DECAY PATTERNS OF WEATHERED QUARTZ SANDSTONES: EVIDENCE OF GYPSUM INDUCED STRUCTURAL CHANGES

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Decay Patterns of Weathered Quartz Sandstones: Evidence for Gypsum Induced Structural Changes

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Abstract

Black gypsum crusts and thin black layers are considered to be typical weathering phenomena located on the surface of quartz sandstones. Black crusts are generelly found in sheltered areas not directly exposed to water runoff, but frequently soaked by rainwater. In contrast, thin black layers occur in zones which were subject to direct wetting by rain. Usually, enrichment of gypsum takes place not only on superficial crusts but also within the intergranular pore spaces of the stone substrate underneath crusts and thin black layers.

Gypsum crystallization within the pore spaces may change the microstructural features of sandstones as well as dry-wet cycles leading to shrinking-expansion phenomena of gypsum, thus, causing decohension of silicate cemented detrital grains within the natural stone. The use of microscopic methods is helpful to characterize erosion features associated with crusts, thin black layers and inward gypsum migration. The surface samples were taken from ”Leineschloß” in Hanover, ”St. Marienkirche” in Zwickau und Erfurt Cathedral (Germany).

The damage observed in the quartz sandstones under investigation is the result of a stone-gypsum interaction. Stone material incorporated within gypsum crusts has lost its primary grain bond. Beyond that, cyclic crystallization pressure and shrinkage-extensinal stresses of gypsum are the potential causes for fracturing surface near quartz grains. These cracks are supposed to be generated during the initial stage of damaging processes. Simultaneously, the development of secondary intergranular porosity is involved in these processes. Thus, the microstructural damage is not visible on the stone surface. If conventional cleaning is planned, the superficial decohension of mineral content in silicate cemented sandstones should be borne in mind.

1 Introduction

Black crusts and thin black layers are wellknown weathering phenomena on natural building stones in urban environments. Apart from air pollution, their occurrence is highly influenced by exposition and by the intrinsic properties of the stone, such as chemical composition (reactive substances), mineralogical composition (bonding, grain size distribution) and physical properties (e.g. porosity, permeability).

Crustal build-ups on quartz sandstones are common in sheltered wet areas not exposed to surface washing, specially in recesses below cornices and ledges. Occasionally accumulation of salt is present in the lower part of runoff zones. Black staining results in the accumulation of airborne particles like ferruginous fly ashes, porous carbonaceous cenospheres and soot, being embedded within growing gypsum crusts. Algae growth is observed rarely. After the death of organisms the green colour of chlorophyll turns to black, reflecting former environmental conditions which probably have changed with changing climatic conditions. Other particles trapped in black crusts are colourless or slightly coloured fly ashes, soil dust and resedimented minerals from the building stones themselves (NEUMANN 1994).

Contrary, thin black layers appear to be homogeneous and do not mask the original surface contours of the building stones. Two types of black layers can be distinguished: **(1)** In urban environments the surface layers on building stones consist mainly of ferrugenous and carbonaceous compounds from different sources (hydrocarbons, soot) due to a high degree of air pollution. Other anorganic compounds like fly ash and resedimented minerals can be detected. In comparison with alteration crusts, the particles are less in diameter and occur in a lower amount (NORD & TRONNER 1991, 1992, NEUMANN 1994). **(2)** They also may originate from microbiogenically created patinas, because of a repeated colonization of algae and other microorganisms (VISSER 1992, KRUMBEIN 1993, NEUMANN 1994). Mostly, thin black layers are less permeable, thus, acting as hydrofobic layers.

Thin black layers are more common on facades of quartz sandstones than black gypsum crusts. Usually they are located on surfaces directly wetted by rain. Due to gypsum enrichment beneath the black surface layers, gypsum is likely to migrate into the intergranular spaces of the sandstones. In areas highly affected by runoff like the upperside of cornices, soluble salts are washed out.

The most important decay patterns are scales or flakes being covered with thin black layers. The stone beneath is severely influenced by a high gypsum content in the pore spaces. Gypsum crusts are detached normally with incorporated quartz grains or were showing transitions to typical scale formation.

Much recent work has considered swelling-shrinkage phenomena of argillaceous sandstones influenced by watersoluble salts, whereas only a few studies deal with damages caused by inward gypsum migration and crystallization within pore spaces of quartz sandstones. Thus, the decay mechanisms occuring on quartz sandstones are still not known in detail. The purpose of this paper is to present microscale damage to stone surfaces and some new microstructural features located in the interface between black crusts/thin black layers and the underlying quartz sandstone of several buildings. The results may help to understand decay processes associated with gypsum impregnation and may serve in the preparation of experimental shrinking-expansion studies of weathered quartz sandstone samples.

2 Materials and methods

This study was part of a BMBF (Ministery of science and research) research programme concerned with deterioration of building stones from several monuments in Germany. Samples were taken from "Leineschloß" in Hanover, "St. Marienkirche" in Zwickau und Erfurt Cathedral. The geological names of the quartz sandstones under investigation and their chronostratigraphic units are shown in tab. 1.

Tab.1: Investigated monuments

Monument	investigated sandstone	geologic-time unit	date of insertion
Leineschloß	wealden sandstone	lower cretaceous	1816 - 1842
Church Saint Mary	Elbe sandstone	upper cretaceous	1885 - 1891
Erfurt Cathedral	Seeberg Sandstone	Rhaetian	< 1900

Samples are mostly removed according to more or less complete profils around cornices, taking into account the different expositions. Investigated areas are:

- Leineschloß: the masonary directly above the bank reinforcenment of the Leine river in the south and the great and little "Portikus" in the northeast of the building,
- church Saint Mary: one pillar in the north and one in the south of the nave,
- Erfurt Cathedral: the building in the south of the high choir.

The investigations were executed predominantly on surface samples and a selected number of dryly drilled cores considering the weathering phenomena described. At a depth of 15cm into the stone the cored sample provides information of the undamaged stone fabric. All sandstones show a siliceous grain bonding and point contacts between the grains. In samples taken from the Leineschloß in Hannover VISSER (1992) found 3-12% authigenic quartz cement. The extent of a claymineral cement was neglectable. Some samples of the investigated quartz sandstones contain small quantities of feldspar and kaolinite or illite in the intergranular pores.

Polarized optical microscopy and scanning electron microscopy (SEM) equipped with an energy dispersive x-ray attachment (EDS) were carried out in order to characterize the microstructural changes and the morphology of gypsum crystals in the surface area of the investigated sandstones. The examinations are performed on thin sections and pieces of stone broken perpendicularly to the surface.

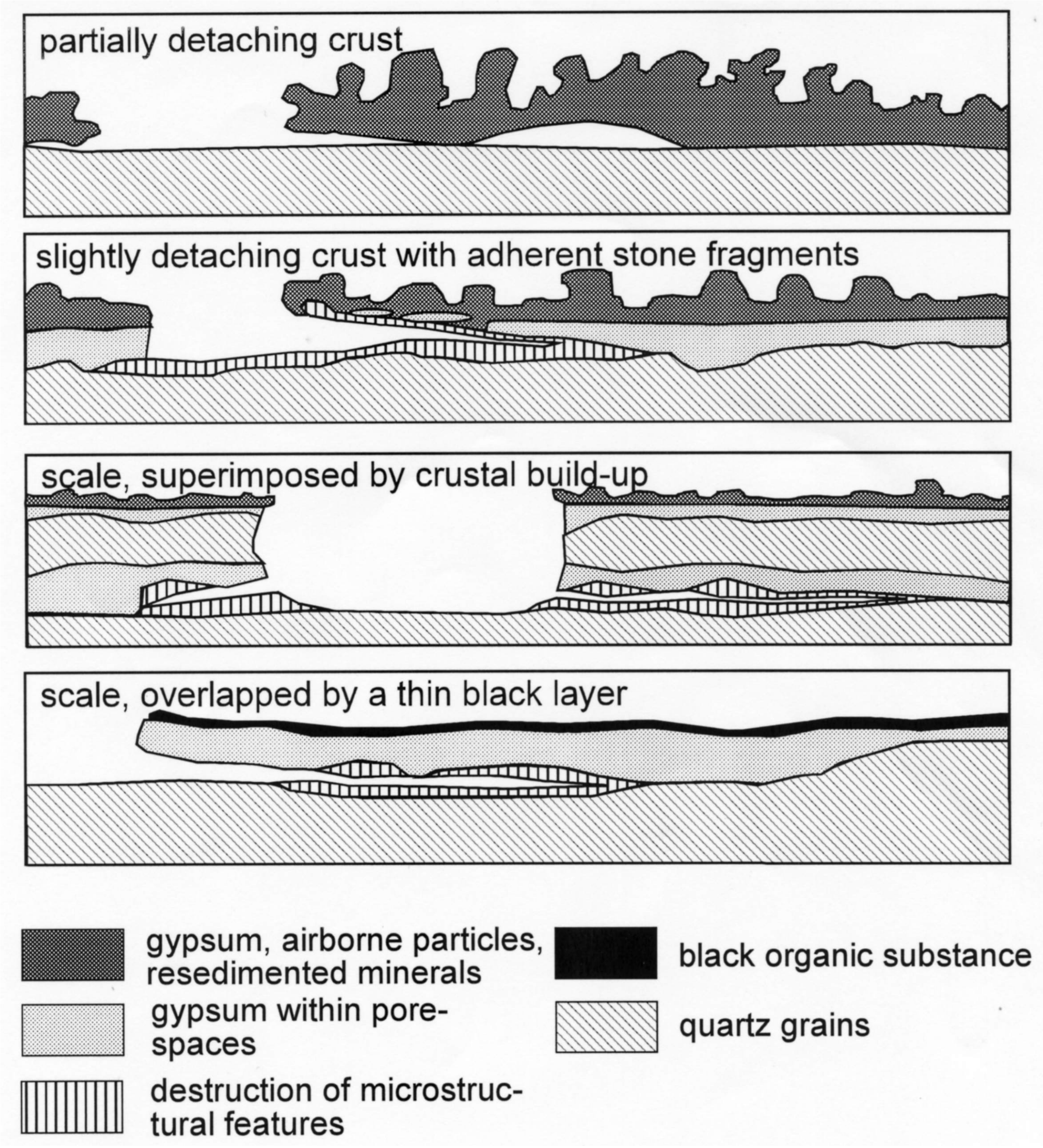

Fig. 1: Different types of microstructural changes (schematic illustration of cross sections)

3 Results

3.1 Black gypsum crusts

A review of different typs of crusts and thin black layers and associated structural changes of the surface area is documented by schematic illustrations in fig. 1. Macroscopically visible back weathering may appear due to loss of crusts with or without adherent stone material. Only few crust build-ups under cornice overhangs or ledges do not show incorporated stone material, but all of them are characterized by outward gypsum growth on the stone surface (Fig. 2/3). The alteration crusts vary in thickness between 0,5 and 10 mm. Detached gypsum crusts intergrown with quartz grains from the sandstone are mainly observed in transition zones of sheltered areas not directly exposed to water runoff and rain exposed surfaces. These locations are characterized by a high moisture content and by a higher SO_2 uptake, not being washed out quantitatively.

Fig. 2:

Partially detaching crust under a cornice, Erfurt cathedral (ER3)

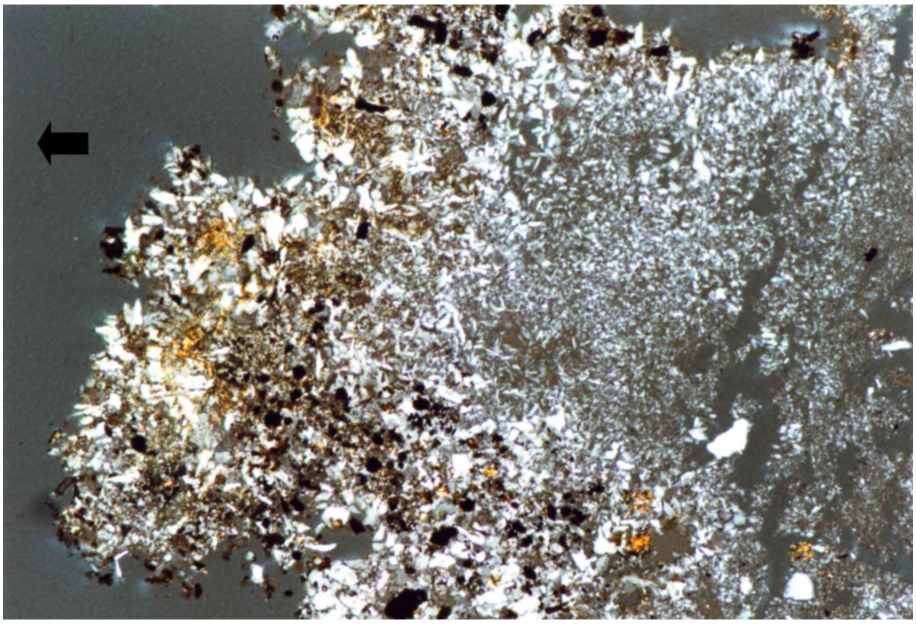

Fig. 3:

Thin section of sample ER3 (arrow points to the surface). X nicols.

A characteristical feature of detached crusts with adherent stone components is the destruction of their primary internal fabric by a secondary gypsum supported fabric. Additionally, a secondary porosity was generating. Often quartz grains with intracrystal microcracks are observed. Between this layer and the stone substrate several fissures have been detected, parallel oriented to the surface. They are follwed by a small zone of granular desintegration. The detached crusts are completely gypsum cemented and show blistering. Sometimes they seem to roll up from the subsurface.

Often transitional forms to contour scaling are recognized. A small gypsumlayer intergrown with microstructurally alterated stonesubstrate was covering stonematerial not visibly disaggregated, without or with minor gypsum fillings in the pores. Underneath, the scale is markedly desintegrated loosing its primary grain bonding. A secondary stabilization by means of gypsum precipitates is negligible. Macroscopically, platy stone elements get detached parallel to the surface (Fig. 1, third diagram). In contrast to the above mentioned crusts showing maximum thicknesses of 2 mm, these contour scales reach values up to 5 mm (the outward crustal growth is not considered).

The same microstructural changes are recocognized in crust build-ups intergrown with the building stone. Macroscopically the investigated ashlars seem to be undamaged. Usually the internal destruction of the microfabric resulted in a loss of grain bond gradually moving inward from the crust-stone interface. Isolated grains or clusters of quartz grains are fixed in a network of gypsum crystals (Fig. 4), with a parallel arrangement of the constituents in respect to the surface. Perpendicularly grown gypsum crystals show suturated boundaries. Microcracks in quartz grains are rarely observed. In an advanced stage of damaging the quartz grains have lost any contact, being fixed in a gypsum supported fabric.

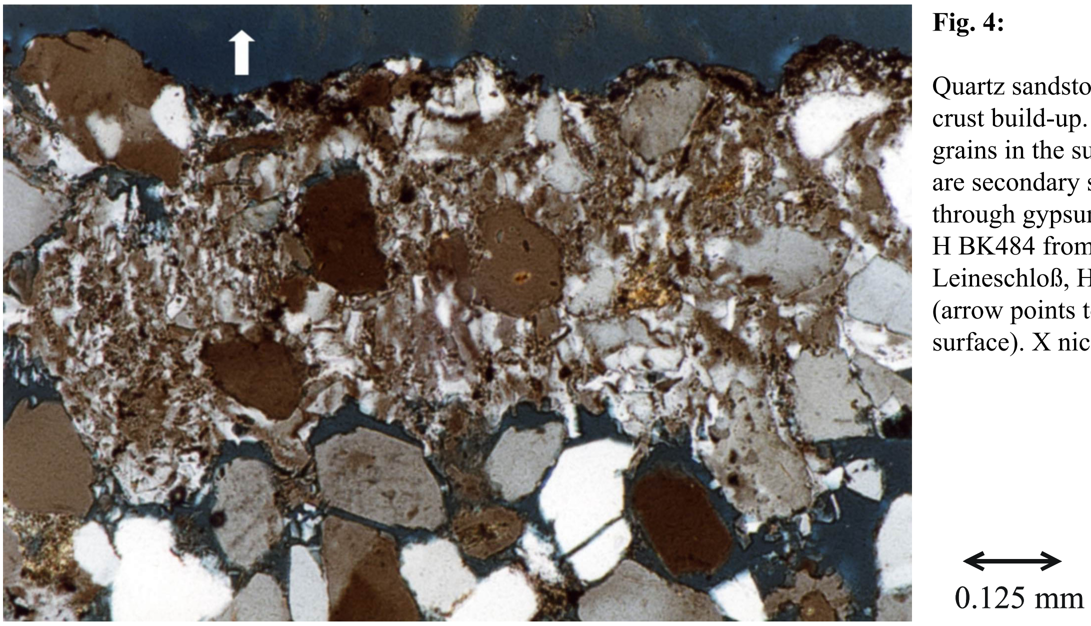

Fig. 4:

Quartz sandstone with a crust build-up. Quartz grains in the surface area are secondary stabalized through gypsum. Sample H BK484 from Leineschloß, Hanover (arrow points to the surface). X nicols.

Another type of secondary microfabric originates from locations with a high moisture and gypsum content. Gypsum crystallization seems to record an inward growth from the stone surface, completely filling the pores, as far as visible to a depth up to 3 mm. The gypsum crystals often appeared to be cryptocrystalline. Occasionally clayminerals or organic matter, are found between the gypsum precipitates marking the original pore space of the primary microfabric right before disintegration. The microscopical examination of a sample from church Saint Mary in Zwickau suggests, that clear gypsum crystals were growing on the pore fillings towards the quartz grains as documented in fig. 5. In fact the expansion of mineral phases within the fabric might generate higher values perpendicular to the surface than to the parallel direction. Only individual gypsum crystals were showing point contacts to the quartz grains caused by a different rate of growth. Thus, circulating secondary pores were developing. The sample was located within the transition zone of masonry and the cornice of the plinth, which was strongly affected by the uptake of sulfate saturated water in the area of runoff.

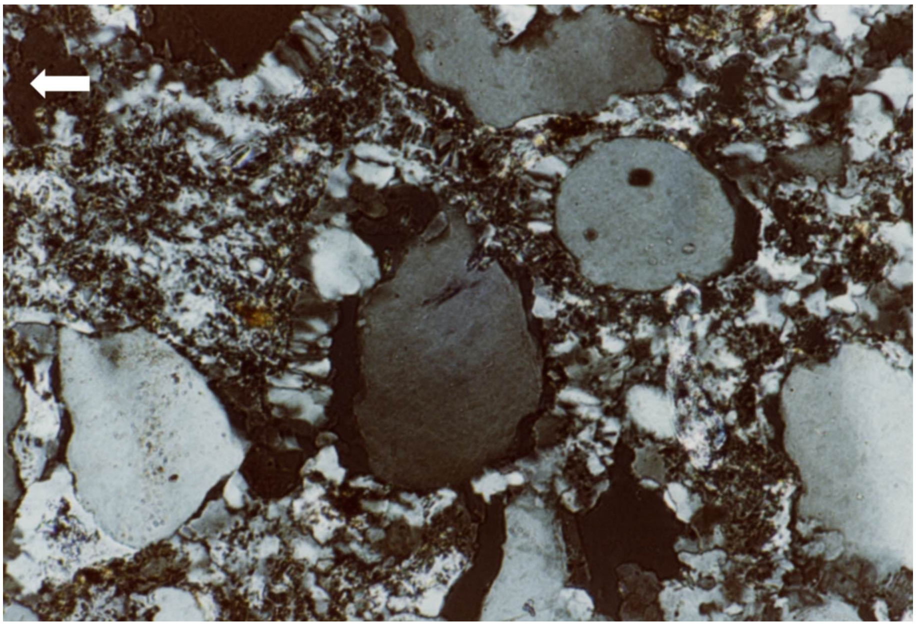

Fig. 5:

Structural changes of a quartz sandstone. Secondary gypsum stablized fabric. Sample Z 15c from church Saint Mary, Zwickau (arrow points to the surface). X nicols.

Identical microstructural patterns were visible at the little ”Porticus” of the Leineschloß, presumably caused by percolating water as a result of a damaged roof. The weathering condition of the sample shown in fig. 6 is typical for a moderate rain sheltered position. On the back side of the above mentioned sandstone, contour scales separated from the stone substrate, covered by thin crustal overgrowths (Fig. 7). The structural change of the quartz sandstone takes place closely to the surface. The distribution of gypsum crystals is restricted to this area as well. It is assumed, that the content of percolating water on both sides of the building stone might increase to similar values, but the evaporation in front of the quartz sandstone is different to that of the backside. Thus causing differing structural alteration forms.

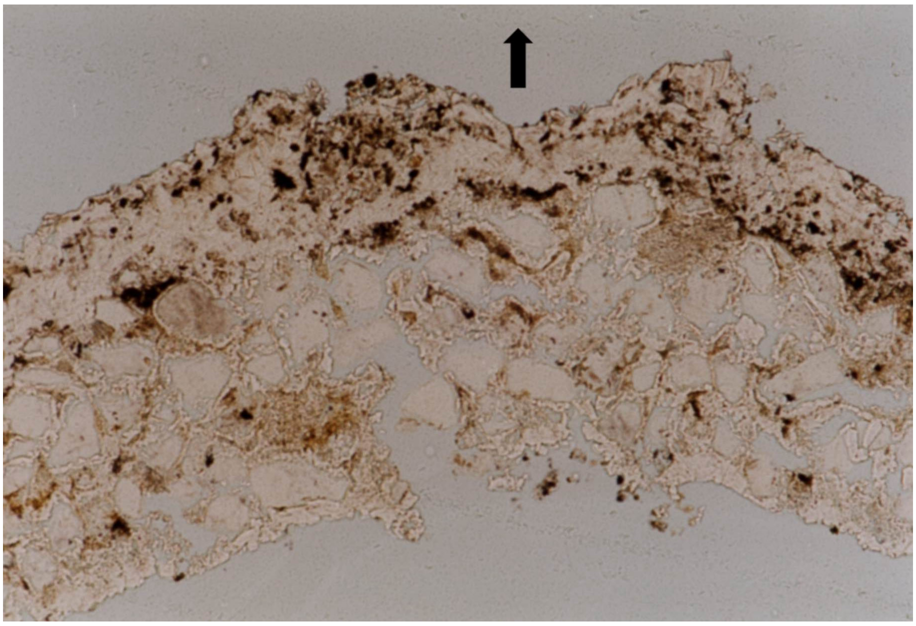

Fig. 6:

Detaching crust build-up with incorporated stonematerial. High gypsum content. Sample H 43, Leineschloß in Hanover, little Porticus (arrow points to the surface). // nicols.

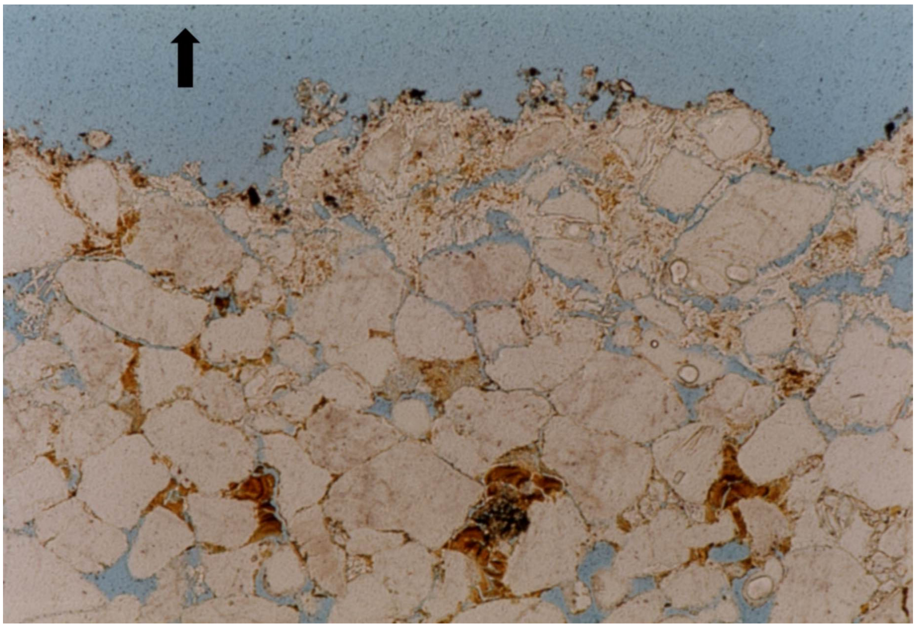

Fig. 7:

Exfoliation (backside not visible) covered by a crustal overgrowth and partially microstructural alteration. Sample H 43, Leineschloß in Hanover, little Porticus (arrow points to the surface). // nicols.

3.2 Thin black layers

On sandstone facades with a black staining the most common damage is exfoliation of the surface area of the quartz sandstone, as illustrated in fig. 8. Neglecting the different origin, thin black layers normally range in thickness from 0,02 mm to 0,2 mm. Usually, the pore space beneath thin black layers is characterized by gypsum impregnation. However, a great variety of structural changes is reflected in the petrofabric. As demonstrated in Fig. 9, for example, gypsum and calcite (brown coloured compound, // nicols) completely filled pores within the exfoliating area. Underneath algae growth occured after detaching. It is suggested that the algae assimilation was responsable for the calcite precipitation (NEUMANN 1994). In other samples a high content of gypsum crystals seems to have affected the interior sides of scales, resulting in a severely disaggregated zone.

Fig. 8:

Scaling of the stone surface, overlapped by a thin black layer, Leineschloß, Hanover.

In the surface area, up to a depth of 1 mm into the stone, the destruction of the fabric is moderate, in comparison to the crust build-ups with incorporated stone material. In shape the crystals may vary from acicular, platy and tabular to poikilitic forms. A great diversity of crystal forms exists.

In areas without macroscopically visible damage the primary microstructure is destroyed frequently and replaced by a secondary gypsum supported fabric. If the depth of desintegration is considered, there is an analogy to the thickness of the investigated scales (Fig. 10). In these zones fracturing is evident within quartz grains.

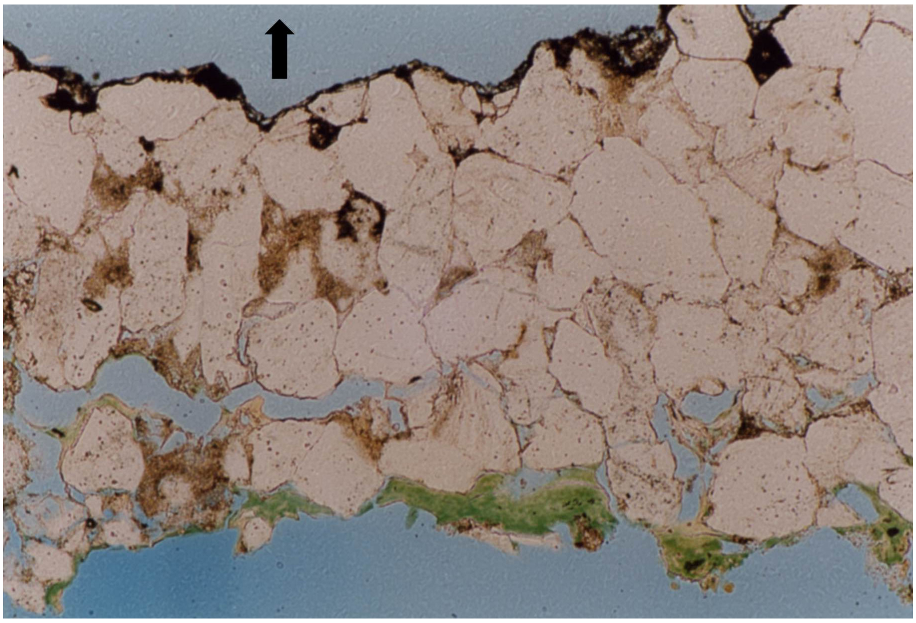

Fig. 9:

Cross section from exfoliation shown in Fig. 8. Sample H 67 (arrow points to the surface). // nicols.

In the transition zones between not desintegrated surface zones and those having experienced changes of the primary fabric, the pores contain acicular gypsum crystals. Within completely filled pores suturated boundaries of gypsum crystals are common. Transitionally the crystals change to cryptocrystalline aggregates. If the primary stone fabric was destroyed, the cryptocrystalline gypsum filling was found to represent the original pore morphology. These pore fillings are overgrown by gypsum crystals more or less perpendicular to the surface, stabilizing the disaggregated quartz grains.

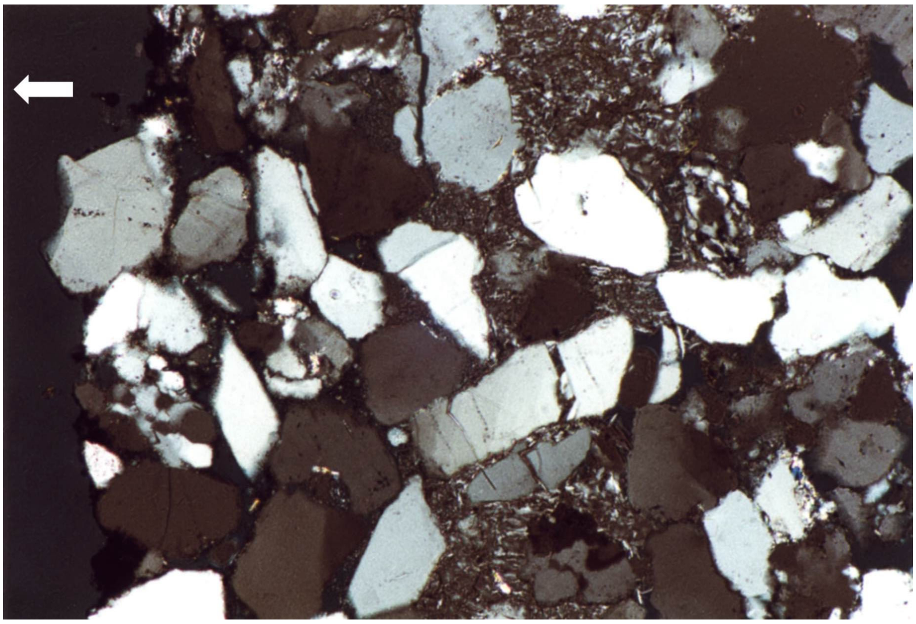

Fig. 10:

Stone surface with a thin black layer. Macroscopically without damage. In the middle and right part microstructural changes are visible (secondary stabilized gypsum supported fabric, microcracks in quartz grains). Sample H 78 from Leineschloß, Hannover (arrow points to the surface). X nicols.

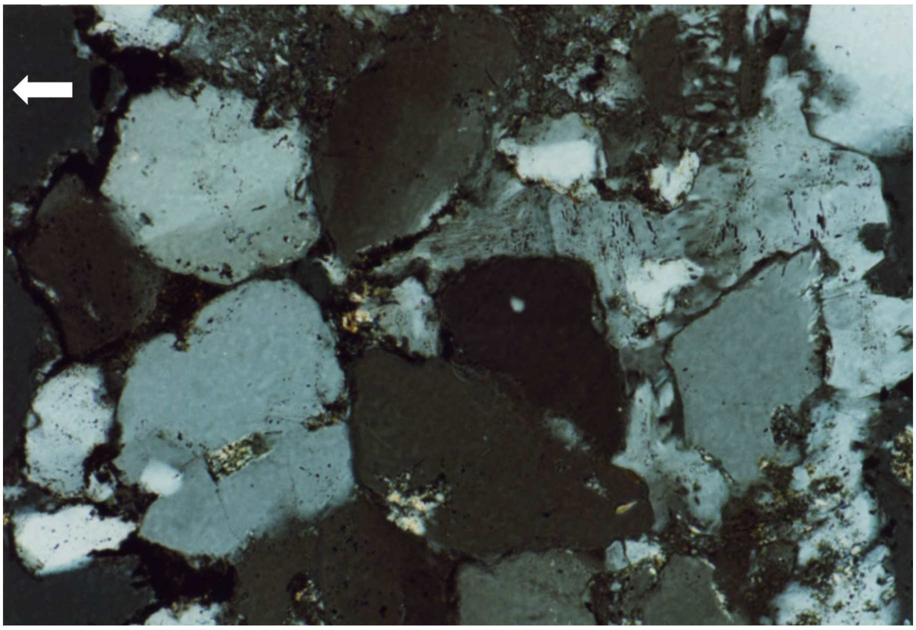

Fig. 11:

Poikilitic gypsum crystal in the pore space of a scale. Sample H 83 from Leineschloß, Hanover (arrow points to the surface). X nicols.

Microscopical investigations of the petrofabric support by documentary evidence (Fig. 12) that thin black layers develop into crust build-ups as a result of changing weathering conditions. A first step towards crustal formation is the generation of a thin black layer covering the stone surface. A certain joint mortar, being adjacent to the investigated sample (sample H 80a, Leineschloß, Hanover) already has lost its mortar-stone adhering force, resulting in fissure generation. For that reason, sulfate saturated solutions start to penetrate witin the stone substrate, the most likely mechanism of decohesion. Stone components are fractured by means of the gypsum growth and seperated from the underlying stone by the newly developing crust.

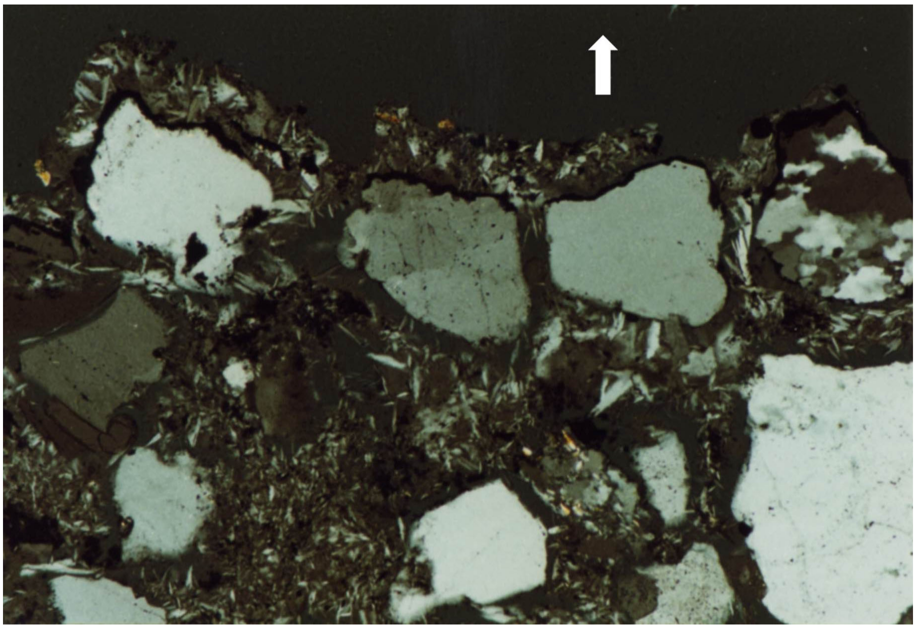

Fig. 12:

Development of a thin black layer into a crust build-up. Sample H 80a from Leineschloß, Hanover (arrow points to the surface). X nicols.

3.3 Cracks in quartz grains

Gypsum enriched surface zones of sandstones mostly seem to be characterized by larger quantities of fractured quartz grains. The generation of intracrystalline microcracks in detrital quartz, in turn, causes further microstructural changes. SEM revealed a width of these cracks ranging from 1 µm to 100 µm. Generally the amount of cracks depends on the position of gypsum crystals in surface near pore spaces. Thus, building stones covered by thin black layers developing into alteration crusts are suitable objects of investigation.

Microcracks in quartz are rarely found in subfluorescences just beneath the stone surface. In contrast, an increased development of cracks is present at a certain depth of about 0,5 up to 2 mm beneath the surface, where gypsum crystallization and an advanced destruction of the primary fabric is obvious. Quantitative analysis (Tab. 2) clearly reveals a correlation of microcrack frequency and weathering forms, as well as the degree of microstructural changes.

Tab. 2: Percentage of microcracks (selected samples)

sample	weathering patterns	microcracks [vol%]	investigated depth [µm]	remarks
H 101	detaching crust with incorporated stonematerial	5	0 - 1400	underside of a cornice, rain sheltered
H 100	scale, superimposed by crustal build-up	20	0 - 400	first ashlar under the cornice, slightly sheltered, south of Leineschloß
H 43	detaching crust with incorporated stonematerial	24	0 - 600	outward position, slightly shelterd area,
H 35	scale, superimposed by crustal build-up	32 4	0 - 1000 2300 - 3900	inward position, sheltered area; both affected by percolating water caused by a damaged roof Leineschloß, little Porticus
H 78	Thin black layer	15	0 - 750	wetted by rain, macoscopically no damage visible, microscopically strongly destroyed, south of Leineschloß
H 67	scale, overlapped by a thin black layer	11	0 - 800	fabric of contour scale, south of Leineschloß
Z 15a	thin black layer, partially flaking	15	0 - 800	5 cm above Z 15b/c
Z 15b/c	detaching crust with incorporated stonematerial	5	0 - 1000	accumulation zone of sulfat-saturated water (runoff), church Saint Mary, Zwickau

4 Discussion of the results

Microscopical examinations of microscale damages to quartz sandstones surfaces demostrate the utmost importance of gypsum crystallization within intergranular pore spaces, strongly depending upon architectural elements and exposition. From the above mentioned investigations, a secondary gypsum stabilisation of the damaged stone fabric becomes evident, though the compessive strength of the quartz-gypsum contacts is much lower than the primary silicate grain bonding. Macroscopically visible weathering forms, such as the 'rolling up' of detaching crusts or thin exfoliated surface layers are supposed to be initiated by the crystallographical behavior of the individual gypsum crystals, leading to physically induced damage phenomena in the subsurface zones.

Microscopical methods are useful tools to visualize the extent to which stone is disaggregated on µm-scale under crusts or thin black layers, which can not be seen macroscopically on the facades. Petrographical examinations clearly demostrate that the degree of microscale damage substantially depends on the material parameters, the individual properties of each stone used as building material and, beyond that, allow to differentiate real deterioation phenomena from tooling-induced surface patterns. For example, the fabrication technique may have led to a considerable degree of surface roughening. In this context it should be taken into account that cleaning of a damaged stone surface with conventional cleaning methods, removing mechanically the crusts or thin black layers, may possibly produce a visible loss of stone material. In order to preserve the weakened surface zones laser cleaning is suggested.

The examinations of damage features of the quartz sandstones under investigation revealed a basic question: how to explain the decay mechanisms that control the breaking up of the primary silicate grain bondings? Beyond the classical salt decay mechanisms, the linear crystallization pressure, NÄGELE (1992) assumed a supplementary 'hydrostatic' pressure of the growing gypsum crystals. Another important damaging process is the repetitive expansion of the gypsum enriched surface zones leading to shear stresses and disintegration in underneath layers. The mentioned weathering phenomena occur due to differences in the moisture related behaviour of the surface zone, rich in gypsum, and the underlying sound stone (SCHUH 1987). The results from dilatation experiments on calcarous sandstones are similar to those of quartz sandstones, showing comparable low expansion - shrinking values of both, the quartz and calcite cement. We assume, that the expansion-shrinking experiments by SCHUH (1987) performed with samples showing a high gypsum content and at least partially a secondary stabalized fabric. No hint is given, that microscopically investigations have been carried out so far.

Only few studies have considered the effects of weathering processes upon quartz sandstones and therewith the degree of alteration of the primary stone fabric. The microscopical examination gives evidence of considerable changes of the petrofabric, thus, allowing a first interpretation of the observed decay mechanisms. The depth of gypsum crystallization within intergranular pore spaces has been determined, depending upon the inward gypsum migration. It is suggested that the following mechanisms have affected the sandstones to a different degree: wet-drying cycles (time, amplitude), the amount of water uptake and runoff and the amount of gaseous SO_2 deposition, leading to various types of fabric alterations. In the pores of the subsurface zone lower crystallization pressures are required to break up the primary grain bonding, in comparison to deeper zones. In the latter, elongate or tabular crystals were growing until they contact each other or the surrounding quartz grains. With an increasing gypsum content the growth pressure of the crystals led to suturated crystal boundaries, gradually transforming to a cryptocrystalline gypsum fabric, because the compressive strength of the quartz grains is much higher. In this state of development the pressure against certain quartz grains tends to propagate on surrounding quartz grains, initiating cracks that pass through some quartz grains being linked by pointcontacts, rather than following intercrystalline boundaries.

Above all, the cyclical expansion of gypsum pore-fillings during rain events and cyclical crystal growing in dry periods was responsable for the loss of the primary grain bond, considering the complex nature of these processes. Besides, volumetric changes will occur, caused by freezing of entrapped water within the newly generated decohesion zone. To prove the validity of the first assumption, experimental work has to be done using the microscopically analysed samples presented in this study. Thus, shrinking-expansion experiments on weathered quartz sandstones with wellknown microstructural alteration patterns and crystallization experiments using the sound stones will be future tasks.

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