

Atomistic simulation of metal-carbonate cluster formation

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It is now widely recognized that the carbonate mineral constituents of many biomineralized tissues form by a two-stage crystallization process that involves the nucleation and structural reorganization of transient amorphous phases. The extent to which similar crystal growth processes occur *ex vivo* is not yet fully realized; however, they may be prevalent in both natural and engineered environments where fluids can become highly-supersaturated with respect to M (II)CO₃ phases (e.g. soil pore waters, CO₂ sequestration reservoirs etc.). The nature of the amorphous to crystalline transition remains controversial, as both solid state and dissolution / re-precipitation mechanisms have been proposed. Yet, an understanding of the underlying processes driving the structural reorganization is essential to interpretation of compositional signatures that are frequently used as indicators of Earth's climate history.

This study uses molecular dynamics simulations to investigate the nucleation and structural evolution of metal-carbonate clusters in aqueous solution. We examine both CaCO₃, which exhibits extensive polymorphism, and FeCO₃, which does not. Comparison of these two end-member systems provides an opportunity to identify common processes related to the amorphous to crystalline transition, and perhaps discern those that are involved in polymorph selection. Clusters are grown from unbiased simulations of highly concentrated solutions, and in an ion-by-ion fashion using umbrella sampling. We report changes in the cluster hydration state and distribution of ion-pair bonding environments as a function of cluster size and simulation time.

Thermobarometry of Hawaiian spinel peridotite xenoliths

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Mantle peridotite xenoliths found within the rejuvenated stage lavas on the island of O'ahu, Hawaii provide a unique window into the oceanic mantle. These peridotites are thought to represent variably metasomatized fragments of the Pacific lithosphere, while some samples with highly unradiogenic ¹⁸⁷Os/¹⁸⁸Os may be fragments of an ancient recycled oceanic lithosphere that is brought up by the plume [1]. Here we present high precision Ca concentration data on high purity olivine separates from Hawaiian peridotites obtained by standard addition HR-ICP-MS. Together with clinopyroxene (cpx) and orthopyroxene major and trace element data, we attempt to reconstruct the P-T range of the Hawaiian spinel peridotites in order to better constrain the compositional variability of the Hawaiian lithosphere with depth. We use the Ca-in-olivine barometer [2] and the cpx-opx thermometer (T_{BKN})[3]. The Ca distribution between olivine and cpx (D^{Ca}_{ol/cpx}) shows no correlation with calculated equilibration temperatures. It also shows no correlation with other highly incompatible elements (e.g. Sr, Ba, Ce) while the D^{Ce}_{ol/cpx} approaches 0.0005, close to experimental values [4]. These data argues against any disturbance of the olivine Ca contents by post-melting processes and are taken to reflect equilibration at mantle P-T. Pressures calculated for the SLC peridotites show a deeper origin, (up to 32kbar) than the Pali vent peridotites (7 to 15kbar). This is consistent with the presence of deeper garnet pyroxenites found at SLC. Interestingly, the Cr-in-CPX barometer [5], shows an overall similar pressure range as the Ca-in-olivine barometer, even in spite of the Cr-in-CPX barometer not having been calibrated in the spinel stability field. Further work will constrain the relationship between P-T, depletion and isotope systematics in the Hawaiian lithosphere and the processes that lead to its present compositional heterogeneity.

[1] Bizimis *et al.* (2007) *EPSL* **257**, 259–273. [2] Kohler & Brey, (1990) *GCA* **54**, 2375–2388. [3] Brey & Kohler (1990) *J. Petrol.* **31**, 1353–1378. [4] McDade *et al.* (2003) *Phys. Earth Planet. Init.* **139**, 129–147. [5] Nimis & Taylor (1998) *Contributions to Mineralogy & Petrology* **139**, 541–554.