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INTRODUCTION

Skarns are recognized as important products and indicators of metamorphic conditions, with the most common skarns resulting from the intrusion of felsic magmas into calcareous wallrocks. Skarn deposits contain critical information regarding the sources of fluids and dissolved components, as well as the physio-chemical processes by which pre-existing crust and intruding magma interact. The nature of this interaction is fundamentally controlled by the protolith composition, temperature, spatial distance from the contact and temporal evolution of fluids (e.g. Clechenko and Valley, 2003). In the Mineral King pendant, we characterize the metasomatic fluid flow processes controlling growth, zoning and nucleation of skarn minerals as well as the igneous history of the exposed Empire quartz diorite pluton and associated skarn to determine the nature of intrusion and evolution of the hydrothermal system (e.g., Einaudi and Burt, 1982; Bowman, J. R., 1998; and Meinert et al., 2005).

Excellent outcrop exposure at Empire Mountain (Fig. 1), provides a rare opportunity to examine the shallow (1-2 kbar; Nadin and Saleeby, 2008) intrusion of the Early Cretaceous Empire quartz diorite into calcareous wallrocks. The three dimensional exposure at Empire Mountain displays the relationships between the intruding Empire pluton, skarns and calc-silicate wall rocks. We present new U-Pb geochronology data and Ti-in-zircon temperature estimates for the Empire quartz diorite pluton, and we evaluate trace element and oxygen isotope analyses of skarn-forming minerals and the pluton that record rock-fluid interactions at Empire Mountain.

GEOLOGIC SETTING

The Lower Mesozoic metavolcanic and metasedimentary rocks of the Mineral King roof pendant are located among the calc-alkaline granitoid belt of the former southern Sierra Nevada arc (Lackey and Loewy, this volume, Fig. 1). Busby and Saleeby (1987) summarized the stratigraphic and magmatic evolution of the Mineral King area, documenting the Triassic-Jurassic metamorphic units which are highly deformed, steeply dipping pendants between Cretaceous plutons. The hypabyssal intrusion of the Early Cretaceous Empire quartz diorite into calcareous wallrocks resulted in the pervasive calcic skarn mineralization (unit CS₅) of the Empire Mountain pendant. The protoliths of calc-silicate units CS₁ to CS₅ are thought to have recorded period of volcanic and tectonic quiescence (Busby and Saleeby, 1987). Busby and Saleeby (1987) reported an U-Pb zircon age of 107 Ma for the Empire pluton, and overlapping ages of 99 Ma and 98 Ma for the east and west binding plutons, the Eagle Lake quartz monzodiorite and the Sawtooth Peak granite, respectively (Fig.1). Mackenzie (1983) conducted an extensive study of the Mineral King mining district, and reported mineral phases and field relationships consistent with those documented in this study. Pb-Zn-Ag sulfide deposits and associated skarns of the Empire Mine (Fig. 1) classified by Mackenzie (1983) were thought to have formed through a two-stage process of prograde skarn development followed by fracturing of roof pendant rocks, where declining temperature and pH fluctuations in meteoric water controlled the development and replacement of skarn mineral assemblages with later stage open-space precipitation. We intend to build upon his interpretation and develop a model of skarn formation and retrograde mineralization.
FIELD RELATIONSHIPS

At Empire Mountain, there is a well-exposed, three-dimensional view of the relationships and contacts between the three major rock types: the Empire quartz diorite, skarns dominated by red-brown or tan-brown garnetite, and calc-silicate rock (Fig. 2). Representative light to medium grey quartz diorite samples from the unaltered cupola zone of the Empire pluton show little modal variation, with ~40% plagioclase, ~20% alkali feldspar, ~10% quartz, and ~30% ferromagnesian minerals (biotite, hornblende and orthopyroxene, in decreasing order). Map unit CS₅ is a massive, iron-rich calc-silicate rock with a very fine average grain size (<0.2 mm), so mineral identification is difficult. However, garnet is ubiquitous and abundant proximal to the Empire Mine (Fig. 1), consistent with the findings of Mackenzie (1983).

In contrast, former originally calcareous wallrock from the ridgetop pendants has been completely replaced by calc-silicate skarn minerals, with garnet significantly more abundant than clinopyroxene (Site B, C; Fig. 2). In the field, a vertically stratified color change is observed within the calc-silicate rock. Composed of small (~1 mm), euhedral garnet, the upper unit of the pendant is a red-brown garnetite (Site C; Fig. 2), while the lower unit is tan-brown garnetite (Site B; Fig. 2). The tan-brown garnetite is fine-grained and mostly granoblastic grossular garnet; in contrast, the red-brown unit displays early granoblastic andradite and late grossular vein fillings, where the observed growth direction displays end member oscillations and fills in late vein areas (Fig. 3D). A sub-horizontal, 1 – 3 m thick zone of vug-filling, large, euhedral garnets (approximately 10 - 15 cm in diameter) and late stage quartz (Fig. 3C) marked the approximate boundary between the two garnetite units (Fig. 1). The large garnet crystals within the quartz matrix display macroscopic 2 – 5 cm zoning.

Figure 1. Geologic map of Mineral King (modified from Saleeby et al., 1993) draped over topography in Google Earth. Map shows the dominantly Triassic-Jurassic metavolcanic and metasedimentary units intruded by three Cretaceous plutons that make up the metamorphic wallrocks of the King Sequence. Empire Mountain pendant study area is boxed in white.

Figure 2. Geologic map of Empire Mountain pendants draped over topography in Google Earth and oblique photo displaying field relationships. Site A) West contact between calc-silicate (CS5) rock and Empire quartz diorite (QD); Site B) Tan-brown garnetite pendants; Site C) Empire Mountain consisting mostly of red-brown garnetite; Site D) Later stage concentrated subhedral to euhedral epidote and calcite, observed at high angles to garnetite contact.
in color from bright red cores to tan-brown rims. The position of the sub-horizontal boundary zone between garnetite units of different compositions suggests that fluid pressures might have opened space between protolith bedding planes and precipitated garnet and quartz in that space. The macroscopic zoning observed in garnet, observed both on the pendant scale and in large garnet crystals from the boundary zone, indicates that variations in fluid composition played an important role in the hydrothermal system. The well-exposed sub-horizontal contact of the Empire quartz diorite with supradjacent CS$_5$ garnetite is highly variable. In the sub-horizontal transition zone between these two units, the calcareous wallrock exhibits sharp contacts with several lens-like blobs of quartz diorite (Fig. 3A) and is coarse-grained, garnet-rich, with large calcite filled vugs (1 – 3 cm diameter). Where this interaction is best exposed, the quartz diorite pervasively intruded and appears to have initiated the ductile deformation of the garnetite. However, west of this transition zone (<50 m from Fig 3A) in the cupola zone of the quartz diorite, apparent products of spalling from the overlying calc-silicate pendant, occur as xenoliths of the garnetite within the Empire quartz diorite. In these exposures, the calc-silicate rock becomes progressively dark red-brown garnet rich toward the quartz diorite contact over 5 cm – 0.5m (Fig. 3B), suggesting that color zonation is not due to major element compositional variations in the original calc-silicate, but more likely formed by progressive fluid infiltration and intense metasomatic reactions (Atkinson and Einaudi, 1978). Endoskarn mineralization (mineralization within the pluton) is not widespread and is only observed at a few localities adjacent to the contact, where it is likely that fluid flow from the wallrock affected the intrusion.

Several features near the garnetite–Empire quartz diorite contact appear to post-date original skarn formation. For example within 3 or 4 m of the contact, concentrated subhedral to euhedral epidote and calcite occur at high angles to the contact within the garnetite (Site D; Fig. 2). Within the pendant garnetite, garnet is a solid mineral, with angular fractures that suggest brittle deformation post-crystal growth; while the presence of actinolite [(Ca$_2$)(Mg,Fe)$_5$(Si$_8$O$_{22}$)(OH)$_2$], calcite (CaCO$_3$), quartz (SiO$_2$), and epidote [(Ca$_2$)(Al$_2$Fe)(Si$_2$O$_7$)(SiO$_4$O(OH))] within the garnetite appear to have mineralized utilizing a post-skarn formation fracture system (Fig. 4).

The tabular shape of these 2 – 4 m wide zones, the breciated garnetite, the frequent euhedral nature of epidote and calcite mineralization, and the outcrop distribution relative to the quartz diorite contact suggest that this mineralization occurred due to channelized flow of magmatic, meteoric, and/or connate fluids within the brittlely-deforming calc-silicate rock. These zones probably were cored by faults or fractures within the metamorphic rock, which provided channel pathways for fluids and may have been created by hydraulic fracturing of the rocks.

**ANALYTICAL METHODS**

We collected samples of the Empire quartz diorite
pluton, associated skarns and calc-silicate units near the Empire Mountain roof pendant at various distances (<1 m to >1000m) from the exposed pluton-wall-rock contact (Fig. 2). Fifteen of these samples were cut into billets for thin sections and sent to Spectrum Petrographics Inc. in Vancouver, Washington. Major and minor, and 17 trace elements were determined for eleven whole rock powdered samples by X-ray fluorescence (XRF) at Pomona College following the method of Johnson et al. (1999).

For geochronology and elemental zircon analyses with the Sensitive High Resolution Ion Micro Probe Reverse Geometry (SHRIMP-RG), a representative sample of the Empire quartz diorite (10MD-17) was crushing and zircon was separation using standard methods of gold table, heavy liquid and Frantz magnetic separation. Zircon grains were handpicked, mounted, and loaded into the SHRIMP-RG at the SUMAC facility at Stanford University. Ion beam working conditions and quantitative analysis of isotopic ratios and of trace elements was performed as described in Barth and Wooden (2010).

Qualitative and quantitative composition data were gathered using a JOEL JXA-8200 electron microprobe (EMPA) at the University of Texas, in Austin. Numerous highly magnified (40x - 130x) backscattered-electron images (BSE) were obtained from polished thin sections from two samples of skarn mineralization (Fig. 5). The UT electron microprobe analysis and image collection was conducted in spot mode, running at 15 kV and 1.5 e-7 A, following similar method as Page et al. (2010).

Oxygen isotope analyses of the zoned garnet, associated skarn minerals and calc-silicates were performed using a 30W CO2 laser at University of Texas, at Austin, following techniques described by Sharp (1990). Oxygen isotope ratios were measured with a ThermoElectron MAT 253 mass spectrometer. Sample δ18O values are reported in standard per mil (%o) nota-
tion relative to Vienna Standard Mean Ocean Water (VSMOW). The analyses were standardized against the University of Wisconsin Gore Mountain garnet standard (UWG-2, Valley et al., 1995).

**SHRIMP-RG U-PB AND TI-IN-ZIRCON**

Sensitive High Resolution Ion Micro Probe Reverse Geometry (SHRIMP-RG), analysis of the representative sample of Empire quartz diorite (10MD17) yielded a single age population within error and combine to give a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 108.5 ±1.0 Ma (with MSWD = 1.8 and probability = 0.033). This study also analyzed Ti-in-Zircon for the Empire pluton sample and an estimate of emplacement temperature was proposed based on the Ferry and Watson (2007) calibration. The high Ti concentration (28 ± 6 ppm) of zircons from the magnetite - bearing pluton indicate likely magmatic temperatures of 874±23°C. This temperature is the hottest Ti-in-zircon temperature yet reported from a Sierran granitoid (Fu et al., 2008).

**δ¹⁸O ISOTOPIC SIGNATURES OF THE SKARN SYSTEM**

Skarn minerals from different parts of the system were sampled for δ¹⁸O analysis to determine the relative magmatic and meteoric components in hydrothermal fluids during the evolution of the skarn system. Samples of andraditic garnet, grossular garnet, epidote, calcite, and quartz were sampled, with the hope that the relative timing of mineralization determined by field relationships could provide context for the changes in fluid composition. For reference, zircon from the Empire quartz diorite display values of above 6.0‰ δ¹⁸O, which is a good proxy value for magmatic fluid.

δ¹⁸O data from zoned skarn garnet reveal early cores of andraditic garnet have a meteoric signature (near 0‰ δ¹⁸O), while rims from the same crystals are grossular-rich and indicate an increasing magmatic component (2 - 3‰ δ¹⁸O). These values are significantly below the expected δ¹⁸O values for garnet precipitation in equilibrium magmatic fluids (above 4.0‰ δ¹⁸O). Epidote and calcite values, which precipitate late in the system’s evolution, also display strong meteoric fluid signatures for each mineral (3‰ and 5 - 7‰ δ¹⁸O, respectively).

**SKARN EVOLUTION**

Mineralization in the Empire Mountain skarn system records two stages of metamorphism that were controlled by the shallow (1-2 kbar) and hot (>800°C) intrusion of the Empire quartz diorite. The proximal garnet>clinopyroxene exoskarn is the most proximal zone of classic skarn zoning, relative to the intruding pluton (Meinert et al., 2005). Since other more distal zones (with increasing vertical distance from the pluton, clinopyroxene>garnet, wollastonite, then
unaltered marble), it is likely that most of the skarn deposit has been eroded since formation.

The granoblastic andraditic cores observed in the garnetite pendant are evidence of the early crystallization of this anhydrous calc-silicate mineral during prograde metamorphism, while the more grossular-rich rims and veins most likely filled in during a second period of garnet growth during retrograde mineralization. The initial formation of garnet and lesser diopside during prograde metamorphism likely promoted permeability due to the strength of garnet (Meinert et al., 2005), permitting the complete replacement observed in the Empire Mountain pendant. Field relationships suggest that this period of mineralization was synchronous with a change from ductile to brittle deformation, suggesting that even during prograde metamorphism and intrusion, cooling of the system was already taking place.

During retrograde mineralization in skarn systems that are dominated by brittle deformation expected in a cooling system, andradite is often overgrown by quartz, calcite, magnetite and pyrite, whereas diopside is replaced by actinolite, quartz and calcite (Meinert et al., 2005). The observed tabular zones of abundant hydrous skarn minerals (epidote and actinolite), quartz and calcite in the Empire pendant therefore are hypothesized to represent retrograde mineralization structurally controlled by faults, joints or intrusive contacts.

Oxygen isotope data strongly indicate that both prograde skarn mineralization and later retrograde mineralization were never in equilibrium with magmatic fluids, but were instead in equilibrium with meteoric fluids, completely unlike any major skarn system worldwide (e.g., Einaudi and Burt, 1982; Meinert et al., 2005). The \( \delta^{18}O \) values of Empire Mountain skarns are highly unusual and only four other locations in the world report low \( \delta^{18}O \) values of primary garnet minerals (Jamtveit and Hervig, 1994; Crowe et al., 2001; Clechenko and Valley, 2003). In the shallow (<10 km) intrusion of a massif anorthosite, Clechenko and Valley (2003) document the distinct morphology and (0.8 – 6.3‰) \( \delta^{18}O \) values of Willsboro skarn garnets, and propose an open system in which shallow circulation of meteoric water was dominant. The zoned Empire Mountain garnets are a new low-\( \delta^{18}O \) locality and the first recognized in the western U.S. These data support our hypothesis that very hot crystallizing pluton was able to ascend to shallow and therefore relatively cool crustal levels, permitting the unusually early initiation of brittle deformation, which allowed the involvement of meteoric fluids throughout the evolution of the hydrothermal system, yielding the large garnetite skarn pendant at Empire Mountain.

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