Linking the Intragrain Oxygen Isotope Record to the P-T-Deformation History of Grenville-age Shear Zones, Adirondack Mountains, New York, USA

Chloë E. Bonamici*, John W. Valley, Reinhard Kozdon and Takayuki Ushikubo
University of Wisconsin-Madison, Department of Geoscience, Madison, Wisconsin, USA 53706
*bonamici@geology.wisc.edu

Summary

We report the first results of high-precision oxygen isotope analyses by ion microprobe on titanite porphyroclasts and zircons from the Carthage-Colton mylonite zone (CCMZ) in the Adirondack Mountains of New York, USA. Traverses across titanite porphyroclasts from inside smaller, ultramylonitic shear zones within the CCMZ show oxygen isotope compositional profiles that decrease smoothly outward from grain cores toward grain rims, suggesting development by isotopic diffusion rather than metamorphic growth or recrystallization. The shape and amplitude of these profiles vary depending on shear zone width, the type of deformation microstructures present, and the magnitude of $\delta^{18}O$ disequilibrium between shear zones and adjacent wall rocks. We suggest that oxygen isotope profiles formed in response to changes in fluid composition and fluid abundance within the shear zones as a result of their evolving deformational microstructures. Meanwhile, zircons are metamorphic in origin and 2-4‰ higher in $\delta^{18}O$ than magmatic zircons of AMCG (anorthosite–mangerite–charnockite–granite) suite rocks prevalent in the Adirondacks (Valley et al., 1994), such as the Diana syenite in which the shear zones are developed. Zircons are in equilibrium with the cores of titanite porphyroclasts and experienced little or no exchange due to slower diffusion.

Introduction

The Adirondack Mountains of New York expose deformed metaigneous and metasedimentary rocks of Grenville age. The NW Adirondack Lowlands and central Highlands are juxtaposed across the Carthage-Colton mylonite zone, a major, NNE-striking structure developed within the Diana syenite complex. The CCMZ ultimately accommodated NW-directed displacement of the Adirondack Lowlands and consequent exhumation of the Adirondack Highlands during Ottawan time (ca. 1090-1020 Ma; Mezger et al., 1992; Streepey et al., 2001; Selleck, 2005); however, the duration of deformation, thermal evolution, and fluid history of the CCMZ remain outstanding issues, in particular as they relate to rates and mechanisms of late synorogenic exhumation (Mezger et al., 1991; Johnson et al., 2005; Selleck et al., 2008).

Estimates of deformation conditions along the CCMZ range from greenschist to granulite facies, suggesting that shearing on this structure initiated in the hot middle crust and continued during cooling and tectonic uplift (Johnson et al., 2005). Constraining the earlier, higher-temperature part of CCMZ deformation is complicated by such a protracted history and requires careful identification of early structures. Previous work by Cartwright et al. (1993) showed that shear zones in the Diana complex near Harrisville, NY retain an O-isotopic compositions consistent with high-T shearing. U-Pb dating of metamorphic titanite (by TIMS and SHRIMP) from the Harrisville outcrops yields a range of ages spanning Ottawan deformation, but with a distinct age population at ca. 1050 Ma that likely dates the onset of extension (Johnson et al., 2005; Chappell et al., 2006). Cartwright et al. (1993) also documented O-isotope disequilibrium between shear zones and adjacent, less-deformed rock, from whole-rock $\delta^{18}O$ and mineral-separate $\delta^{18}O$ data.

Theory and/or Methods

Fractionation of oxygen isotopes amongst phases depends largely on temperature and the bonding states within the phases (e.g., Chacko et al., 2001). Isotopic diffusion is a kinetic phenomenon that occurs in response to changes in temperature and composition and can produce intragrain isotopic zonation (e.g., Cole and Chakraborty, 2001). The shapes and amplitudes of the resultant isotopic profiles therefore potentially record information about the conditions and duration of metamorphic events and/or the composition and abundance of infiltrating fluids (Eiler et al., 1993; Valley, 2001). Previously, observation of subtle isotopic zonation in natural samples was hampered by the limitations of analytical precision; however, improvements in SIMS analysis now routinely allows for high-precision ($\pm$ 0.3‰) *in situ* analyses on the scale of 10 microns (Valley and Kita, 2009).

We collected samples from ultramylonite shear zones (with widths varying from a few millimeters to greater than 10 m) and adjacent, less-deformed wall rocks in the same outcrops previously described by Cartwright et al. (1993) near Harrisville, New York. Whole-rock samples were analyzed by laser-fluorination and gas-source mass spectrometry to identify shear zones that are isotopically shifted with respect to wall rocks. We chose titanite grains for microanalysis by inspection of microstructures in thin section. Representative titanite grains were analyzed by electron microprobe for core and rim compositions. To identify intragrain O-isotope zonation, we then performed traverses across several titanite porphyroclasts on a Cameca IMS-1280 ion microprobe at WiscSIMS, analyzing for 2 oxygen isotopes at closely spaced intervals (Kita et al., 2009). Cores and rims of wall rock titanite grains were also analyzed, though the small size of most wall rock grains (< 100 μm) did not allow for detailed traverses. Zircon grains were imaged by SEM-CL to identify compositional zoning and then spot-analyzed for $\delta^{18}O$ by ion microprobe.

Conclusions

1. The difference in whole-rock $\delta^{18}O$ between shear zones (SZ) and their adjacent wall rocks (WRX) increases from Δ(SZ-WRX)=0‰ in narrow (<3 cm) shear zones to 1‰ in intermediate (>10 cm) and >3‰ in wide (>5 m) shear zones. Since shear zones and wall rocks are the same lithology (Diana syenite), these observations are consistent with a positive correlation between the extent of O exchange and the width of a shear zone.

2. All shear zones display significant grain-size reduction; however, some shear zones retain microstructural evidence for subsequent grain growth, the extent of which increases with shear zone width.

3. Ion microprobe traverses of titanite porphyroclasts from shear zones show a smooth, 1-2‰ decrease in $\delta^{18}O$ from core to rim, consistent with diffusive exchange. When compared with profiles predicted by a simple one-dimensional, semi-infinite medium diffusion model and Morishita et al. (1996) titanite diffusion data, the profiles suggest that diffusive exchange occurred at < 650°C, assuming a period of diffusion ≤ 20 m.y. If correct, these results are consistent with shearing and fluid infiltration after the thermal peak of Ottawan metamorphism at ca. 1050 Ma.

4. The relationship between shear zone-wall rock $\delta^{18}O$ disequilibrium, microstructure, and shear zone width suggests that O diffusion occurred in response to varying degrees of fluid-rock interaction during high-temperature deformation along the CCMZ.

5. Metamorphic zircons from this part of the CCMZ have distinctly higher $\delta^{18}O$ than magmatic zircons typical of the Adirondack AMCG suite rocks. $\delta^{18}O$ values indicate that zircons formed in isotopic equilibrium with the cores of titanite porphyroclasts. Thus, zircon $\delta^{18}O$ may record growth in the presences of infiltrating fluids.

6. These results are consistent with the following history. High $\delta^{18}O$ fluids infiltrated shear zones at temperatures lower than the thermal maximum of ca. 1050 Ma granulite facies metamorphism and equilibrated with newly forming zircons and titanites. The rims of titanites exchanged by diffusion with surrounding wall rocks during subsequent cooling and uplift. Further study aims to determine cooling rates.
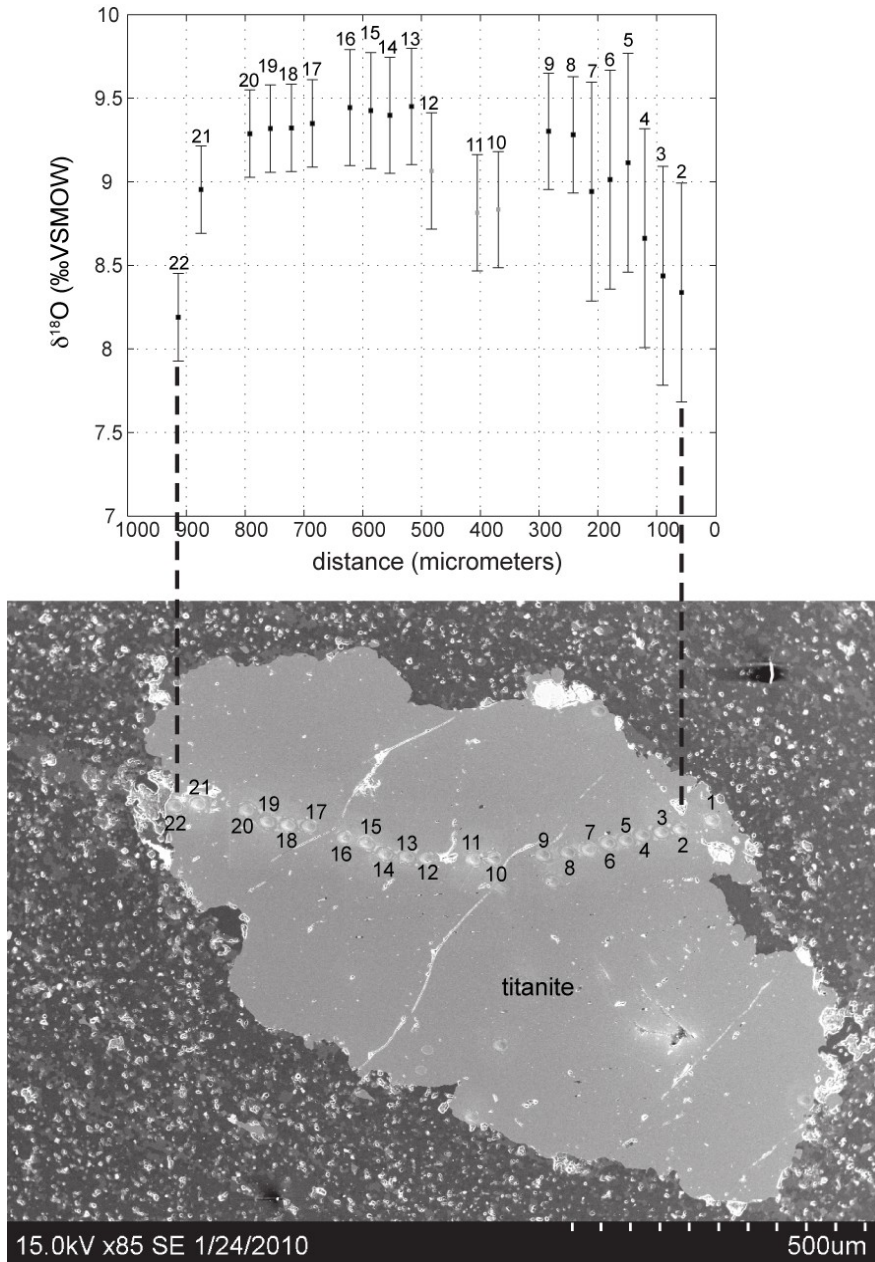

Figure 1: Smooth rim-to-rim $\delta^{18}O$ profile developed in a titanite porphyroclast from a ~3 cm wide ultramylonitic shear zone within the Carthage-Colton mylonite zone near Harrisville, New York. Error bars are 2SD. Secondary electron SEM image shows the locations of ion microprobe analysis pits. Data from pit #1 on the extreme right end of the traverse is not shown, because it

falls in a recrystallized domain at the grain margin and is not considered to be part of the intragrain profile. Pits #10-12 near the center of the traverse with significantly lower $\delta^{18}O$ (gray symbols) intersect Fe-oxide inclusions (seen by SEM after analysis).

References
Cartwright, I., Valley, J.W., and Hazelwood, A., 1993, Resetting of oxybarometers and oxygen isotope ratios in granulite facies orthogneisses during cooling and shearing, Adirondack Mountains, New York: Contributions to Mineralogy and Petrology, 113, 208-225.

Chacko, T., Cole, D.R., and Horita, J., 2001, Equilibrium oxygen, hydrogen and carbon isotope fractionation factors applicable to geologic systems, *in* Valley, J.W., and Cole, D.R. (eds.), Stable Isotope Geochemistry: Reviews in Mineralogy and Geochemistry, 43, 1-82.

Chappell, J.L., Bickford, M.E., Selleck, B.W., Wooden, J.L., Mazdab, F., and Heumann, M.L., 2006, High-temperature shearing and pegmatite formation during Ottawan extensional collapse, northwestern Adirondack Mountains, New York: Geological Society of America Abstracts with Programs, 38 (7), 385.

Cole, D.R. and Chakraborty, S., 2001, Rates and mechanisms of isotopic exchange, *in* Valley, J.W., and Cole, D.R. (eds.), Stable Isotope Geochemistry: Reviews in Mineralogy and Geochemistry, 43, 82-223.

Eiler, J.M., Valley, J.W., and Baumgartner, L.P., 1993, A new look at stable isotope thermometry: Geochimica et Cosmochimica Acta, 57, 2571-2583.

Johnson, E.L., Selleck, B.W., DeLorraine, B., and Lupulescu, M., 2005, The nature and significance of the Carthage-Colton Shear Zone and related late-to-post tectonic granites and ore deposits; Adirondack Mountains, New York. Friends of the Grenville Field Trip guide.

Kita N.T., Ushikubo, T., Fu, B., and Valley J.W., 2009, High precision SIMS oxygen isotope analyses and the effect of sample topography: Chemical Geology, 264, 43-57.

Mezger, K., Rawnsley, C.M., Bohlen, S.R., and Hanson, G.N., 1991, U-Pb garnet, titanite, monazite, and rutile ages: implications for the duration of high-grade metamorphism and cooling histories, Adirondack Mts., New York: Journal of Geology, 99, 415-428.

Mezger, K., van der Pluijm, B.A., Essene, E.J., and Halliday, A.N., 1992, The Carthage-Colton Mylonite Zone (Adirondack Mountains, New York): the site of a cryptic suture in the Grenville Orogen?: Journal of Geology, 100, 630-638.

Morishita, Y., Giletti, B.J., and Farver, J.R., 1996, Volume self-diffusion of oxygen in titanite: Geochemical Journal, 30, 71-79.

Selleck, B.W., McLelland, J.M., and Bickford, M.E., 2005, Granite emplacement during tectonic exhumation: the Adirondack example: Geology, 33, 781-784.

Selleck, B.W., Peck, W.H., McLelland, J.M., Bergman, M., and Conti, C., 2008, Late Ottawan (ca. 1035 Ma) hydrothermal signatures in the southeastern Adirondack Lowlands: new geochronological, stable isotope, and fluid inclusion results: Geological Society of America Abstracts with Programs, Northeastern Section – 43rd Annual Meeting (27-29 March), 27-2.

Streepey, M.M., Johnson, E.L., Mezger, K., and van der Pluijm, B.A., 2001, Early history of the Carthage-Colton shear zone, Grenville Province, Northwest Adirondacks, New York (U.S.A.): Journal of Geology, 109, 479-492.

Valley, J.W., 2001, Stable isotope thermometry at high temperature, *in* Valley, J.W., and Cole, D.R. (eds.), Stable Isotope Geochemistry: Reviews in Mineralogy and Geochemistry, 43, 365-413.

Valley, J.W., Chiranzelli, J.R., and McLelland, J.M., 1994, Oxygen isotope geochemistry of zircon: Earth and Planetary Science Letters, 126, 187-206.

Valley, J.W. and Kita N.T., 2009, *In situ* Oxygen Isotope Geochemistry by Ion Microprobe, *in* Fayek M. (ed.), MAC Short Course: Secondary Ion Mass Spectrometry in the Earth Sciences, 41, 19-63.