



## Fluid mediated transformation of aragonitic cuttlebone to calcite

C. Perdikouri, A. Kasioptas, and A. Putnis

Institut fuer Mineralogie, University of Muenster, Corrensstrasse 24, 48149, Muenster, Germany (cperd\_01@uni-muenster.de)

The aragonite to calcite transition has been studied extensively over the years because of its wide spectra of applications and of its significant geochemical interest. While studies of kinetics (e.g. Topor et al., 1981), thermodynamics (e.g. Wolf et al., 1996) and behavior of ions such as Sr and Mg (e.g. Yoshioka et al., 1986) have been made there are still unanswered questions regarding this reaction especially in the cases where the effects of fluid composition are considered.

It is well known that when heated in air, aragonite transforms by a solid state reaction to calcite. The aragonite cuttlebone of the *sepia officinalis* that was used for our experiments undergoes a phase transition at  $\sim 370\text{--}390^\circ\text{C}$ , measured by *in situ* heating experiments in a Philips X'pert X-ray powder diffractometer equipped with a HTK 1200 High temperature oven. Successive X-ray scans were taken at isothermal temperatures at  $20^\circ\text{C}$  intervals. A similar temperature range was found by Vongsavat et al. 2006, who studied this transition in *Acropora* corals. It is possible however to promote this transition at considerably lower temperatures by means of a fluid mediated reaction where the replacement takes place by a dissolution-precipitation mechanism (Putnis & Putnis, 2007). We have successfully carried out hydrothermal experiments where cuttlebone has been converted to calcite at  $200^\circ\text{C}$ . Using the PhreeqC program we calculated the required composition of a solution that would be undersaturated with respect to aragonite and saturated with respect to calcite leading to dissolution of the aragonite and to a consequent precipitation of the new calcite phase, similar to the experiments described in an earlier study (Perdikouri et al, 2008). This reaction is not pseudomorphic and results in the destruction of the morphology, presumably due to the molar volume increase. A total transformation of the cuttlebone produced a fine calcite powder.

The cuttlebone exhibits a unique microstructure, made up of interconnected chambers. The aragonite grown during biomineralization of the cuttlebone is interlaced with a  $\beta$ -chitin organic phase that provides the framework for the morphology that is observed. Experiments carried out with the same constant conditions but for different periods of time have revealed the evolution of the transformation to calcite. At shorter reaction times the product was made up of calcite powder and of well preserved aragonite septa, as was confirmed by powder X-ray diffraction. In other words, the vertical pillars appear to react at faster rates than the horizontal septa. It has been reported by Florek et al. 2008 that the septa contain higher quantities of  $\beta$ -chitin. The aim of this study is the investigation of these observations and the determination of the effect of the organic component on the kinetics of the aragonite to calcite transformation.

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