Crystallography in Art and Conservation - a Synergy Story

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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. The artifact can also promote the degradation, especially when it exhibits a metal-glass contact zone. Historic glasses are chemically not stable. When an aqueous surface film is formed by moisture, the glass partially deteriorates yielding an alkaline solution that leads to severe corrosion of metals, which is called *glass induced metal corrosion*.[2] Due to the microcrystalline and multiphase character of the corrosion phases, their characterization is challenging.[3] Hence reliable reference data for the phase identification are scarce and in many cases the chemical composition of the corrosion products is unknown, but these data are essential in order to develop suitable conservation strategies for historic objects.

In the first example we present the investigation of the corrosion phase "Zinc C" found on various historic brass objects in the metal-glass contact zone (Figure 1, a, b). By an *ab initio* structure determination from X-ray powder diffraction (XRPD) data supported by complementary spectroscopic analyses the phase composition could be revealed as $Zn_4Cu_3(Zn_{1-x}Cu_x)_6(HCOO)_6(OH)_{18}\cdot 6(H_2O)$.[4] The occupational disorder between zinc and copper (Figure 1, c, green polyhedra) explains the variable metals ratio and the spread of this corrosion phase among various objects from different collections. Metal corrosion was also conducted intentionally in order to produce pigments like verdigris (Figure 1, d, e)[5], by corrosion of copper metal with acetic acid. As this procedure leads to multiphase mixture, we synthesized distinct verdigris phases in aqueous solution and characterized them (Figure 1, f).[6-8]

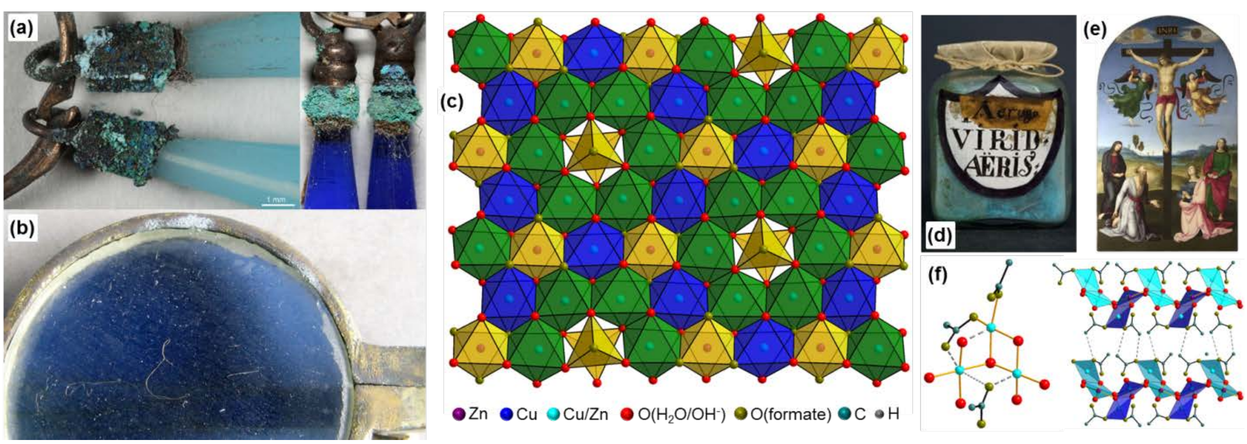

Figure 1. Historic brass objects exhibiting severe corrosion in the metal-glass contact zone: (a) Earrings from the Hamburg museum, (b) Richardson spectacles 19th century from the Basel Historic Museum; (c) excerpt of the crystal structure of the corrosion phase $Zn_4Cu_3(Zn_{1-x}Cu_x)_6(HCOO)_6(OH)_{18}\cdot 6(H_2O)$; (d) historic verdigris pigment vessel, (e) "The Mond Crucification" by Raphael ca. 1502/03 ©National Gallery London, (f) excerpt from the crystal structures of the verdigris phases $1Cu(CH_3COO)_2\cdot 2Cu(OH)_2\cdot 0H_2O$ and $2Cu(CH_3COO)_2\cdot 1Cu(OH)_2\cdot 5H_2O$.

Calcareous heritage objects like historic Mollusca shells[9], eggs[10], ancient pottery (Figure 2, a) or marble reliefs (Figure 2, 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. A systematic structural investigation of these efflorescence phases revealed calcium carboxylate zig-zag chains (Figure 2, 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.[11]

In summary, the investigations on corrosion phases found on cultural heritage objects led to the discovery of many hitherto unknown compounds with complex crystal structures. One of the most striking examples is the seemingly simple $Ca(CH_3COO)_2 \cdot ½H_2O$, that crystallizes in a 11794.5(3) Å³ unit cell with a triple helix motif (Figure 2, e) analogous to the collagen proteins.[12] In addition, global structural motifs that were revealed in these studies indicate that a lot of more compounds are to be discovered.

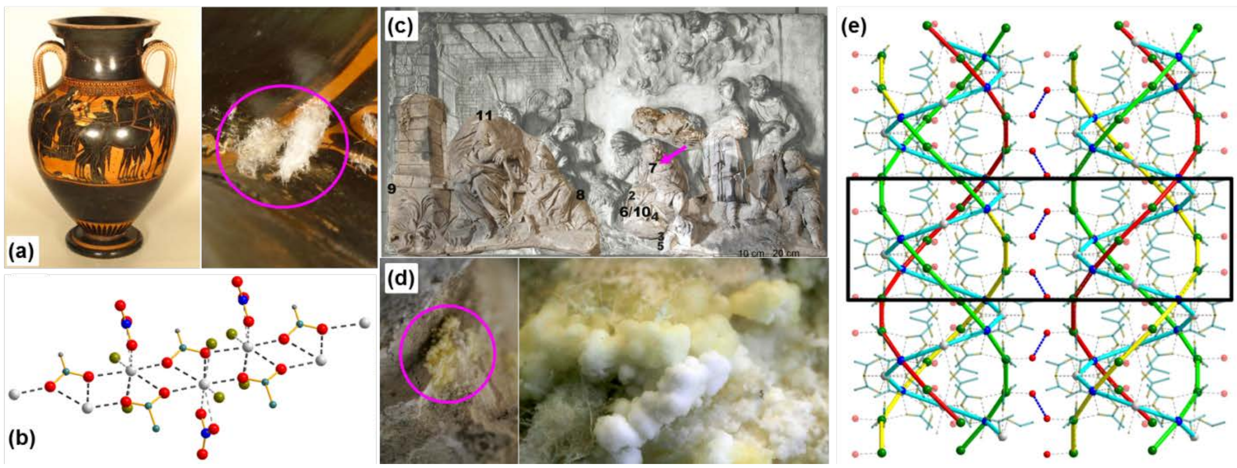

Figure 2. Attic black figured amphora from the Antikensammlung Munich with a white efflorescence phase on its surface ©Anton Buhl; (b) excerpt of the crystal structure of the efflorescence phase $Ca_2(CH_3COO)(HCOO)(NO_3)_2 \cdot 4H_2O$; (c) Fragmented relief 'Adoration of the Shepherds' by G. Torretti, (d) the relief exhibits efflorescence phases ©Rathgen Forschungslabor, Staatliche Museen zu Berlin – Preußischer Kulturbesitz; (e) excerpt of the crystal structure of the efflorescence phase $Ca(CH_3COO)_2 \cdot 0.5H_2O$ exhibiting a triple helix motif.

References

1. L. T. Gibson, et al., *Corros. Sci.*, **2010**, *52*, 172-178.
2. G. Eggert, *Corr. Eng. Sci. Techn.*, **2010**, *45*, 414-419.
3. S. Bette, et al., *Inorg. Chem.*, **2017**, *56*, 5762-5770.
4. S. Bette, et al., *Eur. J. Inorg. Chem.*, **2019**, *2019*, 920-927.
5. D. A. Scott, et al., *Rev. Conserv.*, **2001**, *2*, 73-91.
6. S. Bette, et al., *Dalton Trans.*, **2017**, *46*, 14847–14858.
7. S. Bette, et al., *Dalton Trans.*, **2018**, *47*, 8209-8220.
8. S. Bette, et al., *Z. Anorg. Allg. Chem.*, **2019**, *645*, 988-997.
9. N. H. Tennent, et al., *Stud. Conserv.*, **1985**, *30*, 73-85.
10. S. Bette, et al., *Dalton Trans.*, **2019**, *48*, 16062-16073.
11. S. Bette, et al., *Corros. Sci.*, **2018**, *132*, 68-78.
12. S. Bette, et al., *Angew. Chem., Int. Ed.*, **2020**, *submitted for publication*.