



Experimental replacement of aragonite by hydroxyapatite

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Hydrothermal treatment of aragonite with $(\text{NH}_4)_2\text{HPO}_4$ solution has been shown to produce hydroxyapatite (HAP) with an overall identical and thus pre-determined morphology (Kasiopas et al, 2008). The preservation of the morphology is an outcome of the pseudomorphic nature of this particular reaction. We have investigated the mechanism of the replacement of aragonite by HAP using single, natural, inorganic aragonite crystals. Isothermal experiments were carried out with small crystals placed and sealed in autoclaves with $(\text{NH}_4)_2\text{HPO}_4$ solution. After the experiments the aragonite crystals are partly replaced by a new phase. X-ray powder diffraction confirmed that the product phase is indeed HAP; however electron microprobe measurements revealed that the HAP is probably non-stoichiometric. Even when completely converted to HAP, scanning electron microscopy showed that the fine-structure of the aragonite has perfectly been retained. It was also observed that the HAP product phase exhibited a high porosity and was separated from the aragonite parent phase by a sharp interface (on the micrometer scale).

The replacement of aragonite by HAP in an aqueous solution can be described in terms of a coupled dissolution-precipitation mechanism that takes place at an inward moving reaction front (Putnis & Putnis, 2007). The porosity in the HAP product phase allows the solution to reach the reaction interface.

In addition, we have performed experiments with $(\text{NH}_4)_2\text{HPO}_4$ solutions prepared with H_2O enriched with 97 at.% ^{18}O . The solutions were pre-heated separately to equilibrate the oxygen isotopes in the solution. Raman spectroscopy of the HAP product was used to identify the different vibration modes in the PO_4^{3-} molecule due to the exchange of ^{16}O with ^{18}O atoms. Apart from the main $\nu_1(\text{PO}_4)$ band located near 962 cm^{-1} , we observed four new bands near 945, 931, 919 and 908 cm^{-1} . We have attributed the generation of these new bands to four different degrees of ^{18}O atomic substitutions in the PO_4^{3-} molecule. The bands that show the highest intensity are those corresponding to three and four ^{18}O atoms substituting for ^{16}O in the PO_4 molecule. A non-equilibrated phosphate solution was also used in the replacement experiments in order to observe the simultaneous processes of replacement and $\text{H}_2^{18}\text{O}-\text{P}^{16}\text{O}_4$ exchange in solution. Differences in the intensity of the four vibration modes offer kinetic information on the replacement mechanism when compared with kinetic data of the $\text{H}_2^{18}\text{O}-\text{P}^{16}\text{O}_4$ exchange reaction obtained from *in situ* Raman investigations (Geisler et al., 2008).

Geisler T., Kasiopas A., Menneken M., Perdikouri C., Putnis A, *Journal of Geochemical Exploration* (2008)

Kasiopas A., Perdikouri C., Putnis C.V., Putnis A, *Mineralogical Magazine* 72, 77-80 (2008)

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