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Textural re-equilibration during marble replacement by Ca-oxalate

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One treatment proposed to preserve Ca-carbonate containing building materials draws on the natural action of lichens etc., which have been found to produce protective layers of Ca-oxalate crystals on marble and limestone surfaces (e.g., Del Monte el al 1987). To study the Ca-oxalates produced during these types of reactions we have conducted abiotic experiments on Carrara marble cubes in oxalic acid concentrations between 1 to 500 mM in Teflon-lined steel autoclaves at temperatures between 20 and 90 °C.

Scanning electron microscopy (SEM) investigations of the replacement products show that above 10 mM oxalic acid the reaction rim is composed of two distinct layers. These layers have very different textural characteristics. The outer layer consists of large (up to 10 μm), imperfectly packed crystals whereas the inner layer comprises submicron-sized, rounded grains with minimal interconnected porosity. Characterization using Raman microscopy demonstrates that both of these layers are composed of the monohydrate Ca-oxalate mineral whewellite ($CaC_2H_4.H_2O$).

Secondary electron images obtained during the SEM study and the constant width of the inner rim during longer duration experiments implies that the outer layer develops from the inner whewellite crystals via a textural re-equilibration mechanism. Determination of differences in the fraction of the ^{18}O incorporated into the different whewellite layers during experiments with an ^{18}O-enriched solution demonstrates that the textural re-equilibration is solution mediated. In depth analysis of the Raman spectra also indicates that the inner rim crystallites have a lower crystallinity compared to the larger outer rim crystals, providing a potential driving force for the textural re-equilibration.

[1] Del Monte et al. 1987 *Sci. Total. Environ.* 17-39.