Mechanisms of Calcite Replacement by Whewellite: Implications for the Conservation of Building Stone

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INTRODUCTION.

Calcium oxalates are commonly found in the alteration crusts of stone monuments. From a macroscopic point of view, these layers have a smooth, uniform appearance, although a more detailed observation reveals a porous and irregular surface. The oxalate patinas cover the original surfaces reproducing fine details such as the signs of the instruments used for their carving (Del Monte et al., 1987). Observations of natural patinas on calcitic stone surfaces seem to suggest that these patinas play a preservative role on marbles and limestones; calcium oxalates replace calcite in the stone surface producing less reactive layers towards chemical attack due to its lower solubility (e.g. Del Monte and Sabbioni, 1983; Del Monte et al, 1987). Thus, this natural process could be used in the design of conservation treatments that mimic the natural process taking place in the environment (Doherty et al., 2007). However, the lack of an in-depth mechanistic knowledge of the calcium carbonate-calcium oxalate transformation has limited the development of effective conservation protocols for calcitic building stones. Knowledge of the factors that control texture and porosity developed during the replacement and the adhesion of the product layer to the substrate seems critical before considering the application of such treatments in real cases. It is the aim of this work to investigate the mechanism of the replacement of calcite by whewellite ($CaC_2O_4·H_2O$), including the possible epitaxial relationships between the substrate and the product. This has been done on experimental samples using a combination of Scanning Electron Microscopy (SEM) and bidimensional X-Ray Diffraction (2D-XRD).

METHODOLOGY.

Replacement reactions in Teflon® reactors.

The replacement experiments were performed at room temperature (23 ±1 °C) in sealed Teflon® reactors. Two types of reactors were used with internal volumes of 50 and 250 mL, respectively. Fragments of optical quality Iceland Spar single crystals (ca. 0.020 ± 0.005 mg) were weighed and placed into the reactors before the reaction solutions were added. 50 mL and 250 mL of reaction solutions were introduced into the Teflon reactors. After the reaction, the reactors were opened and the solids were rinsed with ethanol and dried overnight at 60 ºC. Experiments were performed at pH 3 starting from aqueous oxalate-bearing solutions with oxalate concentration of 1 mM and with reaction times ranging from 1 day to 2 weeks.

Textural and two-dimensional X-Ray diffraction analysis of reacted solids.

A JEOL 6300F Field Emission Scanning Electron Microscope (FESEM) was used for surface morphology and texture examinations. Solids were carbon-coated and examined in the FESEM in both secondary electron and backscattered electron mode. 2D-XRD analyses were performed to establish the three-dimensional orientation of calcite and Ca-oxalate overgrowth using an X-ray single crystal diffractometer equipped with a CCD area detector (D8 SMART APEX, Bruker, Germany). Pole densities/figures for the main calcite and whewellite reflections were calculated from the registered frames using XRD2DScan software (Rodriguez-Navarro, 2006).

RESULTS AND DISCUSSION.

SEM examinations of surfaces and cross-sections of reacted samples show that calcite is progressively replaced by calcium oxalate (whewellite, as confirmed by 2D-XRD analysis). The replacement product is polycrystalline. Figure 1 shows the typical morphologies of these newly formed crystals growing on the calcite surface during the early precipitation stages.

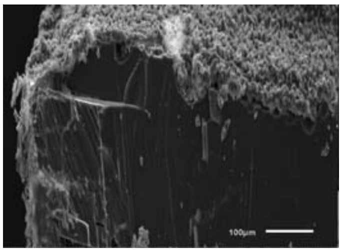

fig 1. *SEM secondary electron image of a calcite crystal partially replaced by whewellite. The whewellite crystals are clearly oriented on the calcite surfaces, and dissolution of the parent calcite is seen by the formation of deep etch pits.*

The product crystals appear clearly oriented on the calcite substrate, forming a thick coating (Fig 1). From the analysis of the pole figures obtained from the bidimensional XRD analysis and calculated for the main calcite and whewellite reflections (Figure 2), it can be concluded that whewellite crystals precipitated onto Iceland Spar crystals with their {100} and {010} planes parallel to {10 :4} calcite faces. Epitaxial relationships will be further developed in the next section. Dissolution of the parent phase is seen by the development of deep etch pits on the substrate surface underlying the newly formed phase. SEM images of cross-sections show that partially replaced crystals retain the external dimensions and crystallographic - characteristics of the initial calcite, i.e. calcium oxalate pseudomorphically replaces calcite. The replacement rim showed limited, apparently non-connected porosity, with most of the empty spaces observed in the reaction product related to the formation and widening of fractures.

palabras clave: Calcita, Whewellita, Reemplazamiento, Piedra ornamental.	*key words:* Calcite, Whewellite, Replacement, Building stone.

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These fractures are frequently observed both within the replacement rim and within the still unaltered calcite crystals (Fig. 3).

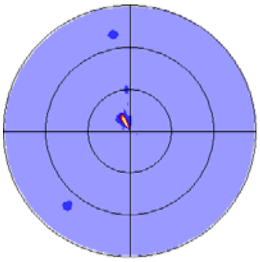

fig 2. *(010) pole figure from whewellite showing a maxima that indicates that these planes are oriented approximately parallel to the (104) calcite plane.*

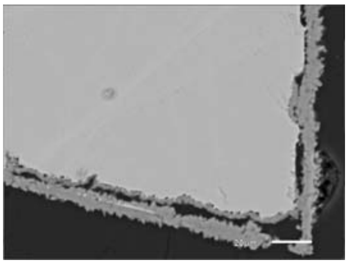

fig 3. *SEM-backscattered electron image showing a cross section of a calcite crystal partially replaced by whewellite.*

With increasing reaction time, the replacement product detaches from the calcite surface and breaks up into fine particles. The fragility of the reaction product may be the combined result of its low adhesion to the substrate and the presence of cracks. Fracture formation and the observed limited porosity may be the consequence of a positive volume change in the replacement reaction, most probably due to the higher molar volume of whewellite compared to calcite. These fractures are critical in the progress of the replacement reaction as they provide additional pathways (to porosity) for the solution and expose fresh, unreacted calcite surfaces that react rapidly with the surrounding solution. Nevertheless, the formation of cracks must be avoided if this methodology is to be used as a treatment for the preservation of building stones. Because the change in volume occurring during a replacement reaction is also related with the relative solubility of the parent and product in the reaction fluid, we are currently testing different reaction parameters (pH and oxalate concentration) in order to obtain a coherent replacement layer. The textural evidence described above clearly demonstrates that the replacement of calcite by whewellite is a pseudomorphic interface-coupled dissolution-reprecipitation process (Putnis, 2002). As shown by Xia et al. (2009), the coupling between the dissolution and precipitation in replacement reactions is achieved by a combination of substrate-assisted nucleation and solution chemistry at the reaction interface. The fast dissolution of calcite at the low pH conditions of our experiments raises the activity of calcium in the solution at the interface with the solid, increasing its supersaturation degree with respect to whewellite and therefore enhancing its nucleation. Furthermore, the structural similarities between calcite and whewellite seem to promote epitaxial nucleation of the latter on calcite surfaces, decreasing the energy barrier for whewellite nucleation. Epitaxial relationships and structural matching between these phases will be explored in the next section. Our observations point towards a "Volmer-Weber" mechanism of epitaxial growth, in which the overgrowth precipitates as thick three-dimensional crystals and that typically occurs when there is a weak adhesion between substrate and overgrowth.

Epitaxial relationships.

For (010) whewellite and $(10\bar{1}4)$ calcite faces a very good matching was observed along $[101]_{COM}$ and $[010]_{Cc}$ (misfit -0.05 %) and along $[100]_{COM}$ and $[\bar{4}41]_{Cc}$ (misfit of 4.26 %), the angular misfit between both directions being -5.31 °. These misfit values are clearly within the limits required for epitaxial nucleation from solution. Similarly, a good structural matching was found along whewellite [001] and calcite [010] PBCs (misfit = -1.35 %) in $(100)_{COM}$ and $(10\bar{1}4)_{Cc}$, but it was difficult to find simultaneous matching along other directions in these faces. Overall, these data suggest a crystallographic control on the overgrowth of whewellite onto calcite, with two possible epitaxial orientations, in accordance with the XRD analysis of the overgrowth: $(010)_{COM} \parallel (10\bar{1}4)_{Cc}$, $[100]_{COM} \parallel [\bar{4}41]_{Cc}$, and $(100)_{COM} \parallel (10\bar{1}4)_{Cc}$, $[001]_{COM} \parallel [010]_{Cc}$. These orientations are in agreement with those most frequently observed in the SEM images of partially replaced crystals.

CONCLUSIONS.

The interaction between oxalate-bearing solutions and calcite cleavage surfaces follows the typical pattern of a pseudomorphic, interface-coupled dissolution-reprecipitation reaction, with the dissolution of the substrate and the subsequent precipitation of whewellite crystals, which grow epitaxially on the $(10\bar{1}4)$ calcite surface. There are two orientations of the whewellite crystals on the calcite surface: $(010)_{COM} \parallel (10\bar{1}4)_{Cc}$, $[100]_{COM} \parallel [\bar{4}41]_{Cc}$, and $(100)_{COM} \parallel (10\bar{1}4)_{Cc}$, $[001]_{COM} \parallel [010]_{Cc}$. The coupling between the dissolution and precipitation reactions in replacement processes is a consequence of substrate-assisted epitaxial nucleation and solution chemistry at the reaction interface. Under the conditions of our experiments, formation of cracks and subsequent detachment of the replacement rim was observed, most probably due to the increase in volume occurring upon the reaction. Changes in the chemistry of the replacement fluid can modify the relative solubility of the parent crystal and the product and lead to the eventual development of a porous, coherent interface. The results of this research are expected to represent a source of information for the design of protective treatments for calcitic stones based on the precipitation of calcium oxalate upon calcite dissolution, and highlight the reaction parameters that must be optimize before such a treatment can be effectively implemented.

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