Fluid compositions reveal fluid nature, metal deposition mechanisms, and mineralization potential: An example at the Haobugao Zn-Pb skarn, China

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ABSTRACT

Fluid inclusion compositions obtained from laser ablation–inductively coupled plasma–mass spectrometry at the Haobugao Zn-Pb skarn in northeastern China provide constraints on fluid origin, evolution, and metal deposition mechanisms and an example of evaluating mineralization potential. Metal concentrations in the prograde fluids were high (up to 1.4 wt% Zn and 1.8 wt% Pb) but remained in solution, likely due to the high temperatures (440–575 °C) and salinities (35.4–45.3 wt% NaCl equivalent). Absolute concentrations of elements (e.g., Rb and Na) and mass ratios (e.g., Zn/Na and K/Na) reveal that the early, prograde fluids were magmatic, consistent with the oxygen isotope composition of fluids (δ\(^18\)O\(_{\text{H}_2\text{O}}\) = 5.5‰–8.5‰). Later mixing with a meteoric fluid caused dilution and Zn-Pb deposition, as revealed by lowered element concentrations and Pb/(Na + K) and Zn/(Na + K) ratios in the sulfide-stage fluid inclusions. Elevated Ca/K ratios in sphalerite-hosted inclusions indicate fluid-carbonate reactions that buffered fluid pH, also facilitating Zn-Pb precipitation. Although cassiterite and molybdenite occur locally at Haobugao, mass balance calculation shows low metal endowment (maximum 2900 t Sn and 2200 t Mo) of the system. Furthermore, the generally unchanged Sn/(Na + K) and Mo/(Na + K) ratios from pre- to late-mineralization fluids suggest that the fluids were never saturated in Sn and Mo. Therefore, finding much Sn or Mo at Haobugao is unlikely. This demonstrates a potential tool for evaluating the metal endowment of a mineral prospect, which may guide exploration.

INTRODUCTION

Compositions of single fluid inclusions (FIs) measured by proton-induced X-ray emission (Ryan et al., 1991) and laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS; Audétat et al., 1998; Heinrich et al., 1999) have been used to investigate magmatic hydrothermal fluid compositions (e.g., Audétat, 2019), to infer fluid types (e.g., Samson et al., 2008) or pulses (e.g., Baker et al., 2004; Kouzmanov et al., 2010), to define hydrothermal processes (e.g., Audétat et al., 1998; Heinrich, 2005), and for thermodynamic modeling (e.g., Bertelli et al., 2009). This study expands the usage of fluid compositions determined by LA-ICP-MS to examine the full fluid evolution of the Haobugao Zn-Pb skarn system in northeastern China from the early pre-mineralization prograde stage through the sulfide stage to the final post-ore stage. The examination reveals the proportion of different fluids (e.g., magmatic, meteoric, and formation) in the hydrothermal system over time, the metal deposition mechanisms, and the resource potential of some less-abundant metals. The Haobugao deposit evolved from an early high-temperature (~575 °C) prograde stage through to a retrograde low-temperature post-ore overprinting mineral assemblage (~150 °C), making it suitable for such a study. The approach presented here may also apply to other skarns that contribute to the world’s supply of W, Sn, Zn-Pb, Mo, Cu, Au, and Fe (Meinert et al., 2005; Chang et al., 2019).

DEPOSIT GEOLOGY

The Haobugao skarn deposit (44°37’N, 119°16’E) in Inner Mongolia, northeastern China (Fig. 1A) contains 0.29 Mt Zn averaging 4.24% Zn, 0.15 Mt Pb (2.25% Pb), and 2.91 Mt Fe (28.7% Fe), with subordinate Cu and Ag and minor newly discovered Mo and Sn (Sun et al., 2018). The Haobugao deposit is related to an Early Cretaceous biotite granite porphyry stock that emplaced into intercalated silstone and/or shale and limestone of the Permian Dashizhai Formation (Fig. 1B). The skarn is an ~800-m-long, ~900-m-deep, steeply dipping tabular body. It fully replaced the limestone bed near the intrusion and partially replaced it at distal locations along the limestone-siltstone and/or shale boundary (Fig. 1B; Fig. S1 in the Supplemental Material). The paragenesis includes a pre-mineralization prograde garnet-pyroxene stage, followed by an Fe (magnetite) mineralization stage accompanied by retrograde amphibole-epidote-ilvaite-quartz alteration, a sulfide (sphalerite-galena-pyrite and minor chalcopyrite–carnotite) mineralization stage with further retrograde chlorite-quartz-calcite alteration, and a post-ore stage of barren calcite veins (Figs. 1C–1E; Figs. S2 and S3). Minor molybdenite and cassiterite were deposited in the late Fe stage and early sulfide stage. The prograde stage is zoned, with a garnet-dominant zone near the intrusion, an intermediate pyroxene-rich zone, and a distal wollastonite ± siderite zone at the marble front.

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\(^1\)Supplemental Material. Methods, results, Figures S1–S6, and Tables S1–S6. Please visit https://doi.org/10.1130/GEOLOG.13262843 to access the supplemental material, and contact editing@geosociety.org with any questions.

Fig. 1. (A) Location of the Haobugao skarn deposit, northeastern China. (B) Schematic cross section of Haobugao (details are provided in Fig. S1 [see footnote 1]).

Groups of individual FIs in a particular growth zone of the host mineral or in the same pseudosecondary trails are considered a fluid inclusion assemblage (FIA; Goldstein and Reynolds, 1994). Where growth zones and pseudosecondary trails are absent, FIs in a cluster with similar phase ratios and microthermometric measurements are also treated as a FIA in this study (Figs. 1F–1H and 1I).

RESULTS
Sample information, analytical details, and the microthermometric and fluid composition data are available in the Supplemental Material. Brine (type B) inclusions in pyroxene homogenize to liquid after halite disappearance, with homogenization temperatures \( T_h \) of 421–575 °C for the 19 FIs, and salinities of 35.4–45.3 wt% NaCl equivalent. LA-ICP-MS analyses show that they contain 0.3–1.9 wt% Zn and 0.5–1.8 wt% Pb. Concentrations of Mo and Sn are significantly lower; 21–84 and 27–122 ppm, respectively (Tables S2–S4; Fig. S4).

For the boiling assemblages with both brine and vapor inclusions (types B and V) in pyroxene, calculated trapping pressures (Steele-MacInnis et al., 2012) are 500–525 bar (average 513 bar). The high-temperature prograde stage was likely under near-lithostatic conditions (Fournier, 1999), therefore the formation depth is estimated at ∼1.9 km. This depth is similar to the ∼2.0 km emplacement depth of the causative intrusion, calculated using a hornblende geobarometer (Ridolfi et al., 2010; Table S5). For the brine FIs without coexistent vapor inclusions, the pressure (513 bar)–corrected trapping temperature is estimated at 250–260 °C for the 19 FIAs, and salinities of 1.2–4.2 wt% NaCl equivalent. They are depleted in most elements (e.g., <31 ppm Zn and <22 ppm Pb), with Mo and Sn below detection limits.

The pressures calculated from type L FIAs in calcite are used to estimate the depth for the prograde skarns. This agrees with the observation that many Zn-Pb stage minerals postdated by later calcite (calcite–siderite–galena) veins or interstitial filling. (E) Massive ore composed of calcite–siderite–galena (gn) veins or interstitial filling.

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lower concentrations of the elements, such as meteoric water, and indicates that these elements remained undersaturated during this stage, likely due to the high temperatures and salinities maintaining high solubilities of the elements. The \( \delta^{18}O_{H_2O} \) values of the fluids (5.5‰–8.5‰) indicate a magmatic origin (Meinert et al., 2003), which is consistent with the near-lithostatic conditions under which external fluid involvement was unlikely.

The sulfide-stage fluids have significantly lower salinities (2.2–9.5 wt% NaCl equivalent) than the prograde fluids. They are likely the mixing product of the prograde brine and meteoric water, as indicated by the gradual decrease in the \( \delta^{18}O_{H_2O} \) values from prograde to post-ore stage, which are not explainable by mixing with formation water. Compiled fluid compositions for initial fluid are based on compositions of prograde-stage brine and vapor inclusions, assuming that they are the boiling product of 10 wt% NaCl equivalent single-phase fluid. pyx—pyroxene; sp—sphalerite; cal—calcite.

Fluids in skarn and porphyry mineralization systems

3. (C,D) Comparison of Haobugao fluids with typical formation water on Rb versus Na and Zn/Na versus K/Na plots. Gray arrows show fluid evolution trends from prograde to post-ore stage, which are not explainable by mixing with formation water. Compiled fluid compositions for B–D are from basins and skarn or porphyry deposits from: 1—North America and the Gulf of Thailand (Samson et al., 2008, and references therein); 2—western Honduras (Samson et al., 2008); 3—northern Finland (Niiranen et al., 2005); 4—northern and central Mexico (Haynes and Baker, 1999; Baker and Lang, 2003) because the As/(Na + K) and Li/(Na + K) ratios of the Zn-Pb-mineralizing fluids are significantly lower than those from that of type V FIAs. Reconstructed values of initial fluid are based on compositions of prograde-stage brine and vapor inclusions, assuming that they are the boiling product of 10 wt% NaCl equivalent single-phase fluid. (Fig. 2A). The cooling gradually drove the system into a brittle state (Fournier, 1999) and the prograde skarns had abundant interstitial vapor inclusions, which is consistent with the near-lithostatic conditions under which external fluid involvement was unlikely.

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(Figs. 1C and 1D), suggesting formation at similar paleodepths. A pressure correction of 2–12 °C has been made using the trapping pressure 192 bar for the type L FIAs (Table S2).

The measured oxygen isotope compositions (\( \delta^{18}O \)) of prograde pyroxene and garnet are 3.7‰–6.7‰, and the calculated \( \delta^{18}O_{H_2O} \) values are 5.5‰–8.5‰ (Table S6). The measured \( \delta^{18}O \) values for magnetite in Fe mineralization stage are –5.5‰ to –3.4‰, corresponding to \( \delta^{18}O_{H_2O} \) values of 1.9‰–4.4‰ (Table S6). The \( \delta^{18}O \) values for the sulfide stage calcite and quartz are 5.9‰–8.4‰, with the calculated \( \delta^{18}O_{H_2O} \) values being –0.4‰ to 3.2‰ (Table S6).

**FLUID SOURCES, EVOLUTION, AND METAL DEPOSITION**

The fluid salinities (35.4–45.3 wt% NaCl equivalent) and element (e.g., Na, K, Rb, Cs, Zn, Pb, Sn, and Mo) concentrations of the prograde-stage brine remain nearly constant over the temperature range of 550–440 °C (Fig. 3A). This excludes mixing with fluids with
vary only slightly (Fig. 3), indicates Zn-Pb mineralization occurred simultaneously with fluid mixing. If Zn and Pb were not deposited during mixing, their ratios to Na + K would have stayed roughly the same as those of other elements despite dilution. During mixing, the salinity decrease destabilized the Zn and Pb chloride complexes, lowering the metals' solubilities by several orders of magnitude (Kouzmanov and Pokrovski, 2012). The decreased temperature and increased pH during mixing also reduced the Zn-Pb solubilities (Bertelli et al., 2009). Therefore, mixing could have resulted in rapid Zn-Pb deposition (Seward and Barnes, 1997).

Fluid-carbonate reaction, revealed by fluid Ca/K ratios, may have also facilitated Zn-Pb deposition. The Ca/K ratios in sphalerite-hosted FIAS at Haobugao are 0.3–1.9, significantly higher than those of typical magmatic fluids recorded in porphyry Cu (Mo, Au) deposits (mostly <0.4; Fig. 2B). The higher Ca/K ratios are believed to be a result of carbonate dissolution by weakly acidic magmatic-hydrothermal fluids. The increasing Ca/K ratios from proximal to distal skarns (Fig. 2B) are consistent with a gradual elevation of Ca relative to K through the dissolution of carbonate along the path from the causative magmas. Haynes and Kesler (1988) attributed the relatively high Ca/K ratios in skarns in Mexico to contributions from sedimentary rock–derived fluid (i.e., formation water), which has higher Ca/K ratios than magmatic fluids (Fig. 2B). However, Rb versus Na and Zn/Na versus K/Na plots show that there is no evidence of formation-water involvement during the fluid evolution in the Haobugao deposit (Figs. 2C and 2D). Fluid-carbonate reactions buffered fluid pH, which also promoted sulfide deposition (Bertelli et al., 2009; Kouzmanov and Pokrovski, 2012).

In the post-ore stage, the fluids contain very little of the ore metals (<31 ppm Zn and <22 ppm Pb) because most of them had precipitated out during the mineralization.

Evaluating the Economic Potential of Sn and Mo

Composition of fluids can be used to assess the mineralization potential of a full hydrothermal system. At Haobugao, continuing exploration recently found some local cassiterite and molybdenite (Fig. S2), which inspired the speculation of a magmatic-hydrothermal ore deposit: Insights with LA-ICP-MS analysis of fluid inclusions: Science, v. 279, p. 2091–2094, https://doi.org/10.1126/science.279.5359.2091.


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