

In situ oxygen isotope analysis of monazite as a monitor of fluid infiltration during contact metamorphism: Birch Creek Pluton aureole, White Mountains, eastern California

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ABSTRACT

Monazite from the hydrothermal aureole of the Cretaceous two-mica Birch Creek Pluton in the White Mountains of eastern California records the infiltration of magmatic fluids into the metasedimentary Early Cambrian Deep Spring Formation. Monazite in the Birch Creek Pluton displays concentric, euhedral magmatic zoning, $\delta^{18}\text{O} = 8.7 \pm 0.2\text{‰}$, and Th-Pb magmatic ages of 78.0 ± 0.7 Ma. The middle Deep Spring Formation ~ 0.5 km east of the contact underwent moderate- to low-temperature alteration by F-rich magmatic fluids; monazite displays patchy zoning but has similar $\delta^{18}\text{O}$ values ($8.7 \pm 0.4\text{‰}$) and Th-Pb ages (78.3 ± 1.6 Ma) to monazite in the Birch Creek Pluton. In contrast, monazite from the upper Deep Spring Formation ~ 0.6 km west of the contact and outside the mapped hydrothermal zone shows concentric zoning, $\delta^{18}\text{O} = 5.2 \pm 0.3\text{‰}$, and partially reset detrital ages from 583 to 1069 Ma. Deep Spring Formation monazite within the hydrothermal alteration zone dissolved and reprecipitated during magmatic fluid infiltration, whereas monazite outside the zone was unaffected. In contrast, Deep Spring zircon within the hydrothermal alteration zone preserved its magmatic zoning and Cambrian-Precambrian U-Pb ages. Zircon can reliably date events prior to hydrothermal activity, whereas monazite, being more susceptible to alteration by fluids, is useful for mapping the extent and timing of fluid infiltration events.

Keywords: monazite, contact aureole, stable isotopes, metamorphic processes, hydrothermal alteration.

INTRODUCTION

Hydrothermal alteration of monazite is an important process because it disturbs the monazite U-Th-Pb systems commonly used for dating (Spear and Pyle, 2002). Plutons act as sources of heat and fluid that can alter and isotopically reset monazite in country rock. Characterizing the response of monazite to well-defined, discrete events, such as magma intrusion, can lead to better interpretations of monazite ages in less well defined settings.

Monazite provides for precise and reliable dating of hydrothermal events because of its incorporation of high concentrations of Th and its high closure temperature for Pb diffusion (Schandl and Gorton, 2004). For example, Rasmussen and Fletcher (2002) documented the low-temperature growth of monazite in carbonaceous shales in response to intrusion of dolerite sills and associated hydrothermal fluid infiltration, which opens up the prospect of dating mafic intrusions that have no datable minerals. Rasmussen et al. (2001) demonstrated that monazite can precipitate from low-temperature, oxidizing hydrothermal fluids in

the aureoles of granitic intrusions. Both studies attributed monazite growth to fluid mobilization and precipitation of rare earth elements (REE).

Commonly, monazite partially or completely recrystallizes, resulting in "patchy" zoning and partial or complete resetting of the U-Th-Pb systems (Townsend et al., 2000); this process often seems associated with fluid activity. Radiogenic lead can be lost through diffusion, dissolution-precipitation, and recrystallization, causing monazite to yield variable U-Pb and Th-Pb ages. Investigators often attribute discordance to diffusive Pb loss; however, the occurrence of monazite inheritance in granites and recent experimental measurements of Pb diffusivity in monazite (Harrison et al., 2002) indicate that the closure temperature of monazite is too high for diffusive Pb loss to be responsible for discordance in most cases. Dissolution-reprecipitation in the presence of an aqueous fluid seems to be the most common resetting mechanism. Seydoux-Guillaume et al. (2002) experimentally duplicated this process by annealing monazite in

saline aqueous fluids at 1000 °C and 700 MPa, causing complete resetting of the Th-Pb system in the parts of the grains that dissolved and reprecipitated.

The exchange of oxygen with H₂O during dissolution-precipitation of monazite in aqueous fluid may change the oxygen isotope composition of monazite, making it possible to use monazite to identify (using oxygen isotopes) and date hydrothermal events. We used a multicollector ion microprobe for in situ $\delta^{18}\text{O}$ analysis and Th-Pb dating of monazite and U-Pb dating of zircon from samples collected from a granitic pluton and a metasedimentary unit in its metamorphic aureole to characterize the response of monazite and zircon to infiltration of magmatic fluid.

GEOLOGIC SETTING AND SAMPLING

The Birch Creek Pluton is a Late Cretaceous two-mica granite in the White Mountains of eastern California (Fig. 1). It was intruded into Late Proterozoic and Early Cambrian metasedimentary rocks and produced a contact metamorphic aureole with spatially heterogeneous hydrothermal alteration zones in the country rock. The Birch Creek Pluton and its metamorphic aureole contain monazite and zircon and have been thoroughly studied to understand the relative timing of emplacement and resulting metasomatism (Barton, 2000), thus making it an ideal candidate for testing the effects of fluids on monazite and zircon. Mildly acidic, oxidizing, and saline magmatic fluids infiltrated country rocks at temperatures of ~ 250 – 500 °C and pressures of ~ 0.15 – 0.25 GPa (Barton, 2000), conditions at which monazite in granitic systems has been shown to be susceptible to hydrothermal alteration (Poitrasson et al., 2000). We characterized the response of pre-existing monazite in one lithologic unit in the country rock, the Early Cambrian Deep Spring Formation, which is relatively homogeneous, is exposed over several kilometers along a traverse perpendicular to the contact, and has relatively simple mineralogy (Barton, 2000).

Phases known to be involved in reactions that produce or consume monazite are absent in this unit (allanite, epidote, garnet, and xenotime) or present in very small quantities (apatite), reducing the possibility that heterogeneous reaction was a significant growth mechanism.

Samples of the Central Suite (CS-1 and CS-2) and Border Suite (BS-1 and BS-2) of the Birch Creek Pluton were collected along an E-W traverse (Fig. 1). In addition, we collected two samples of the Deep Spring Formation country rock: a quartzite from the middle member ~0.5 km from the contact on the east side of the pluton within the hydrothermal alteration zone (Dma-1), and a sandstone from the upper member on the southwest side ~0.6 km from the nearest exposed contact (DU-1) and just outside the zone of principal hydrothermal alteration (Barton, 2000). Petrographic descriptions are provided in Appendix DR1.¹

METHODS

Major and trace element analyses of whole rocks were performed by Actlabs using instrumental neutron activation analysis and inductively coupled plasma-mass spectrometry. Oxygen isotope analyses of whole rocks were performed by Actlabs.

Monazite and zircon were separated from fresh samples from the Birch Creek Pluton and the Deep Spring Formation using standard techniques. Handpicked grains of monazite and zircon were mounted in epoxy with monazite standards 554 and Brazil and zircon standard AS3 (Loflin, 2002). The polished mounts were carbon coated and imaged using backscattered electrons on a Hitachi S-4200 scanning electron microscope at Vanderbilt University. A Cameca SX-50 electron microprobe at the University of Tennessee, Knoxville, was used to quantitatively analyze monazite grains and to produce cathodoluminescence images of zircon grains.

In situ oxygen isotope analyses, and ²³²Th-²⁰⁸Pb ages on monazite and ²³⁸U-²⁰⁶Pb ages on zircon, were acquired using the Cameca IMS 1270 ion microprobe at the University of California, Los Angeles, on gold-coated sample mounts. Analysis spots were chosen on the basis of backscattered electron and cathodo-

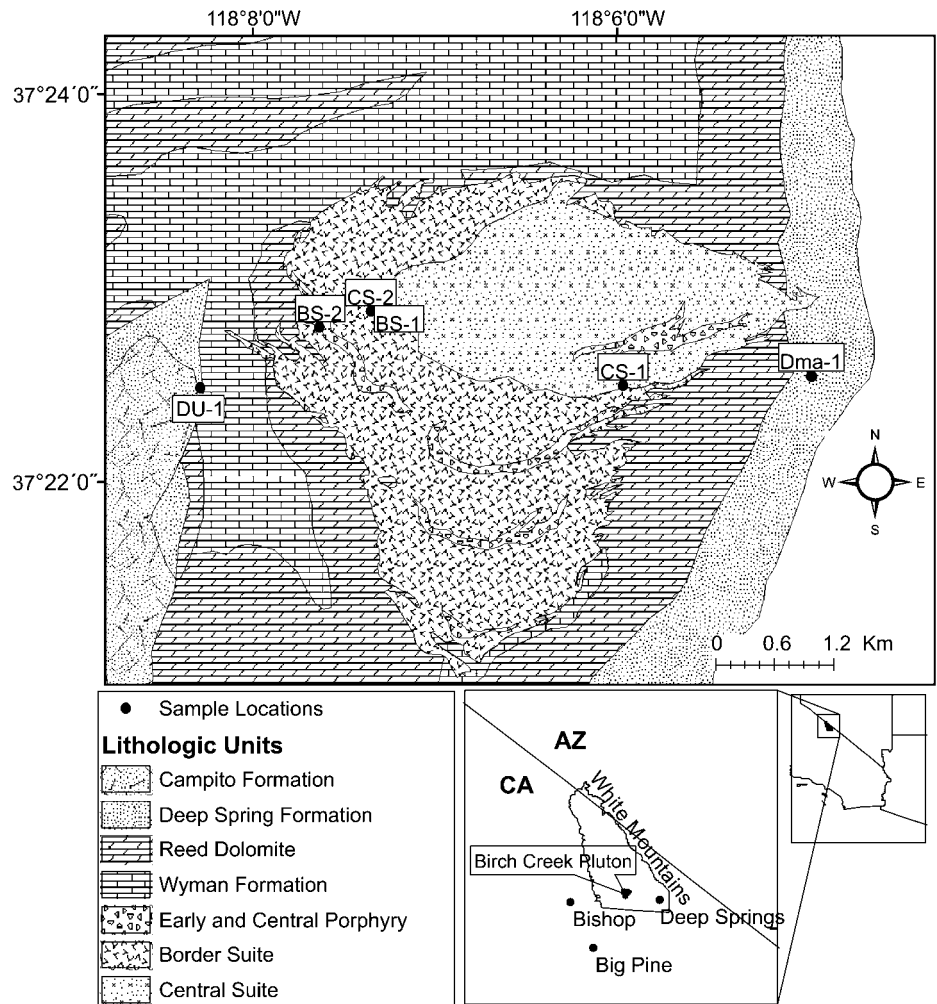


Figure 1. Generalized geologic map of the Birch Creek Pluton and surrounding host rocks.

luminescence images. Results are reported with 1σ analytical errors. Oxygen isotope analyses were acquired using a Cs^+ beam and a multicollector array that allowed for simultaneous counting of ¹⁶O and ¹⁸O (Greenwood et al., 2003). The spot size was 25 μm , and the internal precision of a single analysis was typically 0.2‰ or better (Appendix DR2; see footnote 1). All $\delta^{18}O$ values are expressed relative to standard mean ocean water (SMOW). Monazite Th-Pb and zircon U-Pb ages were acquired using a negative ion oxygen beam focused to a $15 \times 20 \mu m$ ellipse according to the methods of Quidelleur et al. (1997).

RESULTS

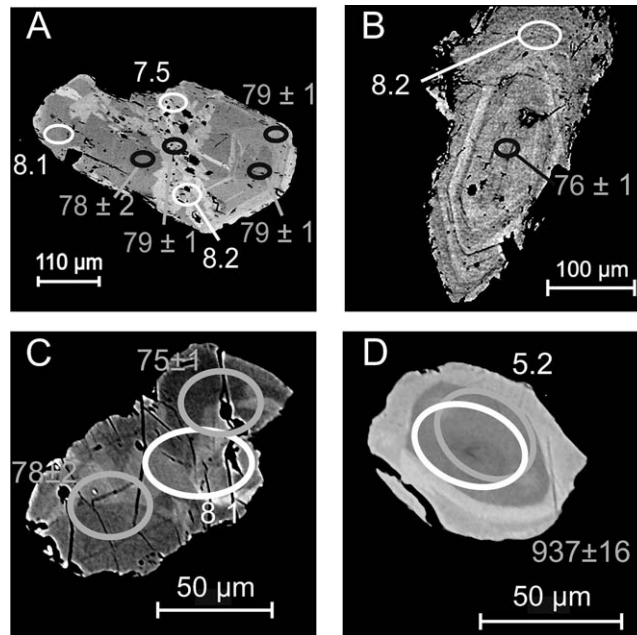
All four samples of the Birch Creek Pluton are strongly peraluminous, high-K, calcalkaline granites (Appendix DR3; see footnote 1). The granites have ~100× chondrite light rare earth elements (LREE) and are depleted in heavy rare earth elements (HREE) (2–4× chondrite), and they lack Eu anomalies. The two samples from the Deep Spring Formation are significantly different in composition, with DU-1 sandstone from the upper member hav-

ing much higher Fe and lower Si than Dma-1 quartzite from the middle member, consistent with its higher biotite content (Appendixes DR1 and DR3). These samples have flatter REE patterns than the granites, with similar LREE but higher HREE contents (8–50× chondrite).

Zircon grains within the Birch Creek Pluton are euhedral crystals 50–300 μm long and 20–50 μm wide. Cathodoluminescence images show thin, concentric magmatic rims and patchy, brighter inherited cores. Ion microprobe ²³⁸U-²⁰⁶Pb ages (Appendix DR4) of rims range from 68 to 182 Ma, with two peaks in the cumulative probability plots at 89 Ma (weighted mean = 88 ± 4 Ma, $n = 5$, mean square of weighted deviates [MSWD] = 0.22) and 165 Ma (weighted mean = 164 ± 25 Ma, $n = 5$, MSWD = 1.3). The 89 Ma peak broadly corresponds to emplacement of the Birch Creek intrusion, whereas the 165 Ma peak may represent inherited zircons from the large Beer Creek Pluton (ca. 175 Ma, Ar-Ar, K-Ar; Barton, 2000), which crops out as close as 1 km east of Birch Creek. A concordia plot of all Birch Creek Pluton zircons shows con-

¹GSA Data Repository item 2006134, Appendixes DR1, petrography; DR2, oxygen isotope analysis procedures; DR3, chemical compositions of Birch Creek samples; DR4, U-Pb ages of zircons; DR5, Th-Pb ages of monazites; DR6, chemical compositions of monazites; and DR7, oxygen isotope compositions of monazites, is available online at www.geosociety.org/pubs/ft2006.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, USA.

Figure 2. Backscattered electron images of monazite grains, with Th-Pb analysis points and ages and 1σ errors in gray and black, and oxygen isotope analysis points and $\delta^{18}\text{O}$ values in white. **A:** Border Suite monazite grain BC-BS1-01. **B:** Central Suite monazite grain BC-CS2-01. **C:** Middle Deep Spring Formation monazite grain BC-Dma-1-14 proximal to contact. **D:** Upper Deep Spring Formation monazite grain BC-DU-1-05 distal to contact.



cordant magmatic ages and a discordia line defined by three inherited core analyses. The upper intercept of the discordia line is well defined at 1690 ± 36 Ma, whereas the lower intercept of 80 ± 76 Ma has a large uncertainty but implies Pb loss from the inherited zircon cores roughly coeval with emplacement of the Birch Creek Pluton. In contrast, no zircons from the Deep Spring Formation yield ages younger than ca. 1000 Ma. Measured ages fall into three groups: 1.0–1.2 Ga, 1.65–1.78 Ga (consistent with the upper intercept of discordia), and a single analysis at ca. 2.7 Ga.

Birch Creek Pluton monazite commonly shows concentric euhedral magmatic zoning (Fig. 2B) that is overprinted by an altered, inclusion-rich secondary zone (Fig. 2A). $^{208}\text{Pb}/^{232}\text{Th}$ ages of primary and secondary monazite are indistinguishable (Appendix DR5; see footnote 1), ranging from 76 Ma to 83 Ma, with one inherited core from the Central Suite with an age of 1537 ± 150 Ma. The mean age for the Border Suite of the Birch Creek Pluton is 78.8 ± 0.7 Ma ($n = 19$, MSWD = 1.7), whereas the mean age for the Central Suite is 76.4 ± 0.7 Ma ($n = 9$, MSWD = 0.4). These ages are significantly younger than the ca. 89 Ma magmatic zircon ages. Monazite compositions from the two Deep Spring Formation samples are distinct: in the Early Cambrian middle Deep Spring Formation, ~0.5 km east of the contact and within the spatial limits of hydrothermal alteration (Barton, 2000), monazite displays patchy zoning (Fig. 2C) and has ages (78.3 ± 1.6 Ma, $n = 17$, MSWD = 8) within the error of measurement of the granite. In contrast, monazite from the upper Deep Spring Formation ~0.6 km west of the contact

and outside the hydrothermal alteration zone shows concentric zoning and ages from 583 to 1069 Ma (Fig. 2D). Deep Spring monazite also shows distinct differences in composition (Appendix DR6; see footnote 1): distal monazite is dominated by huttonite (ThSiO_4) substitution, whereas proximal monazite is dominated by brabantite ($\text{CaTh}[\text{PO}_4]_2$) substitution as is typical for metamorphic monazite (Spear and Pyle, 2002). In comparison with distal monazite in the upper Deep Spring Formation, proximal monazite has lower Si, Th, Pb, and U; higher HREE; and slightly higher LREE and P concentrations.

We hypothesized that infiltrating aqueous magmatic fluids dissolved and reprecipitated monazite in the proximal middle Deep Spring Formation, resetting its Th-Pb clock and changing its composition and internal zoning, while leaving monazite in the distal upper Deep Spring unaffected. To test our hypothesis, we used the multicollector ion microprobe at UCLA to obtain in situ oxygen isotope analyses of Birch Creek Pluton and Deep Spring Formation monazite (Appendixes DR2 and DR7; see footnote 1). Results show that monazite from the Border and Central Suites of the Birch Creek Pluton do not have significantly different $\delta^{18}\text{O}$, and they are grouped together to obtain a mean value of $8.7 \pm 0.2\text{‰}$ ($n = 69$, MSWD = 0.7), 1.7‰ lighter than Birch Creek Pluton quartz ($10.4 \pm 0.1\text{‰}$, $n = 32$). Proximal middle Deep Spring Formation monazite has a similar $\delta^{18}\text{O} = 8.7 \pm 0.4\text{‰}$ ($n = 30$, MSWD = 2.0), whereas distal upper Deep Spring Formation monazite has significantly lower $\delta^{18}\text{O} = 5.2 \pm 0.2\text{‰}$ ($n = 30$, MSWD = 1.2). Analysis of variance (AN-OVA) tests using Dunn's pairwise multiple

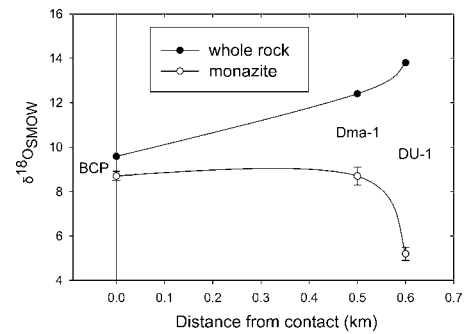


Figure 3. Oxygen isotope composition of monazite, plotted with 95% CL (confidence limit) calculated from multiple analyses, and whole rock plotted as a function of distance from the margin of the Birch Creek Pluton (BCP). Averages of all Birch Creek samples are plotted at a distance of zero kilometers. SMOW—standard mean ocean water.

comparison method show that at the 95% significance level, the Birch Creek Pluton and proximal Deep Spring Formation monazites do not have significantly different $\delta^{18}\text{O}$, but both have significantly different $\delta^{18}\text{O}$ from distal Deep Spring monazite. Whole rock $\delta^{18}\text{O}$ decreases toward the contact, from 13.3‰ for distal to 12.4‰ for proximal to an average of 9.6‰ for Birch Creek samples. Oxygen isotope compositions of both monazite and whole rock were shifted from initial values defined by the distal DU-1 sample toward those of the Birch Creek Pluton (Fig. 3). Whole rock and monazite oxygen isotopes record the exchange of oxygen between proximal samples and infiltrating magmatic fluids derived from the Birch Creek.

DISCUSSION

Petrographic evidence, such as sericitization of plagioclase, suggests that fluids infiltrated both the proximal Dma-1 and distal DU-1 samples of the Deep Spring Formation, but Dma-1 lacks layering and has fewer phases and larger grains, whereas DU-1 preserves its sedimentary layering, all suggesting that Dma-1 attained higher temperatures than DU-1. However, it was not higher temperatures alone that caused monazite to recrystallize in Dma-1 and not in DU-1, as the shifts in oxygen isotope compositions of monazite and whole rock provide evidence for open system behavior. That the $\delta^{18}\text{O}$ values of proximal monazite and whole rock are closer to values for the source of the magmatic fluid than their distal equivalents suggests that proximal rocks underwent a higher integrated fluid flux.

Figure 4 summarizes the isotopic evidence by plotting oxygen isotope composition versus Th-Pb ages of monazite. The most proximal middle Deep Spring Formation monazites overlap with Birch Creek Pluton monazite at 74–82 Ma and $\delta^{18}\text{O} = 7\text{--}11\text{‰}$ (with one out-

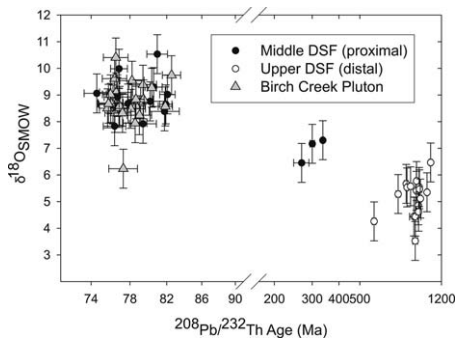


Figure 4. Distinct differences in Th-Pb age (plotted on a logarithmic scale) and oxygen isotope composition for monazite from samples from the Birch Creek Pluton and from Deep Creek Formation (DSF) country rock proximal (~0.5 km) and distal (~0.6 km) to the contact. Only data for which Th-Pb ages and $\delta^{18}\text{O}$ values were measured on the same grain are plotted (with 1σ errors), a small subset of the samples analyzed.

lier from the Birch Creek at 6.2‰). In contrast, distal upper Deep Spring monazites cluster in a distinct field at 820–1070 Ma and $\delta^{18}\text{O}$ ~3.5–6.5‰. One possible explanation for this discrepancy is that the middle part of the Deep Spring, unlike the upper part, had no preexisting monazite. However, precipitation of all middle Deep Spring monazite from infiltrating magmatic fluid at 74–82 Ma does not explain the three middle Deep Spring monazites that plot as mixtures of altered and unaltered monazite with strongly modified ages and intermediate $\delta^{18}\text{O}$ (Fig. 4).

Another possible cause of the changes in monazite oxygen isotope composition is diffusive exchange with coexisting phases in response to increased temperatures near the contact. However, the closure temperature for oxygen diffusion in monazite under hydrothermal conditions (535 °C for a 100- μm -diameter grain and a cooling rate of 100 °C/Ma; Cherniak et al., 2004) is higher than peak metamorphic temperatures in the Deep Spring Formation, making it unlikely that diffusion could have significantly changed the $\delta^{18}\text{O}$ of monazite. Multiple analyses of single grains show no evidence of heterogeneity in oxygen isotope composition in monazite. Furthermore, diffusive exchange of oxygen would not explain the apparent shift in whole rock oxygen isotope composition (though we acknowledge that the initial $\delta^{18}\text{O}$ values of DU-1 and Dma-1 may not have been equal). Finally, the resetting of the Th-Pb system can only be explained by dissolution-precipitation or recrystallization,

as the diffusivity of Pb in monazite is too low for significant Pb loss, even at peak metamorphic temperatures near the contact (Harrison et al., 2002). Closed system recrystallization is ruled out as the cause of the monazite $\delta^{18}\text{O}$ shift because it could not have caused the observed change in whole rock $\delta^{18}\text{O}$. Thus, dissolution-precipitation is left as the only possible explanation for the observed shift in $\delta^{18}\text{O}$ of proximal monazite. Proximal sample Dma-1 lies within the hydrothermal alteration zone mapped by Barton (2000) and contains hydrothermally altered monazite, whereas distal sample DU-1 is outside the hydrothermal alteration zone and contains mostly unaltered monazite, suggesting that infiltrating high-temperature magmatic fluids were responsible for monazite alteration and resetting. Our observation that zircon is less susceptible to resetting than monazite during contact metamorphism suggests that zircon is most reliable for dating events prior to hydrothermal activity, whereas monazite, being more susceptible to hydrothermal alteration, is useful for mapping the extent and timing of fluid infiltration events. Because it is susceptible to dissolution-precipitation and isotopic resetting in the presence of magmatic fluids, monazite can be used to date and map the circulation of fluids.

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