‘Clumped isotope’ thermometry for high-temperature problems

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Paleothermometers for shallow-crustal environments ($50 \leq T \leq 300$°C) are generally empirical, semi-quantitative, or depend on knowledge of the compositions of pore-fluids. Carbonate clumped isotope thermometry (i.e., paleotemperature estimates based on ordering of ^{13}C and ^{18}O in solid carbonate minerals) potentially provides a means for quantitative, thermodynamically-based temperature estimates in shallow crustal environments, independent of knowledge of or assumptions regarding compositions of co-existing fluids. Application of clumped isotope thermometry at high-temperatures faces several hurdles: limits to precision; relevant calibrations; and preservation (i.e., ‘blocking temperature’).

Analyses of synthetic and natural calcite and dolomite suggest that both conform to a single continuous relationship between temperature and extent of ^{13}C-^{18}O ordering between 0 and 1100°C. These data extend previous findings that a wide variety of biogenic and a-biogenic calcites, aragonites and carbonate-apatites approximately follow a single temperature dependent calibration of the carbonate clumped isotope thermometer. However, the temperature dependence is not precisely linear in dimensions of Δ_{47} vs. T, T^{-1} or T^{-2}. The actual T-dependence resembles but is not identical to that predicted by first-principles theory. Minimum analytical errors in T are ~1-2 ° below 50°C, 3° at 100°C, 5° at 160°C and 10° at 270°C. Routine errors are ~2x greater.

Apparent temperatures of calcites from slowly cooled marbles suggest a ‘blocking temperature’ of ~200°C. This is consistent with studies of a variety of shallow-crustal rocks, which preserve a range of apparent temperatures that seem to be dictated by their extents and conditions of recrystallization. Experimental investigations of the kinetics of ^{13}C-^{18}O ordering in calcite are consistent with this conclusion, but reveal unexpected evidence for a first-order intracrystalline isotope exchange reaction that leads to partial re-equilibration at ≤350°C.

This tool will be useful for a variety of problems involving crustal rocks from depths of ≤8-10 km, including: fault friction, subduction geotherms, origins of blueschists, hydrothermal systems, Buchan metamorphism, basin thermal histories, oil, gas and coal genesis, and fossil extremophiles.

Sulfur cycling in contaminated subsurface ecosystems: Linking stable isotopes to microbial ecology

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Over the past 50 years an increased anthropogenic input has altered groundwater quality. The microbial degradation of contaminants is the only sustainable mechanism of self-purification of contaminated groundwater systems. However these processes, particulary the controls, are poorly understood and an improved understanding is necessary in order to save groundwater as future drinking water resource. In this study we focused our work on the biogeochemistry of sulfur and hypothesized that sulfur cycling is a driving factor in the degradation of contaminants in subsurface ecossystems. We have characterized groundwater sulfate, hydrogen sulfide, sulfite and elemental sulfur across a high resolution depth profile across a tair oil contaminated aquifer at a former gas worksite. Furthermore, we linked our results to the aquifer microbial community patterns to identify the complex sulfur cycle in the subsurface ecosystem. The isotope data in the $\delta^{18}O$ of groundwater sulfate suggest that in the uppermost few centimeters of the saturated zone, which is characterized by elevated hydrogen sulfide and sulfite concentrations, sulfur cycling proceeds mostly via the reaction of reduced sulfur species with oxygen, with the latter stemming from the overlaying unsaturated zone. Underneath the plume core, a region characterized by a strong decrease in contaminant concentartions and elevated $\delta^{34}S$ values in groundwater sulfate, hydrogen sulfide may be oxidized by Fe(III) minerals to elemental sulfur, and to a lesser extent to sulfite. By coupeling the microbial community distribution to $\delta^{34}S$ fingerprints in groundwater sulfate and hydrogen sulfide we found clear evidence that elemental sulfur is repeatedly reduced to hydrogen sulfide which may be accompinied by the oxidation of organic contaminants, followed by the oxidation of the reduced sulfur species to elemental sulfur by Fe(III) minerals.