SOURCES OF SULPHATE SALT EFFLORESCENCES AT HISTORICAL MONUMENTS - A GEOCHEMICAL STUDY FROM FREIBERG, SAXONY

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SUMMARY
Analyses of salt efflorescences, mortars and plasters show the dominance of magnesium sulphate compounds at historical buildings in Freiberg. Their high hydration / dehydration activity under moderate climatic conditions is leading to damages of stone and mortar. Magnesium sulphates are related to dolomitic limestones, used for the lime production in the Freiberg region over centuries. A stable isotope study of sulphur in the efflorescences and in the natural and industrial environs shows possible influences of various sources and their mixing effects.

1. INTRODUCTION
The city of Freiberg is the centre of an old mining region. Since 1168, when silver was first time found there, mining for Ag, Pb, Zn ... and smelting of the mainly sulfidic ores has been going on with varying intensity. In the wealthy city lots of churches and profane buildings have been built over centuries, as the Cathedral St. Mary, the Freudenstein Castle and others. Today some parts of those historical buildings are damaged by the decay of building materials. In a lot of cases, such damages of natural stone, mortars and plasters are connected with soluble salts. Salt efflorescences can be found on the material's surfaces in different positions, at the facade of the historical buildings as well as in their interior on the walls and the floors. The following local geochemical study has been made to find out the nature of those soluble salts and their possible relations to the building materials and the environment.

2. ANALYTICAL METHODS
Samples were taken from historical buildings of various ages and building materials all over the city from various positions (different altitudes, exterior and interior places). Efflorescences were scratched off, further samples were taken from the mortars and plasters. Efflorescences were characterized by X-ray diffraction (XRD). Soluble salts have been extracted from the dried, powdered samples of mortars and plasters with deionized water (stirred for 2 hours, then filtered). The ions were determined by ion chromatography as well as the ions from some selected efflorescence samples, which have been soluted in deionized water. Investigations on the stable isotope ratios of sulphur ($^{34}$S, related to the Diablo Canyon troilite standard) have also been made on selected samples of efflorescences, using a method published by Krouse & Tabatabai 1986. Mortars and plasters have been characterized by XRD and differential thermal analysis (DTA) and by the chemical analysis of the binding agent (cf. Wisser & Knöfel 1987).

3. RESULTS
3.1 Efflorescences
The efflorescences were dominated by magnesium sulphates (found in 41 of 43 samples). XRD analyses showed various amounts of hydration water in the analysed phases (epsmite with 7 H$_2$O, hexahydrite with 6 H$_2$O and starkeyite with 5 H$_2$O), which are influenced by the relative humidities in the atmosphere of the exterior and in the laboratory as well. Fig. 1 shows the stability diagramm of different states of hydration. The changing relative humidity and their effects on MgSO$_4$ samples can be simulated under laboratory conditions (fig. 2). For those investigations one original efflorescence sample was taken in a moist cellar room, immediately after prepared for X-ray analysis and covered by a foil in situ. In this sample only...
epsomite was found. After this first analysis, the foil was taken off, and the sample was analysed again after 30 and 90 minutes (laboratory climate: 21 °C / 45 % r.h.). The appearance of hexahydrite peaks demonstrates the rapid process of dehydration. Epsomite is completely dehydrated to hexahydrite after 90 minutes. In a further step, the sample was put in a 20% r.h. atmosphere (for 5 days), but no further dehydration could be detected. In the end, the sample has been exposed to an atmosphere of 65 % r.h. for one day. Diagramm 5 (fig. 2) shows the re-appearance of epsomite and demonstrates the complete reversibility of the dehydration/hydration process.

This laboratory simulation shows practically the activity of magnesium sulphate phases under moderate climatic conditions, as they can be found on facades. They are connected with changes in volume and can lead to hydration pressures within the stone or mortar fabric.

Gypsum was also found in 41 of 43 samples, but in a much lower amount. In two samples, syngenite (K₂Ca[SO₄]₄) and thenardite (Na₂SO₄) were found to be the dominating phases. Those samples were taken from the recently restored city wall and are clearly related to modern portland cement mortars (cf. Arnold 1985).

The chemical analyses of some selected samples of efflorescences show very high sulphate (32-45 weight-%), but generally low chloride, nitrate, potassium and sodium contents (less than 1 weight-%). High Mg contents show again the dominating role of magnesium sulphates within the efflorescences (fig. 3). Ca (mainly bound in gypsum) is found in clearly lower amounts than Mg.

Sulphur stable isotope ratios have been analysed for some selected sulphate samples of the efflorescences. The δ³⁴S values are varying between -1.8 and +8.6 %o, with two maxima in the ranges between -1.8 and +2 %o and between +3 and +6 %o.

3.2 Mortars, plasters
Sulphates have also been found to be the dominating components in the extractions of soluble salts from mortars and plasters. Only in one of 16 investigated samples nitrate was the dominating salt component. The Mg/Ca ratio of the soluble component in the mortars and plasters from the exterior (< 4; fig. 3) is lower than that in the efflorescences (> 4; fig. 3). That means, that gypsum is relatively enriched vs. magnesium sulphate in the mortars and plasters. Some mortar samples from the interior show Mg/Ca ratios comparable to the efflorescences (> 4; fig. 3).

Characteristic XRD and DTA analyses of the binding agents from the historical mortars are shown in figure 4 and 5. Chemical analyses show high MgO contents in most of the mortar samples (up to 15 weight-%). It is bound in hydromagnesite and, maybe, in further amorphous magnesium carbonate compounds (Siedel 1994).

Older historical mortars have the typical ratios binding agent : aggregate of 1:1 to 1:2, while mortars from the early 20th century have a ratio of 1:3 to 1:4. Within the aggregate, quartz, mica, feldspar (sometimes chlorite) have been found.

4. SOURCES OF THE SALT EFFLORESCENCES - DISCUSSION OF THE RESULTS

To find out the sources of the salt efflorescences, the following possibilities have to be discussed:

- soluble parts of the (more or less weathered) building materials themselves
- ions transported with the rising damp from the ground
- wet or dry deposition of air polluting substances.

Cations and anions should be regarded separately.

4.1. Cations
The dominating cations in the efflorescences are generally Mg and (minor) Ca, always bound in sulphate compounds, independent of the different building materials, that are used in every special case (gneiss, sandstone, tuffstone, brick...). Natural Mg and Ca contents of the main building stones (gneiss, sandstone) are not too high and are chemically bound in relatively stable silicates.
On the other hand, the chemical and mineralogical investigations of the unweathered binding agent of joint mortars from various places and of different ages showed high amounts of Mg and the related phases in X-ray and DTA analysis (figs. 4, 5). Hydromagnesite, as found in the mortars, is a product of the carbonation of dolomite lime binders.

Some studies on the behaviour of dolomite lime plasters and mortars in weathering in the exterior show the differences between the magnesium and the calcium component in the binding agent (Hoffmann & Rooß 1976, Niesel & Schimmelwitz 1971). Calcium carbonate is changed to gypsum, magnesium hydrocarbonate is changed to magnesium sulphate (epsomite/hexahydrite), with different solubilities of the sulation products. Gypsum (less soluble) is relatively enriched near the mortar surface, while large portions of the magnesium sulphates (better soluble) are transported by water to the evaporation zone at the mortar's or stone's surface. Thus, they are the dominating salts in the efflorescences.

The different solubilities of MgSO₄ and CaSO₄ are reflected in the variation of the Mg/Ca ratio in the efflorescences and in the soluble components of the mortars. Higher Mg/Ca ratios are found in the efflorescences, because the water had preferentially soluted the magnesium component from the mortars. Lower Mg/Ca ratios of soluble components are found in the mortars from the exterior. They show, that the less soluble component (gypsum) is relatively enriched in the "leached" mortar fabric. In places without any intensive exposition to rain water (interior) the Mg/Ca ratios of the mortars are higher because of the less intensive transport factor.

It must be concluded, that the characteristic chemical patterns of the analysed mortars (high magnesia contents) are the reason for the magnesia-dominated sulphate compounds in the efflorescences. The origin of the "dolomitic" mortars, which have obviously been used in Freiberg over centuries can be explained by the local history. In ancient times, the availability of limestone for lime production has been restricted by the worse possibilities of transport over long distances. Thus, the quarries were situated as near as possible to the building yards. Looking at the geological situation around Freiberg, the most possible sources for lime production are paleozoic limestone lenses within the crystalline complex of the Erzgebirge Mts. and the phylitic series at its margin (Lengefeld, Hermsdorf, Memmendorf, Braunsdorf...). Relations to the Lengefeld quarries are shown by documents from the 16th and 17th century. The analyses in table 1 show the dolomitic nature of those limestones.

### Table 1 CaO and MgO contents of some limestones used for lime production in the surroundings of Freiberg (analyses from descriptions of the geological maps).

<table>
<thead>
<tr>
<th>Deposit</th>
<th>CaO [weight-%]</th>
<th>MgO [weight-%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lengefeld, Erzgebirge Mts. (Cambrian)</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td>Hermsdorf, Erzgebirge Mts. (Ordovician)</td>
<td>28.7...45.2</td>
<td>6.0...18.1</td>
</tr>
<tr>
<td>Braunsdorf, Wilsdruff-Nossen Slate Mts.</td>
<td>no analysis</td>
<td>15...20</td>
</tr>
</tbody>
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4.2. Anions

The absolutely dominating anion of salt compounds in the efflorescences is sulphate. Sulphur contents in the building materials are rather low. For example gneiss, often used as a mural stone in Freiberg, has a sulphur content of 0.06 weight-% on average.

To find out where the sulphur comes from, a preliminarily stable isotope study was made. The results are shown in fig. 6. A comparison with sulphur isotope data from soils, ores and waste products of the Freiberg mining and metallurgical plants and from aerosols, snow and brown coal (used as a fuel in households and factories) was made. It shows, that single samples could not be simply related to defined influences of the environment. There are wide ranges of the $\delta^{34}S$ values and lots of mixing effects. On principle both, air pollution and the natural background (soils, water) could be of any influence. To find out the sulphate sources in a special case, the special situation on the building and the direct environs have to be investigated more detailed.
5. CONCLUSION

The chemical patterns of salt efflorescences at historical monuments in a certain geographical area do not only demonstrate the influences of industrial air pollution within the last hundred years. Besides, they show connections to the chemical and mineralogical composition of locally important building materials and to the natural background (soils, water), which should be considered while making a concept for restoration.

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REFERENCES


Figure 1: Stability of different states of hydration for magnesium sulphate, after Schmölzer 1936 and Gmelin 1939.

Fig. 2: Laboratory simulation of the dehydration / hydration process of magnesium sulphate, controlled by XRD (E - epsomite, H - hexahydrite). 1 - original sample, covered by foil, 2 - after 30 minutes in the laboratory atmosphere, 3 - after 90 minutes in the laboratory atmosphere, 4 - after 5 days in 20% r.h., 5 - after 1 day in 65% r.h.
Fig. 3 Magnesium / calcium ratio in the soluble component of salt efflorescences, mortars and plasters.

Fig. 4 Typical XRD analysis of the enriched binding agent of a historical mortar from Freiberg (quartz belongs to the aggregate). Cc - calcite, Hm - hydromagnesite, Qz - quartz.
Fig. 5 Typical DTA diagram of the binding agent of a historical mortar from Freiberg. The effects between 300 and 600 °C are related to hydromagnesite.

Figure 6: Ranges of sulphur isotope ratio δ³⁴S for sulphate salt efflorescences at historical buildings in Freiberg and the possible sources of sulphur.