



## Crystallographic relationship during hydrothermal conversion of calcitic sea urchin spine into apatite

Pedro Alvarez-Lloret (1), Alejandro B Rodríguez-Navarro (1), Giuseppe Falini (2), Simona Fermani (2), and Miguel Ortega-Huertas (1)

(1) University of Granada, Mineralogy and Petrology, Granada, Spain (pedalv@ugr.es), (2) Dipartimento di Chimica "G. Ciamician", Alma Mater Studiorum Università di Bologna, via Selmi 2, 40126 Bologna, ITALY.

Mineral replacement reactions play a very important role in many natural processes and also have important technological and industrial applications. Mineral replacement occurs at a large scale in the formation of hydrothermal transformation and metamorphic replacement formations (Putnis, 2009). During these replacement reactions, one mineral can be replaced by another with a different composition while preserving the external morphology and microstructural properties (e.g. porosity) of the original material, forming what is known as a pseudomorph. These mineral replacement reactions can take place by an "interface-coupled dissolution precipitation" reaction in which the dissolution rate of a parent phase is related with the precipitation of the product phase (Kasioptas et al., 2010; Xia et al., 2009). We analysed the crystallographic relationships during hydrothermal conversion of a calcitic sea urchin spine into apatite. We identified a pseudomorphic mineral replacement mechanism involving a superficial dissolution of calcite and a subsequent overgrowth of oriented carbonated hydroxylapatite (HA) nanocrystals. Cross-section images of these converted spines show that the dimensions of the HA crystals increase the further they are from the outer surface. This replacement process is favoured by an increase in porosity which enables both fluid and mass to be transported by diffusion, thereby allowing the replacement reaction to progress toward the interior of the spine. These recrystallization reactions take place on the surface of the calcite single crystal which acts as a substrate for the epitaxial nucleation of HA crystals. The epitaxial relationship observed between the parent calcite crystal and the newly formed apatite crystals can be defined as (0001) apatite // (01-18) calcite and [10.0] apatite // [-44.1] calcite. The apatite crystals are related by the three fold axis arising from the trigonal symmetry of the parent calcite crystal. There is therefore a strong structural control which favours the conversion of calcite into apatite. This process co-exists with the formation of apatite crystals which are not structurally related to the calcite crystal and which may precipitate within the porosity of the material. The analysis of crystallographic relationships is a fundamental step towards understanding mineral replacement reactions, which can be used for the synthesis of artificial materials with predefined shapes and microstructural characteristics, a technique that may have interesting technological and industrial applications.

### References:

- Putnis, A. *Rev. Mineral. Geochem.* 2009, 70, 87-124.  
Kasioptas, A.; Geisler, T.; Putnis, C.V.; Perdikouri, C.; Putnis, A. 2010 *J. Cryst. Growth* 312, 2431-2440.  
Xia, F.; Brugger, J.; Ngothai, Y.; O'Neill, B.; Chen, G.; Pring, A. 2009 *Cryst. Growth Des.* 9, 4902-4906.