SEM STUDY OF THE DETERIORATION OF MONUMENTAL STONES IN VIENNA

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Kurzfassung

Kalkarenitische Proben von mehreren Bauwerken im Stadtgebiet von Wien bzw. in einer Kleinstadt nahe Wiens, die alle deutliche Verwitterungserscheinungen aufwiesen, wurden mittels des Rasterelektronenmikroskopes (REM) untersucht, um anhand mineral- und gefügemorphologischer Beobachtungen Aussagen über die Korrosionsmechnismen treffen zu können. Dabei wurden sowohl der korrodierte Oberflächenbereich, als auch das intakte Steininnere studiert.

Im Querschnitt von der Verwitterungskruste zum unverwitterten Stein fällt bei allen Proben auf, daß die äußere Kruste kompakt ist und dahinter eine Zone erhöhter Porosität folgt. Diese für den Steinzerfall besonders kritische Zone leitet zum unverwitterten Steininneren über.

Anhand einer Reihe von REM-Photos wird gezeigt, daß in der dichten Außenkruste das Mineral Gips ($CaSO_4 \cdot 2H_2O$) vorherrscht, das hier in Form tafeliger Kristalle oft rosettenförmig auf Calcit aufwächst und als Reaktionsprodukt zwischen diesem und den schwefelhaltigen Luftschadstoffen aufzufassen ist.

Auch in der Zwischenzone ist Gips vertreten und bewirkt hier zum Teil eine mechanische Zerstörung der verbliebenen Calcitkristalle.

Die unverwitterten Teile der Steinproben zeigen eine breit gefächerte Korngrößenverteilung; die Begünstigung dieses Umstandes für den Steinzerfall ist in der höheren Lösungsrate kleiner Mineralkörner zu suchen, die aber ihrerseits das Bindemittel für größere bilden, sodaß diese in der Folge leicht aus dem Gesteinsverband herausbrechen.

Weiters wird anhand von REM-Photos die mechanische Gefügezerstörung durch das Wachstum der Gipskristalle dokumentiert, die ebenfalls vor allem in der bindemittelverarmten Zwischenzone von Bedeutung ist.

Die Beobachtung der beschriebenen Phänomene führt zu dem Schluß, daß in allen Fällen Wasser maßgeblich an den Korrosionsprozessen beteiligt war.

Abstract

Scanning Electron Microscopy (SEM) was used to study the deterioration of limestones from monumental buildings in Vienna. The examination was carried out on specimens from the decayed surface and also from the sound interior of the stone.

The evidence found indicates that the main deteriorating processes occurred in the presence of water: chemical dissolution due to acid rain and mechanical disruption induced by the crystallization of the soluble salts, products of the above reaction.

1. INTRODUCTION

Some of the most important monuments in Vienna are built of calcarenites from the tertiary Leithakalk formation in the neighbourhood of Vienna. Mostly, these are fairly porous, pure limestones (>97 % $CaCO_3$) (1). Because of their calcitic nature they are susceptible to the attack of acid rain. It is important to recognize that acid rain is not just a solution of acid air pollutants in rain water. The term "acid rain" involves a very complex system of different corrosive agents: rain water acidified by the air pollutants; gaseous sulfur and nitrogen oxides produced by combustion of fuels; aerosols of these oxides; and combinations of all these factors (2).

The attack of the calcite by "acid rain" results not only in the chemical dissolution of the calcium carbonate but also in the production of calcium sulfate and nitrate. Calcium nitrate is a very soluble salt and will wash away readily from the surface of the stone. Calcium sulfate, on the other hand, can crystallize as the fairly insoluble gypsum ($CaSO_4 \cdot 2H_2O$), and tends to accumulate in areas that are not exposed to direct rain impact. The fact that this salt is more soluble than the original calcite, occupies a larger volume, and has different mechanical and thermic properties, make it one of the most important deterioration inducing agents in limestones (3, 4, 5, 6).

This paper illustrates by scanning electron microscopy (SEM) the changes that have occurred on the surface and within the matrix of these limestones exposed for at least a century to the urban atmosphere in Vienna. Deterioration mechanisms are discussed based on the SEM evidence.

2. EXPERIMENTAL

Samples of four monumental buildings in Vienna: St. Stephen's Cathedral, Neues Rathaus (City Hall), a Post Office building (Ungargasse) and Rudolf Hospital, were collected in 1984. Samples from the "Wiener Tor", a town-gate in Hainburg, a small town in the outskirts of Vienna, were also obtained at the same time. Specimens of the exposed surface, and of the unweathered stone (taken from the interior of the stone samples at a depth of about 10 cm) were prepared. All the specimens, except the external exposed surfaces, were examined in fractured surfaces. The specimens were mounted on aluminium stubs and sputter coated with 10 nm of gold.

Fig. 1 shows a cross section of the weathered stone from the exterior hardened black crust to the interior sound stone. The surface crust is fairly compact but behind it the stone shows loss of cohesion and much

higher porosity. This sample was taken from the Wiener Tor in Hainburg which was constructed around 1250. It is to be noted that this sample, coming from a rural area, does not show the pervasiveness of gypsum in the matrix of the stone, as was observed for all the other samples which were taken from the historic center of Vienna.

Fig. 2 shows the appearance of the surface of the external black crust. The crust is mainly composed of gypsum with residues of combustion pro-

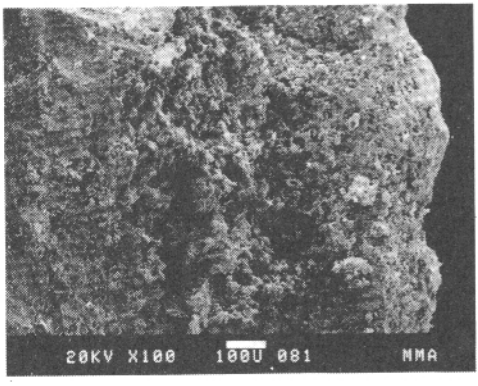

Fig.1: Cross section of the exposed surface of a weathered stone. The photomicrograph shows from right to left: the compact outer crust, a decohesion zone and the sound stone

Abb.1: Querschnitt durch den Oberflächenbereich einer korrodierten Steinprobe. Das Photo zeigt von rechts nach links die kompakte Kruste, die bindemittelverarmte Zwischenschicht und den unverwitterten Stein

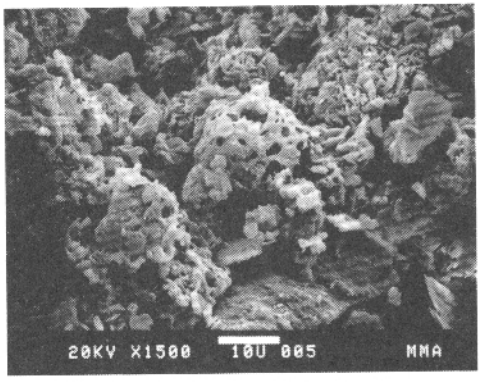

Fig.2: External surface of the outer crust. Note the piece of fly-ash among the platy gypsum crystals

Abb.2: Oberfläche der Außenkruste. Zu beachten ist das Flugaschenteilchen zwischen den tafeligen Gipskristallen

ducts, e.g., fly-ash. Fig. 3 is a detail of the habit of the gypsum crystals forming characteristic rosettes. Fig. 4 shows the appearance of these rosettes when they grow along a flat surface of another crystal, e.g., a calcite grain. These photomicrographs were taken from samples of the Post Office building (Ungargasse), constructed around 1840.

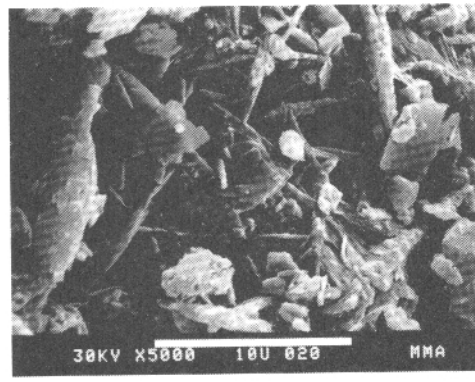

Fig.3: Detail of the growth of platy gypsum crystals in the characteristic rosette form in the outer crust
Abb.3: Detailaufnahme der Anordnung tafeliger Gipskristalle in charakteristischer Rosettenform in der Außenkruste

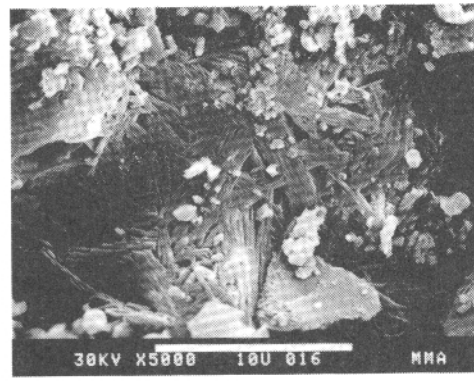

Fig.4: Detail of the appearance shown by the platy gypsum crystals when they grow against a flat surface, i.e., the surface of a calcite crystal
Abb.4: Tafelige Gipskristalle, die auf einer ebenen Oberfläche (Calcitfläche) aufwachsen

Fig. 5 illustrates the deteriorated stone beneath the black crust. To be noted is the surface growth of gypsum on the calcite crystals. Fig. 6 shows the detail of a calcite crystal being corroded and stressed by the growth of gypsum. The samples from which these photomicrographs were taken came from the St. Stephen's Cathedral, from a detail presumably reconstructed ca. 1880.

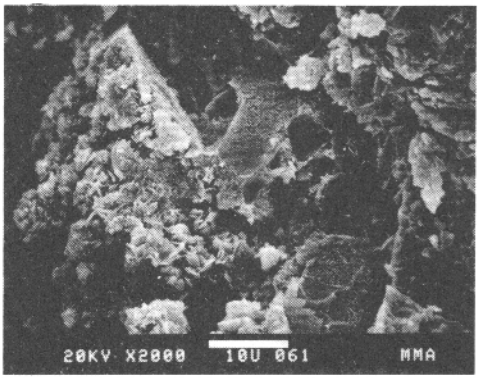

Fig.5: Growth of gypsum on calcite. Note the clean fracture of a calcite crystal that probably formed during sample preparation. This photomicrograph was taken in the decohesion zone

Abb.5: Gipswachstum auf Calcit. Die glatten Spaltflächen des Calcitkornes dürften auf die Probenpräparation zurückgehen. Diese Aufnahme stammt aus dem Bereich der bindemittelverarmten Zwischenzone

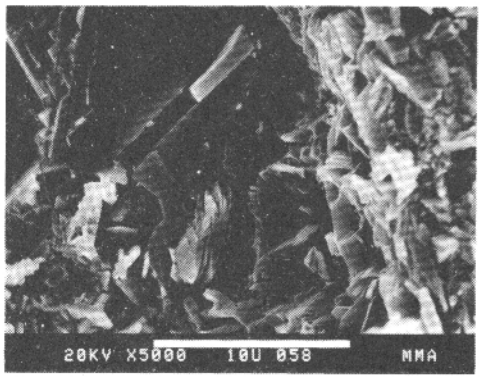

Fig.6: Detail of a calcite crystal showing fractures induced by the growth of gypsum

Abb.6: Detailaufnahme eines infolge Gipswachstums gespaltenen Calcitkristalls

Fig. 7 shows part of a calcite shell that surrounded a larger calcite or quartz grain. Fig. 8 is a detail of the etched surface of the calcite crystals in the interior of this shell. These photomicrographs were taken from a sample of the Rudolf Hospital (ca. 1884).

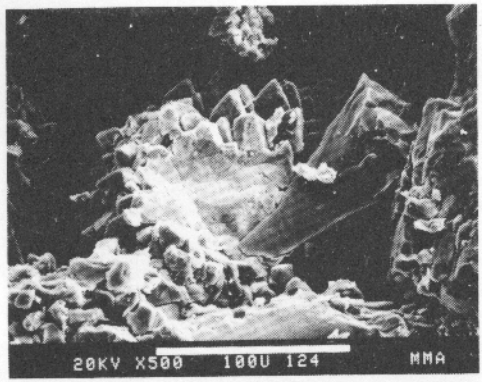

Fig.7: Photomicrograph showing a depression in a calcite shell that surrounded a larger grain. The loss of these grains produces the large porosity in the decohesion zone

Abb.7: Abdruck eines großen, bereits ausgebrochenen Kornes auf einem Schalenrest. Der Verlust solcher Körner bewirkt u. a. die hohe Porosität der bindemittelverarmten Zone

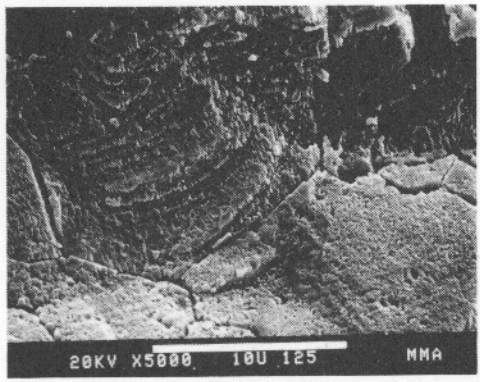

Fig.8: Detail of the etching in the inner surface of the calcite shell in Fig. 7

Abb.8: Detail aus Abb. 7. Die angelöste Schale zeigt Ätzmuster

Fig. 9 shows the large distribution in calcite crystal sizes that can occur in these limestones. This photomicrograph was taken from a sample of sound stone from the Post Office building.

Fig. 10 shows a general view of the structure of these calcarenites: peloids and bioclasts are held together by a micritic binder. This sample is from a sound stone specimen from the Rathaus, constructed ca. 1880.

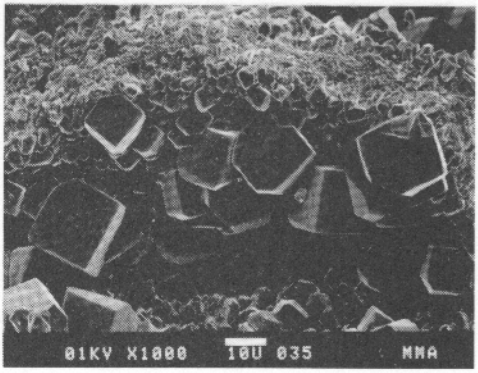

Fig.9: Photomicrograph showing the large distribution of crystal sizes of the calcite in the sound stone
Abb.9: Beispiel für die beträchtlichen Korngrößenunterschiede im unverwitterten Stein

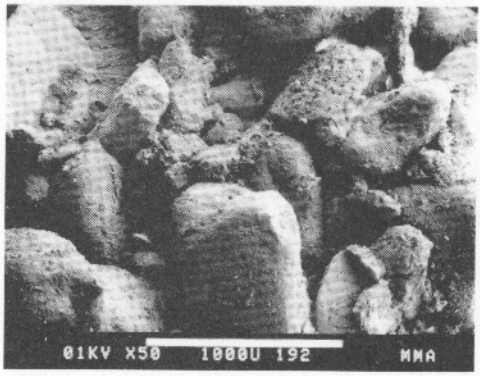

Fig.10: Low magnification view showing the typical microstructure of the investigated calcarenites
Abb.10: Die für die untersuchten Kalke typische Mikrostruktur bei geringer Vergrößerung

3. DISCUSSION AND CONCLUSIONS

The SEM examination of these limestones indicates that the main deteriorating processes occured in the presence of water.

All calcareous materials are susceptible to dissolution by acids. The dissolution rate of calcite can be either a surface controlled or a diffusion controlled reaction depending on pH and undersaturation of the solution, among other variables (7). In either case the dissolution rate will increase as the available surface of calcite increases. Smaller particles, having a much larger specific surface, will take less time to dissolve than larger particles (8). Particle size is therefore important as it will determine the rate at which the calcite grains will be dissolved. Furthermore, if, as is the case in these calcarentites, there is a wide particle size distribution (Fig. 9), this distribution will become wider as dissolution proceeds (9). Also to be remembered is that solubility can increase as particle sizes decrease significantly (10).

The net result of the attack on these calcarenites by acid air pollutants in the presence of water is that the smaller grains will dissolve away much faster than the larger ones. Even though larger grains still remain, the structure will have lost cohesion and these larger grains will eventually fall out (Fig. 7). Limestones with a wide particle size distribution will therefore decay at a faster rate than those in which all particles are uniformly small. The loss of cohesion and the resulting increase in porosity can be seen in Fig. 1 in the area behind the surface crust. This is the area of "true" deterioration and it is especially dangerous since the decay is not visible on the stone surface and can therefore proceed unheeded until major damage occurs. This figure illustrates the description given for the weathering of limestones and calcareous sandstones and the formation of surface crusts (3, 11). It also illustrates the model used for the calculation of the rate of deterioration of porous bodies based on diffusion phenomena and chemical reaction which predicts a surface attack, formation of a compact layer and a dissolution zone behind it (12).

The discussion so far has only dealt with the chemical dissolution of the calcite. A second deteriorating agent is introduced by the formation of gypsum. Any time the stone gets wet, at least part of the gypsum accumulated on the surface will dissolve and the solution will enter the stone pore system through capillary action. When the stone dries, the water evaporates and the gypsum will recrystallize wherever the evaporation took place. If the stone has a high porosity, the evaporation of the water will take place in the pore system, rather than on the surface of the stone. The gypsum, on crystallizing in the pore system will induce mechanical stresses in it (Fig. 5, 6) (3, 13). The repeated dissolution-recrystallization of gypsum crystals will eventually break down the stone matrix. The amount of damage will be proportional to the amount of salt that penetrates into the stone, the number of wet-dry cycles the stone goes through, and the mechanical resistance of the stone. As the mechanical resistance is lowered through decohesion of the calcite grains, the stress induced by the crystallization of gypsum

becomes a significant contributing factor in the deterioration of these limestones.

Buildings that are in an urban environment, such as the samples discussed from the historic center of Vienna, because of their exposure to higher concentrations of air pollutants will have a higher concentration of gypsum in them. They will therefore deteriorate faster because of the combined action of the two mechanisms involved: chemical dissolution and mechanical stress induced by the crystallization of the gypsum.

In summary, these calcarenites are especially susceptible to deterioration due to acid air pollutants because of their large particle size distribution, the micritic character of the binder and their high porosity. This last feature contributes to the crystallization of the gypsum salts in the interior of the stone inducing mechanical stresses into an already weakened stone matrix.

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