Replacement of anhydrite by hydroxyapatite: kinetic and textural characteristics

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Interface-coupled dissolution-precipitation (ICDP) reactions lead to the pseudomorphic replacement of minerals in a wide range of geological settings, exerting a significant impact in geochemical cycles (Putnis 2002). ICDP reactions play a major role in the diagenetic evolution of sedimentary rocks, specially of limestones and evaporites. Recent experimental works have studied ICDP reactions that lead to the formation of CaCO₃ pseudomorphs after anhydrite (CaSO₄), upon interaction of the latter phase with carbonated aqueous solutions. These pseudomorphs are highly porous polycrystalline aggregates that mainly consist of calcite (Roncal-Herrero et al. 2018; Altree-Williams et al. 2017). The formation of a large volume of interconnected microporosity that balances the molar volume loss associated to the anhydrite-calcite transformation as well as the specific arrangement of this microporosity, influenced by the existence of epitactic relationships between anhydrite and calcite, facilitate the progress of the ICDP reaction.

Here, we study the ICDP reaction that leads to the formation of hydroxyapatite (Ca₅(PO₄)₃(OH)) pseudomorphs after the interaction of anhydrite with phosphate-bearing aqueous solutions at temperatures 90 to 180°C during times that range from one hour to five weeks. The X-ray diffraction Rietveld analysis of the transformed samples indicates that the kinetics of the pseudomorphic transformation of anhydrite into hydroxyapatite strongly depends on temperature. Thus, while at 180°C a 100% transformation yield is attained in few hours, it takes five weeks of interaction at 90°C. Scanning Electron Microscopy imagining of transformed samples shows the very good preservation of both, the original external shape and microtopographic features of anhydrite crystals. On cross-cut sections of partially replaced by hydroxyapatite anhydrite crystals we observe that the transformation advances from the surface inwards, with sharp separating the by replaced layer from the unreacted anhydrite core. Furthermore, this replaced layer is structured into a compact ~ 50 µm thick outer rim, which consists of coalescent small (~ 5 µm) hydroxyapatite crystals, and a progressively thickening inner region formed by hydroxyapatite columnar crystals in a stockade-like arrangement. This latter region is highly porous. We interpret these results taking into consideration the differences in solubility and molar volume between anhydrite and hydroxyapatite as well as the similarities/differences between the crystal structures of these phases. By comparing the characteristics of different ICDP reactions that involve anhydrite in sedimentary basins we derive implications about the diagenetic evolution of calcium sulphate evaporites.
