Sources of Magnesium Efflorescence on Ceramics

ABSTRACT

Magnesium formate dihydrate was detected by Raman microscopy as efflorescence on terracotta figures with replacements made of Sorel's magnesia cement consisting of basic magnesium chlorides as binder phases. On this alkaline, not water-proof material, formaldehyde from indoor air pollution can react directly to formate via the Cannizzaro reaction causing the efflorescence.

Hairy, wooly aggregates of curved needles, resembling thecotrichite, were found on Attic black-figured vases and identified as magnesium sulfate hexahydrate, mineral name: hexahydrite. As no gypsum was present, migrating salts from the architecture in a necropolis are considered as a magnesium source. The appearance is not due to a certain material, but due to crystallisation on a porous substrate with a dry surface.

Samples of efflorescence should generally be kept in order to enable subsequent instrumental analysis, which may add to the objects' 'biographies'.

KEYWORDS

Ceramics · Efflorescence · Hexahydrite · Magnesium formate · Magnesium oxychloride · Magnesium sulphate · Sorel · Whisker

AUTHORS

Gerhard Eggert*
Emeritus Professor of Objects' Conservation
Institute of Conservation Sciences
State Academy of Art and Design Stuttgart
gerhard.eggert@abk-stuttgart.de

Judith Berning
MA Student
Objects' Conservation Programme
State Academy of Art and Design Stuttgart
judithelisabeth.berning@stud.abk-stuttgart.de

Andrea Fischer
Senior Lecturer
Objects' Conservation Programme
State Academy of Art and Design Stuttgart
andrea.fischer@abk-stuttgart.de

Jörg Stelzner
Researcher/Objects' Conservator
Institute of Conservation Sciences
State Academy of Art and Design Stuttgart
joerg.stelzner@abk-stuttgart.de

Sebastian Bette
Researcher/Chemist
Max Planck Institute for Solid State Research
s.bette@fkf.mpg.de

**Corresponding Author*

INTRODUCTION

Conservators of archaeological ceramics sometimes have to deal with salt deposits and efflorescence. Qualitative analysis of the salt anions is covered in textbooks (Buys and Oakley 2011; Odegaard, Carroll, and Zimmt 2000) and is routinely performed, although results are not of much consequence for desalination. Cations are neglected in this approach. But perhaps they can also tell us something about the 'biography' of the object? This paper discusses two case studies where different efflorescences of magnesium salts were detected by instrumental analysis.[i] What can we learn from them, and where does the magnesium come from?

Magnesium, if present in clay, is tightly bound in the ceramic matrix; mobilisation and dissolution by atmospheric humidity is highly unlikely and never reported. As seawater contains some magnesium, approximately 1.3 g/kg, deposits on marine ceramic finds may contain magnesium carbonate (Pradell et al. 1996); however, in both cases discussed in this paper, the objects had not been waterlogged with sea water. Therefore, there must be other explanations for the presence of the magnesium salts that were detected.

Figure 1. *Angel figure No. 31, cold-painted terracotta, H 10.0 cm. Franziskanermuseum Villingen-Schwenningen · Courtesy C. Hauer, State Academy of Art and Design Stuttgart*

CASE STUDY I: MAGNESIUM FORMATE ON FOLK ART TERRACOTTA FIGURES

The figures

A collection of cold painted terracotta nativity figurines in the Franziskanermuseum Villingen-Schwenningen exhibited surprising and unusual white crystalline efflorescence (Figure 1). In order to study what happened, these were selected as winter semester 2017/18 projects in the Bachelor of Arts Objects' Conservation Programme at the State Academy of Art and Design Stuttgart (ABK).

Such figures were made in winter for private use at home in the 19th century by three generations of the Ummenhofer family (Auer 2002, 14). They are known as 'Guller figures'[ii] after the nickname of one of the family members. The figures were modelled in clay as this was an inexpensive material that was widely available. During modelling, the figures were supported using a wooden rod inserted into a hole at the bottom. The figures were reinforced internally with iron wires, which can easily be seen on X-ray radiographs (Figure 2). Cross sections reveal that, after drying and firing in a pottery kiln, the figures were cold painted on a thin chalk ground and then varnished, possibly to imitate a potter's glaze (Istas 2011, 17). The figures were heavily covered with dust

Figure 2. *X-radiograph of angel figure No. 31 · Courtesy V. Schaible, State Academy of Art and Design Stuttgart*

and mould. The varnish had yellowed and cracked considerably and obscures the original paint, which is often flaking. Corrosion of the interior iron and its resultant volumetric increase caused cracking of the body.

Extremities were often missing and later replaced with a heterogeneous, slightly reddish cement with white inclusions, after which the figures were completely repainted. All replacements showed the white crystalline efflorescence, often causing the underlying paint to flake (Figures 3, 5, and 6). The usual anion tests for chloride, sulfate, nitrate, and carbonate were negative. Instrumental analysis by Raman microscopy identified magnesium formate dihydrate ($Mg(HCOO)_2 \cdot 2H_2O$) as an extremely rare mineral called dashkovaite. This compound has not previously been reported in the literature on the conservation of ceramics. According to the Art and Archaeology Technical Abstracts (AATA) database (aata.getty.edu), magnesium formate dihydrate was only reported once before in the field of conservation science: on a dolomite ($CaMg(CO_3)_2$) containing sandstone as a result of 'cleaning' treatment using formic acid (Zehnder and Arnold 1984).

Sorel's magnesia cement

Energy dispersive X-ray analysis in the scanning electron microscope (EDX-SEM) of the replacements detected magnesium, chlorine, and oxygen as being the only heavier elements present in significant quantities. This elemental composition suggests Sorel's (1867) magnesia cement as the unusual material used to create the replacements. This putty is made by mixing magnesium oxide (MgO), 'magnesia', with a concentrated magnesium chloride ($MgCl_2$) solution and consists of basic magnesium chlorides as binder phases (Freyer 2017). The main binding components are the 3-1-8 and the 5-1-8 phases formed according to the equations:

$$3MgO + MgCl_2 + 11H_2O \rightarrow 2[Mg_2(OH)_3Cl \cdot 4H_2O] = 3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$$

$$5MgO + MgCl_2 + 13H_2O \rightarrow 2[Mg_3(OH)_5Cl \cdot 4H_2O] = 5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$$

In the presence of humidity, carbon dioxide from the air is absorbed by this hydroxide compound. This carbonation leads to chlorartinite, $Mg_2(CO_3)(OH)Cl \cdot 2H_2O = Mg(OH)_2 \cdot 2MgCO_3 \cdot MgCl_2 \cdot 4H_2O$ (Freyer 2017, 324). Indeed, chlorartinite, but no basic magnesium chloride phases, was the only crystalline material identified by X-ray powder diffraction (XRPD) in samples of the replacements.

Sorel's magnesia cement is stronger than Portland cement and is still used today for special applications, such as industrial heavy-load floors. Magnesia cement can easily be mixed with fillers such as sawdust in *Steinholz* (German, literally 'stone wood') floors. The use of Sorel's magnesia cement has only rarely been reported in the context of restoration. Thornton (1998) discusses use as early gap filling materials without, however, providing examples of applications. From the end of the 19th century until 1975, magnesium oxychlorides have been used under the trade name 'Meyer cement' for marble repair on the Acropolis. Maravelaki-Kalaitzaki and Moraitou (1999) observed severe deterioration in the outdoor environment:

> (1) expansion of mortars leading to break-up of the marble as a result of the carbonation of oxychloride phases; (2) disintegration of mortars exposed to washing and staining

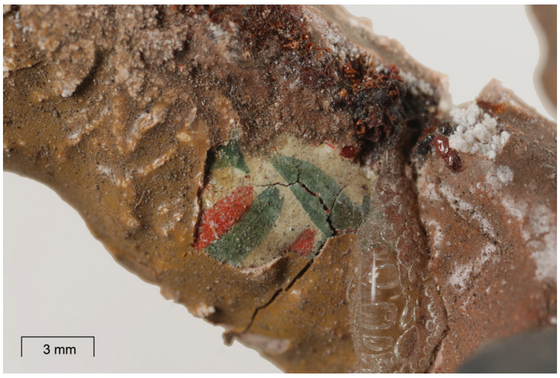
> of marble due to the release of magnesium chloride; and (3) in mortars sheltered from rain action, efflorescence due to the sulfation of mortar constituents that yields hydrated sulfate salts of magnesium and calcium with different water molecules; their hydration, crystallization, and rehydration during microclimatic shifts imply volume changes and the release of corrosive solutions leading to formation of cracks and staining.

Such drastic decay is not observed indoors. In the Berlin Antiquities Collection, magnesia cement has also been used for marble repair (Fendt 2012).

Leaching of chloride is a limiting factor in the application of the cement as it may cause metal corrosion. Chloride is not directly coordinated to magnesium, instead it is present in interstitial places within the structure of basic magnesium chlorides. Iron dowels in the terracotta figures showed typical signs of chloride corrosion known from archaeological iron, i.e. reddish brown drops or pustules exuding from the surface, known as weeping iron (Figures 3 and 4) (Scott and Eggert 2009, 101-102, Plate 39).

A direct treatment of the cold painted terracotta with formic acid is extremely unlikely to be the source of the formate. However, Sorel's magnesia cement can contain unreacted magnesium oxide, or 'caustic magnesia', which is known to directly produce formate from formaldehyde via the Cannizzaro reaction catalysed by bases (Busca et al. 1987; Peng and Barteau 1989). Unreacted MgO and alkaline cement degradation products may catalyse the direct reaction of formaldehyde from indoor air pollution to formate in the same way as is found in glass-induced metal corrosion, where formates predominate (Fischer et al. 2018). Hence, it is possible to regard this efflorescence as a kind of dosimeter, as it reflects the cumulative impact of C_1 carbonyl pollutants, formaldehyde and formic acid, collected at least over decades. If this interpretation is correct, then we can expect to see further examples of magnesium formate due to Sorel replacements on objects that are kept indoors long enough. (You are most welcome to send us your efflorescence samples!)

It is important to differentiate between magnesia cement, invented in 1867 (Sorel 1867), and Stanislas Sorel's (1855) similar first version



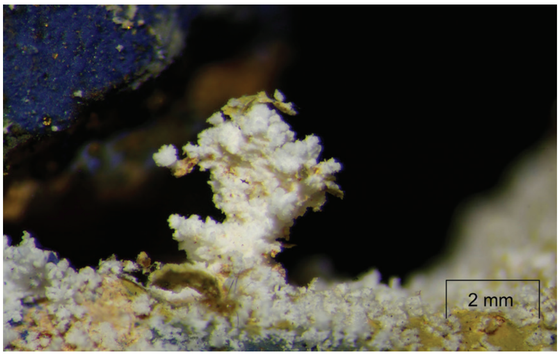


Figure 3. *(top) Detail of the angel's wing showing flaking overpaint, white efflorescence, and rust-brown scales of chloride corrosion · Courtesy C. Hauer, ABK*

Figure 4. *(above center) Rust scales on the angel figure · Courtesy C. Hauer, ABK*

Figure 5. *(below center) Light micrograph of magnesium formate efflorescence on angel No. 29, cold-painted terracotta, H 7.0 cm. Franziskanermuseum Villingen-Schwenningen · Courtesy C. Hauer, ABK*

Figure 6. *(below) Efflorescence on the horn of an ox figure, no No., cold-painted terracotta, H 6 cm. Franziskanermuseum Villingen-Schwenningen · Courtesy S. Hoffmann, ABK*

of cement made from the corresponding zinc compounds, i.e. zinc oxide and chloride, which are more expensive as raw materials. Ready-made zinc hydroxychloride products are still commercially available today (Lithos Arte), are used for stone repair, and were recently tested by Tennent et al. (2014) as replacement material for tiles. Therefore, the term 'Sorel cement' is ambiguous as it may refer to either formulation. In order to be completely clear, the word 'zinc oxide' or 'magnesia' should be added to the description. It would be very interesting to perform tests to compare these two materials for their suitability in ceramic restoration applications.

CASE STUDY II: MAGNESIUM SULFATE ON BLACK-FIGURED ATTIC VASES

Vulci vases with whiskers

Anton Buhl (personal communication, 26 May 2016) reported efflorescence on four classical black-figured vases in the Staatliche Antikensammlungen München, Nos. SH 1369, SH 1398, SH 1400, and SH 1413 (Lullies 1939) that visually resembled the calcium acetate thecotrichite in its hairy, woolly appearance (Eggert et al. 2016). All but SH 1400 were known to have been excavated by the Candelori brothers on their own ground in the Etruscan necropolis near Vulci. The Candelori collection of vases was acquired in 1831 for Ludwig I, King of Bavaria, by his agent J.M. von Wagner (Buhl and Knauß 2007).

Some of the salts caused dramatic flaking of the surface (Figure 7). Surprisingly, Raman microscopy and XRPD never found any of the expected thecotrichite. On SH 1413, a hitherto unknown calcium acetate was detected (Eggert, Bette, and Dinnebier, forthcoming) whose crystal structure was determined from XRPD data (Bette et al. 2018). Efflorescence on the three other vases consisted of magnesium sulfate hexahydrate ($MgSO_4 \cdot 6H_2O$), mineral name: hexahydrite (Figures 7, 8, and 9). Magnesium sulfate occurs in various states of hydration depending on temperature and relative humidity (RH) (Steiger et al. 2011, Figure 4). Most abundant is the heptahydrate epsomite, commonly called Epsom or bitter salt; the deliquescence point of the pure compound is 89 percent RH. Magnesium sulfate is notorious for its damaging effect on building stones and is used in a standardised weathering test (BS EN 1367-2:2009). But why does it occur on Attic vases?

Source of magnesium sulfate

Gypsum is traditionally used for replacements in ceramics conservation. Gypsum, geologically often a seawater evaporite or derived from dolomite, may contain varying amounts of magnesium, 'a few percent $CaCO_3$, $MgCO_3$, and $CaMg(CO_3)_2$ may be present, depending on the provenance of the raw gypsum.' (Lucas 2003, 58). As magnesium sulfate is far more soluble than calcium sulfate dihydrate (gypsum), selective dissolution and redeposition is theoretically possible but would require a very high relative humidity. Magnesium sulfate efflorescence on gypsum has been observed in the laboratory even with soluble magnesium oxide contents below 1 percent (Ahlers 2003, 1). However, despite the frequent use of plaster of Paris, no reports of magnesium sulfate whiskers could be found in the conservation literature. And, most important, the vases had no replacements at all. As there is no other known treatment with the potential to introduce magnesium into the vases, it must have already been present before excavation. It should be noted that two of the three vases are known to come from a necropolis. They might have come into contact with migrating salts from the architecture. Depending on the humidity, salts present, pore size, and height above ground, magnesium sulfate can be deposited in certain areas. As vases from Vulci can be found in many collections all over the world, it would be interesting to see how often magnesium sulfate is present on objects from this site.

For thecotrichite, it was rationalised that needle-like growth depends on crystal structure with an elongated elementary cell (Wahlberg et al. 2015). However, the case study reported here shows that the crystal morphology, i.e. the aggregates of curved whiskers, do not reliably identify the composition of the material, as this efflorescence comprises a totally different compound. Whisker growth has been demonstrated experimentally for a number of other soluble inorganic salts on ceramic sherds impregnated with concentrated solutions (Borchardt-Ott and Kleber 1959). Whisker formation depends only on the speed of drying, not on the crystal structure; even common table salt, sodium chloride, can form hair. In stone conservation, the model of Zehnder and

Figure 7. *Needle efflorescence and flaking surface of the Attic black-figured belly amphora SH 1369, H 26 cm. Staatliche Antikensammlungen München · Courtesy A. Buhl*

Figure 8. *White efflorescence on a fragment of the Attic black-figured belly amphora SH 1398, H 28 cm. Staatliche Antikensammlungen München · Courtesy A. Buhl*

Figure 9. *White efflorescence on Attic black-figured belly amphora SH 1400, H 32 cm. Staatliche Antikensammlungen München · Courtesy A. Buhl*

Arnold (1989, Figure 2) for the different shapes of efflorescence independent of composition is now widely accepted: whiskers grow only on a salt-laden microporous substrate when the surface is completely dry, otherwise more bulky aggregates are precipitated.

CONCLUSION

The identification of anions in salts on ceramics can tell us about soil logging, e.g. chloride from arid or semi-arid soils, or former de-sintering with acids (Buys and Oakley 2011, 89-90). Various calcium acetates derive from calcareous deposits when objects are exposed to acetic acid, e.g. from storage in wooden cabinets (Eggert, Bette, and Dinnebier, forthcoming). Interestingly however, magnesium salts may also reveal a story: magnesium salts can occur on marine finds, as a result of magnesium-containing replacements comprising gypsum or Sorel's magnesia cement, or hygric contact with migrating salts in archaeologically associated architectural elements. If cleaning with formic acid can be ruled-out, formation of magnesium formate is an indicator of indoor air pollution.

Efflorescence on ceramics comes with a cause, and identifying the efflorescing salts can reveal details of the object's 'biography'. Analysis beyond simple qualitative anion detection may very well be worthwhile. If efflorescence analysis cannot be performed initially, storing samples of the efflorescence for later analysis is recommended. You do not know your future questions; however, your samples may provide the answer!

ACKNOWLEDGEMENTS

We gratefully acknowledge the discussions and information exchange with the Stuttgart BA students Alice Costes, Ana Carolina Diaz, Milad Gholampour, Carina Hauer, Solveig Hoffmann, Julia Kuppel, Patricia Marxer, and Helene Schneider who studied and treated the terracotta figures. We are indebted to Anton Buhl, conservator at Staatliche Antikensammlungen München, who provided information on the Attic vases and samples of the efflorescence.

NOTES

[i] There seems to be no qualitative test for magnesium in the conservation literature. Those in chemistry books, e.g. Feigl 1958, require some experience to perform.

[ii] 'Guller' means rooster in the local dialect.

REFERENCES

Ahlers, U. 2003. Magnesium im Gips. Clausthal-Zellerfeld: Papierflieger.

Auer, A. 2002. Gullerfiguren: Villinger Tonfiguren der Familie Ummenhofer. *Villingen im Wandel der Zeit* 25: 14-18.

Bette, S., G. Eggert, A. Fischer, J. Stelzner, and R.E. Dinnebier. 2018. Characterization of a new efflorescence salt on calcareous historic objects stored in wood cabinets: $Ca_2(CH_3COO)(HCOO)(NO_3)_2 \cdot 4H_2O$. *Corrosion Science* 132: 68-78.

Borchardt-Ott, W. and W. Kleber. 1959. Über das Whisker-Wachstum anorganischer Salzkristalle. *Zeitschrift für Physikalische Chemie* 2110(1): 79-92.

Buhl, A. and F. Knauß. 2007. Hermes und der Delphin: Die folgenreiche Bildergänzung eines Stamnos in München. In *Konservieren oder Restaurieren – Die Restaurierung griechischer Vasen von der Antike bis heute*, eds. M. Bentz and U.A. Kästner, 57-62. München: Beck.

Buhl, A. 2016. Staatiche Antikensammlungen München, personal communication to Gerhard Eggert at Interim meeting of ICOM-CC *Glass and Ceramics* Working Group, Wrocław, Poland, 26 May 2016.

Busca, G., J. Lamotte, J.C. Lavalley, and V. Lorenzelli. 1987. FT-IR study of the adsorption and transformation of formaldehyde on oxide surfaces. *Journal of the American Chemical Society* 109(17): 5197–5202.

Buys, S. and V. Oakley. 2011. *Conservation and restoration of ceramics*. Oxfordshire: Routledge.

Eggert, G., A. Fischer, N. Wahlberg, R. Dinnebier, T. Runčevski, R. Kuiter, M. Schüch, S. Kampe, E. Sulzer, and A. Wollmann. 2016. Efflorescence X? Case solved: $Ca_3(CH_3COO)_3Cl(NO_3)_2 \cdot 6H_2O$! The research history, identification, and crystal structure of thecotrichite. In *Recent advances* *in glass and ceramics conservation 2016*, eds. H. Roemich and L. Fair, 135-144. Spólka: POZKAL Spólka.

Eggert, G., S. Bette, and R.E. Dinnebier. Forthcoming. Curious compounds: The variety of calcium acetate efflorescence on calcareous objects. Manuscript, State Academy of Art and Design, Germany.

Feigl, F. 1958. Chapter III: 35. Magnesium. In *Spot tests in inorganic analysis.* fifth revision, English edition, 223-229. Amsterdam: Elsevier.

Fendt, A. 2012. *Archäologie und Restaurierung: Die Skulpturenergänzungen in der Berliner Antikensammlung des 19. Jahrhunderts*, volume 1, 333-335. Berlin: De Gruyter.

Fischer, A., G. Eggert, R.E. Dinnebier, and T. Runčevski. 2018. When glass and metal corrode together, V: Sodium copper formate. *Studies in Conservation* 63(6): 342-355.

Freyer, D. 2017. Chapter 10: Magnesia building material (Sorel cement): from basics to application. In *Cementitious materials: Composition, properties, application*, ed. H. Pohlmann, 311-331. Berlin and Boston: de Gruyter.

Istas, Y. 2011. *Zizenhausener Terrakotten. Die Sammlung des Stadtmuseums Stockach, Katalog zur Ausstellung Stockach, Stadtmuseum im Alten Forstamt* (5.07.-5.11.2011). Konstanz: werk zwei Print + Medien.

Lucas, G. 2003. The special features of high temperature gypsum as building material. *ZKG International* 56: 54-65.

Lullies, R. ed. 1939. *Corpus vasorum antiquorum. Deutschland, volume 3. München, Museum Antiker Kleinkunst, volume 1.* München: C.H. Beck.

Maravelaki-Kalaitzaki, P. and G. Moraitou. 1999. Sorel's cement mortars: Decay susceptibility and effect on Pentelic marble. *Cement and Concrete Research* 29: 1929–1935.

Odegaard, N., S. Carroll, and W.S. Zimmt. 2000. *Material characterization tests for objects of art and archaeology.* London: Archetype.

Peng, X.D. and M.A. Barteau. 1989. Adsorption of formaldehyde on model magnesia surfaces: Evidence for the Cannizzaro reaction. *Langmuir* 5(4): 1051–1056.

Pradell, T., M. Vendrell, W.E. Krumbein, and M. Picon. 1996. Altérations de céramiques en milieu marin: les amphores de l'épave romaine de la Madrague de Giens (Var). *Revue d'Archéométrie* 20: 47-56.

Scott, D.A. and G. Eggert. 2009. *Iron and steel in art: Corrosion, colorants, conservation*. London: Archetype.

Sorel, S. 1855. Procédé pour la formation d'un ciment très-solide par l'action d'un chlorure sur l'oxyde de zinc. *Comptes rendus hebdomadaires des séances de l'Académie des sciences* 41: 784-785.

Sorel, S. 1867. Sur un nouveau ciment magnésien. *Comptes rendus hebdomadaires des séances de l'Académie des sciences* 65: 102-104.

Steiger, M., K. Linnow, D. Ehrhardt, and M. Rohde. 2011. Decomposition reactions of magnesium sulfate hydrates and phase equilibria in the $MgSO_4$-H_2O and Na^+-Mg^{2+}-Cl^--SO_4^{2-}-H_2O systems with implications for Mars. *Geochimica et Cosmochimica Acta* 75(12): 3600-3626.

Tennent, N.H., L. Calcutt, T.P. Oliveira, M.W. Overhoff, S.R.M. Pereira, K.E. van Lookeren Campagne. 2014. The evaluation of zinc hydroxychloride cement pastes for the conservation of damaged tiles. In *ICOM-CC 17th Triennial Conference Preprints, Melbourne, 15–19 September 2014*, ed. J. Bridgland, article 0503, 7 pages. Paris: International Council of Museums.

Thornton, J. 1998. A brief history and review of the early practice and materials of gap-filling in the west. *Journal of the American Institute for Conservation* 37(1): 3-22.

Wahlberg, N., T. Runčevski, R.E. Dinnebier, A. Fischer, G. Eggert, and B.B. Iversen. 2015. Crystal structure of thecotrichite, an efflorescent salt on calcareous objects stored in wooden cabinets. *Crystal Growth and Design* 15(6): 2795–2800.

Zehnder, K. and A. Arnold. 1984. Stone damage due to formate salts. *Studies in Conservation* 29(1): 32-34.

Zehnder, K. and A. Arnold. 1989. Crystal growth in salt efflorescence. *Journal of Crystal Growth* 97: 513—521.