones indicates the enrichment of silica gel as an evidence of over-consolidation of the surface (b, arrows)

14. ábra: A WN minta SEM-BSD felvétele és Si-eloszlási térképe. Az okker részek a Si (zömében kovagél és némi kvarc) eloszlását mutatják (a). A Si-ban gazdag felszín alatti zóna nagy mennyiségű kovagél jelenlétére (b, nyilak) és a felszín túlszilárdítására utal

It happens when the consolidant migrates back towards the surface as a consequence of too fast evaporation resulting from inadequate curing. The fluid ethyl silicate concentrates in the sub-surface zone and after the evaporation of ethanol the solid silica gel remains back in large quantities in the pores below the surface. In this case, atypically for an ethyl silicate consolidation, many pores also became completely filled with the gel provoking not just an over-consolidated outer zone, but also a barrier for moisture migration. Degradation happens, when the moisture enters the stone from the back and cannot leave through the surface. Finally, water retention can cause frost damage in winter, which also happened in the case of the stone column “Spinnerin am Kreuz”.

Effects of improper water repellent treatment – sample NK, Neunkirchen

Despite several interventions in the last decades on the Holy Trinity Column in Neunkirchen, Lower Austria, different parts exhibited massive flaking and scaling in the mid 2010s. The most affected parts are made of porous calcarenite composed predominantly of microfossil fragments. This Middle Miocene facies can be found in several historical stone quarries on the western side of the Leitha Mts. (Rohatsch 2005b).

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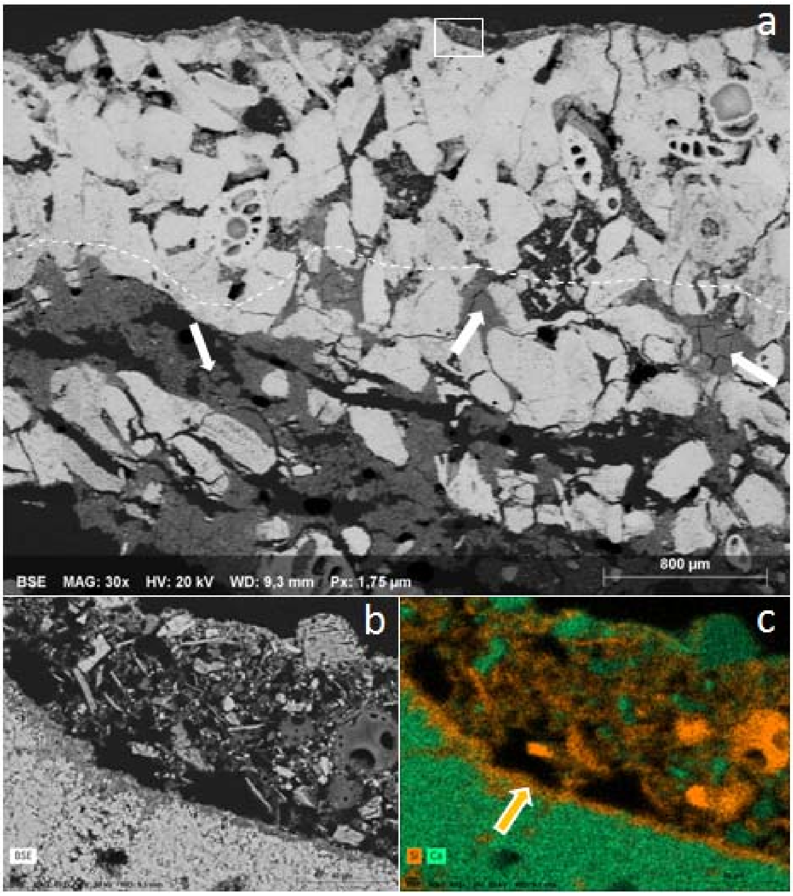

Fig. 15.: SEM-BSD image and element mapping of sample NK. Arrows show crack- and pore-filling secondary salt and dust deposits, the dotted line indicates the approx. depth of penetration of the water repellent agent (a). The surface is coated with a silicon resin-based slurry (b). Element mapping (Ca [calcite]: green, Si: orange) indicates the presence of a thin water-repellent layer on the top of the substrate (c, arrow)

15. ábra: Az NK minta SEM-BSD felvétele és Si-eloszlási térképe. (a) A nyilak a repedés- és póruskitöltő termékeket, a szaggatott vonal a hidrofóbizáló szer feltételezhető behatolási mélységet mutatja. (b) A felszínen egy szilikonalapú bevonat található. (c) Az elemeloszlás (Ca [kalcit]: zöld, Si: narancs) a kőfelszínt bevonó hidrofób rétegre utal (nyíl)

In situ observations indicated the formation of thin flakes on the surface suggesting a hard and impermeable outer zone. The back side of the detached stone is marked by a massive crack system filled with a mixture of damaging salts and fine dust washed into and deposited in the crack (**Fig. 15a**). The dominance of calcium, alkalis and sulphur in the EDS spectra (Linke 2016) suggests the presence of gypsum and alkali sulphates as secondary products. Additionally, the surface is covered with a 50 to 100 µm thick coating (i.e. protecting layer), where high amounts of lightweight silica filler and a binder rich in Si indicates the use of silicon resin-based slurry (Linke 2016). The pores between the surface and the crack system are almost completely free of any secondary products, suggesting that a barrier for moisture and salt solutions exists several millimetres below the surface. Careful element mapping (**Fig. 15a**) showed the presence of finely distributed Si in the microporosity up to a depth of 2 mm. Also, between the stone and the coating a 5 to 10 µm thin silicon-rich layer was detected (**Fig. 15b-c**). Enrichment of Si in the porosity refers either to the use of ethyl silicate consolidant (see samples TU and WN), or the use of a silan/siloxane-based water-repellent agent, or the combination of both.

Since characteristic silica gel deposits could not be observed, the detected Si enrichments were interpreted as a tracer of a hydrophobic treatment.

Fig. 16.: Water droplet test performed on the broken surface of sample NK. Due to large contact angles (i.e. hydrophobic treatment) the water droplet cannot penetrate the pores (stereo microscopy)

16. ábra: Vízcsepp-teszt az NK minta törött felületén. A megnövekedett nedvesítési szög (hidrofób kezelés) következtében a vízcsepp nem tud a pórusokba behatolni (sztereomikroszkópos kép)

To control this assumption, a simple water droplet test was performed on the fresh broken surface of the sample. The water droplet on the broken surface (**Fig. 16.**) caused by a large (i.e. >90°) contact angle, proved the hydrophobic property of the stone up to a depth of 3 mm. The basic idea behind a hydrophobic treatment is to protect a porous mineral material from infiltrating moisture. Normally, a hydrophobic system works properly if there is no other way for the water to penetrate the stone than the outer (treated) surface. Nevertheless, moisture may enter the objects from different directions and sources (Ban et al. 2018). Additionally, a water repellent treatment works in both directions, thus it does not only prohibit the infiltration of e.g. meteoric water, but also act as a barrier for outward moisture movement. The outwards migrating water, containing in most cases dissolved salts, stays behind the hydrophobic horizon and the evaporation takes place at the hydrophobic barrier below the surface. Subsequent crystallization of mineral components forms damaging salts and crystallization pressure causes delamination or flaking of the substrate. Additionally, the increased accumulation of moisture favours freeze-thaw damages in winter (Nimmrichter 2007, Nimmrichter & Linke 2008). The consequences of the inadequate use of hydrophobic treatment on porous building stones are well-known phenomena (Nimmrichter 2007, Ban et al. 2018) and represent one of the most intensely researched topics among restorers and conservation scientists.

Table 2.: Appearance and cause of weathering in the studied sandstone types

2. táblázat: A mállás megjelenési formái a vizsgált homokkő változatokban

Sample	Macroscopic weathering phenomenon	Cause of degradation at the macro / micro scale
KR	scaling in mm thick layers	improper drainage, PC joint mortars / effect of freeze-thaw cycles + mineralogy
TU	scaling in mm thick layers / granular disintegration	repeated stone consolidation / reduction of porosity in the sub-surface zones + effect of freeze-thaw cycles and subsequent salt damage
SG	scaling in mm to cm thick layers	removal of historical sacrificial layers / effect of freeze-thaw cycles at micro scale + formation of gypsum
KB	scaling and granular disintegration	use of structural concrete element / effect of damaging salts and freeze-thaw cycles
WN	scaling in mm thick layers	improper application of stone consolidation / reduction of porosity in the sub-surface zones + effect of freeze-thaw cycles
NK	scaling in mm thick layers	application of water repellent treatment / reduction of water permeability + damage due to salts and freeze-thaw cycles

Conclusions

In the present paper the weathering characteristics of historically significant porous sedimentary rocks (i.e. subarkose and biocalcarenite types) from Austria were investigated using different methods of microscopy. The selected examples (**Table 2.**) focused on the weathering processes and subsequent damages caused by the combination of natural and anthropogenic interventions (i.e. maintenance, conservation activities, etc.). Based on the results the following conclusions can be drawn:

- mineralogical composition and physical properties (i.e. low to medium hardness and high porosity) determine a low to moderate resistance against physical weathering processes in the investigated stones;
- the weathering phenomena result in flaking or, rarely, granular disintegration in the case of both rock types;
- the presence of mica in the subarkose may intensify the effect of frost damage by forming effective nucleation sites for ice crystallization due to highly acute mica wedges. Additionally, due to excellent cleavability, mica crystals may also form weak zones in the stone;
- the use of ethyl silicate consolidants may alter the capillary properties of the sandstone, which in combination with gypsum dissolution and re-crystallization processes, induces a dense outer layer. Subsequent freeze-thaw-cycles below the dense outer layer will increasingly execute their damaging effect;

- although gypsum of secondary origin was observed in many samples, its role as the primary cause for the damage could not be confirmed in most cases. Examples from a sandstone containing coarse dolomite cement and gypsum, but no magnesium sulphate as a sulphation product, suggest that gypsum did not form by the direct chemical reaction of SO_4 ions and carbonate minerals of the stone;
- the removal of porous, mineral sacrificial layers (i.e. lime coats) from the surface of a sandstone sensitive to thermal/hygric dilatation, resulted in increased formation of cracks and disintegration of the texture;
- integration of Portland cement-based (structural) elements into a masonry made of sandstone resulted in changing the direction of moisture movement and increasing the water load in the porous stone. Additionally, soluble salt components were also mobilized from the cementitious materials and transported to the porous stones, provoking salt damages;
- inaccurately executed stone consolidation frequently causes the so-called over-consolidation of the substrate´s surface. In extreme cases this leads to an outer zone of low permeability as shown in the case of a porous biocalcarenite. Subsequent frost damage may cause severe flaking of the surface;
- the use of a water repellent treatment may also cause damages when not executed thoroughly. Especially soft and porous limestone types are exposed to secondary damages due to hydrophobic coatings or flooding with water repellent agents. Moisture migrating behind the hydrophobic surface/zone causes damage due to salt crystallization and/or freeze-thaw cycles;
- examples showed that besides mineralogical composition and microstructure of the stones as well as natural weathering processes, not properly planned and executed maintenance and conservation activities can also accelerate or even provoke damages. Therefore, instead of aspiring to find long-lasting solutions, regular examination and fast interventions are of outmost importance to keep historic monuments in a good condition in the future.

Acknowledgements

The author thanks Johann Nimmrichter and Matea Ban for their support in providing information about the conservation activities at the objects as well as Marta Guzowska for her critical comments and suggestions for improvement on the manuscript.

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