

Controls on the isotope composition of trace metals in calcite - New tools for paleo-reconstructions

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Divalent metals including Ba, Mg, Sr, Cd, Co, Cu, Mn, and Zn exhibit contrasting ion size, diffusivity, hydration energy (or rate of exchange of water molecules in their hydration sphere), and affinity to hydrolyze or form inorganic and organic ligands. A large number of past studies have shown that these contrasting properties affect calcite-fluid partition constants, and how these partition coefficients vary with calcite growth rate.

In an effort to extend these observations to isotopic fractionation we have performed a number of related experimentally studies showing how crystal growth rates, and fluid pH and speciation impact the isotopic composition of the divalent metals incorporated into the calcite lattice. For example, the extent of Mg isotope fractionation between calcite and the fluid phase increases considerably with **decreasing** calcite growth rate¹. In contrast, Ba, Sr, and Zn isotope fractionation increases with **increasing** calcite growth rate. Equally, Ca and Mg isotope fractionation increase with calcite and magnesite growth rate, respectively². The distinct behavior of Mg stems from the reduced lability of water molecules in its coordination sphere compared to Ca, Ba, Sr, or Zn, and provides new insight on carbonate growth mechanisms. Moreover, Mg kinetic isotope fractionation can be quantified using three isotope diagrams³ which allow the precise determination of equilibrium fractionation factors and provides a new tool to quantify the growth rates of calcite precipitated in the deep past. Such tools also provide insight into the saturation state of the fluids present when the calcite precipitated. Similarly, the measurement of Zn and Cu concentration and isotope compositions during calcite growth at fixed rates, pH, saturation state, and concentration of selected inorganic and organic ligands, allow quantification of the equilibrium isotope composition of Zn and Cu incorporated in the lattice and its dependence on the aqueous fluid composition. Such observations provide new insight into the metal incorporation mechanisms during calcite growth. Our experimental calibrations, validated by the quantification of Mg, Zn and Cu chemical and isotope fractionation in calcite-precipitating springs, are providing new and powerful tools to reconstruct paleo-environmental conditions from the isotope compositions recorded in carbonate sediments.

[1] Mavromatis *et al.* (2013) *Geochim. Cosmochim. Acta* (in press). [2] Pearce *et al.* (2012) *Geochim. Cosmochim. Acta* **92**, 170-183. [3] Young *et al.* (2002) *Geochim. Cosmochim. Acta* **66**, 683-698.

Serpentinization, Microbial Activities, and Carbon Flow in the Deep Biosphere

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Serpentinizing ultramafic rocks are conduits for the exchange of carbon and energy between the deep Earth and the surface environment and are ubiquitous, occurring on each of the continents and over vast portions of the seafloor. Serpentinization commonly generates high pH (>11), highly reducing conditions rich in hydrogen and methane that can sustain deep subsurface microbial communities which play important roles in controlling the composition and mobility of carbon-bearing compounds. Due to a complex interplay of nutrient sources and sinks and because they are perched near the limits of life, the significance of microbial processes in serpentinites has proven difficult to constrain. Recently, concerted studies of serpentinites in both continental and marine settings have begun to identify the functional potential of serpentinite-associated microbial communities, their energy sources, and their impacts upon carbon speciation. Metagenomic and functional genomic analyses document evidence of both consumption and production of hydrogen and methane in certain environments and in some cases for microbially-mediated sulfur and iron red-ox transformations. These studies also provide evidence for CO and CO₂ assimilation and the potential for the fermentation of organic matter derived from deep Earth materials. These data provide important targets for quantification of subsurface biogeochemical processes and their impact upon the characteristics of circulating fluids and their host rocks. By linking microbiological data with geochemical data, these studies also provide the opportunity to develop new paradigms for understanding microbial adaptations and evolution in the deep subsurface environment.