DAMAGE TO FRESCOES CAUSED BY SULPHATE-BEARING SALTS: WHERE DOES THE SULPHUR COME FROM?

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Abstract—Crystallization of sulphates in the form of gypsum and mirabilite/thenardite is one of the main causes of the accelerated disintegration of historic frescoes. The sulphur, which is necessary for these processes, may originate from a large number of different sources. Although the nature and velocity of the processes causing the damage, as well as the possible transport pathways of the salt-forming ions, can be determined with reasonable accuracy, reliable information on the origin of the ions is seldom forthcoming. Sulphur isotope ratios were determined for various construction materials and salts from the church at Eilsum (Lower Saxony, Germany) where the romanesque frescoes have suffered serious damage. The studies showed clearly that sulphate on the walls inside the church, in contrast to that on the outside walls, originates mainly from the ground beneath the church from where capillary rise takes place within the walls. This information on sources and pathways of salt-forming ions may contribute towards developing a programme of remedial measures.

1 Introduction

As with historic buildings, which are subject to increased weathering in current atmospheric conditions, works of art within buildings, such as frescoes, are increasingly threatened by disintegration. An interdisciplinary research project has, therefore, been initiated with the object of discovering the reasons for the disintegration of mural paintings, particularly those executed in fresco. It is hoped that in this way a contribution will be made towards their conservation.

The romanesque mural paintings in the Evangelical Reformed church at Eilsum (near the North Sea coast in Germany) were selected for study, since they showed serious disintegration and restorative measures seemed to

be urgent. Figures 1 and 2 are two photographs of the same subject, one taken 18 years after the other; these demonstrate how quickly disintegration is progressing: about 70% of the paint layer present after the last restoration has disappeared within this short time.

Scientific studies showed that the damage was mainly caused by soluble salts, particularly sulphates such as gypsum ($CaSO_4 \cdot 2H_2O$) and thenardite (Na_2SO_4). Gypsum occurs in

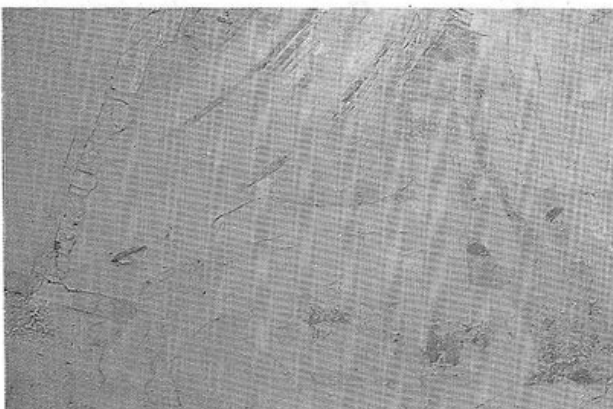*Figure 1   Fresco subject (a bull) a few years after the mural painting was uncovered (photograph: IfD, Hannover).*

Figure 2   The same subject 18 years after the photograph shown in Figure 1 was taken (photograph: J. Autenrieth, Munich).

various forms as a crust, blister or pore filling and thus contributes to the destruction of the paint layers and the supporting plaster layers. One of the initial steps towards repair and restoration of a damaged fresco is detection of the sources and pathways of the salt-forming ions; only then can the frescoes be protected by stopping further supply of salt. If further sulphate transport to the mural paintings is not stopped, then sulphate can continue to react with calcium, which is present in abundance, to form gypsum.

Although it is now possible to discover the causes of damage and salt concentration, it is still very difficult to determine the origin of the salt ions, in this case particularly the sulphate. Possible sources of the sulphur are:

—sulphate and sulphur dioxide (SO_2) from the atmosphere,
—sulphate from the soil,
—sulphate from gypsum additives in the paint layers,
—sulphate from building materials,
—sulphate from groundwater, rainwater or seawater.

Stable isotopes may provide an indication of the sources of the sulphur and the pathways used by it. Because of the great number of possible sources of the sulphur isotopes, a mixing effect must be expected, making it normally impossible to assign the sulphur to one single source. However, preliminary tests have shown that in the case of the Eilsum church, identification of a single source does seem to be possible.

Among the numerous publications dealing with the subject of stable isotopes, there are only a few that deal with the origin of sulphur in the case of weathering damage to buildings and objects of art [1–3]. These investigations are all restricted to the exterior parts of the building which are directly exposed to the atmosphere. So far, no publication has discussed the origin of the sulphur which contributes to the disintegration of mural paintings inside churches, although the role of sulphate is just as important here as on the outside of buildings. This paper presents an initial attempt to determine the origin of the sulphur (in sulphate) on the walls inside a building and on mural paintings, using the

variation of the ratio of two stable sulphur isotopes.

2 Fractionation of sulphur isotopes

Isotopes are atoms containing the same number of protons—and electrons—but varying numbers of neutrons. ^{32}S and ^{34}S, for instance, are two isotopes of sulphur each containing 16 protons but the former 16 and the latter 18 neutrons in its nucleus. 'Stable' isotopes are 'non-radioactive' species of isotopes; all sulphur isotopes are stable. Four sulphur isotopes have been found with a wide range of abundances: among all sulphur isotopes on the earth, ^{32}S has a concentration of 95·02%, ^{33}S of 0·75%, ^{34}S of 4·21%, and ^{36}S a concentration of 0·02%.

Isotope fractionation means partitioning of isotopes between two compounds to produce different isotope ratios. Isotope fractionation takes place as a result of certain reactions that

a) *have* an isotope effect *and*
b) do not reach completion.

There are two main mechanisms responsible for the fractionation of sulphur [4, 5]:

1 Chemical exchange reactions between sulphur compounds. Generally, the nucleus of an atom is responsible for the physical properties of the element, while the extranuclear characteristics influence its chemical behaviour. Since the electron numbers and arrangements in isotopes of the same element are identical, the chemical properties of these isotopes are very similar, while certain physical and physico-chemical differences exist due to the mass difference between isotopes. ^{34}S is more strongly bound than ^{32}S; therefore the compounds have physical properties that are not identical. This is the reason why compounds which differ in their isotopic composition may show different degrees of enrichment. This type of fractionation often depends on temperature.

2 Kinetic isotope fractionation based on differences between the reaction rates of isotopes with different masses. A kinetic isotope effect can be observed when a

chemical reaction rate depends on the atomic mass of reacting compounds at characteristic stages of the reaction. In the case of the bacterial reduction of SO_4^{2-} via SO_3^{2-} to S^{2-}, this mechanism causes a very strong fractionation of sulphur isotopes.

Isotope exchange reactions can generally be described using chemical equilibrium equations. But instead of measuring an equilibrium constant, it is more convenient to use a fractionation factor, i.e. the ratio of two isotopes in two chemical compounds. For practical purposes a delta value is defined, relating the measured isotope composition of two compounds to the isotope ratio of a standard sample.

In the case of the sulphur isotopes ^{34}S and ^{32}S the degree of fractionation expressed by the delta value is

$$\delta^{34}S[\permil] = \frac{(^{34}S/^{32}S)_{sample} - (^{34}S/^{32}S)_{Std}}{(^{34}S/^{32}S)_{Std}}$$

where Std = Standard (Diablo Canyon troilite: FeS from the Diablo Canyon iron meteorite, used worldwide as a laboratory standard for the absolute determination of $^{34}S/^{32}S$ isotope ratios).

Delta values describing the natural fractionation of two sulphur isotopes cover a wide variation range of up to 155‰. The 'heaviest' sulphates in sedimentary rocks have $\delta^{34}S$ values of about +90‰ while the 'lightest' sulphides give δ values of around −65‰.

3   Results

Sample selection was suited to the problem; most of the samples were of the plaster.

Samples in which sulphur was found in the form of gypsum or thenardite were prepared as bulk samples; in some of the soil samples and in the rainwater and groundwater samples, the sulphate was precipitated in the form of $BaSO_4$. The samples were analyzed by the Geochemistry Institute of Göttingen University using a Finnigan MAT251 gas mass spectrometer with a precision of ±2%.

The analytical results, together with a short description of the samples, are given in Table 1. Figures 3 and 4 show the locations of the various samples mentioned in Table 1.
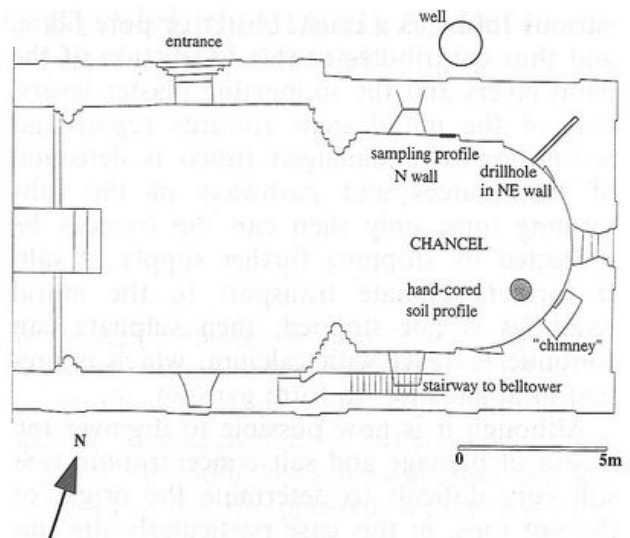

Figure 3   Ground-plan of the chancel area at Eilsum church. The sketch shows the unheated part of the church containing the romanesque frescoes.
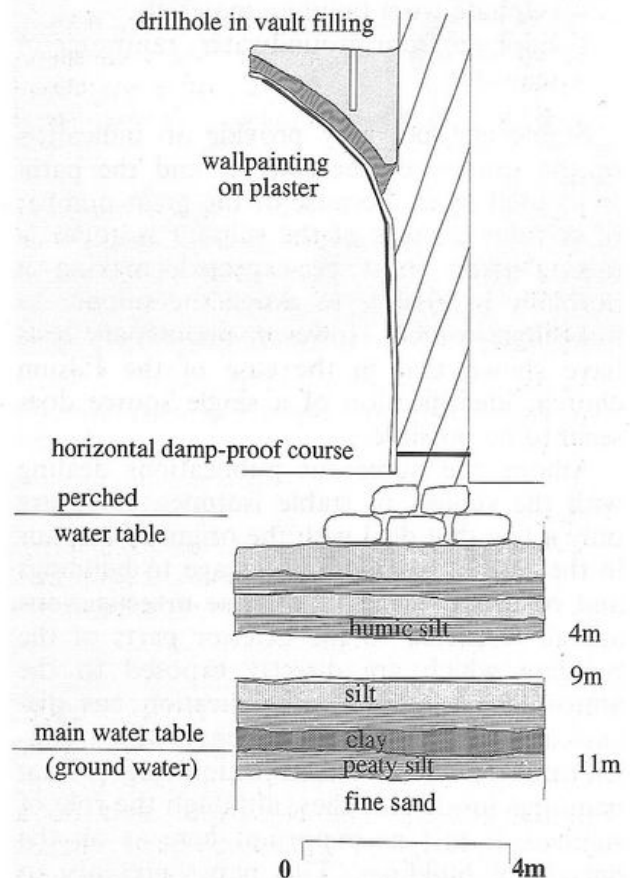

Figure 4   Schematic section through the ground, the foundations and the wall of the church showing the two water-tables.

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Table 1 Analytical results and sample descriptions

Sample	$\delta^{34}S[‰]$	Short description
Building materials		
Ei002	2·80	Interior, north wall of chancel, 0·40m above the floor, plaster
Ei008	−0·97	Interior, north wall of chancel, 1·95m above the floor, plaster
Ei011	−1·27	Interior, north wall of chancel, 2·82m above the floor, plaster
Ei126	0·20	Interior, north wall of chancel, 5·57m above the floor, plaster
Ei152	0·99	Interior, north wall of chancel, 0·80m above the floor, plaster
Ei158	−1·00	Interior, north wall of chancel, 3·70m above the floor, plaster
Ei274	−1·28	Old plaster with encrustation, north wall above the door
Ei299a	−0·59	Drillcore no. 2 in the northeast wall, plaster only
Ei207	0·46	Plaster sample from a hollow in the southeast wall used as a chimney
Ei51a	2·58	Outside, apse wall, south side, 3·3m from the ground, brick
Ei51b	2·14	Outside, apse wall, south side, 3·3m from the ground, mortar
Ei136	2·37	Outside, south wall, mortar
Ei236	−1·64	Drillcore no. 2 in the northeast wall (0·66–0·77m, i.e. average sample)
Ei80	4·56	Sample taken with a drilling rod from the loose vault filling above the ceiling, 0·55m in front of the north window of tower; sampling depth 0–0·09m
Ei84	3·07	Hole drilled into the vaulted ceiling from above, 0·55m in front of north window of tower (sampling depth 0·90–1·05m)
Salts		
Ei130	−1·13	Interior, salt from Ei8
Ei146	−0·87	Interior, hard white encrustation on wall
Ei204	1·21	Interior, salt encrustation (cauliflower-like) on brick wall in stairway to bell tower
Ei265	−2·10	Interior, cauliflower-like blisters
Soil		
Ei162	6·63	Soil profile, south side of church, 2m from the wall (0–1·00m)
Ei177	4·39	Soil profile, east side of church (2·70–4·05m)
Ei177s	−1·85	Soil profile, soluble sulphate only
Ei177i	6·64	Soil profile, insoluble sulphur-bearing substances only
Ei183	1·87	Soil profile, east side of church (10·60–11·00m)
Ei183s	−1·48	Soil profile, soluble sulphate only
Ei183i	1·76	Soil profile, insoluble sulphur-bearing substances only
Ei185	6·62	Soil profile drilled through floor of apse (0–0·20m)
Ei188	6·97	Soil profile drilled through floor of apse (1·50–3·00m)
Water		
Ei264	6·37	Groundwater taken at depth of about 2m in a well about 50m east of the church
Ei331	9·18	Groundwater taken from the well east of the main entrance
Ei294	4·66	Rainwater collected on 17–18 July 1990

In Figure 5 the results are grouped under the different substances and according to whether the samples were taken inside or outside the church. The church is built on a *'warft'* (an artificial hill constructed against North Sea storm tides as is usual in coastal regions). The foundations of the church are in contact with the surface soil layers (Figure 4) from which the three soil profile samples (Figure 3) originate. These soil samples are, however, not in contact with the groundwater, which occurs at a depth of about 11m beneath an impermeable clay layer.

4 Discussion of the results

All the samples collected in the chancel except Ei002 show $\delta^{34}S$ values smaller than 2‰ (most
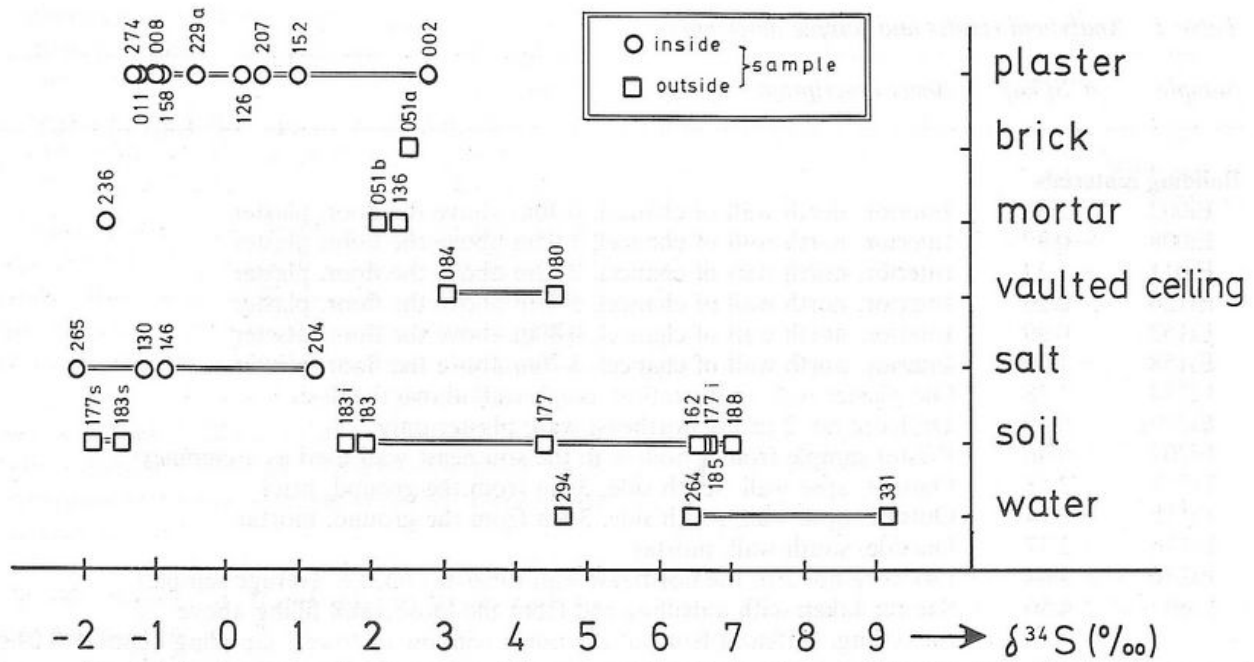
Figure 5 Sulphur isotope ratios in some substances collected in and around the church at Eilsum. The sample numbers refer to the 'Ei' sample numbers in Table 1; 'i' means insoluble matter, 's' means soluble sulphate.

of them are negative), whereas the samples collected outside the church always have a $\delta^{34}S$ greater than 2‰. Sample Ei002 comes from the immediate neighbourhood of the horizontal damp-proof course that has been built into the walls of the church in order to stop rising damp. During this difficult building operation, mortar and plaster, both probably containing cement, were used, thus introducing potentially hazardous ions into the walls; elevated concentrations of K^+, Na^+ and SO_4^{2-} in sample Ei002 confirm this assumption.

The sulphur isotope ratios for the plaster and salt samples are mostly negative and thus correspond to the isotope values of the drill core samples from the chancel. Mortar sample Ei236 is interesting; it was collected from the middle section of a drill-hole in the northeast wall. It shows a distinctly more negative δ value than mortar and brick from the outside of the church wall.

Some soil samples were divided into two parts, one containing the soluble, the other the insoluble sulphates. The sulphur isotope ratio for the soluble sulphates in the soil lies within the range of the mortar samples from inside the building, whereas the rainwater and the two groundwater samples show distinctly

higher positive values. This is understandable: the insoluble sulphates in the soil samples are unrelated to the groundwater ($\delta^{34}S = 6·4$ and 9·2), which occurs at a depth of more than 10m and is separated from the overlying soil layers by an impermeable clay. Equally, the soluble sulphates in the soil samples are unrelated to the fresh rainwater ($\delta^{34}S = 4·66$).

The soil samples span the widest range of $\delta^{34}S$ values. This is presumably due to intensive fractionation within the humic soil layers. Anaerobic sulphur bacteria are the main catalysts in the reduction chain from sulphate to sulphite and then to sulphide. Thus the isotope values of the soil bulk samples and the insoluble portion of the soil samples are isotopically much 'heavier' than those of the soluble sulphate portion. This suggests the presence of sulphur in the soil as a sulphide (pyrite), which was confirmed by X-ray diffraction.

Due to the proximity of the North Sea (only a few kilometres away), the sulphur isotope ratios could be expected to have been influenced by the sea. However, as the $\delta^{34}S$ value of seawater sulphate is about +20‰ worldwide [6], the supply of the seawater as an aerosol via the atmosphere is unlikely to

have markedly affected the values.

Only one sample of rainwater was investigated (Ei294). Although this is, of course, not representative, it fits into the range of other rain samples collected away from the influence of the sea [7]. The 'heavier' δ values for the outside samples (brick, mortar, loose material above the vaulted ceiling) probably result in general from the mixing of ascending sulphate with sulphur transported by rainwater and other 'anthropogenic' emission sources.

Thus we propose the following sulphate transport model. Soluble sulphate from the ground beneath the church rises gradually via the foundations into the brickwork and from there mainly uses the mortar as a pathway for upward movement. The salts crystallizing in the exterior walls derive from a mixture of this sulphate with sulphate and gaseous oxides of sulphur (SO_x) transported in the atmosphere, whereas the salts found on the interior walls are predominantly derived from the ground. In the interior of the church, gaseous SO_x or sulphate supplied as dust seem to have played a minor role. These results agree with measurements carried out by Arnold who found that the proportion of harmful substances transported into a building by air is negligible compared to that transported by air onto the outside surfaces of the same building (the ratio is about 1:80)[8].

Our studies have provided evidence that the sulphur in those sulphate-bearing salts which are responsible for most of the disintegration of the mural paintings in Eilsum does not derive from air pollution, but originates in the ground beneath the church. The possibility that certain substances in the building materials also contribute to the disintegration, although only to a minor extent, cannot be excluded. This result is surprising since a horizontal damp-proof course has been built into the church at Eilsum. Cores drilled during the course of other investigations, however, provided evidence that the damp-proof course within the walls is not continuous. In addition, no care was taken to provide a barrier to damp rising through the plaster on the interior walls; accordingly, this critical zone in particular forms an ideal 'capillary ladder' for the rise of salt-forming ions to the frescoes.

Comparable results have been obtained during studies on the church at Idensen, near Hannover.

To identify the origin of the sulphur in cases of this kind, it is not sufficient to study the substances contained in the building materials and in the ground [9]. Often, historic buildings have been subject to capillary rise of solutions over several centuries and, consequently, even minor concentrations of harmful substances in the environs may have led to considerable accumulations at the surface.

It is hoped that these studies will prove useful for restorers and curators of historic buildings when they must make decisions as to where long-term remedial measures should be directed. Studies are being made on other objects to check the reliability of the isotope analysis method as a means of determining the source of harmful salts. It is necessary to develop a sampling strategy for this kind of investigation, in order to provide reliable information at low cost.

Acknowledgement

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Résumé—La cristallisation des sulfats sous forme de gypse et de mirabilite/thénardite est l'une des principales causes de détérioration accélérée des fresques anciennes. Le soufre, qui est nécessairement impliqué dans ce processus, peut provenir d'un grand nombre de sources différentes. Bien qu'on puisse déterminer avec assez d'exactitude la nature et la rapidité du processus qui provoque l'altération, ainsi que les voies de transport possibles des ions qui forment le sel, une explication fiable de l'origine de ces ions est rarement avancée. Pour ce faire, on a déterminé les rapports isotopiques du soufre provenant des différents matériaux de construction et des sels, l'ensemble étant prélevé à l'église d'Eilsum (Basse Saxe, Allemagne), où les fresques romanes avaient souffert d'altérations importantes. Les études ont montré à l'évidence que le sulfate des murs à l'interieur de l'église, par opposition à celui des murs extérieurs, provenait principalement du sol sur lequel le bâtiment était construit et montait par capillarité dans les murs de celui-ci. Ces renseignements sur les sources et les chemins des ions formant le sel peuvent contribuer à élaborer un traitement curatif.

Zusammenfassung—Die Kristallisation von Sulfaten als Gips und Mirabilit/Thenardit ist eine ganz wesentliche Ursache dafür, daß historische Wandmalereien einem beschleunigten Zerfallsprozeß unterworfen sind. Der Schwefel, der hierzu benötigt wird, kann dabei aus zahlreichen verschiedenen Quellen stammen. Obwohl Aussagen zu Art und Geschwindigkeit der Schadensbildung sowie mögliche Transportwege der salzbildenden Ionen gemacht werden können, sind sichere Hinweise auf die Herkunft der schädlichen Salzionen nur in Ausnahmefällen möglich. In der Kirche von Eilsum (Ostfriesland) mit gravierenden Schäden an romanischen Fresken wurden die Schwefelisotopenverhältnisse an verschiedenen Baumaterialien und Salzen gemessen. Sie zeigen klar an, daß Sulfat an den Innenwänden—anders als im Außenbereich—überwiegend aus dem Untergrund der Kirche stammt, von wo es kapillar in den Mauern aufsteigt. Solche Hinweise auf Quellen und Wege schädlicher Salzionen können wichtige Beiträge für Sanierungskonzepte sein.