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Virtual Event
September 21-23
2020
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Apatite and Zircon Compositional Constraints on the Petrogenesis of the Huojihe Porphyry Mo Deposit, Lesser Xing'an Range, NE China

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Summary

Northeastern (NE) China is an important Mo resource region in China, with more than 80 Mo deposits and occurrences. To better understand the key factors leading to porphyry Mo deposit formation in such a relatively short time (mainly Jurassic to Early Cretaceous) and in a limited area (NE China), the Huojihe deposit that is one of the representative deposits from many Mesozoic porphyry Mo deposits in the Lesser Xing'an Range, NE China, was selected for investigation in an attempt to clarify the possible metal deposition mechanisms. The combination of whole rock geochemistry and mineral-chemical and isotopic analyses of zircon and apatite in this study has provided considerable insight into the characteristics of the causative magma and ore-forming mechanisms responsible for the Huojihe porphyry Mo deposit. Notably, magmatic apatites crystallized from H_2O-saturated melt, whereas some might have been hydrothermally altered during the porphyry Mo mineralization and didn't experience any hydrothermal alteration, are used to constrain the physiochemical conditions of the initial pre-degassing magmas, combined with the magmatic zircon analyses.

Introduction

In recent years, many new porphyry Mo deposits have been discovered in NE China, making northeastern China the largest Mo ore region in China (Shu et al., 2016; Chen et al., 2017). These deposits are generally characterized by Mo-only or Mo-dominated with little or no Cu. Many of them have Jurassic to Early Cretaceous ages and have been suggested to be related to magmatic events during the subduction or subsequent slab rollback of the Paleo-Pacific oceanic plate (Wu et al., 2011; Ouyang et al., 2013; Shu et al., 2016; Zhai et al., 2018). One of

the major puzzling questions is for what reasons such large-scale porphyry Mo mineralization can occur in a relatively short time (mainly Jurassic to Early Cretaceous) and in a limited area (NE China). Whether there is any inherent Mo enrichment of the source region and/or any pre-degassing magma processes leading to high-Mo melts remains enigmatic. Previous work has been largely focused on the geology characteristics, geochronology, ore-forming fluids, and regional metallogenic setting of these porphyry systems (e.g., Shu et al., 2016; Chen et al., 2017; Gao et al., 2018, and references therein), while little has touched on the characteristics of the initial pre-degassing magmas responsible for the porphyry Mo mineralization in this region. Melt inclusion composition should be a direct and intuitive proxy of the physicochemical features of the parental ore-forming magmas, which has been applied in various Climax-type porphyry Mo deposits from North America (e.g., Lerchbaumer and Audétat, 2013; Mercer et al., 2015; Audétat and Li, 2017; Zhang and Audétat, 2017a, b). However, little information on melt inclusions has been reported for the porphyry Mo deposits in NE China, which hampers the understanding of the Mo concentrations of the causative melts.

Zircon and apatite are common magmatic accessory minerals and relatively stable over a wide variety of geological processes including weathering, transport, and weak hydrothermal alteration (Belousova et al., 2002a, b; Cook et al., 2016); therefore magmatic zircon and apatite can preserve considerable physicochemical information of their equilibrium magmas, which have been widely used to quantify magma oxidation state, trace magma source, evaluate magma fertility, and reflect degrees of magma fractionation (Watson, 1980; Ballard et al., 2002; Piccoli and Candela, 2002; Dilles et al., 2015; Lu et al., 2016; Pan et al., 2016; Zeng et al., 2016; Chelle-Michou et al., 2017; Richards et al., 2017; Azadbakht et al., 2018; Shu et al., 2019). However, it has been documented that acids can very likely alter the magmatic apatite and as a result, the compositions would be partly or completely changed (cf. Harlov, 2015). Moreover, even for magmatic apatite, various element contents (especially volatiles) will dramatically change in volatile-saturated silicate melt during the crystallization or degassing process. Therefore, apatite crystals equilibrated under H_2O-saturated conditions can't preserve a record of initial melt compositions (Stock et al., 2018; Audétat, 2019), and only these magmatic grains crystallized under volatile-undersaturated conditions have been selected for component analysis to indicate the characteristics of the ore-forming parental melt.

In this paper, systematic element and isotopic compositions have been analyzed in apatite and zircon from the granitic intrusions related to the Mo mineralization in Huojihe. Zircon Hf and apatite (and also whole rock) Sr-Nd isotopes were used to reveal the magma source regions, while the elemental compositions of both minerals have provided insights into the nature of the ore-forming magmas. The results from this study are helpful in understanding the possible factors controlling the Mo mineralization in Huojihe, and probably in other porphyry Mo deposits in NE China and worldwide.

Samples and Methods

In this study, three biotite monzogranite samples and one granodiorite sample were selected for apatite geochemical and *in situ* Sr-Nd isotopic analyses, one biotite monzogranite sample was selected for zircon U-Pb dating, Hf isotope, and trace element analyses, and four samples (including two biotite monzogranite and two granodiorite samples) were collected for whole rock compositional and Sr-Nd isotopic analyses.

Results and conclusions

Zircon U-Pb dating shows that ore-bearing biotite monzogranite from Huojihe deposit was emplaced in the early Jurassic (ca.181.6 Ma), which is consistent with the previous molybdenite Re-Os age and granodiorite U-Pb age. The mineralized granitic rocks share homogeneous geochemical compositions, and can be classified as oxidized high-K calc-alkaline, I-type granite. The intrusion samples have similarly initial $^{87}Sr/^{86}Sr$ ratios of 0.7072–0.7075 and slightly negative $\varepsilon_{Nd}(t)$ values from -2.3 to -1.4, reflecting a uniform magma source. The least-altered apatites show similar (or slightly enriched) initial $^{87}Sr/^{86}Sr$ ratios (0.7080–0.7108) and $\varepsilon_{Nd}(t)$ values (-4.0 to -1.8), whereas the hydrothermally altered apatites are characterized by significantly higher initial $^{87}Sr/^{86}Sr$ ratios (0.7091–0.7119) and more negative $\varepsilon_{Nd}(t)$ values (-4.9 to -4.4), probably due to the interaction between the hydrothermal fluids and wall rocks. The zircon $\varepsilon_{Hf}(t)$ values range from -0.9 to 1.7, corresponding to a restricted range of T_{DM2} ages from 1279 to 1120 Ma. The Sr-Nd-Hf isotope results suggest that the parental magmas associated with the Mo mineralization were originally derived from partial melting of the Mesoproterozoic lower crust with a subordinate contribution from the depleted mantle. The early Jurassic magmatism and Mo mineralization were very likely related to the flat-slab subduction of the Paleo-Pacific plate.

The low Ga and Ce and high Eu contents in the magmatic apatite reflect a oxidized magma in Huojihe, which is also supported by the high zircon Ce_N/Ce_N^* (22–568) and Eu_N/Eu_N^* (0.38–0.71) values. Two available partition coefficients for S between apatite and oxidized melt are used to estimated the absolute sulfur concentrations in the mineralization-related melt based on apatite SO_3 contents. The models return relatively low magmatic sulfur concentrations in Huojihe (20–100 ppm), indistinguishable from those of larger or smaller deposits or even barren magmatic bodies. Using the estimated magmatic sulfur concentrations, a minimum volume of 10–50 km^3 magma has been suggested to be necessary to produce the Huojihe Mo deposit based on mass balance modelling. Besides, the Mo concentration in the original magma have also been roughly estimated (2–10 ppm) based on the magma size and the contained Mo in Huojihe. Although our data show relatively low Zr/Hf, Nb/Ta, and Th/U ratios in zircon, and low Fe/Mn, La/Yb, and Th/U ratios in apatite that reflect a high degree of fractionation of the host magmas, no obvious Mo enrichment was observed in the residual melt. Comparing our data with several other mineralized systems of various size and barren systems, no systematic differences in the S and Mo contents of the parental melts was observed in any of the complied mineralized or barren occurrences, suggesting no special S and Mo enrichment are required to form even large porphyry Mo systems.

To conclude, all the evidence presented above suggests magmatic accessory minerals including zircon and apatite are useful to constrain the age, origin, and composition of the magmas responsible for porphyry Mo mineralization. It is suggested that pre-degassing enrichments of Mo and S in the original magma are not necessarily important in the formation of the Huojihe Mo deposit, and that factors other than melt composition, including (but not limited to) a large-sized magma chamber with high magmatic oxygen fugacity, may be the essential prerequisites to form a porphyry Mo system.

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