Sub-micron-scale variations in Ti abundance in zircon

Amy E. Hofmann, A.J. Cavosie, Y. Guan, J.W. Valley, & John M. Eiler

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 granulite 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 co-vary 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.