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Accessory Minerals Compositional Constraints on the Formation Conditions of Magmas Related to Porphyry Mo mineralization, Daheishan deposit, NE China

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Summary

In Northeastern (NE) China, there are more than 80 porphyry Mo deposits, making it the largest Mo ore region in China. However, the major factors controlling the large-scale porphyry Mo mineralization in this region are still unclear, and 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. Daheishan is one of the typical porphyry Mo deposits in the Lesser Xing'an-Zhangguangcai Range, NE China, and the magmatic features and ore-forming processes remain obscure, which presents an excellent opportunity to study the possible factors controlling the Mo endowment. In this contribution, we present a detailed study of mineralogy, whole rock and mineral compositions, and isotopes from the Daheishan Mo deposit, followed by discussions on petrogenesis of the causative intrusions, characteristics of ore-forming magma, and ore precipitation mechanisms. The results from this study would give a clear constraint for the Mo mineralization in Daheishan deposit and provide better insight into understanding the ore-forming mechanisms for other porphyry Mo deposits in this region and worldwide.

Introduction

NE China has become the largest Mo ore region in China (total Mo>11.4 Mt) due to abundant new discoveries, over the last decade, of large to giant Mo-only or Mo-dominated polymetallic deposits. Most of these Mo deposits in northeastern China are porphyry type with generally Mesozoic ages (Ouyang et al., 2013; Shu et al., 2019), such as Chalukou (2.46 Mt Mo; Duan et al., 2018), Caosiyao (1.79 Mt Mo; Wu et al., 2017), Daheishan (1.09 Mt Mo; Zhou et al., 2014), Luming (0.89 Mt Mo; Chen and Zhang, 2018), and Huojihe (0.28 Mt Mo; Xing et al., 2020). Many studies have been carried out on these Mo deposits, mainly concentrating on their geologic characteristics, geochronology, whole rock geochemistry, and isotopic signature, as well as studies of ore-forming fluids and regional metallogenic setting (Zeng et al., 2014; Han et al., 2014; Chen et al., 2017; Gao et al., 2018, and references therein); however, to date only a few papers have focused on the characteristics of the ore-related parental magmas and the key controls on the Mo mineralization in this region (Ouyang et al., 2020; Xing et al., 2020). Although the direct and intuitive understanding of the physicochemical features of the initial mineralization related magmas is melt inclusions (e.g., Lerchbaumer and Audétat, 2013; Mercer et al., 2015; Audétat and Li, 2017; Zhang and Audétat, 2017a, b; Ouyang et al., 2020), accessory minerals (e.g., apatite, titanite, and zircon) in ore-related intrusions can also provide indirect evidence on the nature of the ore-forming magmas; this is due to the extremely sparse melt inclusions in these porphyry Mo deposits in NE China.

Apatites and titanites are important accessory minerals in granitic rocks, both of which are major carriers of various key trace elements (i.e., halogens, S, As, Fe, Mn, Ga, Sr, and REEs) (Nagasawa, 1970; Henerson, 1980; Nakada, 1991). They are relatively resistant to alteration and weathering and therefore preserve their original geochemical signatures even after weak hydrothermal alteration (Belousova et al., 2002a, b; Selvig et al., 2005; Cook et al., 2016). Hence, magmatic apatite and titanite record and preserve important geological information of their equilibrium parental magmas (cf. Watson, 1980; Tiepolo et al., 2002; Piccoli and Candela, 2002; Mathez and Webster, 2005; Pan et al., 2016, 2018; Azadbakht et al., 2018; Xing et al., 2020). For example, the Ga content, Ce and Eu anomalies of titanite and apatite have been widely used to evaluate the oxidation state of magma (e.g., Cao et al., 2012; King et al., 2013; Chelle-Michou et al., 2014; Pan et al., 2016, 2018), halogen and sulfur compositions in magmatic apatite have been applied to estimate volatile compositions in melt (cf. Coulson et al., 2001; Pan and Fleet, 2002; Chelle-Michou et al., 2017; Richards et al., 2017), the concentrations of Sn, W, and Mo in titanite are important indicators for evaluating magma fertility for these metals (cf. Pan et al., 2018), and the Sr/Y, La/Yb, and Dy/Yb ratios are utilized to indicate the magmatic water contents (e.g., Lu et al., 2016; Nathwani et al., 2020). Furthermore, apatite and titanite Nd isotopic compositions can shed light on the magma source (Gregory et al., 2009; Zeng et al., 2016).

Samples and Methods

Twelve granitic samples in this study were collected from the surface outcrops of the Daheishan deposit in order to perform whole-rock compositional, minerals (apatite, titanite) geochemical, and *in situ* Nd isotopic analyses. Six fresh granitic samples, including four of Qiancuoluo granite porphyry (166.6 Ma) and two of Qiancuoluo biotite granodiorite (169.9 Ma), were selected for whole rock major and trace element composition analyses. Samples used for major and trace elements analyses of the apatite and titanite were selected from these twelve fresh granitic rocks expect one granite porphyry with weak potassic alteration and one with weak sericite alteration.

Results and Conclusions

Whole rock geochemical data show that the causative plutons in Daheishan deposit share homogeneous compositions, and both are characterized by peraluminous high silica, alkali rich compositions, belonging to high-K calc-alkaline, I-type granites with adakitic affinities. Magmatic apatite and titanite from the intrusions show similar $\varepsilon_{Nd}(t)$ values from -1.1 to 1.4, corresponding to a restricted range of T_{DM2} ages from 842 to 1039 Ma. Combining with the tectonic setting, the Nd isotopic compositions reflect the ore-forming intrusions have a relatively uniform magma source, indicative of formation from parental magmas dominantly derived from melting of the juvenile lower crust with minor depleted mantle materials.

The low Ce and high Eu contents in magmatic apatite and titanite suggest that the mineralization-related magmas has a high oxygen fugacity. These results are also supported by the high Fe_2O_3/FeO (>1) ratios of the whole rock, as well as the low Ga concentrations in apatite (9–52 ppm), but high Ga concentration in titanite (36–122 ppm). The high Sr/Y ratios of whole rock, relatively high δEu/Y, La/Yb, and low Dy/Yb ratios of apatite, titanite, and zircon in Daheishan are interpreted to reflect the high magmatic water contents. Using two published partition coefficients for S between apatite and oxidized silicate melt, we estimated the absolute S concentration in pre-degassing melt was 15–88 ppm, which display no systematic difference with the subeconomic and barren occurrences. Based on the mass balance constraints on estimated S, a minimum volume of 33–193 km^3 magma are required to form the Daheishan deposit. In addition, a rough estimate of magmatic Mo concentrations via magma chamber size and Mo inventory in Daheishan show an apparent Mo-poor character of the mineralized magmas (2–13 ppm), which is consistent with the low Mo contents in titanite (11–53 ppm). Comparing many other porphyry Mo/Mo-Cu, subeconomic, and barren systems, we conclude that a large volume of magma (at least several tens to hundreds of km^3) with high oxygen fugacity and water contents are more likely the key controls on Mo endowment, while the pre-degassing enrichments of Mo and S in parental magma are not essential prerequisites for formation of the Daheishan Mo deposit. The findings in this study can apply to evaluate whether a magmatic system has the potential to form Mo mineralization.

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