Growth rate effect on Sr/Ca and Mg/Ca partitioning between calcite and fluid: *In situ* data

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Sr/Ca and Mg/Ca (Me/Ca) abundances in speleothems, foraminifera, coccolith, and mollusks have been extensively used as paleotemperature proxies. However, inconsistencies exist between different Me/Ca-temperature calibrations which imply disequilibrium exchange of Sr/Ca and Mg/Ca between fluid and calcite, thereby jeopardizing their use as paleoclimate proxies unless the overriding physico-chemical and biological effects on elemental partitioning can be calibrated.

This study complements existing experimental data on Sr and Mg partitioning that are mostly based on bulk analysis of calcite precipitated at different rates. In our alternative approach, the advancing rate of the crystal surface was determined by sequentially spiking calcite-precipitating fluids with rare earth element (REE) dopants. *In situ* secondary ion mass spectrometry (SIMS) analyses of Me/Ca were performed on single crystals of experimentally grown calcite at relative external reproducibilities for both ratios of ~1 % (1s. d.). REE patterns reveal concentric domains of calcite growth. The growth rate of calcite generally decreases with time - i.e. crystal rims advanced at slower rates than cores. Fluids were sampled periodically for Me/Ca, dissolved inorganic carbon, and pH.

SIMS profiles across individual calcite crystals displayed depleted Sr/Ca and elevated Mg/Ca at crystal rims relative to interiors. The partition coefficient of Sr/Ca ($K_d^{Sr/Ca}$) increases by ~100±2% with increasing growth rate over the range of 1 to 8 μm/day (at 25°C). In contrast, $K_d^{Mg/Ca}$ decreases by ~33±16% over the same range.

Our results suggest that Sr (Mg) are enriched (depleted) in the near-surface region of calcite relative to the bulk crystal lattice. This observation is consistent with previous *in situ* data and the surface entrapment model [1, 2], which underscores that Sr/Ca and probably Mg/Ca in natural carbonates are not a direct proxy for marine and terrestrial temperature, and require corrections for the dependency of partitioning behavior on crystal growth rate.

[1] Gabitov & Watson (2006) *G-cubed* **7**, 11. [2] Watson (2004) *Geochim. Cosmochim. Acta* **68**, 1473–1488.

Zircon rim response to metamorphic and hydrothermal regime-change

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A significant advance in zircon geochronology is the recognition of different types of neoblastic growth and recrystallization during tectonism and mineral-fluid interaction. Such domains can form in zircon and other accessory minerals as a consequence of alteration and dissolution-precipitation processes across a range of P-T conditions, and as low as ~200 °C particularly when in the presence of fluids. Distinct chemical and isotopic signatures associated with these alteration regimes can reveal valuable geological information regarding the timing and source of fluid influx, as well as mineral-fluid interaction at the sub-grain level. Application of SIMS depth-profiling now permit unparalleled spatial resolution analysis (down to ~0.2 μm) of these thin alteration zones. Complementary LA-ICPMS depth-profiling allows detection of geochemical changes accurately down to ~5 μm. Depth-profiling of unpolished zircon or other accessory crystal species measures changes in radiogenic (U-Pb), stable isotopic ($\delta^{18}O$) and chemical (REE) signatures that translate into concentration-depth profiles as drilling progresses into the crystal's interior. One application is to resolve the source and timing of fluid-flow responsible for lode Au deposits of the Canadian Abitibi Province. Depth-profiling techniques successfully uncovered <3 μm alteration domains in wall-rock zircon, occurring as light REE-enriched "rims", and Th/U and ^{18}O values suggest that alteration involved limited crustal recycling. Zircon rim ages are significantly younger than host rock ages, and correlate to intensely mineralized and deformed quartz-carbonate-Au shear veins. Subsequent zircon alteration correlating to thin, shallow-dipping and less altered and mineralized vein networks occurred 20 m.y. later, and represents a late hydrothermal fluid pulse at the end of retrograde metamorphism. A similar approach revealed an episode of Eocene metamorphism (metasomatism?) in the western Cyclades of the Aegean, an area known for iron- and sulfide-ore skarn deposits. A dominant zircon population had a spongy structure created by complete recrystallization of the pre-existing crystal, possessing low Th/U and flat and depleted HREE patterns, and yielding Eocene ages with $\delta^{18}O$ ~7‰. Detailed pre- and post-analytical imaging is necessary to document crystal structures and mineral outgrowths. Depth-profiling on zircon is a successful, yet nascent application for the dating of mineral deposits and fluid flow.