Trace element and isotopic (S, Pb) constraints on the formation of the giant Chalukou porphyry Mo deposit, NE China

QINGQING ZHAO1†, DEGAO ZHAI1,2,* ANTHONY E. WILLIAMS-JONES2, and JIAJUN LIU1‡

1State Key Laboratory of Geological Processes and Mineral Resources, and School of Earth Sciences and Resources, China University of Geosciences, Beijing, 100083, China
2Department of Earth and Planetary Sciences, McGill University, Montreal, Quebec H3A 0E8, Canada

ABSTRACT

Porphyry-type Mo deposits have supplied most of the Mo to the world. However, the source of the Mo and the controls on its enrichment in such deposits is still a matter of great debate. In this study, we present in situ trace element and isotopic data for a giant porphyry Mo deposit (the Chalukou Mo deposit in NE China) and use these data to address these issues. Three primary paragenetic stages of mineralization were recognized at Chalukou: (Stage I) K-feldspar + quartz + minor pyrite (Py-I) + minor molybdenite (Mol-I); (Stage II) quartz + sericite + molybdenite (Mol-II) + pyrite (Py-II); (Stage III) quartz + chlorite + epidote + fluorite + pyrite (Py-III) + galena + sphalerite + minor chalcopyrite. The bulk of the molybdenite was deposited in Stage II. In situ S isotope analyses of the sulfide ores show that the $\delta^{34}S$ values vary from –5.2 to +7.8‰ (mean = +2.9‰) and correspond to $\delta^{34}S_{\text{H}_{2}\text{S}}$ values from –2.4 to +3.3‰ (mean = +1.1‰). These values are consistent with a magmatic source for the sulfur. In situ Pb isotope compositions of the sulfide ores are almost identical to those of the local Mesozoic granites and other magmatic-hydrothermal ore deposits in this region, suggesting a close genetic association between the Mo mineralization and felsic magmatism.

Pyrite from the three stages of mineralization differs significantly in its trace element composition. The first generation, Py-I, has a high Cu content (8.7 ± 49.6 ppm; where the first value is the median and the second is the standard deviation) and Mo content (6.9 ± 3.8 ppm). Pyrite-II has the lowest Cu concentration (1.3 ± 2.1 ppm) and a relatively high Mo concentration (5 ± 128 ppm), and Py-III has a high Cu content (8.7 ± 37.1 ppm) but the lowest Mo content (0.05 ± 5.7 ppm). From this, we infer that pyrite recorded the chemical evolution in the Mo/Cu ratio of the ore fluid and that this ratio reached a maximum in Stage II, coinciding with the widespread saturation of the fluid in molybdenite. The evolution of the Mo/Cu ratio in pyrite implies that the fluid was undersaturated in chalcopyrite at the high temperature of Stage I, despite the Cu concentration of the fluid apparently being at its high level, and chalcopyrite only saturated later, at a lower temperature. Molybdenite, however, because of its lower solubility, saturated early (Stage I) and in the subsequent stage (Stage II) was supersaturated in the fluid.

There is a significant enrichment of Mo in the syn-ore intrusions at Chalukou compared to the pre-ore monzogranite. The very low Sr/Y ratios for the Chalukou syn-ore intrusions, which are in sharp contrast to the high Sr/Y ratios of the pre-ore monzogranite and those of porphyries related to Cu deposits, suggest that fractional crystallization of plagioclase may have been a key factor in generating the syn-ore magmas. Molybdenum is a highly incompatible metal and will concentrate in the crust, and assimilation of old continental crust, therefore, may explain the Mo enrichment of the syn-ore intrusions and ultimately the formation of the giant Chalukou deposit.

Keywords: Sulfur and lead isotopes, trace element chemistry, porphyry Mo deposits, magma and fluid evolution, metal source and enrichment

INTRODUCTION

The genesis of porphyry-type deposits has been a subject of debate since their discovery (Camus 1975; Carten et al. 1988; Clark et al. 1990; Mathur et al. 2000; Richards 2003, 2011; Sillitoe 2010; Lee and Tang 2020). Much of this debate has centered on the sources of the ore metals and the processes of enrichment, particularly for the giant deposits (Audétat et al. 2000; Lee et al. 2012; Chiaradia 2014; Chang et al. 2018; McFall et al. 2019). Early models for the formation of porphyry deposits focused on processes relating to subduction (Clark et al. 1990; Blevin 2002; Richards 2003, 2011; Sillitoe 2010; Olson et al. 2017), but as some porphyry deposits form in post-collisional settings, it has become clear that their genesis needs to be viewed through a wider lens (Hou et al. 2015; Yang et al. 2015; Yang and Cooke 2019; Xu et al. 2021). Whether porphyry-type deposits emplaced in different tectonic settings have different metal sources is a point of contention (Zheng