ALTERATION OF WALL PAINTINGS AFFECTED BY SOLUBLE SALTS

VERFÄRBUNGSEFFEKTE AUF HISTORISCHEN WANDMALEREIEN, HERVORGERUFEN DURCH KRISTALLISATION VON SALZEN

ALTERATION DE PEINTURES MURALES AFFECTEES PAR DES SELS SOLUBLES

Friedrich Grüner

SUMMARY

White and vitreous discolorations were investigated on samples of historic wall paintings from the museum of ethnology in Munich and from St. Anton - Maria Himmelfahrt, Garmisch - Partenkirchen. The wall paintings of the 19th century in the museum of ethnology were covered until 1992 with sacking and wooden vitrines. Water penetration from the roof led to high moisture contents. In St. Anton in Partenkirchen, frescoes on the ceiling were affected by high humidity, shown by microbiological metabolism. The church is not heatable during winter seasons.

In both cases, microscopical and SEM /EDX - investigations showed dense layers of gypsum sinters on the surface of the paint layers. Tests for amino acids in the investigated paint layers were carried out. No evidence for the use of binding media (casein, glue) containing amino acids was found.

The discolorations observed in the dark pigment layers are caused by the crystallisation of gypsum sinters. This will be favoured by the physico - chemical characteristics of the natural earth pigments used. They are made up of a mixture of clay minerals, for example kaolinite, silicate minerals and the colouring pigment. Clay minerals show a much higher absorption potential for moisture and dissolved salt ions, here sulphate, than silicates. These conditions favour the crystallisation of large gypsum crystals displaying their equilibrium forms.

ZUSAMMENFASSUNG

Es sind weißliche und glasige Verfärbungen an Malschichtproben in Wandmalereien des Völkerkundemuseums in München und in St. Anton - Maria Himmelfahrt, Garmisch - Partenkirchen untersucht worden. Die Wandmalereien des Völkerkundemuseums aus dem 19. Jh. sind bis 1992 mit Vorhängen aus Sackleinen und Holzvitrinen verdeckt gewesen. Wassereinbrüche haben zu einer zeitweisen starken Durchfeuchtung geführt. In St. Anton in Partenkirchen sind freskale Deckengemälde ebenfalls hohen Luftfeuchtebelastungen ausgesetzt, wie mikrobiologische Bildungen (Schwarzschimmel, etc.) zeigen. Die Kirche ist nicht beheizbar.

In beiden Fällen sind durch mikroskopische und REM / EDX - Untersuchungen dichte, die betroffenen Malschichtoberflächen fast vollständig bedeckende Gipssinterbildungen festgestellt worden. Testuntersuchungen zum Nachweis von Aminosäuren als organische Bindemittelbestandteile (z.B. Kaseine, Leime) in den Malschichten verliefen negativ.

Die Farbveränderungen der dunklen Malschichtpartien werden auf die Bildung von Gipssinterschichten zurückgeführt, die durch die physiko - chemischen Eigenschaften der verwendeten natürlichen Erdpigmente stark begünstigt wurden. Erdpigmente enthalten hohe Anteile an Tonmineralen, die durch ihr gegenüber Silikatmineralen erhöhtem Adsorptionsvermögen von Feuchtigkeit und gelösten Salzen, hier Sulfate, besonders günstige Voraussetzungen für die Bildung und Verwachsung einzelner Gipskristalle in ihren Gleichgewichtsformen bilden.

RESUME

Des décolorations vitreuses et blanchâtres de peintures murales historiques ont été étudiées sur des échantillons de mur du musée d'ethnologie de Munich et de St. Anton - Maria Himmelfahrt à Garmisch - Partenkirchen. Les peintures murales du 19ème siècle du musée d'ethnologie étaient couverts par des rideaux en toile et des vitrines en bois jusqu'en 1992. La pénétration d'eau au niveau du toit a conduit à de hautes teneurs en humidité. A St. Anton à Partenkirchen, les fresques du plafond étaient également exposées à une forte humidité, comme le montre le métabolisme microbiologique. L'église n'est pas chauffable pendant l'hiver.

Dans les deux cas, des enquêtes microscopiques MEB / EDX ont montré la présence de couches denses de concrétions de gypse à la surface des couches de peinture. Des essais ont été menés pour déceler des acides aminés dans les couches de peinture étudiées. Aucune évidence de l'emploi d'acides

aminés dans la composition des matières agglutinantes (caséine, colle) des couches de peinture n'a été trouvée.

Les décolorations observées dans les couches de pigment sombres sont causées par la cristallisation de gypse, favorisée par les propriétés physico-chimiques des pigments naturels terreux employés. Ils sont composés d'un mélange de minéraux d'argile, par exemple le kaolinite, de silicates et du pigment. Les minéraux d'argile ont un potentiel d'adsorption d'humidité et d'ions de sel (sulfates) dissous beaucoup plus élevé que les silicates. Ces conditions favorisent la cristallisation de grands cristaux de gypse exposant leurs formes d'équilibre.

1 INTRODUCTION

The effects of weathering by salt crystallisation processes in historic wall paintings is an old but still unsolved conservation problem. Historic mural paintings can be characterised as a system often made of highly porous materials. The precious paint layer forms the upper level on a sequence of different layers (for example from bottom to top):

- masonry built up with porous bricks or natural stones and joints filled with lime mortar, or a frame of wooden laths
- layers of plaster (arricio, intonaco), consisting of mostly high porous lime mortars,
- the paint layer on the top (secco paintings). In fresco paintings, the colour is painted directly into the damp intonaco and is hardened together with the lime of the plaster (bueno frescoe technique).

Deterioration caused by higher salt concentrations leads very often to visible damaging problems:

- efflorescences (varying from more or less thick salt crusts, salt pustules to fluffy efflorescences)
- powdering and granular disintegration of the paint layer, flaking of paint particles of different size
- development of dark spots and zones of higher humidity.

Numerous studies have been carried out on theoretical aspects of crystallisation and hydration of salts in natural stones and plaster structures. In practice, very often salt bursting tests are carried out for testing natural stones, bricks and mortars in spite of degradation by salt weathering processes. There are only few investigations on the disintegration processes of frescoes and the binding media of secco - technique wall paintings. Some experimental work on the disintegration of fresco paintings was done by Majewski [1970]. A comprehensive study on the role of soluble salts in wall paintings was carried out by Arnold & Zehnder [1987].

This article presents examples for salt weathering by the formation of dense gypsum sinter crusts on wall paintings. The resulting alterations (e.g. discolorations) in wall paintings however are often interpreted as binding media decrepitations.

2 ALTERATION OF WALL PAINTINGS FROM THE 19TH CENTURY IN THE MUSEUM FOR ETHNOLOGY, MUNICH, CAUSED BY SALT WEATHERING

The former bavarian national museum, now museum for ethnology, exhibits 143 wall paintings of different painting techniques from the 19th century. In 1950 the condition of the paintings was described as partly seriously damaged. Only parts of the wall paintings were accessible, up to 1992 most of them were covered with sackings cloth or covered with additional ceilings or vitrines. Water repeatedly penetrated into the ceilings and damaged the paintings. In 1995, the BLfD in Munich began with the documentation of the wall paintings for conservation and restoration treatments [oral communication, J. Pursche, BLfD].

The paintings investigated now are frescoes, but in dark parts, an additional layer of tempera with casein, egg or plant gums as organic binding media was

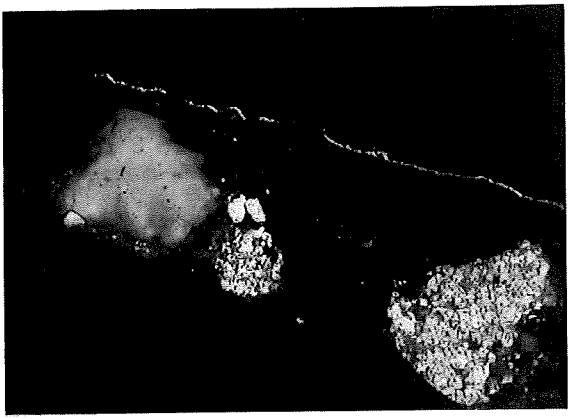

Fig. 1: View of thin section (sample no. 2537, P1) under crossed polarised light. In the lower parts a large quartz grain of greyish colour and calcitic matrix of the plaster is shown. A thin crystalline sinter of gypsum (enlightened) lies on the surface of the paint layer (dark). Approximate magnification 85x.

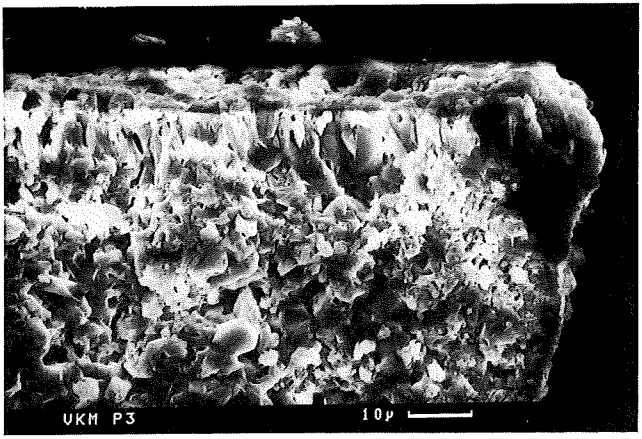

Fig. 2: View on cross section of sample 2537 / P1. The surface (top part of photograph) is covered with prismatic gypsum crystals.

assumed. Very dark colours with high covering power are difficult to work out in real fresco technique and are often painted over in secco technique.

In dark parts of some paintings, greyish and cloudy alterations in form of thin films occurred. The restoration team assumed ageing and disintegration effects of the binding media. Only little was known about the restoration history, e.g. former cleaning agents and application of consolidants. Cleaning with acidic or strongly alkaline solutions (e.g. sulphurous caustic soda, barium hydroxide, etc.) was a widely spread method and assumed here.

Microscopical examinations of a dark green sample (no. 2537 / P1) showed white and fluffy efflorescences and a very fine - grained, nearly translucent "coating" of the whole sample (figs. 1 - 3). Some microbiological colonisation was also recognised. Energy - dispersive x - ray (EDX) analyses of discrete salt crystals on the surface of the sample showed high amounts of the elements Ca, S, O (fig. 5), which can be interpreted as gypsum crystals. In some parts, fluffy efflorescences of Mg - sulphates of unknown hydration state (for example epsomite: $MgSO_4 * 7 H_2O$, kieserite: : $MgSO_4 * 6 H_2O$, etc.) occured upon the gypsum sinter crust. Mappings of the sample surface with SEM/EDX for elemental distributions were carried out. The translucent and overall covering of the sample however gave a very uniform and dense sulphur and calcium distribution (fig. 4). Only in areas with microbiological influence, the sulphur and calcium distribution was reduced.

In a vertical crack profile, the pigment content of the paint layer could be analysed. The elements detected give evidence for a mixture of clay minerals (alumino - silicates), iron silicates and calcite typical for natural green earth pigments. A small part of the sample was prepared for cross section and, in a second step, was later on mounted on glass and prepared for thin section analysis (Preparation thickness: 20 - 30 µm). Microscopical investigation under crossed polarised light clearly showed a gypsum crust of 2-3 µm in thickness (fig. 1).

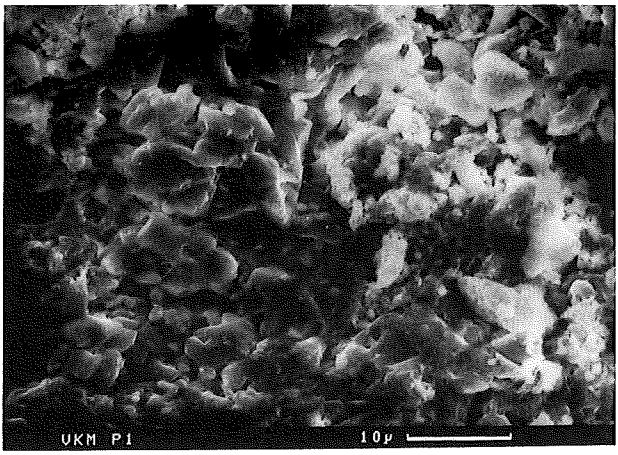

Fig. 3: Top view of the crust aggregated by well - shaped gypsum crystals, sample 2537 / P1.

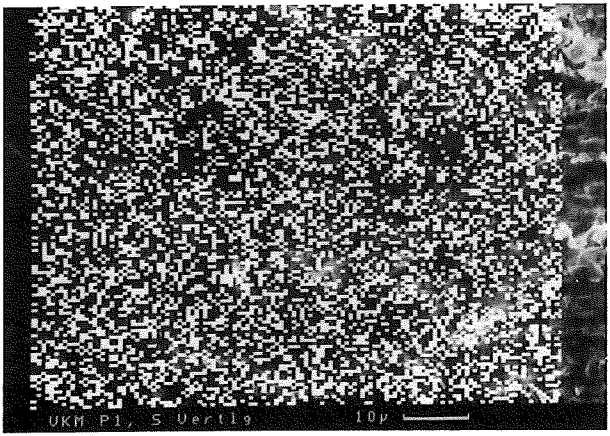

Fig. 4: Distribution of sulphur on a representative part of the surface of sample 2537 / P1.

The investigation of further wall paintings of different expositions in the museum included brown coloured earth pigments (including iron oxides and the heavy minerals rutile and sphene), dark green paint samples consisting of a mixture of green earth pigments and bone black indicated by higher phosphor contents in x - ray analyses and a dark red paint sample (mixture of red ochre with bone black). Each sample showed the formation of a sinter of gypsum on the surface.

In one case however, a greyish discoloration took place in a field of about two square meters at the rim of the painting (sample no. 2540 / P4, fig. 6). This zone was covered by a wooden vitrine for many years. Microscopic view of the surface showed sugar-like efflorescences. The energy dispersive x - ray spectrum showed high amounts of the elements Mg, S and Oxygen, indicative for epsomite or other hydrated phases of magnesium sulphate minerals.

A very sensitive microchemical test for amino acids was carried out on two samples (2537 / P1, 2539 / P3). A small part of each sample was treated with hydrochloric acid under sealed conditions at elevated temperatures and than filtered. The solution was dropped on a chromatographic plate tested with ninhydrin reagent. No positive colour reaction was recognised. With this test, it was possible to exclude organic binding media like casein and glue as constituents of the paint layer.

The plaster consists of two layers, a fine - grained intonaco, some mm in thickness and a coarse - grained arricio. Mineralogical x - ray diffraction analysis showed calcite, dolomite and quartz as constituents of the binding media fraction ($\leq$ 0,063 mm). Small amounts of gypsum were identified. Analysis of the highly water soluble ions chloride, nitrate and sulphate were photometrically done on eluates of the plaster. While the chloride and nitrate contents were in the range of 0.01 to 0.02 wt.-%, the sulphate content reached 1.0 wt.-%. The origin of the high sulphate content is unknown, but there are

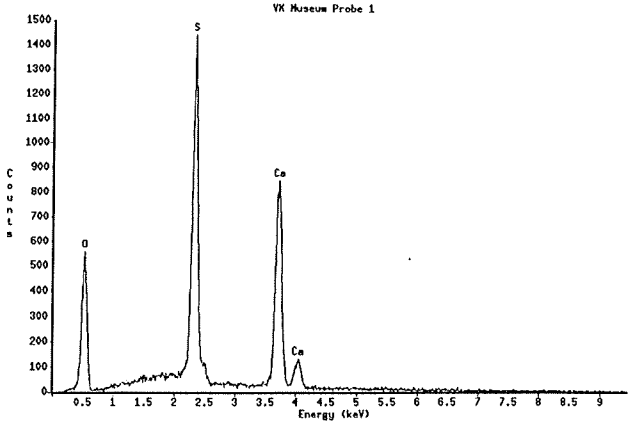

Fig. 5: EDX - spectrum of the gypsum sinter crusts covering the surface, sample 2537 / P1.

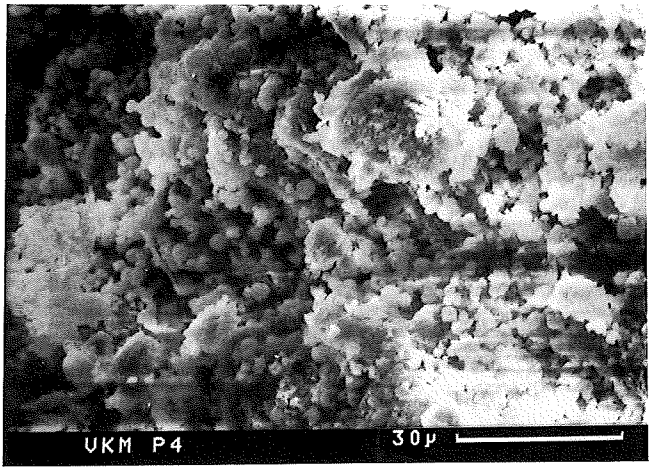

Fig. 6: Sample 2540 / P4 with magnesium sulphate (probably epsomite) covering the surface.

indications for cleaning with corrosive agents like "sulphurous caustic soda", etc. in the 1930's.

In this case, the greyish and cloudy alterations in zones painted with dark colours could be identified as thin salt crusts of µm size , mainly made up of gypsum. In one case magnesium sulphates were dominant. According to the long assumed covering of the wall paintings with sacking and vitrines and periodical water infiltration through the ceiling, a stable microclimate with high relative humidity should have developed. These are favourable conditions for the intergrowth of large crystals displaying their equilibrium forms. No evidence for disintegration or collapse of organic binding media was found.

3 WHITE DISCOLORATIONS ON FRESCO PAINTINGS, ST. ANTON - MARIA HIMMELFAHRT, GARMISCH - PARTENKIRCHEN

The main part of the pilgrimage church St. Anton near Garmisch - Partenkirchen was built from 1734 to 1736. The frescoes at the ceiling were painted by Joh. Ev. Holzer in 1736 [Käßer, 1985]. The church cannot be heated during winter season. In the 1950's, the fresco has been cleaned and conserved.

Several parts of the frescoes showed severe problems of alterations: white and greyish lightenings of dark brown pigments, of which three different examples will be shown.

In the first case a sample (2726 / GAP 22) was taken in a white, tear shaped zone. In the unpublished restoration report from A. Wolf (in the early 1950's) a carbonate bound varnish used to cover dark patches in a cloud coloured in dark yellow below a putto was noted (fig. 7). Scanning electron microscope investigations showed an intense and dense crystalline crust on the painted surface (fig. 8). Elemental analysis with EDX showed calcium, sulphur and

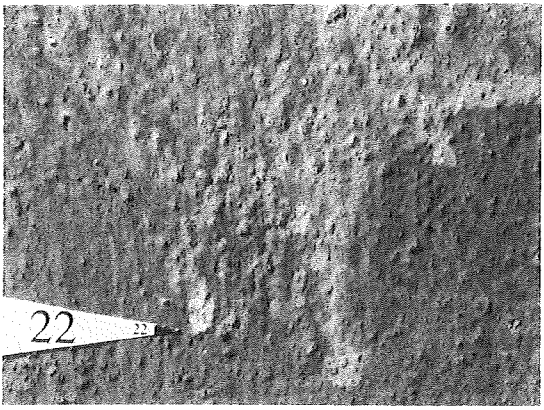

Fig. 7: Detailed view of the area of sample 2726 / GAP 22 showing white discolorations and drops of varnish.

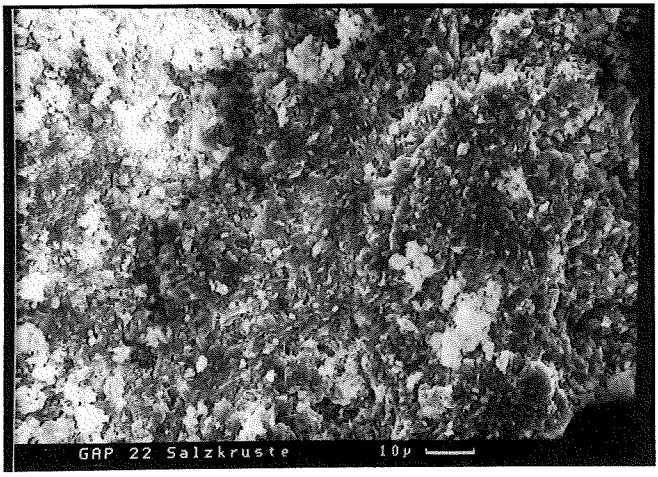

Fig. 8: Dense sinter crust of gypsum on the surface (sample 2726 / GAP 22).

oxygen as main constituents. The white drops and adjoining areas are covered by gypsum, which should be a reaction product of the carbonate constituent of the fresco and a corrosive cleaning agent.

Another example shows samples 2723 / GAP 23 and 2724 / GAP 24, which were taken in the dark brown coloured habit of St. Antonius. A thin vitreous layer on the surface was macroscopically visible. Different crystalline gypsum formations were distinguishable. Fine - grained gypsum crystals with well shaped crystallographic forms and platy, dense gypsum films were observed (fig. 9).

In the south eastern part of the fresco, a woman with a dark red robe is shown. A shadow was painted in a dark grey colour in a fold (fig. 10). It was assumed that the colour of the shadow was too bright for the intention of Joh. Ev. Holzer (pers. Communication, J. Pursche, BLfD). The pigment was supposed to be discoloured brown coal (so-called "Kasseler Braun"). It was possible to identify the pigment by SEM / EDX analysis; it consists mainly of high amounts of iron oxides and only little calcite, mostly altered to gypsum (figs. 11, 12). In the lightened parts of the sample very fine grained gypsum efflorescences were identified on the surface.

4 CONCLUSIONS

The affection of wall paintings by soluble salts is noted by several authors since many years. In 1987 Arnold and Zehnder published an extensive article about the salt species usually appearing in walls and the indication of their origin [Arnold & Zehnder, 1987]. For wall paintings, the following sources are of greatest interest: influence of polluted atmosphere (including smoke and soot from candle lights), materials used for repair and conservation (e.g. portland cements, water glass, corrosive cleaning agents, etc.), rising dampness (water in soils are normally diluted salt solutions, enriched in nitrate

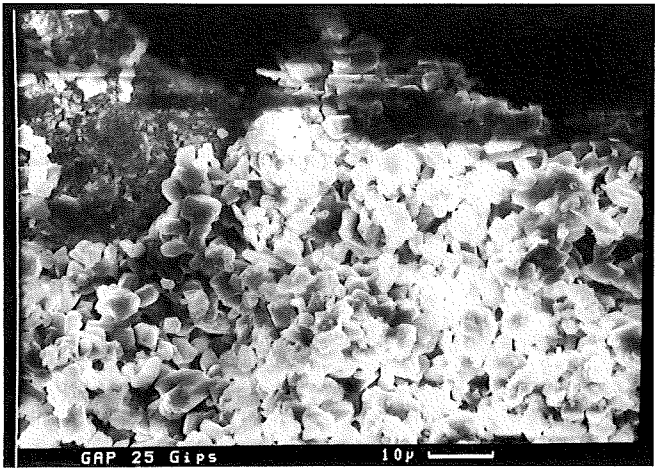

Fig. 9: Fine - grain aggregates of gypsum crystals with partly well shaped crystallographic forms, sample 2723 / GAP 24.

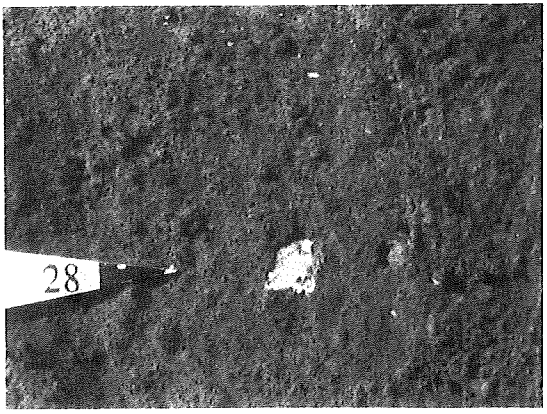

Fig 10: Detail of the fresco showing a woman's robe, painted in intensive red colour. An overlying shadow was painted in a fold in dark grey colour.

and chloride by human activities), original building materials (e.g. sandstones from Switzerland may contain up to 1500 ppm of sulphates [Zehnder, 1982] and biological metabolism. Another important factor is the use of dolomitic lime mortars for the underlying plasters; if in contact with sulphate ions dissolved in pore water, the formation of magnesium sulphates like epsomite and hexahydrite will occur [Arnold & Zehnder, 1987]). Just as uprising moisture causes intensive decay in the lowermost parts of wall paintings, the penetration of water through leaking roofs affects numerous wall paintings.

The precipitated salts may crystallise either on or beneath the surface of paint layers and other porous materials. The efflorescences appear in a wide variety of habits and aggregate forms as described in Arnold & Kueng [1985] and in Arnold & Zehnder [1987]. The formation of fluffy efflorescences and whiskers is very common. Normally the crystallisation takes place with serious forms of decay, such as disruption of paint particles of various size from the substrate.

From studies on crystal growth, it is known that crystal morphology is dependent on internal factors (e.g. crystal lattice) and on external factors such as supersaturation and composition of the solution, temperature and relative humidity. Zehnder & Arnold [1988] found out the relationship between crystal morphology of the efflorescences and the wetting properties of the solution. On a wet substrate with a thick film of the solution, the favoured crystal morphology is a granular crust made up of isometric grains, similar to their equilibrium forms and commonly aggregating to more or less thin crusts.

In the examples presented, crystallisation of remarkable amounts of gypsum was found. The investigated samples showed the formation of dense sinters or crusts. Macroscopically, its appearance varies from vitreous sinters to white discolorations. The formation of whiskers or single grains was absent with the exception of crystallising magnesium sulphates.

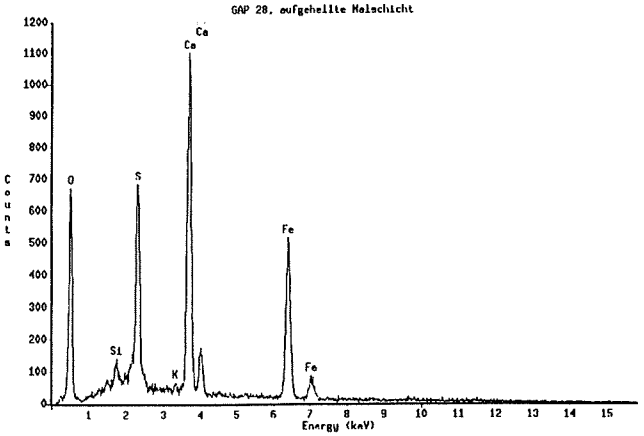

Fig. 11: EDX - spectrum in the altered part of the shadow (sample 2730 / GAP 28, the element spectrum can be interpreted to iron oxides (pigment) and gypsum (altered carbonaceous binding media).

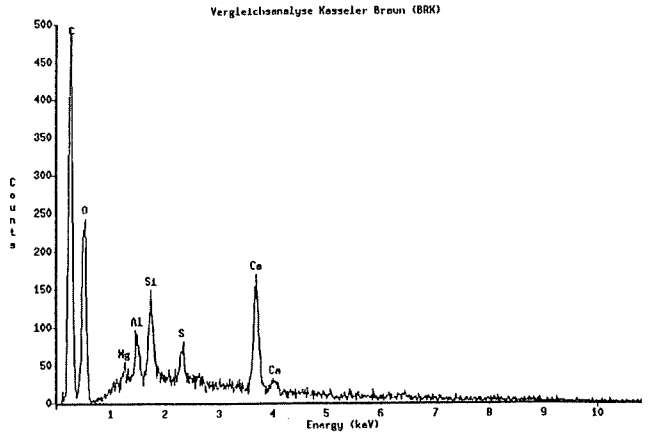

Fig. 12: EDX - spectrum of „Kasseler Braun“ (selled by Kremer Pigmente), showing high amounts of carbon (coal), clay minerals and gypsum.

In the case of the museum of ethnology, longer periods of relative high humidity were reached by water penetrating periodically through the ceiling and the simultaneous covering of the walls with sackings. In St. Anton, no heating is possible during winter and microbiological metabolism is indicative for higher moisture contents of the walls. In relationship with (seasonable) changes in relative humidity and temperature, the wall painting surfaces will show lower or higher moisture (wet films), favoured by high amounts of gypsum ($CaSO_4 * 2H_2O$) in the plasters and paint layers.

The artists of both wall paintings used natural earth pigments for mixing dark brown and green colours. The adsorption of moisture and dissolved salts is not only dependent on the microclimate of the building, but also controlled by adsorption on pore walls and double layer effects in the porous plasters and paint layers. The amount of adsorption depends on the number and potential of surface sites and the amount of internal surface of the materials used. Basically Al - containing minerals, especially clay minerals have very high reactive surfaces and can adsorb higher amounts of dissolved sulphates. Silicates show less absorption. The uptake of sulphate measured on kaolinite, a widespread clay mineral in natural mixtures of earth pigments can increase up to 0,25 wt.-% [Sridharan et al., 1986]. The formation of dense gypsum sinters and crusts on the investigated wall paintings from St. Anton in Partenkirchen and the museum of ethnology in Munich shows clearly these relationships on the physical and chemical characteristics of the earth pigments used in the paint layer which strengthened the crystallisation - dissolution processes.

5 BIBLIOGRAPHY:

Arnold, A. & Zehnder , K. (1987): Monitoring Wall Paintings affected by soluble Salts. - The Conservation of Wall Paintings, Proceedings of a symposium organized by the Courtauld Institute of Art and the Getty Conservation Institute, London 13 - 16 July, 103 - 135

Arnold, A. & Kueng, A. (1985): Crystallization and Habits of Salt Efflorescences on Walls, Part I: Methods of Investigation and Habits. - 5th International Congress on the Deterioration and Conservation of Stone, Lausanne, 25 - 27 September, 1985, 255 - 267.

Käßer, P. (1985):Votiv- und Wallfahrtskirche St. Anton Partenkirchen. - Schnell Kunstführer Nr. 128 (1935), 9. Auflage 1985, 14 S.

Majewski, L. J. (1970): Interim report on an Investigation of Processes of Disintegration of Frescoes. - Application of Science in Examination of Works of Art, Museum of Fine Arts, Boston, 182 - 186

Sridharan, S.; Rao; Sudhavar M.; Gajarajan, V. S. (1986): Influence of adsorbed sulphate on the engineering properties of kaolinite and bentonite. - Clay Res., 5, (2), 74 - 81

Zehnder, K. (1982): Verwitterung von Molassesandsteinen an Bauwerken und in Naturaufschlüssen. - Geotechnische Beiträge Geologie der Schweiz, 61

Zehnder, K. & Arnold, A. (1988): New experiments on salt crystallization. - 6th International Congress on the Deterioration and Conservation of Stone, Torun 12 - 14 september, 320 - 329