

Kinetic of the replacement reaction of anhydrite by calcium phosphates

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Interface-coupled dissolution-precipitation (ICDP) reactions are widely common during the diagenesis of sedimentary rocks, namely, limestones and evaporites. In a broad range of diagenetic sceneries, ICPD reactions result in pseudomorphic replacements that often involve carbonate and sulfate minerals, both as primary and secondary phases [1-2]. Phosphate-rich rocks can be found in sedimentary rocks of all ages since the Early Proterozoic. The origin of some of these phosphate-rich rocks has been related to diagenetic processes [3], which brings up the question of whether ICPD reactions involving the interaction between P-rich aqueous solution and mineral phases common in sediments may have played a role in their formation.

Here, we investigate the hydrothermal interaction between anhydrite, a common component of evaporites, and phosphate-rich aqueous solutions during times set between 1 and 72 hours in the temperature regime between 120 and 200°C. The characterization of the reacted samples by X-ray diffraction (XRD), Scanning Electron Microscopy, Infrared and Raman spectroscopies shows anhydrite crystals are partially to totally replaced by mixtures of hydroxyapatite and β -tricalcium phosphate in proportions that vary with time and temperature. The replacement reaction initiates at the surface of the anhydrite crystals and advances inwards, defining a sharp reaction front. The formation of a significant volume of porosity, which balances the molar volume loss associated to the anhydrite into calcium phosphate transformation, guarantees the continuous communication between the phosphate-rich solution and the reaction front, facilitating the progress of the anhydrite dissolution-calcium phosphate precipitation reaction. The good coupling between the rate of both processes explains the pseudomorphic nature of the replacement, which takes place with an almost perfect preservation of the original external shape of the anhydrite crystal all along the ICDP reaction. Finally, we determine anhydrite replaced fractions as a function of reaction time and temperature using XRD Rietveld analysis and apply the rate constant and the time to a given fraction methods to estimate the empirical activation energy E_a (kJ/mol) for the replacement reaction.

[1] Putnis A. (2002): *Mineralogical Magazine* 66.5, 689-208.

[2] Pedrosa E. et al (2017): *American Mineralogist*, 102(1), 126-134.

[3] Bentor, Y. K. (1980) "Phosphorites—the unsolved problems".