# The variety of calcium bearing efflorescence phases - An explanation by crystal chemistry

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Cultural heritage objects are affected by various corrosion processes during decades and centuries of storage in museums and collections. Atmospheric gases like $CO_2$, moisture or - as wood emits significant amounts of formic and acetic acid[1] - the storage furniture itself can induce corrosion. Calcareous heritage objects like historic Mollusca shells[2], eggs[3], ancient pottery (Figure 1, a) or marble reliefs (Figure 1, c, d) are very sensitive to acetic and formic acid vapours. The corrosion process leads to the formation of efflorescence crystals sometimes crystallizing in pores and cracks, which can cause severe damage to the artifacts. This phenomenon has been known as "Byne's disease" since the end of the 19$^{th}$ century.[4] Both, simple salts like $Ca(CH_3COO)_2{\cdot}H_2O$[5] or $Ca(CH_3COO)_2{\cdot}½H_2O$[6] and complex compounds like calclacite ($Ca(CH_3COO)Cl{\cdot}5H_2O$)[7] or thecotrichite ($Ca_3(CH_3COO)_3Cl(NO_3)_2{\cdot}6H_2O$)[8-9] were found as corrosion phases on calcareous historic objects. Many of these efflorescence phases, however, still remain poorly characterized due to their microcrystalline character and the occurrence of polyphase mixtures.

Our work focuses on the characterization of unknown or hitherto poorly characterized efflorescence phases found on herriatge objects. As the amount of substance that can be removed from the artifacts is usually very small, we also describe the synthesis of the corrosion phases by model experiments. In this study we present the characterization and structure elucidation of complex efflorescence salts like $Ca_2(CH_3COO)(HCOO)(NO_3)_2{\cdot}4H_2O$[10], $Ca(CH_3COO)(HCOO){\cdot}2H_2O$ and $Ca_3(CH_3COO)_4(HCOO)_2{\cdot}4H_2O$[11] that were found on ancient amphorae (Figure 1, a) or historic birds eggs[5] and seemingly simple corrosion phases like $Ca(CH_3COO)_2{\cdot}½H_2O$[12] which crystallizes on marble reliefs (Figure 1, c, d) or ceramics[6]. A systematic structural investigation of these efflorescence phases revealed calcium carboxylate zig-zag chains (Figure 1, b) as the common structural motif, which shows the crucial role of the carboxylic acids in the corrosion processes and explains the great chemical variety of these compounds. The seemingly simple $Ca(CH_3COO)_2{\cdot}½H_2O$ was found to crystallize in a 11794.5(3) Å$^3$ unit cell with a triple helix motif (Figure 1, e) analogous to the collagen proteins.

In summary, the investigations on corrosion phases found on cultural heritage objects led to the discovery of many hitherto unknown or only poorly characterized solid phases with complex crystal structures. In addition, global structural motifs that were revealed in these studies indicate that a lot more compounds are to be discovered.

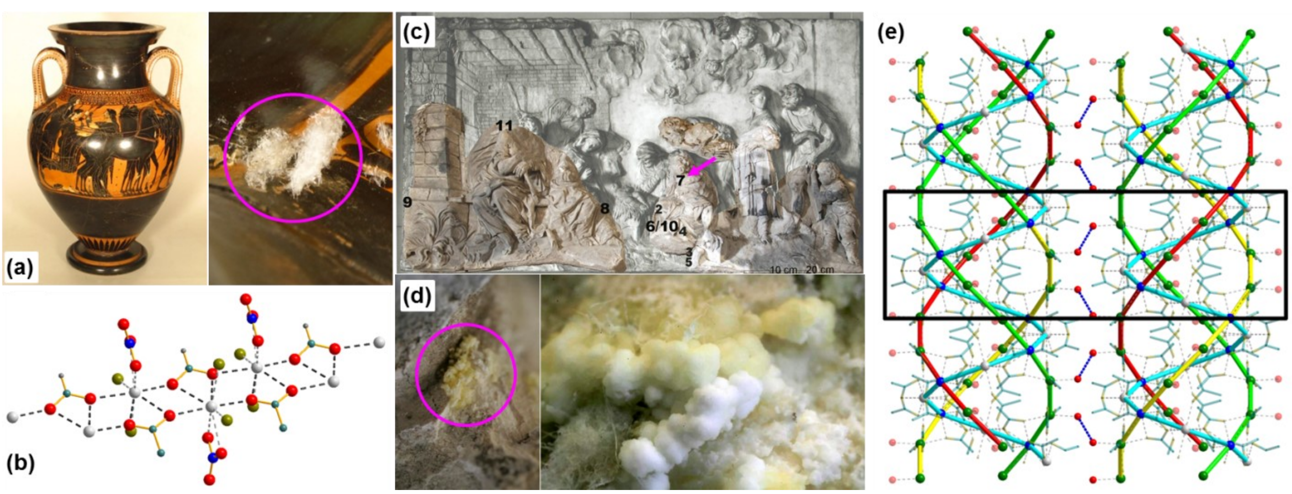


**Figure 1.** Attic black figured amphora from the Antikensammlung Munich with a white efflorescence phase on its surface ©Anton Buhl; (b) excerpt of the crystal structure of the efflorescence phase $Ca_2(CH_3COO)(HCOO)(NO_3)_2{\cdot}4H_2O$; (c) Fragmented relief 'Adoration of the Shepherds' by G. Torretti, (d) the relief exhibits efflorescence phases ©Rathgen Forschungslabor, Staatliche Museen zu Berlin – Preußischer Kulturbesitz; (e) excerpt of the crystal structure of the efflorescence phase $Ca(CH_3COO)_2{\cdot}½H_2O$ exhibiting a triple helix motif.

1. Gibson, L. T.; Watt, C. M., Acetic and formic acids emitted from wood samples and their effect on selected materials in museum environments. *Corrosion Science* **2010,** *52* (1), 172-178.
2. Tennent, N. H.; Baird, T., The deterioration of Mollusca collections: identification of shell efflorescence. *Stud. Conserv.* **1985,** *30* (2), 73-85.
3. Bette, S.; Mueller, M. X.; Eggert, G.; Schleid, T.; Dinnebier, R. E., Efflorescence on calcareous objects in museums: crystallisation, phase characterisation and crystal structures of calcium acetate formate phases. *Dalton Trans.* **2019,** *48*, 16062-16073.
4. Byne, L. F. G., The corrosion of shells in cabinets. *Journal of Conchology* **1899,** *9*, 172-178.
5. Tennent, N. H.; Baird, T., The deterioration of Mollusca collections: identification of shell efflorescence. *Studies in Conservation* **1985,** *30* (2), 73-85.
6. Boccia Paterakis, A.; Steiger, M., Salt efflorescence on pottery in the Athenian Agora: A closer look. *Studies in Conservation* **2015,** *60* (3), 172-184.
7. Giuseppetti, G.; Tadini, C.; Ungaretti, L., La struttura cristallina della calclacite/ Crystalline structure of a triclinic phase of the compound corresponding to calclacite, Ca(CH3COO)Cl.5H2O. *Periodico di Mineralogia* **1972,** *41*, 9-21.
8 Gibson, L. T.; Cooksey, B. G.; Littlejohn, D.; Linnow, K.; Steiger, M.; Tennent, N. H., The Mode of Formation of Thecotrichite, a Widespread Calcium Acetate Chloride Nitrate Efflorescence. *Studies in Conservation* **2005,** *50* (4), 284-294.
9. Wahlberg, N.; Runčevski, T.; Dinnebier, R. E.; Fischer, A.; Eggert, G.; Iversen, B. B., Crystal Structure of Thecotrichite, an Efflorescent Salt on Calcareous Objects Stored in Wooden Cabinets. *Crystal Growth & Design* **2015,** *15* (6), 2795-2800.
10. Bette, S.; Eggert, G.; Fischer, A.; Stelzner, J.; Dinnebier, R. E., Characterization of a new efflorescence salt on calcareous historic objects stored in wood cabinets: Ca 2 (CH 3 COO)(HCOO)(NO 3 ) 2 ·4H 2 O. *Corrosion Science* **2018,** *132*, 68-78.
11. Bette, S.; Müller, M. X.; Eggert, G.; Schleid, T.; Dinnebier, R. E., Efflorescence on calcareous objects in museums: crystallisation, phase characterisation and crystal structures of calcium acetate formate phases. *Dalton Transactions* **2019,** *48* (42), 16062-16073.
12. Bette, S.; Stelzner, J.; Eggert, G.; Schleid, T.; Matveeva, G.; Kolb, U.; Dinnebier, R. E., Corrosion of heritage objects: collagen-like triple helix found in the calcium acetate hemihydrate crystal structure. *Angewandte Chemie International Edition* **2020**.


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