Pressures of skarn mineralization at Casting Copper, Nevada, USA, based on apatite inclusions in garnet

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ABSTRACT

Thermobarometry of metasomatic rocks is commonly challenging, owing to the high variance of hydrothermal mineral assemblages, thermodynamic disequilibrium, and overprinting by subsequent hydrothermal episodes. Here we estimate formation pressures of a Cu-Fe-sulfide–bearing andradite-diopside skarn deposit at Casting Copper (Yerington district, Nevada, USA) using Raman spectroscopy and elastic modeling of apatite inclusions in garnet. Andradite garnet from the Casting Copper skarn contains inclusions of hydroxylapatite, calcite, hematite, magnetite, and ilmenite. Raman spectroscopy reveals that the apatite inclusions are predominantly under tension of ~23 to ~123 MPa at ambient conditions. Elastic modeling of apatite-in-garnet suggests that entrainment occurred at ~10–115 MPa, assuming a trapping temperature of ~400 °C, which is consistent with paleodepth estimates of ~2–3 km. These results provide independent constraints on the conditions of hydrothermal skarn formation at Casting Copper, and suggest that this approach may be applied to other, less-well-constrained skarn systems.

INTRODUCTION

Pressures ($P$) and temperatures ($T$) of ore-forming systems are key factors in determining the style of mineralization and alteration (Mercer and Reed, 2013). However, conventional thermobarometry based on mineral equilibria may be challenging in hydrothermal systems because rocks from these environments typically contain few minerals (Korzhinskii, 1968). Therefore, thermobarometers relying on mineral-mineral equilibria or element partitioning are commonly underconstrained or unavailable. Where viable mineral assemblages for thermobarometry are present, lack of equilibrium (Mercer and Reed, 2013) and/or resetting by subsequent alteration (Goncalves et al., 2013) can be serious impediments to evaluating $P$ and $T$. Fluid inclusions can provide constraints (e.g., Roedder and Bodnar, 1980) but $P$ corrections are rarely well known, and fluid inclusions representative of specific paragenetic events are not always available. In some cases, $P$ of formation can be inferred based on constraints from geologic mapping, which may place tight constraints on depths of formation (Dilles et al., 2000), although translating depth to $P$ requires a known or assumed $P$ gradient, which may also be underconstrained (Roedder and Bodnar, 1980). Consequently, in many cases $P$ of formation of hydrothermal veins and metasomatic replacements are only crudely known.

Skarns are metasomatic calc-silicate rocks that commonly form at the interface between igneous intrusions (often associated with porphyry-style mineralization) and reactive country rocks, especially carbonate rocks. Carbonate-hosted skarns exhibit a classic zonation wherein garnet-only and garnet-pyroxene rocks are the principle high-$T$, high fluid:rock ratio assemblages (Meinert et al., 2005). Skarns are known to form over a wide range of crustal depths; Meinert et al. (2005) reported that skarn formation depths may range from <1 km to >10 km, and that formation depth represents a key control on the size, geometry, and alteration style of skarn deposits.

In this study we revisit thermobarometry of a skarn at Casting Copper, part of the Ludwig skarn system in the Yerington district (Nevada, USA). We analyze the Raman spectra of apatite inclusions enclosed within skarn garnet grains, and use an isotropic elastic model to estimate $P$ of entrainment. Our results corroborate previous estimates based on paleodepth constraints, highlighting a new approach to $P$ estimation in hydrothermal systems and validating the applicability of this barometer to metasomatic rocks.

Study Area: Casting Copper Skarn

The Casting Copper skarn (Fig. 1) is located in the Ludwing area adjacent to the Yerington and Ann Mason porphyry-Cu centers within the Yerington district and is considered broadly coeval with porphyry-Cu mineralization (169.4–168.5 Ma; Dilles et al., 2000). The Yerington district has been dissected and tilted 60°–90°W by Cenozoic normal faulting (Poffett, 1977). Thus, a modern-day plan-view geologic map is essentially equivalent to a Jurassic cross section, providing excellent paleodepth constraints. The formation depth of the Casting Copper skarn is estimated to be ~2–3 km (Einaudi, 1977, 2000; Harris and Einaudi, 1982). Dilles et al. (2000) stated that Cu-Fe-sulfide deposition at Casting Copper probably occurred under hydrostatic $P$ conditions, after andradite formation. The estimated depth of formation of 2–3 km implies a hydrostatic $P$ of ~20–30 MPa; lithostatic $P$ at the same depth would correspond to ~54–81 MPa (Fig. DR1 in the GSA Data Repository1).

The Casting Copper skarn and other adjacent skarns were subjected to two intrusive phases. The intrusion of the McLeod Hill quartz monzodiorite (169.4 Ma) into the Triassic parent limestone created extensive hornfels metamorphism, and the subsequent intrusion of the Luhr Hill granite (168.5 Ma) was responsible for the formation of andradite-pyroxene skarn along with Cu mineralization at Casting Copper (Dilles and Wright, 1988; Einaudi, 2000). The Casting Copper deposit is an Fe-rich skarn characterized by massive andradite and pyroxene with small concentrations of Cu-Fe-sulfides. Nearly pure andradite (Ard) initially replaced calcite in the limestone and was later overprinted by both more grossular (Grs)–rich garnet (~$Ard_{0.5}Grs_{0.5}$) and coarse pyroxene with an average hedenburgite-diopside-johannsenite composition of approximately $Hd_{0.3}Di_{0.7}Jnn$ (Table DR3; Harris and Einaudi, 1982). Where the parent limestone was locally

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1 1GSA Data Repository item 2017314, Figures DR1 and DR2 and Tables DR1–DR4 (supplemental data, sample descriptions, garnet and apatite compositions, and Raman data), is available online at http://www.geosociety.org/datarepository/2017/, or on request from editing@geosociety.org.
more Mg-rich due to dolomitization, subsequent skarn mineralization created more Mg-rich diopside-pyroxene (salite) and garnet (pyrope). Petrographic studies reveal that the garnet grains contain inclusions of hydroxyl-fluorapatite (Figs. 2B–2D), calcite, hematite, magnetite, and ilmenite in addition to sparse aqueous fluid inclusions. Apatite inclusions are ubiquitous and are distributed throughout the garnet from core to rim. Calcite is present as both relict inclusions in the cores of garnet grains and as irregular grains that fill open spaces within the late-stage fine-grained diopside pyroxene (Fig. 2A). Hematite, magnetite, and ilmenite inclusions are rare.

Based on mineral equilibria, Harris and Einaudi (1982) estimated a minimum formation $T$ of 325 °C for andradite at an inferred $P$ of ~50 MPa and $X_{CO_2} = 0.02$. They also noted the lack of wollastonite in these rocks, which would form at a minimum $T$ of 440 °C under these conditions, but its absence in these rocks may be the result of slightly higher $X_{CO_2}$. Earlier Mg-rich skarns more proximal to the McLeod Hill quartz monzodiorite formed at ~550–650 °C (based on phase relations, the presence of monticellite, and fluid inclusion analyses), but this early skarn material is crosscut by the later stage of Fe-rich skarn that dominates at Casting Copper (Harris and Einaudi, 1982). These constraints suggest that the Casting Copper skarn formed in the range of ~325–450 °C. This estimated range is also similar to that of the shallowly emplaced Big Gossan andradite skarn at Grasberg, Indonesia (360–535 °C; Meinert et al., 1997). For $P$ estimates using mineral inclusions, accurate $T$ estimates are important because the elastic model is moderately sensitive to $T$ (Ashley et al., 2017).

METHODS

We collected samples of garnet from the Casting Copper skarn (Fig. 1; Table DR2) and prepared doubly-polished wafers (~500 µm thick) of individual garnet grains. Our strategy for thermobarometry was to analyze the mineral inclusions using Raman spectroscopy to quantify internal $P$ according to the $P$-dependent peak position of the phosphate symmetric-stretching mode ($\nu_3$) (Comodi et al., 2001; Schouwink et al., 2010). The internal $P$ of apatite inclusions at ambient conditions is used to estimate entrapment $P$ using an isotropic elastic model (Guiraud and Powell, 2006). This approach has been previously applied to high-$P$ and Barrovian-sequence metamorphic rocks (e.g., Enami et al., 2007; Ashley et al., 2014, 2015; Kouketsu et al., 2014), but has not yet been tested on hydrothermal metasomatic rocks such as skarns.

We analyzed host garnet and mineral inclusions using electron probe microanalyzer (EPMA) analysis and Raman spectroscopy (Tables DR1, DR3, and DR4). Internal $P$ within mineral inclusions was computed according to a polynomial regression based on experimental data for the $P$-dependent Raman peak shift of the inclusion phase (Ashley et al., 2017). We use the elastic model of Guiraud and Powell (2006), including ideal solid-solution models for inclusion and host (Liu and Mernagh, 1990; Kuebler et al., 2006), as described in the following. Details of our analytical and computational methods are described in the Data Repository.

RESULTS

Many of the analyzed grains exhibit well-developed concentric zoning (visible in transmitted light; Fig. 2C) reflecting variations in the grossular (Al) concentration, but almost all the analyzed inclusions were within thick bands of andraditic garnet. This zonation aids in distinguishing the relative timing of apatite trapping in some garnet grains, indicating that apatite inclusions were trapped from early to late during the growth of the garnet crystals. EPMA analyses show that the garnet grains range in $X_{Adr}$ from 0.65 to 0.97, the balance being grossular. On average, the garnets are ~90 mol% andradite and ~10 mol% grossular and were treated as such for the purpose of elastic modeling (Table DR1; Harris and Einaudi, 1982; Einaudi, 2000).

We focused on apatite inclusions in garnet for thermobarometry because apatite inclusions are abundant, were trapped throughout the duration of garnet growth, and the $P$-dependent Raman peak shift of apatite is well known (Comodi et al., 2001; Schouwink et al., 2010). Apatite inclusions in the Casting Copper garnets ranged from 50% to 96% fluorapatite, the balance being hydroxyapatite, but are, on average, 72% fluorapatite and 28% hydroxyapatite with only trace amounts of CI (Table DR3). Despite the compositional variability, similarities in the bulk moduli of fluorapatite and hydroxyapatite cause nominal deviation in calculated entrapment $P$ (Ashley et al., 2017). Additional refinements assume ideal mixing for apatite of composition $X_F = 0.72$ and $X_{OH} = 0.28$. The apatite inclusions are commonly euhedral and individual facets of the apatite grains can be discerned in transmitted light (Figs. 2B–2E).

Apatite inclusions that were exposed to the surface during polishing were identified using reflected light microscopy (Fig. 2D).

Comparison of the Raman peak position of fully enclosed apatite inclusions to inclusions exposed to the sample surface indicate that the
fully enclosed inclusions are under tension and shifted to lower wave-numbers (Fig. 3), equivalent to ~45 to ~101 MPa with an uncertainty of ±22 MPa (Fig. 4). Heating experiments performed on these enclosed apatite inclusions reveal that the inclusions can be repressurized upon heating to >300 °C and the predicted internal pressure increase matches the observed (Fig. DR2; Ashley et al., 2017) and does not require a correction (cf. quartz inclusions; Ashley et al., 2016).

Entrapment pressure was calculated over a range of T from 325 to 450 °C. At 325 °C, about half of the inclusions restore to negative formation P (which is impossible), indicating that these inclusions must have formed at higher T. At 400 °C, most of the apatite inclusions predict modest positive P, with values ranging from ~10 to 115 MPa, consistent with previous estimates. At 450 °C, all of the inclusions restore to positive P of formation with values ranging from ~55 to 170 MPa, which is slightly higher than previous estimates but within the uncertainty of this technique (Fig. 5).

**DISCUSSION**

The well-developed growth zoning exhibited by several of our garnet grains (Fig. 2C) permits correlating the relative timing of entrapment of individual apatite inclusions. Thus, P obtained from apatite inclusions in successive growth zones may reflect the P-T evolution during garnet growth. Sample CC03, in particular, shows this variation in P and T over time. Of the six pressurized inclusions within this sample, the three inclusions exhibiting the largest tensile stress were all located close together within the same growth zone near the core of the garnet. In the next adjacent zone outward, the single inclusion is under less tensile stress than the preceding three. The final two inclusions were located in a growth zone toward the rim of the garnet grain and exhibited tensile stresses similar to those in the second zone. This trend suggests either an increase in P or a decrease in T during garnet growth (Fig. 4). In addition, some areas of the garnet contain clusters of apatite inclusions grouped together (Fig. 2E), suggesting coeval entrapment. Sample CC01 contains a cluster of three apatite inclusions (Fig. 2E) that have consistent internal P (between −75 and −89 MPa at ambient conditions; Fig. 4).

Some of the garnet grains host apatite inclusions exhibiting consistent internal P, while others exhibit highly variable P (Fig. 4). This variability may be due to postentrapment depressurization (e.g., through fracturing the surrounding host), analytical uncertainties, or variation in P and/or T within the system during the time of formation. It is possible that some of the variation in internal P, especially among inclusions with the greatest tensile stress, is due to edge effects in which tension is focused along the apatite-garnet grain boundary more than the core of the inclusion (DeWolf, 1996). In addition, because the Casting Copper skarn formed at shallow depths, it is possible that periods of hydrostatic P were punctuated by periods of fluid overpressure as magmatic fluids were vented through the system (Burnham and Ohmoto, 1980). If the fluid P periodically exceeded hydrostatic P, we would expect to see significant variability between the internal P of inclusions and their predicted P of formation, which is what we observe among apatite inclusions. As such, statistical analysis of the apatite P, computing the mean estimates among coeval inclusions, appears to be the best approach for estimating P. At the low end of the T scale at 350 °C, the mean P of entrapment is ~17 ± 50 MPa. At this T, many of the inclusions predict that negative formation P is impossible, so it is likely that the majority of inclusions were entrapped at T > 350 °C. At 400 °C,
the mean P of formation is ~62 ± 50 MPa, within the range estimated based on stratigraphy. At 450 °C, the average P of formation is 107 ± 50 MPa, which is much higher than the estimated P of formation provided by Harris and Einaudi (1982). So, for each 50 °C increase in modeling T, the predicted P of formation increases by ~45 MPa. For these reasons, we infer that most inclusions at the Casting Copper skarn likely formed in the T range of 375–400 °C. Despite the range of possible formation T and the variability in inclusion P, the majority of our data fit within an ~100 MPa window that is broadly consistent with previous estimates (Fig. 5).

CONCLUSIONS

The mean trapping P estimated at 400 °C is ~62 MPa ± 50 MPa. Thus, our results corroborate previous estimates of formation P for Casting Copper, and indicate thatapatite inclusions in garnet can be an effective barometer at relatively high T and low P in hydrothermal systems, even with the inherent uncertainties associated with this method. The Casting Copper skarn represents a test case for this approach because the formation conditions are well constrained, and therefore these results suggest that our approach can be extended to other less well-known skarn systems. This approach is thus promising for illuminating the formation P of skarn systems and better constraining genetic and exploration models (Meinert et al., 2005).

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