

# Crystal structure determination of corrosion products on heritage objects

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Heritage objects, i.e. historic art- and craftwork, jewelry, glazed tiles and pigments are exposed to chemical aggression during the exposure to air moisture and acidic pollutant gases or their precursors (e.g. formaldehyde, H<sub>2</sub>CO) over long periods of time. For example considerable amounts of acetic acid vapor are emitted from wooden (especially oak) storage cabinets and display cases. Corrosive media also evolve during the degradation of historic glasses, which are not completely stable. During the exposure to air moisture alkaline surface films are formed by ion exchange with alkali metal ions from the glass network. This provides corrosive media for metals at the metal-glass contact areas and leads to “*glass-induced metal-corrosion on museum exhibits*” (*GIMME*) that recently has been shown to be quite common (1). The corrosion processes cause veritable surface damage on heritage objects and the corrosion products appear as microcrystalline efflorescent salts.

The poor crystallinity of the corrosion products and the occurrence of complex multiphase mixtures hamper a detailed characterization. Hence, the chemical compositions as well as the crystal structures of most solid phases formed during the corrosion process are unknown. Profound knowledge of crystal structures is crucial for conservation and heritage science as it is the basis for qualitative and quantitative phase analysis by X-ray powder diffraction, which provides a efficient way to monitor corrosion processes and for diagnosis of the degradation state of historic art- and craftwork.

The presented work focuses on the crystal structure determination from X-ray powder diffraction data of corrosion products on heritage objects from various museums and collections. Selected solid phases were also obtained as pure substances for detailed characterization by purposive chemical synthesis. In detail, the following crystal structures are presented: thecotrichite, Ca<sub>3</sub>(CH<sub>3</sub>COO)<sub>3</sub>Cl(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, an efflorescent salt occurring on surfaces of porous calcareous objects stored in wooden cabinets (2); Cu<sub>4</sub>Na<sub>4</sub>O(HCOO)<sub>8</sub>(H<sub>2</sub>O)<sub>4</sub>(OH)<sub>2</sub>, a metal-organic framework formed on a series of antique artworks by a glass induced metal corrosion process (3), (4); K(OH)·2PbCO<sub>3</sub>, a layered carbonate belonging to a M<sup>n+</sup>(OH)<sub>n</sub>·2PbCO<sub>3</sub> (with n = 1,2) structure family formed on the lid mounting of a 200 years old beer jug (5) and various copper acetate hydroxide hydrates, (xCu(CH<sub>3</sub>COO)<sub>2</sub>·yCu(OH)<sub>2</sub>·zH<sub>2</sub>O), “*green span*” formed by copper corrosion and also used as pigments.

## References

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