Chronologic microanalysis of monazite

MATTHEW J. KOHN

Department of Geosciences, Boise State University, Boise, ID 83725 (mattkohn@boisestate.edu)

Several techniques have been developed in the last 15 years to determine *in situ* U-Pb, Pb-Pb, and Th-Pb ages of monazite, a common (U,Th)-rich phosphate. Ion microprobe, electron microprobe, and laser-ablation ICP-MS are all capable of providing ages within minutes with effective spatial resolutions of about 10-30 µm, but with highly variable accuracy and precision; microdrilling and ID-TIMS analysis can provide highly precise and accurate ages but is relatively laborious, and typical spatial resolutions are not better than about 50 µm. Numerous advantages attend rapid and spatially resolute monazite chronology, especially the ability to link chemical domains within monazite grains to metamorphic reactions, thereby allowing refined tectonic or petrologic interpretations. Yet, despite continued promise, *in situ* chronologic microanalysis of monazite appears to suffer from calibration issues, particularly for the Th-Pb system. For example, chemically simple monazite grains "dated" by ion microprobe (Th-Pb isotopes) and electron microprobe (bulk U-Th-Pb) at ~400 Ma were later microdrilled in thin section and dated by ID-TIMS (U-Pb isotopes) at 450±2 Ma, i.e. a calibration error of ~10% for ion and electron probes. Similarly, cm-sized pegmatitic monazite grains ranging in age from 100 to 900 Ma were mounted (admittedly atypically) as ~1 mm thick slabs perpendicular to a, b, and c crystal axes and analyzed together by single-collector LA-ICP-MS. Th-Pb calibrations differed by 10-15%, and in one case by nearly 20%. Calibrations depend strongly on placement within the sample chamber (at least 10%), and on crystal orientation (as much as 10%). These effects likely result from heterogeneities of He flow that deliver a different size distribution of ablated particles to the plasma and from crystallographically-dependent differential coupling of the (213 nm) laser. U-Pb calibrations are much less sensitive to sample placement and crystal orientation, but can nonetheless differ among monazite standards by up to 5%. Pb-Pb calibrations are completely insensitive. The effect of grain orientation has implications for the analysis of deformed rocks. In general, most monazite grains older than ~500 Ma can be easily and accurately dated by Pb-Pb with ion microprobe or LA-ICP-MS. Inter-element calibration errors currently compromise the accuracy of younger ages, although for monazite grains ≤ ~25 Ma, large calibration errors from ion microprobe and LA-ICP-MS may be tolerated.

Two (nearly) single-mineral monitors of the activity of rutile, 1: Calibration

M.J. KOHN* AND J.A. CHAMBERS

Dept. of Geosciences, Boise State Univ., Boise, ID 83725, USA (*correspondence: mattkohn@boisestate.edu)

Two recent, highly precise, trace element thermometers (Ti-in-Qtz and Ti-in-Zrc) were calibrated by Watson and coworkers for quartz and zircon in equilibrium with rutile. Yet many rocks lack rutile requiring independent estimates for a(Rt). Although a(Rt) can be calculated in some assemblages based on reactions involving Ti-oxides or titanite, we propose that the cation exchange $Ti^{VI}Al^{IV} = Al^{VI}Si^{IV}$ can be calibrated in muscovite and biotite, and together with quartz serves as a monitor of a(Rt). This unconventional exchange can be derived by combining more commonly proposed Ti substitutions in silicates, including dioctahedral-trioctahedral and Tschermaks. The muscovite and biotite reactions can be formally expressed as:

$$K(AlTi)(Al_2Si_2)O_{10}(OH)_2 + SiO_2 = K(Al_2)(AlSi_3)O_{10}(OH)_2 + TiO_2$$

and

$$K(\square MgTi)(AlSi_3)O_{10}(OH)_2 + SiO_2 = K(\square MgAl)(Si_4)O_{10}(OH)_2 + TiO_2$$

Empirical calibration of these reactions shows that Ti contents of muscovite and biotite in equilibrium with rutile and silica increase strongly with increasing temperature, and decrease moderately with increasing pressure. Titanium contents also decrease with increasing Na in muscovite, and increasing Mg/Fe in biotite. For muscovite, no difference in Ti content is predicted or found for quartz vs. coesite-bearing assemblages. If pressure and temperature are known independently, then a(Rt) can be resolved with an uncertainty of ~0.2; alternatively if Ti contents of Qtz or Zrc are measured, the Ti-in-Qtz and Ti-in-Zrc thermometers can be combined with our equilibria to infer temperature with an uncertainty of 15-30°C. These a(Rt) monitors may be especially useful in high-variance or inclusion assemblages, or for mylonites developed in mica-bearing quartzites or quartzo-feldspathic rocks (Chambers and Kohn, 2009, *GCA,* this volume).