

## Profiling Eoarchean magmatic crustal growth using the elemental and isotopic composition of zircons

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The ability of zircons to maintain their physical and chemical integrity through both sedimentary and metamorphic cycles make them ideal recorders of ancient crustal processes. In particular, recent advances in trace element analytical techniques using high resolution ion microprobes has created the opportunity to not only determine the concentrations of relatively abundant trace elements (e.g. HREE), but to also determine abundances of elements that do not readily substitute for major constituents in zircon and, therefore, provide considerable insight into the degree of alteration of individual zircons. These elements (e.g. Fe, Ca, Al, etc.) can be used along with concordance of the U-Pb system and Th/U ratios to identify the grains that most faithfully record ancient magmatic conditions.

This approach has been applied to both *in situ* and detrital igneous zircons from the Beartooth Mountains of the northern Wyoming Province (MT-WY, USA). These zircons provide insight into Archean crustal evolution in this unique crustal province, which is distinct among all Archean cratons for the evolved Pb isotopic compositions of its Meso- and Eoarchean rocks (model ages to ~4.0 Ga). In order to further constrain processes and reservoirs involved in crustal evolution, we conducted >200 paired trace element and U-Pb isotopic analyses on 3.3 to 4.0 Ga zircons using the SHRIMP RG. Critical observations based on elemental and isotopic data from a subset of carefully screened zircons include: 1) REE, U, and Y abundances, including Eu anomalies, indicate crystallization from moderately evolved (not primitive) magmas; 2) magmatic temperatures based on Ti abundances indicate a range from 660-820°C; and 3) moderately high Hf contents (8,000-12,000 ppm) also suggest crystallization in at least moderately evolved magmas. Significantly, variations in these parameters do not correlate with the ages of the individual zircons over the entire range of ages. In terms of modern analogs, the overall characteristics of these zircons match well with rocks from modern, continental margin arcs. This analogy includes the involvement of older lithosphere in the evolution of Neo-Mesoarchean rocks based on whole rock Sm-Nd and Lu-Hf zircon systematics that yield model ages >4.0 Ga.

## Experimentally determined interdiffusion data of divalent cations in carbonates

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Carbonate minerals are major constituents of terrestrial and planetary bodies, including Mars. The temperature-dependent element and isotope uptake characteristics of these minerals provide the basis for estimations of conditions during crystal growth or recrystallization for a large range of temperatures, which makes carbonates suitable recorders of geological environments and biological processes. Nevertheless, commonly observed compositional zoning suggests that under some conditions carbonate crystals were not able to fully equilibrate. Knowledge of parameters governing element and isotope exchange is crucial to understanding this non-equilibrium record.

We present new experimental data for divalent cation diffusion between carbonate minerals of different composition. Diffusion coefficients have been determined for the binary exchange of Fe-Mg and Mn-Mg and multicomponent interdiffusion [Fe-(Ca+Mg) and Mn-(Ca+Mg)]. Diffusion couples were prepared by depositing a thin film (50-100 nm) of the source material by pulsed laser deposition (PLD) onto a cleaved surface of dolomite crystals (2x2 mm) under vacuum. Samples were annealed for 3-100 hours at 525-625 °C in a stream of CO<sub>2</sub> gas (150-300 sccm/min) using an 1-atm furnace. The near-surface compositions of samples following diffusion anneals were measured using RBS and diffusion coefficients were extracted by fitting the resulting compositional depth profiles.

Experimental results reveal that interdiffusion of divalent cations in carbonates follow an typical Arrhenius relation with values of log D<sub>0</sub> (m<sup>2</sup>/s) ranging from -4.2 to -6.5 for experiments involving Fe diffusion. Corresponding activation energies fall between 215 and 260 kJ/mol. Diffusion experiments on multicomponent Mn-(Ca+Mg) exchange suggest diffusivities which are at least half an order of magnitude faster and yield substantially lower activation energies (<100 kJ/mol). Diffusive closure of carbonates is expected to take place at temperatures below 300 °C for most natural conditions, which highlights their potential to record information on rates and timescales of geological events.