2012

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Repository Citation

D'Errico, M. E., Lackey, J. S., Surpless, B. E., Loewy, S. L., Wooden, J. L., Barnes, J. D., Strickland, A., & Valley, J. W. (2012). A detailed record of shallow hydrothermal fluid flow in the Sierra Nevada magmatic arc from low-δ18O skarn garnets. *Geology, 40*(8), 763-766. doi: 10.1130/G33008.1

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A detailed record of shallow hydrothermal fluid flow in the Sierra Nevada magmatic arc from low-δ18O skarn garnets

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ABSTRACT

Garnet from skarns exposed at Empire Mountain, Sierra Nevada (California, United States) batholith, have variable $\delta^{18}O$ values including the lowest known $\delta^{18}O$ values of skarn garnet (–4.0‰) in North America. Such values indicate that surface-derived meteoric water was a significant component of the fluid budget of the skarn-forming hydrothermal system, which developed in response to shallow emplacement (~3.3 km) of the 109 Ma quartz diorite of Empire Mountain. Values of $\delta^{18}O$, measured in situ across single garnet crystals by secondary ion mass spectrometry, vary considerably (up to 7‰) and sometimes abruptly, indicating variable mixing of meteoric, magmatic, and metamorphic water. Brecciation in the skarns and alteration of the Empire Mountain pluton suggests that fracture-enhanced permeability was a critical control on the depth to which surface waters penetrated to form skarns and later alter the pluton. Compared to other Sierran systems, much greater volumes of skarn rock suggest an exceptionally vigorous hydrothermal system that saw unusually high levels of decarbonation reaction progress, likely a consequence of the magma intruding relatively cold wallrocks inboard of the main locus of magmatism in the Sierran arc at that time.

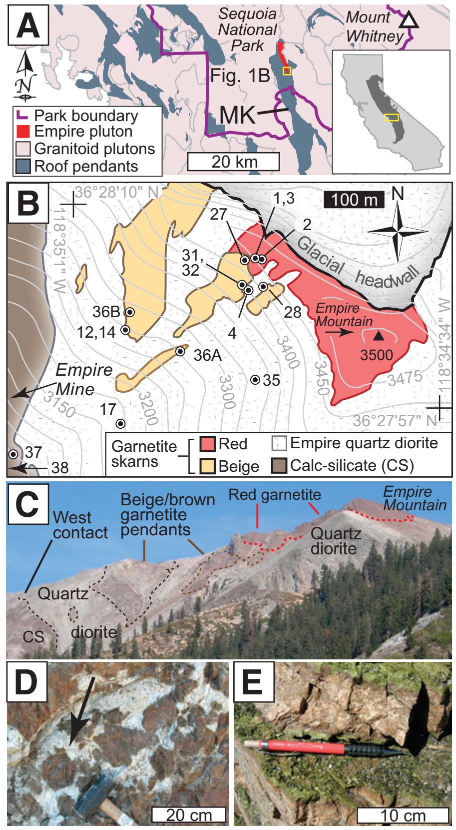

Figure 1. Geologic maps of rock units and sample locations. A: Relative location of Mineral King (MK) and the Empire Mountain study site (California, United States) within metamorphic wallrocks/pendants and Sierra Nevada plutons (inset of Sierra Nevada batholith). B: Empire Mountain field area showing locations of skarn, pluton, and wallrock samples near contacts and within the pluton. Note limit of mapping at glacial headwall denoted by heavy solid line. C: Oblique view of ~400 m of relief showing isolated pendants, the pluton, and color change in the skarn. D: Large garnets in quartz-filled fracture in garnetite. Arrow points to euhedral crystal. E: Secondary epidote veins crosscutting garnetite.

INTRODUCTION

Skarn deposits are directly related to magmatic-hydrothermal activity associated with plutonic bodies and derived fluids, which introduce metals such as Si, Al, and Fe into surrounding carbonate wallrock. Besides the clear economic value of skarns, which are the sites of precipitation of economic metals such as Fe, W, Cu, Zn, Au, and Ag (cf. Meinert et al., 2005), silicate minerals in skarns provide important records of hydrothermal system dynamics in the crust. Such records have proven particularly informative where magmatic and surface (meteoric) waters have mixed during skarn formation, thereby creating large contrasts in fluid chemistries and resulting mineral compositions. Most notably, analyses of skarn garnet reveal large variation of $\delta^{18}O$ values, which include enigmatic negative values (Bowman, 1998; Crowe et al., 2001; Clechenko and Valley, 2003; Meinert et al., 2003, 2005).

Here, we present field, geochronologic, compositional, and oxygen isotope data (both conventional bulk and secondary ion mass spectrometry [SIMS] transects of zoned skarn garnets), documenting the first low-$\delta^{18}O$ skarn recognized in the Sierra Nevada batholith, at Empire Mountain (California, United States), and elucidating a detailed record of the evolution of the skarn-forming hydrothermal system. Our findings shed new light on the nature of shallow hydrothermal fluid flow in the Sierran Arc and other Mesozoic batholiths in the Cordillera.

GEOLOGIC SETTING

The Mineral King Pendant

The Sierra Nevada batholith contains numerous roof pendants and septa of Paleozoic to Cretaceous metasedimentary and metavolcanic rocks (Fig. 1A); in the eastern and central Sierra Nevada, pendants were commonly contact metamorphosed at pressures of 1.5–2.5 kbar and 400–625 °C (e.g., Ferry et al., 2001). The Mineral King pendant, in the south-central Sierra Nevada (Fig. 1B), is composed of marine sedimentary rocks deposited during significant felsic volcanic activity (Busby-Spera and Saleeby, 1987). The pendant is intruded and contact metamorphosed by the ca. 109 Ma quartz diorite of Empire Mountain (D'Errico, 2011; this study), and younger (ca. 98 Ma; Busby-Spera and Saleeby, 1987) plutons bound the pendant to the east and west (Fig. 1A).

The Empire Mountain Skarns

Massive skarn deposits (garnetite with minor clinopyroxenite) are located near the southern contact of the Empire Mountain pluton, where it intrudes calc-silicates and marbles of the Mineral King pendant (Figs. 1A and 1B). Most contacts display grain coarsening in skarn minerals approaching the intrusion, which becomes finer grained adjacent to garnetite, and locally is porphyritic (3–4 mm plagioclase phenocrysts in 300–500 µm quartz-diorite matrix). Red garnetites form the upper 70 m of Empire Mountain, down to the top of the pluton at 3450 m

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GEOLOGY, August 2012; v. 40; no. 8; p. 763–766; doi:10.1130/G33008.1; 4 figures; Data Repository item 2012208. | Published online 15 June 2012.

(Figs. 1B and 1C). Below, large isolated bodies of brown garnetite crop out within the pluton down to 3175 m (Figs. 1B and 1C). At the west contact of the pluton, garnetite typically extends <10 m from the pluton-wallrock contact and thins to <5 m, and at lower elevations, grades into massive clinopyroxenite + wollastonite, and unaltered marble. No significant skarn is developed where the younger Coyote Creek pluton intrudes the same calc-silicate unit to the east, supporting the above field relationships that indicate the Empire Mountain pluton was the sole heat source during skarn formation.

The garnetites show color variation, with early red granoblastic garnet aggregates cut by fractures filled by beige garnet (D'Errico, 2011). Other quartz-filled fractures cut the red garnetite and contain unusually large (15-cm-diameter), euhedral garnets with the same color and growth pattern as the aggregates within the massive garnetite (Fig. 1D), suggesting brittle deformation occurred during garnetite formation. Fracture networks that cut the garnetite (D'Errico, 2011) are also filled by hydrous (secondary) skarn minerals (Fig. 1E), epidote, actinolite, calcite, and quartz, which comprise an assemblage that is typical for late-stage alteration in Sierran skarns (Newberry, 1980), which occurs as temperatures decline (e.g., Einaudi and Burt, 1982; Meinert et al., 2005). The pluton itself is thoroughly crosscut by veins of epidote and quartz, grains of which are commonly euhedral, a result of growth into open cavities in the fractured pluton and skarns (D'Errico, 2011).

RESULTS

Oxygen Isotopes of Garnet

Laser fluorination and SIMS techniques both show unusually low $\delta^{18}O$ values for garnets from the Empire Mountain skarns (Figs. 2 and 3; see the GSA Data Repository[1]). Values of $\delta^{18}O$ for primary red garnet by laser fluorination average –0.3‰ ± 0.8‰, and texturally later beige garnet averages 2.4‰ ± 0.3‰ (Fig. 2A). SIMS analyses show that $\delta^{18}O$ for garnet varies from –4.0‰ to +4.4‰ (Fig. 2B), in good agreement with laser values; $\delta^{18}O$ values within single grains vary markedly (up to 7‰), with intra-crystalline zoning characterized by both abrupt and gradual shifts in $\delta^{18}O$ (Fig. 3). Garnet is dominantly grossular-andradite solid solution (e.g., Fig. 3), typically <5% almandine + pyrope + spessartine (Table DR4 in the Data Repository), and shows weak correlation of higher average Mn/Al with $\delta^{18}O$ (Fig. 2B).

Two garnets from a single rock capture parts of the same cumulative fluid history in the cupola zone of the pluton (Figs. 3A and 3B), showing the lowest values in early red garnet and a broad trend of rimward increasing $\delta^{18}O$ in beige garnet. This $\delta^{18}O$ shift indicates greater proportions of magmatic and/or metamorphic input with time. A third grain (sample 12, Fig. 3C) shows stepwise alternation of increasingly higher and lower $\delta^{18}O$ values over time, thus progressively larger shifts of fluid $\delta^{18}O$, and a fourth grain from the lowest structural level, 36B (Figs. 1B and 3D), has relatively high and stable $\delta^{18}O$ values across 2/3 of the grain, but is then punctuated by a 6‰ decrease followed by a partial rebound of $\delta^{18}O$.

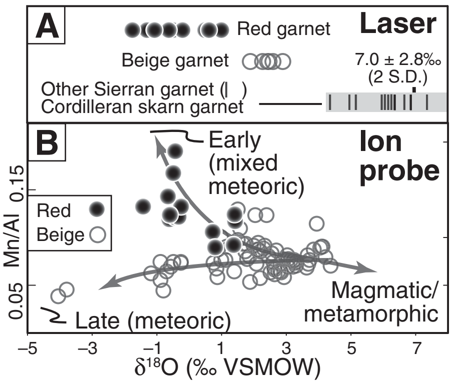

Figure 2. $\delta^{18}O$ values at Empire Mountain, California. A: Laser fluorination mineral and whole-rock $\delta^{18}O$ values, reported in per mil relative to Vienna standard mean ocean water (VSMOW), determined by laser fluorination at the University of Texas–Austin and the University of Wisconsin–Madison. Gray field shows the cordilleran skarn garnet compilation (Table DR1 [see footnote 1]) with "X" symbols showing other Sierran skarn garnet values. S.D.— standard deviation. B: Summary of $\delta^{18}O$ values measured within single grains using the WiscSIMS IMS-1280 ion microprobe (Tables DR2 and DR3) with the method of Page et al. (2010). Values are plotted versus Mn/Al in garnet to show correlation of $\delta^{18}O$ and cation content.

Other Minerals

Clinopyroxene from the skarns also has low-$\delta^{18}O$ values (1.0‰ ± 0.8‰; Table DR1), confirming that low-$\delta^{18}O$ values are a feature of all major skarn minerals. Epidote and quartz $\delta^{18}O$ values from late-stage veins that cut primary garnetite also are low (2.4‰–2.9‰ and 4.6‰–7.5‰, respectively; Table DR1). Calcite in the garnetites has $\delta^{18}O$ values (5.2‰ to 6.6‰) lower than magmatic calcite values (Bowman, 1998), yet calcite in marbles elsewhere in the pendant is 13‰–22‰ (Table DR1). Metavolcanic rocks 500–1500 m from the west contact of the pluton have whole rock $\delta^{18}O$ values of 4.5‰–5.1‰.

The Empire Mountain Pluton

Zircons in the Empire Mountain pluton have a weighted mean $^{206}Pb/^{238}U$ age of 108.5 ± 1.0 Ma (MSWD = 1.8; Table DR5), and $\delta^{18}O$ of 6.7‰ ± 0.3‰ (Table DR1). The $\delta^{18}O$ value of zircon agrees with regional patterns of magmatic $\delta^{18}O$ of Cretaceous plutons in the central Sierra Nevada (Lackey et al., 2008). In contrast, whole rock $\delta^{18}O$ values from the pluton are much lower (4.3‰–5.8‰) than measured whole rock $\delta^{18}O$ values for the central Sierra Nevada. Lithostatic pressure for emplacement of the pluton is estimated at ~1 kbar (Table DR5) using the temperature-corrected Al-in-hornblende barometer of Anderson (1996).

DISCUSSION

Origin of the Empire Mountain Skarns

Skarn $\delta^{18}O$ values are controlled by and record the compositions of infiltrating fluid, which typically is in exchange equilibrium with the adjacent intrusion (Bowman, 1998; Meinert et al., 2003); however, $\delta^{18}O$ values as low as –4.0‰, which are second lowest on Earth next to garnets in Dalnegorsk, Siberia (Crowe et al., 2001), can only be produced with significant involvement of meteoric water. Sedimentary and metavolcanic rocks in the pendant were deposited in a marine setting, an origin that is reflected in the high-$\delta^{18}O$ values of local marbles, hence pendant rocks can be excluded as a potential source of low-$\delta^{18}O$ fluids. Moreover, the pluton was not a source of low-$\delta^{18}O$ fluids: water exiting the pluton at a solidus temperature of 800 °C would have a $\delta^{18}O$ value of 8.3‰ using the quartz-water (Clayton et al., 1972) and quartz-zircon (Valley et al., 2003) fractionations; garnetites generated strictly from magmatic water from the Empire Mountain pluton should have $\delta^{18}O$ values of 5.8‰–6.2‰, based on zircon-grossular equilibrium at 400–625 °C (Valley et al., 2003). Such calculated values agree well with estimates of measured $\delta^{18}O$ values of skarn garnets from systems dominated by magmatic water (Fig. 2A; Bowman, 1998).

Thus, we conclude that the hydrothermal system that developed around the Empire Mountain pluton contained a substantial component of Cretaceous meteoric water that infiltrated because of shallow emplacement of the pluton, and led to the low-$\delta^{18}O$ skarns. The overall field and mineralogical features of the Empire Mountain skarns match those of a handful of Sierran skarns that Newberry (1980) designated as "oxidized," because they (1) contained andradite-rich garnet with low (<5%) almandine-spessartine content, (2) showed intense hydrothermal alteration of both skarns and intrusions, and (3) had Pb and Zn minerals in the retrograde alteration assemblage. Newberry hypothesized these skarns to be shallowly (<4 km) formed, with meteoric water allowing garnet to have relatively high Fe^{3+} content. Whereas the ~1 kbar estimated crystallization pressure of the Empire Mountain pluton is consistent with such

[1]GSA Data Repository item 2012208, data tables and analytical details, is available online at www.geosociety.org/pubs/ft2012.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

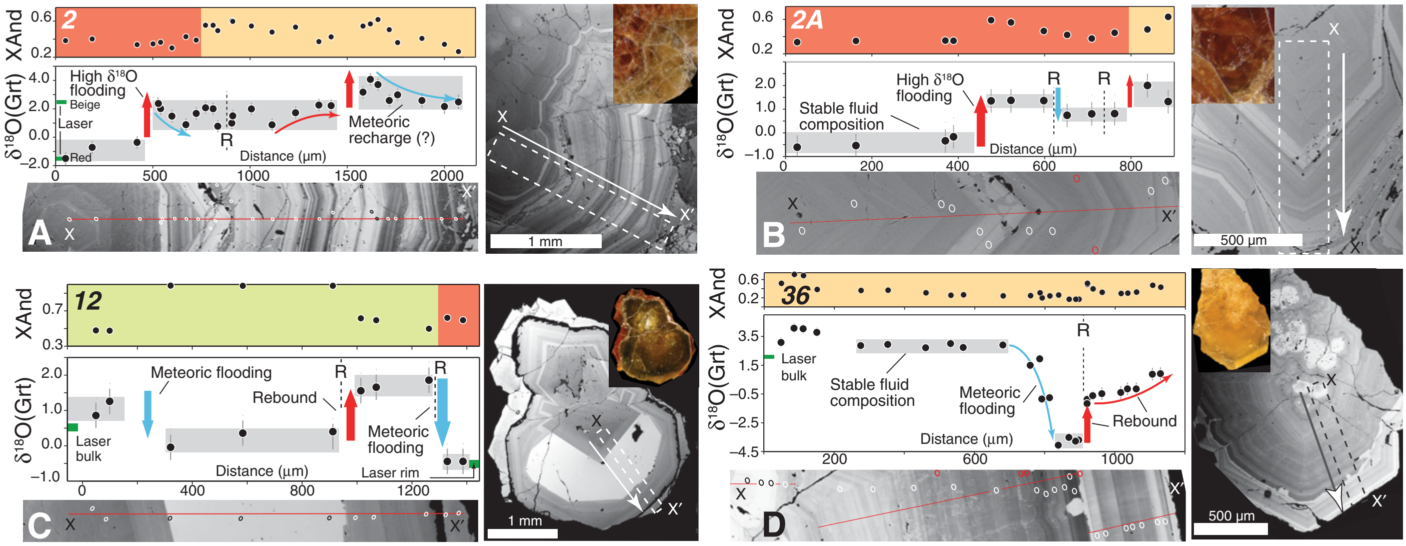

Figure 3. δ18O values of within single garnets. A: Sample 2 (red to beige transition). B: Sample 2A (red-dominated early grain). C: Sample 12 (green to red). D: Sample 36 (beige). Backscattered electron (BSE) image shows micrometer-scale of oscillations that relate to andradite- and grossular-rich domains, with magnified transects showing secondary ion mass spectrometry (SIMS) spots (ovals) and graph with δ18O values and corresponding andradite mole fraction (XAnd) along X–X′ transects. Red ovals are projected onto transects from equivalent BSE bands that were outside the image area. Green bars are bulk δ18O(Grt) values measured by laser fluorination. Color shades in andradite graphs correspond to changes of garnet color. Error bars are ±2 S.D., and often smaller than symbol size. R—resorption rim.

an origin, the low δ18O values of the skarns and pluton whole rock values confirm Newberry's hypothesis that infiltration of relatively oxidized meteoric water in the shallow crust led to their distinct traits.

The paleolatitude of the Sierra Nevada (Hillhouse and Grommé, 2011) gives an approximate δ18O for meteoric water of –7‰ at sea level, an upper limit given that δ18O of meteoric water decreases with elevation (Bowen and Wilkinson, 2002).

Garnet Zoning and Fluid Composition

The overall variation of δ18O values within single garnets reveals changing fluid composition (Fig. 3) consistent with mixing of fluid reservoirs. Previous studies correlated Fe (andradite) with magmatic δ18O values, showing that the compositions of garnet domains reflect alternating dominance of magmatic and meteoric waters (Crowe et al., 2001; Clechenko and Valley, 2003; Page et al., 2010). This does not appear to be the case at Empire Mountain, because (1) δ18O is often constant over intervals where andradite composition varies, (2) major shifts of δ18O values are not reflected by shifts of andradite content (Fig. 3), and (3) there is a *three*-way divergence of SIMS δ18O values and Mn/Al ratios (Fig. 2B).

To explain these complex patterns, we suggest that fluids derived from metamorphic devolatilization reactions contributed a third component to the fluid budget of the hydrothermal system, such that δ18O of garnet was primarily controlled by the variable input of meteoric water, because magmatic and metamorphic water (typically >10‰; Bowman, 1998) are both high-δ18O. Cation composition was likely controlled by the ratio of magmatic to metamorphic water. For example, early red garnet with a relatively high Mn/Al ratio and δ18O values near 0‰ suggests a mixture of meteoric and high-δ18O water (Fig. 2B), with the high Mn/Al contributions being from fluids exchanged with metamorphic rocks, given that the Mn/Al of the pluton is low (D'Errico, 2011). The three component fluid mixture prevents calculation of fluid mass balance proportions of different cations (e.g., Si, Al, Fe) that were transported to the site of skarn formation, but in general, the structural and spatial context of the samples gives an indication of when particular fluid reservoirs dominated.

Formation of an Unusual Hydrothermal System

Contact metamorphism at 1.5–2.5 kbar in much of the central and eastern Sierra is relatively shallow, and yet the extent to which meteoric water was involved at the Empire Mountain system is unprecedented compared to previous studies (e.g., Ferry et al., 2001). Here, we present a model to account for the unusually high budget of meteoric water (Fig. 4), and we

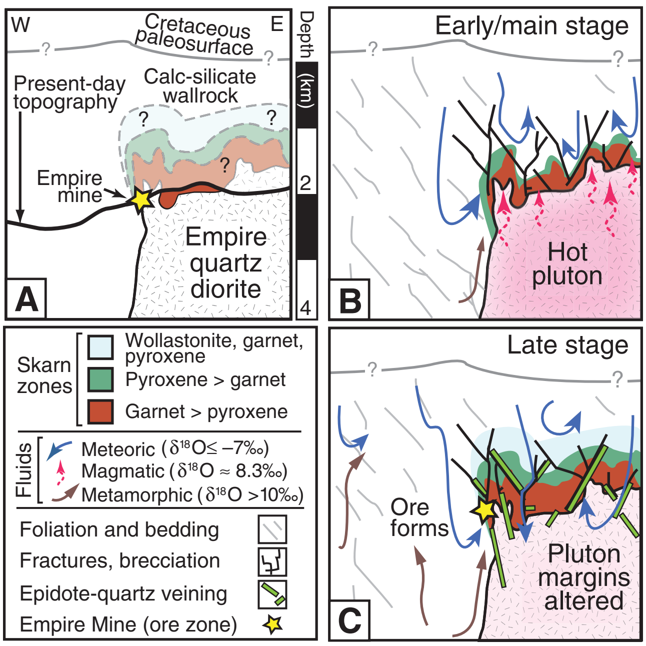

Figure 4. Schematic hydrothermal model of the Empire Mountain skarn system. A: Initial structural and intrusive relationships. B: Early-stage shallow hydrothermal activity with greater proportions of meteoric water. C: Late-stage infiltration of meteoric water and increased metamorphic devolatilization reactions, leading to ore mineralization of ore and pluton alteration. Skarn zones shown are based on data from this study and from studies of calcic skarn systems in the Sierra and elsewhere (e.g., Newberry, 1980; Einaudi and Burt, 1982). See text for discussion of model details.

consider how the timing and placement of the Empire Mountain pluton in the Sierran arc may have allowed for the anomalous character of the system.

Early-stage garnet has the lowest $\delta^{18}O$ values, indicating a greater proportion of meteoric water than at any other time during skarn formation. Thus, fluid mixing within the hydrothermal system was largely confined to above the pluton (e.g., Fig. 4B). Because infiltration of meteoric water to any extent requires well-developed permeability networks at near-hydrostatic pressure, we conclude that emplacement of the magma at ~ 1 kbar lithostatic pressure (~3.3 km) promoted the fracture and brecciation of surrounding wallrocks, allowing meteoric water to infiltrate and mix with magmatic water at top of the pluton (Fig. 4B). Growth of garnet and other skarn minerals would sustain permeability owing to the negative volume change of reactions, and because garnet is relatively strong and sustains open porosity (Meinert et al., 2005).

Late-stage decrease of the meteoric water signal may reflect closure of porosity or potentially a greater input of the metamorphic water (Fig. 4C), which would be enriched in ^{18}O and therefore would offset a presumed decrease in the magmatic water flux of the pluton with time. The within-crystal records of both static and changing $\delta^{18}O$, punctuated by intracrystalline features like resorption surfaces, suggest that, at times, fluid mixtures changed radically enough for garnet to become unstable and dissolve (Figs. 3B–3D). Such marked shifts of fluid composition likely record merging or collapse of fluid flow networks as permeability changed in the system.

Meteoric water continued to infiltrate the hydrothermal system, with cooling allowing secondary fracture networks to open in the skarns and pluton. These late-stage fluid incursions hydrated skarn minerals and altered the pluton (Fig. 4C). Pb-Zn ores were deposited at this time according their association with alteration minerals, a common feature of ores in skarns of the Sierra (Newberry, 1980). The incursion of meteoric water is well recorded in the $\delta^{18}O$ transect of a grain from the lower skarns (Fig. 3D).

We hypothesize that the temperature contrast between the intruding magma and the Mineral King pendant was one factor that led to an unusual permeability network. Because quartz diorite magma will have greater heat for similar water content to granitic magmas (Pietranik et al., 2009), it can be emplaced higher in the crust. In addition, the pluton was emplaced inboard of the main locus of magmatism in the Sierra Nevada at 109 Ma. Thus it would have encountered relatively cold wallrocks in the future Mineral King pendant, thereby enhancing brittle fracture effects, especially if strain rates were high. Lastly, the voluminous garnetite section at Empire Mountain dwarfs those in other Sierran skarns (Newberry, 1980). Therefore, the hydrothermal system appears to have caused more extensive decarbonation than is typical for skarn systems dominated by magmatic water.

CONCLUSIONS

The 109 Ma Empire Mountain skarn, in the south-central Sierra Nevada, is the first low-$\delta^{18}O$ skarn reported from a Mesozoic batholith in North America. Garnets in the deposit record meteoric water throughout all stages of the hydrothermal system, with variable mixing of magmatic and metamorphic water. Unlike other relatively shallow hydrothermal systems in Cordilleran batholiths, the Empire Mountain system suggests that the temperature contrasts associated with shallow intrusion of a relatively mafic magma can facilitate extensive brittle deformation of pendant rocks to allow early infiltration of meteoric water. More broadly, mafic magmatism in Cordilleran batholiths conceivably allowed similar hydrothermal systems to form, leading to enhancement of shallow crustal metamorphic outgassing of CO_2.

ACKNOWLEDGMENTS

We thank H. Werner and K. Nydick for assistance with permitting for field work in Sequoia National Park. J. Starnes and E. Klemetti assisted in the field. In the laboratories, we were assisted by N. Kita, J. Kern (SIMS), M. Spicuzza (University of Wisconsin, laser), T. Larson (University of Texas, laser), and J. Fournelle (EPMA). L. Anderson helped with the barometry. We thank J. Ferry, L. Meinert, and an anonymous reviewer for their comments that helped us present the findings more clearly. The field study was funded by the Keck Geology Consortium (NSF-REU-1062720). The WiscSIMS ion microprobe laboratory is partly supported by National Science Foundation grants EAR-0319230, 0744079, and 1053466, and by the University of Wisconsin–Madison.

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Manuscript received 9 November 2011
Revised manuscript received 13 March 2012
Manuscript accepted 16 March 2012

Printed in USA