

The influence of mineralization pathway on composition and isotope signatures in calcite

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Chemical proxy models are based upon the assumption that isotopic signatures and concentrations of minor and trace elements reflect equilibrium fractionation processes that occurred during mineralization. This picture is rooted in the fundamental assumptions of BCF crystal growth theory—a thermodynamic-based model that was derived for step growth at very near equilibrium conditions. However, the applicability of these assumptions are being called into question with the realization that many carbonate biominerals form by non-classical processes. Here, mineralization begins with accumulation of amorphous calcium carbonate (ACC) in a localized environment that subsequently transforms to the crystal/organic composites we know as skeletal structures. It is not yet known 1) if the transformation involves classical microscopic dissolution-precipitation or an altogether different type of process and 2) the consequences of this process for composition and isotopic signatures.

This study investigates the influence of the ACC to calcite pathway on the Mg content and isotopic signature of calcites. For low solution levels of Mg/Ca, Mg content is insufficient to inhibit step growth and ACC transforms into crystallites of Mg calcites that exhibit the expected linear fractionation with Mg/Ca of initial solutions (0-20 mol% MgCO₃). In contrast, when initial Mg levels are above the threshold for step growth, ACC transforms to nanoparticle aggregates of very high Mg calcite (30-50 mol% MgCO₃). The Mg content of calcites formed by this process is independent of solution chemistry, without evidence of fractionation. The data suggest mineralization is biased to the alternative pathway when the Mg level in the local environment is too high for significant calcite growth beyond nanoparticle sizes. This pathway is allowed because high levels of supersaturation render thermodynamic barriers to nucleation less significant than the larger kinetic barriers. Thus, the alternative pathway is a consequence of interplays between kinetic and thermodynamic factors.

Parallel experiments used enriched isotope labels (⁴³Ca and ²⁵Mg) to distinguish dissolution-precipitation from direct conversion during the ACC to calcite transformation. When solution Mg/Ca is low calcite assumes the isotopic label of the growth media consistent with a dissolution-precipitation pathway. In contrast, very high Mg calcites that grow from high Mg solutions retain a portion of the ACC isotope signature. This suggests the transformation of high Mg ACC occurs by an alternative pathway that involves a substantial fraction of direct transformation. Collectively our data show that mineralization pathway dramatically affects composition. This type of mechanistic understanding of mineralization processes will be necessary to explain proxy behavior and more accurately reconstruct past environmental conditions.

Constraining dehydration rates during regional metamorphism, Townshend Dam, Vermont, U.S.A.

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Progressive dehydration during regional metamorphism can result in pervasive or channelized fluid flow. Given sufficient fluxes, fluid flow may have profound effects on rheological properties of the rock, bulk rock composition, stable and radiogenic isotope compositions, mineralogy, and the kinetics of mineral reactions. Many published studies have used petrologic and stable isotopic data to constrain time-integrated syn-metamorphic fluid fluxes. Here, an integrated geochronologic and thermodynamic analysis is used to estimate the dehydration rate and flux during metamorphism of a pelitic schist from Townshend Dam, Vermont.

Microdrilling based on Mn growth zoning, from large (1-3 cm) garnets from one sample, provides information on the rate and duration of garnet growth. Three to six concentric zones (depending on crystal size) of garnet, were sampled for ID-TIMS Sm-Nd geochronology. A partial dissolution procedure was utilized in order to remove inclusion phases from garnet fractions which were analyzed as NdO⁺ with Ta₂O₅ activation. This yielded clean garnet, with ¹⁴⁷Sm/¹⁴⁴Nd ≤ 3.18. Garnet-matrix isochron ages of individual garnet zones have been previously reported [1], with the duration of garnet growth across the sample ranging from 5.5 to 11.7 Ma, and an average duration of 7.8 Ma.

Garnet growth may be linked directly to dehydration during regional metamorphism. Thermodynamic analysis of this reaction allows calculation of the stoichiometric ratio between garnet formation and water release. The garnet:water ratio depends on the growth reaction, and the P-T path during growth. In our sample, the average water:garnet molar production ratio is 3.3:1 over the duration of garnet growth. Early garnet growth involves the consumption of chlorite, resulting in initially higher water:garnet ratio. Both thermodynamic and textural analysis have determined that ~ 5.5 vol% garnet was formed during the age span stated above. This equates to a release of 1 wt% (or 2.8 vol%) water during garnet formation, similar to water volumes estimated in previous studies from southeastern Vermont [2]. Using the duration of growth (5.5 to 11.7 Ma), a time-averaged dehydration rate of 1.3 to 2.8 x 10⁻¹⁰ moles of water/ cm³ of rock/ year can be calculated.

[1] Gatewood et al. (2011) AGU Fall Mtg., Abstract #V13G-05.

[2] Kohn, M.J. & Valley, J.W. (1994) *GCA* **58**, 5551-5566.