

Thermodynamic feedbacks in kinetic trace metal-calcite solid solution formation

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Calcite precipitated from natural terrestrial fluids typically incorporates trace to mole percent amounts of impurities. The resulting solid solutions have solubilities different from the pure phase. To understand the relationships between trace element concentration and the environment of calcite precipitation, it is necessary to know how thermodynamic controls on solid solution composition also affect mineral precipitation kinetics. These two factors together determine the solid solution composition. To evaluate the feedbacks between thermodynamics and kinetics we developed a microscopic model of ion-kink attachment-detachment rates which predicts the inhibition and incorporation behaviour of impurities, and its relationship to solution composition.

For solution supersaturations typical of biomineralizing fluids in seawater and of most natural surface waters, ion attachment and detachment occur primarily at kink sites along step edges on the calcite surface. The net ion attachment rate is controlled by the density of compatible kink sites (i.e. a carbonate site for a calcium ion) and by the kinetic barrier for ion attachment, which is thought to reflect ion and kink desolvation kinetics. Ion detachment from kink sites occurs when the solid-solid bonds between the ion and the adjacent lattice sites are broken. Lattice strain induced by incorporation of poorly fitting trace elements will speed ion detachment kinetics. Ion attachment kinetics are primarily governed by solution properties, whereas ion detachment is controlled by bond energetics of calcite. At equilibrium, ion attachment and detachment rates are equal, so the detachment frequency can be calculated from the equilibrium ion activities, which in turn are dependent on the composition of the calcite. Ultimately, with some assumptions about the form of the kinetic rate laws, we can derive a model that simultaneously accounts for the trace element incorporation and its effects on calcite growth rates.

Our results indicate that step velocities of strontian calcites vary non-linearly with aqueous Sr concentration due to the effect of lattice strain on Ca detachment kinetics. The growth rate of Mg-bearing calcite with increasing aqueous Mg, on the other hand, is inhibited primarily by kink blocking, and Mg incorporation is typically controlled by the relative rates of Ca and Mg desolvation. This suggests that the Mg isotopic composition may similarly be controlled by dehydration kinetics. This model can be used to constrain the composition of fluid from which a given calcite precipitated.

The geochemical behavior of thallium in mantle-derived basalts

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Thallium (Tl) isotopes are a new stable isotope system that shows great potential as a tracer in igneous systems [1, 2]. One of the main difficulties when doing any geochemical study of Tl is the scarcity of knowledge about the general behavior of this element in various environments. This problem stems from the fact that historically Earth scientists have rarely analyzed Tl. The physical and chemical properties of Tl allows for the possibility that it can act in four different ways, depending on the geodynamic setting: 1) Chalcophile, 2) Lithophile, 3) Fluid mobile, 4) Volatile.

The few studies that have investigated Tl behavior in igneous systems present somewhat conflicting evidence. McGoldrick et al. [3] concluded that sulfur imparts a strong control on Tl concentrations in mid ocean ridge basalts (MORB), which contrasts the general behavior of Tl in more evolved igneous systems, where Tl appears to follow the alkali metals [2]. The more recent studies present more reliable data produced with inductively coupled mass spectrometers (ICP-MS), but the number of data points is either limited or lack some key complimentary geochemical data that might help reveal the processes that control the transport of Tl from the mantle to the Earth's surface [1, 2, 4, 5].

To obtain a more complete understanding of Tl in primitive igneous systems we will present Tl concentration data for a number of MORB glasses, back arc lavas and melt inclusions. These data are complemented by concentrations of alkali metals, water, Cl and S, which will enable us to identify if Tl changes its geochemical affinity in different geologic settings.

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