Sub-micron-scale variations in Ti abundance in zircon

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The Ti-in-zircon geothermometer [1,2] can constrain growth and/or re-equilibration temperatures of zircons and is particularly useful for constraining Archean and Hadean events where detrital zircon is the only surviving mineral. Zircons are often small (ca. <100 µm in the long dimension) and preserve evidence of fine-scale (sub-micron) compositional zonation. Methods for determining Ti abundances in natural zircons typically analyze domains 10s of microns across, which must average fine-scale compositional variations. Although Ti can correlate with coarse cathodoluminescence (CL) zones (e.g., [3]), it is unknown whether Ti exhibits fine-scale variations and thus may be compromised by coarse-scale measurements.

We report Ti abundances in natural and synthetic zircons down to length scales of ca. 250 nm based on measurements made with the Caltech Microanalysis Center Cameca NanoSIMS 50L. All data reported here were calibrated by comparison with primary and secondary standards previously studied in other laboratories. The external precision of our measurements for 2-µm raster images are typically 2%, relative, at 10 ppm Ti, and degrade with decreasing spot size as expected by counting statistics.

We analyzed detrital zircons from Archean metasediment in the Jack Hills (Australia) and from Proterozoic metapelite in the Adirondacks (New York). Ti concentrations commonly vary by factors of 2-3 over distances of ca. 3 µm, conformable to µm-scale CL zonation and corresponding to nominal temperatures of ~700 to ~750 °C. In some cases, banding extends down to sub-micron scales with gradients at least as sharp as a factor -3 in concentration over 250 nm. The preservation of such gradients through granulate facies metamorphism attests to slow diffusion of Ti in zircon. Curiously, compositional variations include ca. 1-2 µm bands of very low Ti content (<2 ppm, corresponding to apparent temperatures of <600 °C). Hf concentrations commonly covary with Ti, but the sense of correlation can be either positive or negative; i.e., there is no general correlation among all data. All zircons studied to-date also contain 1-2 µm-wide bands or ca. 1 µm spots having Ti concentrations up to 80 times that of the background, corresponding to nominal temperatures up to 1200 °C. These presumably reflect sampling of micron or sub-micron inclusions of Ti-rich phases.

Ferrihydrite in porous media – An inner-sphere complexion and transport approach to describe multiple reactions and predict colloid mobilization

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Prediction of colloid release and transport as affected by reactive species remains a significant challenge for field applications. We report experimental and modeling results of ferrihydrite colloid release under the influence of citrate species. Using CD-MUSIC, a 3-plane surface complexion model (1), equilibrium constants were obtained for the three proposed inner-sphere complexes by fitting citrate adsorption isotherm and pH adsorption envelopes. The constants are used in a reactive transport model (implemented in ORCHESTRA (2)) for simulating reaction fronts of dissolved species during injection of citrate in ferrihydrite-coated quartz columns. Simulation results show that sorption alone may not adequately describe the breakthrough curves. Inclusions of ferrihydrite dissolution and re-adsorption of Fe(III) improve the prediction of dissolved species transport. Additionally, matrix diffusion may be needed for a better prediction. The mechanisms of colloidal iron oxide release change over time. At complete breakthrough of citrate, oxide dissolution and interfacial repulsion control particle release from sediment. However, the peak release of colloids, corresponding to the breakthrough front of citrate, was mainly brought by electric double layer forces. These particles underwent detachment-deposition-detachment cycles along the flow path, and emerged in the effluent with the major reaction front. To quantitatively predict colloid release, a semi-empirical linear correlation is proposed, linking the calculated electric potential to experimental colloid release rates. The model works well for the prediction and scaling of field experiments concerned with organic ligand injection in subsurface environments.

References


References