

Influence of kinetics on the oxygen isotope composition of calcite

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Paleotemperature reconstructions rely on knowledge of the equilibrium fractionation of oxygen isotopes between aqueous solution and calcium carbonate. Although oxygen isotope separation is expected on theoretical grounds, the temperature-dependence remains uncertain because other factors, such as slow exchange of isotopes between dissolved CO₂-species and water, can obscure the temperature signal. This is problematic for crystal growth experiments on laboratory timescales and for interpreting the oxygen isotope composition of crystals formed in natural settings.

We present results from experiments in which inorganic calcite is precipitated in the presence of 0.25 μM dissolved bovine carbonic anhydrase (CA). The presence of dissolved CA accelerates oxygen isotope equilibration between the dissolved carbon species CO₂, H₂CO₃, HCO₃⁻, CO₃²⁻ and water, thereby eliminating this source of isotopic disequilibrium during calcite growth. The experimental results allow us to isolate kinetic oxygen isotope effects occurring at the calcite-water interface during mineral growth.

The oxygen isotope composition of precipitated calcite is lighter than dissolved HCO₃⁻ yet heavier than CO₃²⁻ at pH = 8.3. ¹⁸O uptake into calcite varies with precipitation rate, but the observed rate-dependence is lower than in previous studies where calcite is not precipitated in the presence of dissolved CA. These non-equilibrium effects can be explained in terms of isotopologue-specific reaction rate coefficients. We present a framework of ion-by-ion growth of calcite that reconciles our new measurements with measurements of natural cave calcites that are the best candidate for having precipitated under near-equilibrium conditions. Our findings suggest that isotopic equilibrium between calcite and water is unlikely to have been established in laboratory experiments or in many natural settings. The use of CA in carbonate precipitation experiments offers new opportunities to refine oxygen isotope-based geothermometers and to interrogate environmental variables other than temperature that influence calcite growth rates.

First melt inclusion study of the Sudbury Igneous Complex (Ontario, Canada): Evidence for two-liquid immiscibility and constraints on trace element distribution

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The 1.85 Ga Sudbury Igneous Complex (SIC), Ontario, Canada, is an intrusive complex representing a crystallized melt sheet formed during a bolide impact. The SIC has been extensively studied due to its rich endowment in magmatic sulfide ores (Ni-Cu-PGEs). In this study, primary melt inclusions hosted in cumulus apatite within three mafic units of the SIC (gabbro, norite and sublayer quartz diorite) are used to decipher the physical and chemical characteristics of the evolving melt sheet as it crystallized.

The compositions of coeval melt inclusions show 2 distinct types: (1) SiO₂-rich, ranging from tonalitic to granodioritic in composition (60-70 wt% SiO₂, up to 11 wt% FeO); and (2) Fe-rich with syenogabbroic to essexitic to alkali gabbroic compositions (27-49 wt% SiO₂, 16-44 wt% FeO). The liquids are interpreted to represent the products of immiscibility (*c.f.* Skaergaard Intrusion [1]).

$D_{\text{Fe-rich melt/Si-rich melt}}$ values range between ~0.7 and ~2 with the exception of V and Co that partition more strongly into the Fe-rich melt ($D > 4$). Microthermometry shows that complete melting of the inclusion contents occurs at ~1100°C, with homogenization (i.e., minimum trapping T; by bubble contraction) between ~1230 and 1300°C, confirming that apatite is an early liquidus phase in melt and trapped melt over a range of temperatures. Preliminary melt inclusion analyses suggest that the earliest melt phase of the SIC, as represented by sublayer quartz diorite, was enriched in Ni and Cu, up to an order of magnitude higher than those liquids trapped in the units stratigraphically higher in the SIC, and may reflect loss of these metals to early sulfide liquids.

The results of this study may lead to the development of parameters that enhance exploration success in mafic-ultramafic systems where post-magmatic processes have severely limited the application of bulk rock chemistry in understanding their petrogenesis.

[1] Jakobsen *et al.* (2005) *Geology* **33**, 885-888.