Revision 2

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

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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: (I) K-feldspar + quartz + minor pyrite (Py-I) + minor molybdenite (Mol-I); (II) quartz + sericite + molybdenite (Mol-II) + pyrite (Py-II); (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$_{H2S}$ 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 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; Sillitoe 2010; Richards 2003, 2011; 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 (Audéetat et al. 2000; Chiaradia 2013; Lee et al. 2012; 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; 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 et al. 2019). Some studies of porphyry Cu deposits have suggested that the Cu is derived from a mixture of oceanic crust and mantle during subduction (Zhou et al. 2015). Others have concluded that, in arc magmas, there is a negative correlation between crustal thickness and copper content (Chiaradia 2013), which suggests that the required Cu may come from the deep continental crust (Sillitoe 2010). It is thought, however, that in the unusually well-endowed Colorado and Qinling Mo porphyry districts a large proportion of the molybdenum came from recycling of ancient continental crust (Carten et al. 1993; Mao et al. 2011).

The Great Hingan Range metallogenic belt, which lies in the eastern part of the Central Asian orogenic belt (CAOB), hosts numerous porphyry Mo (-Cu), skarn Fe,
epithermal Au-Ag and polymetallic (Ag-Pb-Zn) vein deposits (Chen et al. 2012, 2017; Zhai et al. 2014, 2017, 2019, 2020; Shu et al. 2016; Gao et al. 2016; Xing et al. 2020). More than 80 Mo deposits have been discovered in northeast China (e.g., Chen et al. 2017; Xing et al. 2020), and among them, the Chalukou deposit is the largest (reserves of 2.46 Mt @ 0.087 wt.% Mo; Zhao et al. 2021a). Previous studies have discussed the deposit geology and its tectonic setting (Jin et al. 2014), the age of the mineralization (Nie et al. 2011; Liu et al. 2014b; Zhang and Li 2017; Zhao et al. 2021a), the bulk rock geochemical and Sr-Nd-Hf isotope compositions (Li et al. 2014; Liu et al. 2015a; Liu et al. 2017; Duan et al. 2018), the fluid inclusion characteristics and the H-O-S-Pb isotope data (Liu et al. 2014a; Li et al. 2019). These studies have concluded that the Chalukou deposit was the product of hydrothermal processes related to a set of highly-fractionated magmatic rocks, including monzogranite, granite porphyry, fine-grained porphyry and quartz porphyry, during the subduction of the Mongol-Okhotsk Ocean (Nie et al. 2011; Li et al. 2014; Liu et al. 2017). Issues relating to metal source and the processes of metal enrichment, however, have not been fully addressed. Whether the Mo was supplied by old continental crust, as in the Colorado and Qinling metallogenic belts, or a thickened lower crust enriched by intracrustal magmatic processes in a subduction zone remains unresolved.

In this paper, we report results of a detailed study of the in situ trace element and sulfur and lead isotopic composition of three generations of pyrite and molybdenite in the Chalukou Mo deposit, and use them to determine the metal source, reconstruct aspects of the fluid evolution and gain insight into the Mo enrichment process. The
new results indicate that in situ compositional (including isotopes and trace elements)
analyses of sulfides can provide valuable information on the environment of origin
and chemical evolution (including metal ratios) of the ore fluid.

REGIONAL GEOLOGY

The Chalukou porphyry Mo deposit is located in the Heilongjiang province in NE
China, and occurs within the Great Hingan Range metallogenic belt, which lies in the
eastern part of the CAOB (Fig. 1A). More than 80 Mo deposits have been discovered
in this area, with a combined reserve of 11.4 Mt Mo, making NE China one of the
World's most important Mo metallogenic provinces (Chen et al. 2017; Xing et al.
2020; Shu and Chiaradia 2021).

The rocks exposed in the vicinity of the Chalukou deposit comprise a Precambrian
basement, Paleozoic volcanic-sedimentary sequences and Mesozoic volcanic rocks
(Fig. 1B; Liu et al. 2017). The Precambrian basement has been subdivided into the
Xinghuadukou Group and Dawangzi Formation, with the former being composed of
migmatite, granulite, biotite-plagioclase gneiss, two-mica schist and marble. Zircon
U-Pb analyses provide an age of about 850 Ma for the Xinghuadukou group (Ge et al.
2015). This suite is overlain unconformably by greenschist facies quartz-chlorite
schist, quartz-biotite schist and minor marble of the Dawangzi Formation (Zhou et al.
2011; Liu et al. 2017). The Paleozoic volcano-sedimentary sequences comprise the
early Ordovician Tongshan and Duobaoshan Formations and the Devonian to early
Carboniferous Niqiuhe, Hongshuiquan and Baoligaomiao Formations (Li et al. 2018).
The Ordovician formations consist dominantly of tuffaceous sandstone, siltstone, limestone, andesite, dacite, tuff, minor marble and slate, and were deposited between 490 and 470 Ma (Li et al. 2018). These rocks occur mainly in the eastern Hingan Massif. The Devonian to early Carboniferous sedimentary sequences, which mainly comprise sandstone, bioclastic limestone, shale and slate (Wu et al. 2015; Liu et al. 2017), are widely distributed from the Erguna block to the Hingan Massif. They are overlain by Mesozoic volcanic rocks composed mainly of andesite, rhyolitic tuff and rhyolitic pyroclastic rocks that are widespread in the region (Fig. 1B).

Northeast China is composed of several micro-blocks (Fig. 1B; Chen et al. 2017), i.e., the Erguna, Hingan, Songliao, Lesser Hingan, and Jiamusi blocks. Multiple subduction and collisional events involving these blocks resulted in widespread magmatism (Chen et al. 2017). The Paleo-Asia Ocean that existed between the North China Craton and the Siberian Craton finally closed in the late Permian-early Triassic, leading to the assembly of several microcontinental blocks, i.e., the Lesser Hingan, Jiamusi and Songliao blocks (Johnson et al. 2001; Zeng et al. 2013; Zhao et al. 2021b), and the emplacement of numerous I-type granitoids (Zorin et al. 2001; Chen et al. 2017). The first episode of Mo mineralization in this region was during this period, e.g., the emplacement of the Gaogangshan (~250 Ma, Zhang et al. 2017) and Bilugangan (~237 Ma, Tang et al. 2012) porphyry Mo deposits.

After the closure of the Paleo-Asia Ocean, NE China gradually transformed into a syn- to post-collisional extensional setting, characterized by the widespread occurrence of Mesozoic S-type granitoids (Johnson et al. 2001; Wu et al. 2011). The
second episode of regional Mo mineralization occurred at this time, and is exemplified by the Wudaoling skarn (~194 Ma, Shi et al. 2012) and Luming porphyry Mo deposit (~177 Ma, Chen et al. 2017). This was followed by the south to southeastward subduction of the Mongol-Okhotsk oceanic plate at ~165 Ma (Wang et al. 2017), which eventually led to the closure of the Mongol-Okhotsk Ocean, the timing of which is still unresolved (Chen et al. 2017). Some researchers consider that the Mongol-Okhotsk Ocean was closed in a scissor-like style from west to east between the mid-Jurassic and early Cretaceous (Fritzell et al. 2016; Chen et al. 2017), and associate this closure with the third regional Mo mineralization event (e.g., Chalukou, ~147 Ma, Nie et al. 2011, Caosiyao, ~148 Ma, Wang et al. 2017). Other researchers, however, consider the third Mo mineralization event to be a product of the westward subduction of the Paleo-Pacific oceanic plate (Chen et al. 2017 and references therein).

ORE DEPOSIT GEOLOGY

The Chalukou ore district is 8 km long and 5 km wide, and is divided into the eastern and western exploration zones, which are separated by the Duobukuer River. Exploration has focused mainly on the eastern exploration zone, where the main molybdenum resource is located (Nie et al. 2011).

Local rocks

The tectonostratigraphic sequence exposed in the vicinity of the Chalukou deposit comprises rocks ranging in age from Neoproterozoic to Mesozoic (Fig. 2A; Xiong et
Neoproterozoic metamorphic rocks of the Dawangzi Formation crop out in the center of the ore district and discontinuously to the northeast. These rocks comprise quartz-chlorite schist, quartz-biotite schist, meta-sandstone, and minor marble; a recent zircon U-Pb analysis of quartz-chlorite schist collected from this formation yielded an age of 684.4 ± 9.5 Ma, which represents the formation age of the protolith (Li et al. 2018). The main hosts to the ores are volcano-sedimentary rocks that have been considered to be part of the thick, late Jurassic Guanghua Formation (Liu et al. 2015a). They comprise tuffs of rhyolitic, dacitic and andesitic composition and are particularly well-exposed in the eastern exploration zone where they have a thickness of > 1500 m. Recent zircon U-Pb data for three drill core samples (rhyolite, dacite and tuff) returned ages ranging from 473.9 ± 3.7 to 470.7 ± 2.4 Ma, constraining their formation to the early Ordovician. These ages coincide with those of the regional Duobaoshan Formation (from 490 Ma to 470 Ma, Li et al. 2018). Widespread late Jurassic to early Cretaceous volcano-sedimentary rocks generated from the eruption of the Jinsong caldera (Li et al. 2014), namely those of the Baiyingaolao Formation, comprise andesite, dacite, rhyolite, breccia, tuff and lava; the tuff breccia yielded a zircon U-Pb age of 135 ± 1 Ma (Nie et al. 2011; Liu et al. 2017).

Intrusions

There were three episodes of intrusions in the Chalukou area, i.e., pre-, syn- and post-ore intrusions, as revealed by detailed core logging and cross-cutting relationships (Fig. 2A, B; Liu et al. 2014b). The principal pre-ore intrusion is a
monzogranite, which is only observed in drill core at depths > 600 m below the southeast part of the Chalukou deposit and crops out over an area of > 80 km² outside the ore district (Fig. 2B). A zircon U-Pb radiometric determination yielded an age for the monzogranite of 166 ± 2 Ma (Liu et al. 2014b; Zhao et al. 2021a).

The syn-ore intrusions comprise granite porphyry, quartz porphyry and fine-grained porphyry. The granite porphyry occurs as apophyses or small stocks that intrude the Ordovician volcano-sedimentary rocks and have widths ranging from 3 to 80 m. The quartz porphyry was emplaced in the shallow parts of the deposit as small stocks intruding the Ordovician volcano-sedimentary rocks (~100 m; Fig. 2B), and is compositionally similar to the granite porphyry. A single fine-grained porphyry intruded the Ordovician volcano-sedimentary rocks in the central part of the ore district. This intrusion is only encountered at a depth >600 m (Fig. 2B). Based on zircon U-Pb radiometric determinations, the granite porphyry, quartz porphyry, and fine-grained porphyry are coeval with ages of 152.1 ± 2.2, 148.2 ± 2.2, and 148.1 ± 2.6 Ma, respectively (Li et al. 2014, Liu et al. 2014b; Zhang and Li 2017; Duan et al. 2018, Zhao et al. 2021a).

The post-ore intrusions comprise diorite porphyry and quartz monzonite porphyry, and occur mainly as small dikes (Fig. 2B) that cross-cut the earlier intrusions as well as the Mo orebodies (Li et al. 2014). Zircon from the diorite porphyry and quartz monzonite porphyry yielded U-Pb ages of 132.7 ± 2.5 and 128.4 ± 2.1 Ma, respectively (Li et al. 2014; Liu et al. 2017).
Alteration and mineralization types

The various rock-types exposed in the mine area, including quartz-chlorite schist of the Dawangzi Formation, volcano-sedimentary rocks of the Ordovician Duobaoshan Formation and the Jurassic monzogranite, all experienced intense hydrothermal alteration related to the emplacement of the syn-ore intrusions (granite porphyry, quartz porphyry and fine-grained porphyry). An elliptical alteration zone with a long axis of ~1800 m and a short axis of 400-800 m is observed on the surface, and is characterized by a central silicic core that passes outwards through potassic, phyllic and argillic alteration to propylitic alteration (Fig. 2C; Li et al. 2019). Potassic and phyllic alteration are closely associated with Mo mineralization. Silicification is restricted to the apex of the fine-grained porphyry, where it is spatially associated with unidirectional solidification textures (UST). Only minor disseminated or veinlet Mo mineralization could be observed in this zone (Fig. 3A, B). Potassic alteration developed along the contact between the fine-grained porphyry and Ordovician volcano-sedimentary rocks, and/or between the granite porphyry and Ordovician volcano-sedimentary rocks at depths of >400 m (Jin et al. 2014), in a zone that reaches a width of 1200 m in cross-section. Mineralogically, this zone is identified by the abundance of K-feldspar and quartz (Fig. 3 C, D; Nie et al. 2011; Jin et al. 2014).

Phyllic alteration is present mainly in the lower Ordovician volcano-sedimentary rocks and overprinted the earlier potassic alteration (Fig. 3E). It forms a zone measuring 1200 m in length, 300-400 m in width and ~800 m in depth (Liu et al. 2017). Phyllic alteration is characterized by the mineral assemblage, quartz + sericite
+ fluorite + pyrite ± molybdenite ± calcite. Abundant sericite is observed as halos
(2-10 mm wide) along quartz veins. The argillic alteration is developed irregularly at
the margin of the phyllic zone (Liu et al. 2017) and consists of quartz, calcite and
pyrite with minor galena, sphalerite and chalcopyrite. Propylitic alteration is observed
mainly in the Dawangzi Formation, the lower Ordovician rocks and the monzogranite,
and is manifested by the assemblage epidote-chlorite-calcite.

The economic mineralization in the Chalukou deposit has been subdivided into a
lower Mo mineralized zone and an upper zone of Pb-Zn mineralization (Li et al. 2014;
Liu et al. 2014b; Duan et al. 2018). The Pb-Zn mineralization occurs as quartz-sulfide
veins in Ordovician volcano-sedimentary rocks and is associated with propylitic and
argillic alteration (Jin et al. 2014). This mineralization constitutes a resource of 0.143
Mt Pb @ 0.6 wt.% and 0.013 Mt Zn @ 0.3 wt.% (Liu et al. 2017; Duan et al. 2018).

The Pb-Zn mineralized veins vary in width from 0.2 to 2 m, occur above the Mo
orebodies and locally cross-cut the Mo-bearing veins, indicating a relatively late
timing of emplacement (Liu et al. 2014b). The Mo mineralization, most of which
occurs as stockwork or veins (Figs. 3 and 4 A-C), is hosted by fine-grained porphyry,
granite porphyry, breccia pipes and lower Ordovician volcano-sedimentary rocks. It is
zoned vertically in terms of grade from a thin, low-grade (<0.06 wt.% Mo) domain in
the upper part of the deposit through a thicker, medium-grade (0.06-0.26 wt.% Mo)
intermediate domain, to a thick, high-grade (0.08-0.53 wt.% Mo) domain in the lower
part of the deposit (Fig. 2D; Nie et al. 2011; Zhang and Li 2017).

Mineralization stages
The ore minerals in the Chalukou deposit comprise molybdenite, pyrite and minor sphalerite, galena, chalcopyrite and hematite, and the main gangue minerals are quartz, K-feldspar, plagioclase, sericite, fluorite, calcite, epidote and chlorite. Based on cross-cutting relationships among the different vein-types, and the mineral assemblages, the Chalukou mineralization has been subdivided into three ore stages.

Stage I mineralization consists of quartz veins and minor disseminated mineralization and is represented by the mineral assemblage quartz + K-feldspar + minor pyrite + minor molybdenite ± magnetite ± hematite ± fluorite. The veins (0.5-2 mm) in this stage generally have halos of strong silicification or potassic alteration. Numerous quartz veinlets are observed to cross-cut the USTs that are associated with this stage (Zhao et al. 2021a). Magnetite occurs as subhedral to euhedral grains with obvious growth zones and was replaced by hematite (martite) (Fig. 4D, E). The magnetite and hematite occur as veinlets (Liu et al. 2015a) or irregularly shaped masses in association with quartz. The vein-hosted and disseminated molybdenite (Mol-I) of Stage I occurs as euhedral plate-like crystals (Fig. 5A, B) in potassically altered granite porphyry. The pyrite (Py-I) is in the form of subhedral to euhedral crystals (Figs. 4F, G and 5A, B), and is generally cross-cut and replaced by later molybdenite (Mol-II, Fig. 4F).

The main ore stage (Stage II) is composed of mineralized veins and breccias, which contain molybdenite and minor pyrite, accompanied by quartz, K-feldspar, sericite and fluorite. Veins (0.2-5 cm) in this stage can be subdivided into quartz + molybdenite ± fluorite, quartz + K-feldspar + molybdenite (Fig. 3C), quartz + sericite
Molybdenite (Mol-II) usually occurs along the edges of the quartz + K-feldspar veins, and locally delineates a suture in the vein-center (Fig. 5A, B). These veins are surrounded by sericite halos. In some cases, the vein consists dominantly of molybdenite and contains only minor quartz (Zhao et al. 2021a). The major modes of occurrence of Mol-II are as fine-grained aggregates (Figs. 4F and 5D) and wispy lamellae (Fig. 5 E-G) that vary from 20 to 250 μm in width and 50 to 500 μm in length. These aggregates are associated with pyrite (Py-II), which is coarse-grained, cross-cuts Mol-II or contains inclusions of Mol-II (Fig. 4H).

Stage III veins are composed of quartz, pyrite, galena, sphalerite, chlorite, epidote, fluorite and minor chalcopyrite. Pyrite (Py-III) is coarse-grained and is associated with quartz, galena, sphalerite, and fluorite (Fig. 4B, C, J, K). Chalcopyrite is rarely observed and occurs only as inclusions in sphalerite (Fig. 4I). It may also coexist with galena and/or sphalerite and was replaced by pyrite (Liu et al. 2015a). Galena and sphalerite occur at the margins of pyrite crystals (Fig. 4J).

SAMPLES AND ANALYTICAL METHODS

In situ trace element analyses

The trace element concentrations of pyrite and molybdenite were analyzed in situ using an Agilent 7500a ICP-MS, equipped with a New Wave 193 nm laser at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Beijing. The laser ablation included a pre-ablation period of 5 s to clean
the surface of the samples, 20 s for background measurement, and 45 s for signal
collection. The repetition rate of the laser was 10 Hz and the spot diameter was 36 μm.
The external standard NIST 610 was used for calibration, NIST 612 was used as the
monitoring standard and MASS-1 was used as a blind sample. The integration time
was 8 ms for $^{57}$Fe, $^{63}$Cu, $^{66}$Zn, 15 ms for $^{51}$V, $^{55}$Mn, $^{59}$Co, $^{60}$Ni, $^{71}$Ga, 20 ms for $^{82}$Se,
$^{111}$Cd, $^{115}$In, $^{116}$Sn, $^{121}$Sb, $^{205}$Tl, $^{209}$Bi, 30 ms for $^{75}$As, $^{95}$Mo, $^{182}$W, $^{208}$Pb, $^{238}$U, and 80
ms for $^{107}$Ag, $^{197}$Au and other elements. Details of the analytical method can be found
in Zhang et al. (2019).

In situ sulfur and lead isotope analyses

In situ sulfur and lead isotopic analyses of sulfides (molybdenite, pyrite, galena and
sphalerite) were carried out at the State Key Laboratory of Continental Dynamics,
Northwest University, China. Detailed descriptions of the methods employed in the
analyses can be found in Yuan et al. (2017). The sulfur isotopic measurements were
made using a Nu Plasma 1700 MC-ICP-MS (Nu instruments, UK) coupled to a
RESOlution M-50 laser ablation system (ASI, Australia) equipped with a 193 nm ArF
CompexPro102 excimer laser (Coherent, USA). A spot size of 37 μm was adopted
with a laser repetition rate of 3-4 Hz and an energy density of 3.5-4.0 J/cm$^2$. Each
sample acquisition consisted of background collection for 30 s, followed by ablation
signal collection for 50 s. A standard-sample bracketing method was used to correct
the mass discrimination and instrumental drift. The external standards for sphalerite,
pyrite and galena were NIST NBS123, PY-4, and CBI-3, respectively. The analytical
precision calculated from replicate analyses of unknown samples was better than 0.2‰
In situ lead isotopic analyses were conducted with a Nu Plasma II MC-ICP-MS instrument (Nu Instruments, UK) coupled to a 266 nm NWR UP Femto laser ablation system (ESI, USA). The laser ablation employed a spot size of 15 μm for galena and 50 μm for pyrite and molybdenite, a maximum energy density of 6 J/cm², and a laser frequency of 5-50 Hz. A NIST SRM 997 Tl dry aerosol (50 ng/g, \(^{205}\text{TI}/^{203}\text{TI} = 2.3889\)) standard was used in conjunction with the standard-sample bracketing method to correct for the mass discrimination of the mass spectrometer. Repeated analyses of the NIST SRM 610 glass standard yielded reproducible results with mean \(^{206}\text{Pb}/^{204}\text{Pb}, \(^{207}\text{Pb}/^{204}\text{Pb}\) and \(^{208}\text{Pb}/^{204}\text{Pb}\) ratios of 17.052 ± 0.003, 15.515 ± 0.003 and 36.980 ± 0.007 (1σ, n = 183), respectively.

**Whole-rock lead isotope analyses**

Whole-rock lead isotope analyses of the intrusive rocks were conducted at the Beijing Research Institute of Uranium Geology, China National Nuclear Corporation. The samples were cleaned in deionized water and leached in hot 6 N HCl for 15 to 20 minutes. Then, the samples were dissolved using HF and HClO₄, and treated with a basic anion exchange resin to purify Pb. The Pb isotopes were measured by thermal ionization mass spectrometry using a mass spectrometer (Thermo Finnigan); the measurement accuracy was better than 0.005%. The measured Pb isotope ratios of the Pb standard reference NBS 981 were \(^{206}\text{Pb}/^{204}\text{Pb} = 16.937 ± 0.002, \(^{207}\text{Pb}/^{204}\text{Pb} = 15.457 ± 0.002\) and \(^{208}\text{Pb}/^{204}\text{Pb} = 36.611 ± 0.004\), respectively, and are consistent with the reference values (Todt et al. 1993).
RESULTS

Trace elements

Molybdenite samples from the Chalukou deposit have highly variable trace element concentrations (Table 1; Fig. 6). However, the concentrations are generally lower in Mol-I than in Mol-II (Fig. 6). The median concentrations of V, Cu, Zn, Ag, Sb, and W in Mol-I are < 10 ppm, but the concentrations of some of these metals can range to very high values, e.g., Zn (1250 ppm) (Table 1; Fig. 6), due to the presence of sub-microscopic inclusions. Compared to Mol-I, Mol-II is enriched in almost all the metals analyzed and the median concentrations of V, Cu, Zn, Ag, Sb and W in Mol-II are all over 10 ppm. The median content of Ti in Mol-II is 312 ppm. There is a strong correlation of Ti with Fe. Analysis of some Mol-II crystals yielded anomalously high Ti contents (Fig. 7A), due probably to the presence of submicroscopic ilmenite and/or rutile inclusions.

Both Mol-I and Mol-II have high concentrations of Fe and Pb with median values of 894, 7570 ppm and 269, 4519 ppm, respectively (Table 1). The Co and Ni contents of Mol-I and Mol-II are relatively low, with median values of 0.2, 1.9 ppm and 3.8, 4.4 ppm, respectively. Though Mol-II contains slightly more Co and Ni than Mol-I, both have a Co/Ni ratio <1. There are strong correlations (Fig. 7 B-E) between Fe and Cu ($R^2 = 0.77$), Bi and Pb ($R^2 = 0.97$), Bi and Ag ($R^2 = 0.74$), W and As ($R^2 = 0.73$), and a weak correlation between Sb and Au ($R^2 = 0.35$; Fig. 7F).

Trace element concentrations in pyrite are variable and lower than in molybdenite.
There is a progressive decrease in the contents of Ti, Mn, Zn, Cd, Sn and W from Py-I through Py-II, to Py-III (Fig. 8). The Cu content decreases from a median of 8.7 ppm in Py-I, to a median of 1.3 ppm in Py-II but increases in Py-III to a median of 8.7 ppm. The Py-I samples have the highest Mo contents (6.9 ± 3.8 ppm, where the first value is the median and the second value is the standard deviation, S.D.; Table 1). The Py-II samples have a relatively high Mo content (5.0 ± 128.1 ppm) and the lowest Cu content (1.3 ± 2.1 ppm) of the three pyrite types, whereas the Py-III sample is generally enriched in Cu (8.7 ± 37.1 ppm) and extremely depleted in Mo (0.05 ± 5.7 ppm) (Table 1; Fig. 8).

There are good correlations among Pb, Ag and Bi (Fig. 9A, B) and weaker correlations among Zn, Ti and Mn (Fig. 9C, D). Most elements (e.g., As, Co, Ni and Se, Fig. 10A) show relatively smooth curves in the time-resolved depth profiles. For Pb, Ag and Bi, the spikes could be found in the time-resolved depth profiles of sample C142Q2-3 (Fig. 10B). Samples of Py-I and Py-II have relatively high Co (median values of 12 and 10 ppm, respectively) and Ni (median values of 19 and 5 ppm, respectively) concentrations, and Co/Ni ratios ranging between 0.04 and 7.71 (Fig. 9E). The Py-III samples, however, have much lower Co (median = 0.2 ppm) and Ni (median = 0.6 ppm) contents than Py-I and Py-II, and the Co/Ni ratios are all < 1 (Fig. 9E).

**Sulfur and lead isotope ratios**

The results of the in situ sulfur isotope analyses are reported in Table 2 and
illustrated in Figure 11A. The full dataset has $\delta^{34}$S$_{V-CDT}$ values in the range from -5.2 to +7.8‰; the mean is +2.9‰. The molybdenite is characterized by relatively high $\delta^{34}$S values (+4.2 to +7.8‰) compared to the other sulfides. The 17 spots for Py-I, Py-II and Py-III all yielded similar values, which range from +3.2 to +4.2‰ (mean = 3.7‰), +1.4 to +2.5‰ (mean = 2.1‰) and +1.1 to +4.6‰ (mean = 3.0‰), respectively. Within single pyrite crystals, there is a small but significant $\delta^{34}$S variation from +1.1 to +3.3‰; the cores have typically ~2‰ isotopically heavier values than mantles (Fig. 11A). The sphalerite yielded $\delta^{34}$S values of +0.2 to +2.4‰.

Two spots for galena returned $\delta^{34}$S values of -5.2 and -5.0‰.

The lead isotope compositions of the sulfides are reported in Table 3 and illustrated in Figure 12. The $^{206}$Pb/$^{204}$Pb ratios vary from 18.274 to 18.386, $^{207}$Pb/$^{204}$Pb from 15.518 to 15.597, and $^{208}$Pb/$^{204}$Pb from 38.097 to 38.308. Significantly, the sulfides from Stages I and II (Mol-I, Mol-II, Py-I and Py-II) contain more radiogenic lead than the Stage III sulfides (i.e., Py-III, galena and sphalerite).

**Whole-rock lead isotope ratios**

The whole rock Pb isotope compositions of the syn-ore (granite porphyry, quartz porphyry and fine-grained porphyry) intrusions are similar, with $^{206}$Pb/$^{204}$Pb, $^{207}$Pb/$^{204}$Pb, and $^{208}$Pb/$^{204}$Pb values of 18.442-18.570, 15.549-15.591, and 38.323-38.482, respectively (Table 4; Fig. 12). These values are also similar to those of sulfides, especially the ratios of $^{207}$Pb/$^{204}$Pb, which completely overlap with sulfides in the Chalukou deposit.
Sulfur and lead sources

Sulfur sources. As reported above, the sulfur isotope compositions of the Chalukou sulfides have $\delta^{34}\text{S}$ values ranging from -5.2 to +7.8‰, which decrease in the order molybdenite, pyrite, sphalerite and galena (Fig. 11A; Table 2). In order to calculate the corresponding $\delta^{34}\text{S}$ for $\text{H}_2\text{S}$ in equilibrium with each sulfide, we used the homogenization temperatures of fluid inclusions from previous studies, which are 320 to 480 °C for the early quartz + K-feldspar stage, 260 to 410 °C for the quartz-molybdenite stage, and 200 to 250 °C for the late quartz-pyrite-galena-sphalerite stage (Liu et al. 2014a; Li et al. 2019). The corresponding range and mean $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ values of the different stages are from +2.3 to +3.3‰ (mean = 2.8‰; T= 400°C) for Stage I, from +0.4 to +1.5‰ (mean = 1.1‰; T= 350°C) for Stage II, and from -2.7 to +2.8‰ (mean = 0.8‰; T= 225°C) for Stage III. The narrow range of $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ values centered on 0‰ (-2.7 to +3.3‰, mean = 1.0‰) indicates a magmatic sulfur source (Seal 2006). However, the sulfur isotope fractionation of over 6‰ between coexisting galena and sphalerite in Stage III implies a temperature of 101 °C, which is much lower than the homogenization temperature described above, indicating that the two minerals were not in isotopic equilibrium (Seal 2006).

The $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ values for Chalukou are similar to those reported for other magmatic-hydrothermal ore deposits in the region (Appendix Table A1; Ma 1984; Seal 2006).
Zhao et al. 2016), e.g., the Daheishan porphyry Mo deposit (-0.8 to +3.0‰; Hu et al. 2014), the Badaguan porphyry Cu-Mo deposit (-1.8 to +2.4‰; Mi et al. 2017; Hou 2014; Kang 2015; Gao et al. 2016), and the Wunugetushan porphyry Cu-Mo deposit (-0.1 to +2.8‰; Chen et al. 2011; Zhang et al. 2016). All of these deposits are close to the Derbugan fault, which is the boundary between the Erguna block and the Hingan block and the locus of a large number of Mesozoic granites (Fig. 1B). In contrast, δ³⁴S_H₂S values for deposits in the Duobaoshan ore district, which is located to the east of the Derbugan fault area and characterized by widely distributed Paleozoic rocks (Fig.1B), are generally negative (Fig. 11B), e.g., the Zhengguang gold deposit (-14.2 to +1.6‰; Fu et al. 2014; Gao et al. 2017), the Tongshan Cu deposit (-1.1 to -0.2‰; Liu et al. 2015b), the Sankuanggou skarn Fe-Cu deposit (-4.5 to -0.5‰; Deng et al. 2018), and the Duobaoshan porphyry Cu deposit (-3.2 to -0.5‰; Fu et al. 2014). However, some deposits in the Duobaoshan ore district also have positive δ³⁴S_H₂S values, e.g., the Yongxin gold deposit (+2 to +3.9‰; Yuan et al. 2018).

The above observations indicate that there are differences in the sulfur isotope composition of the fluids forming deposits close to the Derbugan fault and those in the Duobaoshan ore district, although all the deposits in both regions are of magmatic-hydrothermal origin. Moreover, the sulfur isotope values are independent of the ore deposit type, and mineral paragenesis (Chen et al. 2011; Hu et al. 2014; Mi et al. 2017; Yuan et al. 2018). Geologically, the two regions differ significantly. Whereas Paleozoic sedimentary strata are common in the Duobaoshan district, Mesozoic volcanics and granites are dominant in the Derbugan fault area (Fig. 1B).
Furthermore, sulfur isotope data for the Palaeozoic sedimentary rocks in this area show that the $\delta^{34}$S values range from -43.8 to -8.5‰ (mean = -35.48‰; Huang et al. 2018). We therefore infer that there was a considerable contribution of sulfur from the Paleozoic strata in the Duobaoshan area, leading to negative $\delta^{34}$S$_{H2S}$ values (as low as -14.2‰) in several deposits (e.g., the Zhengguang gold deposit; Fu et al. 2014), whereas the dominance of the Derbugan fault area by igneous rocks ensured that deposits in this area had $\delta^{34}$S$_{H2S}$ values close to zero.

**Lead sources.** In order to identify the source of lead and, by extension, the other metals, we have compared the lead isotope compositions of the Chalukou sulfides with those for sulfides from numerous ore deposits in the region, the Mesozoic granite, basalt and trachyte, and the Duobaoshan Formation andesitic tuff (Fig. 12). In general, the in situ lead isotope data are similar to those of previous studies of sulfides using mineral separates at Chalukou and other Mesozoic ore deposits in the region (Appendix Table A2; Guo et al. 2010; Chu et al. 2012; Zhao et al. 2016), all of which plot in a field between the mantle and orogen evolutionary curves (Fig. 12; Zartman and Doe 1981). The Paleozoic deposits, however, tend to have lower $^{208}$Pb/$^{204}$Pb and $^{207}$Pb/$^{204}$Pb ratios at a given value of $^{206}$Pb/$^{204}$Pb, whereas those for the Mesozoic deposits completely overlap the Chalukou data (e.g., Liu et al. 2015b), suggesting that the Chalukou deposit and the other Mesozoic deposits had the same metal source (Hu et al. 2014; Yuan et al. 2018). Moreover, the Pb isotope data for the Chalukou ore minerals are very similar to those for Mesozoic granites in the region (Fig. 12), further indicating a Mesozoic magmatic source for the metals (Hu et al. 2014; Liu et al.
It is also important to note that, compared to the Chalukou sulfides, the Pb isotopic data for the Mesozoic basalt and trachyte show distinctly higher $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios (Fig. 12), making these rocks less plausible candidates for significant sources of metals for the Chalukou deposit.

**Metal signature of the fluid**

**Trace elements in pyrite.** Our results show that the trace element concentrations in pyrite vary widely, underscoring the complexity of the ore-forming fluids (Cook et al. 2013; Mavrogonatos et al. 2020). The Mo contents of Py-I (6.9 ± 3.8 ppm) and Py-II (5 ± 128 ppm) are higher than those of Py-III (0.05 ± 5.7 ppm). The highest Mo content was recorded by pyrite in Stage I and was high enough for the fluid to saturate with molybdenite at high temperature (390-480°C; Li et al. 2019). The high solubility of molybdenite at this temperature, however, ensured that its precipitation was limited, thereby explaining the small proportion of molybdenite deposited during this stage. Although the Cu content of pyrite was high in Stage I, the fluid did not saturate with a Cu mineral (e.g., chalcopyrite). We attribute this to the fact that at the relatively high temperature of Stage I, the solubility of copper minerals like chalcopyrite is too high for them to saturate in the fluid (Landtwing et al. 2005; Williams-Jones and Migdisov 2014). The Mo content of Py-II is slightly lower than that of Py-I, but was high enough in the corresponding fluid for molybdenite to have been strongly oversaturated and deposit the bulk of the molybdenite in Stage II (Fig. 13). This reflects the fact that with decreasing temperature, the solubility of molybdenite decreases sharply (Williams-Jones and Migdisov 2014). The low content of Cu in...
pyrite of Stage II is consistent with the observation that the fluid did not saturate with a Cu-bearing sulfide during this stage. The Mo/Cu ratio recorded by pyrite reached its maximum in Stage II. By Stage III, however, the combination of a sharply higher Cu content in the fluid and lower temperature allowed the fluid to saturate with chalcopyrite. The extremely low Mo content in Py-III precluded precipitation of molybdenite and the Mo/Cu ratio of the ore fluid reached its minimum (Fig. 9F).

From the observations discussed above, we conclude that pyrite recorded the chemical evolution in the Mo/Cu ratio of the ore fluid, and that, in reaching its maximum Mo/Cu ratio in Stage II, pyrite recorded the onset of main stage of molybdenite deposition. We also conclude that the absolute content of metal in the fluid is not the key factor affecting metal precipitation, but that ore mineral saturation controlled by the system temperature is the real key.

**Trace elements in molybdenite.** Several studies have investigated the uptake of trace elements by molybdenite and its use in predicting the trace element signature of ore fluids (e.g., Ciobanu et al. 2013; Huang et al. 2014; Ren et al. 2018; McFall et al. 2019). Molybdenum is present in molybdenite as Mo$^{4+}$, which has a large ionic radius that, together with its high charge, makes it difficult for trace metals such as Fe, Cu, Zn, As, Pb, Co and Ni to substitute for it in concentrations of more than a few tens of ppm (Ren et al. 2018). Because of the relatively high crystallization temperature of molybdenite, the trace element composition of molybdenite could be, nevertheless, important in recording the signature of the mineralizing fluid (Huang et al. 2014).

The trace element contents of Mol-I and Mol-II in the Chalukou deposit are clearly
different. Whereas Mol-I contains up to several hundred ppm of Ti, Mn, Fe, Pb and several tens of ppm of Cu, As, Se, Ag, Sn, and Bi (Fig. 6), Mol-II contains thousands of ppm of Ti, Fe, and Pb, and concentrations of several other trace metals are in the range of tens to hundreds of ppm (Fig. 6). The observation that Mol-II is more enriched in trace metals than Mol-I is consistent with greater metal enrichment in the ore fluid in Stage II compared to Stage I. Given that the bulk of the molybdenite was deposited in Stage II, the high metal content of Mol-II is an important signature of the mineralizing fluid at Chalukou and potentially at other deposits.

The role of magma Mo content

The mechanism of metal enrichment in giant porphyry deposits has been a contentious issue because of the large amounts of metal required to form these deposits (Audétat et al. 2000, 2008; Richards 2003, 2011; Heinrich 2005; Pettke et al. 2010; Hou et al. 2015; Chang et al. 2018). Such large amounts of metal could be extracted from a very large volume of magma with a low metal content, or a smaller volume of magma with a high metal content (Core et al. 2006; Yang et al. 2016). Which of these possibilities reflects reality, however, is still debated (Carten et al. 1988; Stern et al. 2007; Audétat 2010). In the case of Cu, the presence of anhydrite-bearing intrusive rocks in the El Teniente Cu-Mo deposit containing >0.5% Cu supports the argument that the source magma was unusually enriched in this metal (Stern et al. 2007). Thus, the availability of a fertile magma (metal enriched) could be an essential step in forming porphyry deposits (Nadeau et al. 2010; Chiaradia 2013). In the case of Mo, which is a highly incompatible element and, thus, is preferentially
concentrated in the continental crust, a contribution of metal from this source could lead to a fertile magma and thereby help explain the formation of giant porphyry Mo deposits.

Audétat (2010), noting that the Mo content in the initial magma recorded by melt inclusion data is relatively low (5-6 ppm), has argued that the magmas and fluids in mineralized Mo systems are not unusually Mo-rich. Thus, in this model, a large amount of magma would be needed to form a large porphyry Mo deposit. Similar conclusions have been reached by Wang et al. (2014) and Zhang and Audétat (2017). The processes by which metals form giant ore deposits from magmas containing a very low Mo content, however, are still unclear.

In principle, the magmas forming the pre-ore monzogranite or those forming the syn-ore intrusions could have been the source of Mo for the Chalukou deposit. The two analyzed samples of monzogranite have Mo contents of 0.2 ppm, which is lower than that of the average upper continental crust (0.8 ppm, Rudnick and Gao 2014). In contrast, the unaltered syn-ore granite porphyry, quartz porphyry and fine-grained porphyry contain 1-68 ppm (median, 18 ppm), 5-110 ppm (median, 9 ppm) and 3-96 ppm (median, 25 ppm) Mo, respectively (Li et al. 2014). This enrichment of the syn-ore granites in Mo by a factor of 45 to 125 relative to the pre-ore monzogranite and the extremely low Mo content of the latter makes it extremely unlikely that the pre-ore monzogranite magmas were the source of the Mo for the Chalukou deposit (Fig. 13). Thus, although the Mo content of the magmas forming some giant Mo deposits may have been relatively low (Audétat 2010; Zhang and Audétat 2017), our
data leave little doubt that the Mo-rich syn-ore magmas at Chalukou were the source
of the Mo for this deposit.

A feature of the whole-rock geochemical data is the very low Sr/Y ratio (Sr/Y from
0.4 to 37; mean, 7) of the Mo-enriched syn-ore intrusions compared to the pre-ore
monzogranite (Sr/Y from 14 to 69; mean, 37) (Li et al. 2014; Liu et al. 2015a). This
could indicate that the magmas forming the syn-ore intrusions were derived from the
magma after an unusually high degree of fractional crystallization of plagioclase.
Such fractional crystallization would have greatly reduced the Sr content of the
residual magma (Kobylnski et al. 2020), thereby explaining the very low Sr/Y ratios
of the syn-ore intrusions. In turn, this could also explain the extremely strong negative
Eu anomalies of the syn-ore intrusions. Indeed, according to Li et al. (2014),
fractional crystallization of the main rock-forming minerals could have reached up to
50%, which could have significantly enriched the residual magma in Mo. However,
even considering the very high melt/silicate mineral partition coefficients reported for
Mo (35-1080 at 2.61 GPa and 600-800 °C; Bali et al. 2012), the Mo enrichment due
to fractional crystallization would only have increased the concentration of Mo in the
magma to 0.4 ppm.

Although the pre-ore monzogranite and syn-ore intrusions at Chalukou have similar
Sr-Nd-Hf isotope compositions, which permit them being genetically related (Liu et al.
2015a), the negative initial Hf isotope signature (εHf) of the syn-ore intrusions (-1.4
to +0.5) indicates that their magmas assimilated old continental crust, which was not
the case for the pre-ore barren monzogranite (+0.9 to +3.0). As Mo is a highly
incompatible element and, therefore, concentrates in the crust, assimilation of old continental crust likely explains the high Mo concentration of Mo in the syn-ore intrusions (Zhang and Li 2017).

IMPLICATIONS

The trace element chemistry of pyrite and S and Pb isotopic compositions have made it possible to interpret the evolution of hydrothermal fluids during the formation of the Chalukou porphyry Mo deposit. This evolution occurred in three paragenetic stages characterized by distinctive mineral assemblages. The composition of the fluid as recorded by pyrite indicates that the fluids in Stage I and Stage II were enriched in Mo, whereas the fluid in Stage III was highly depleted in Mo. The combination of a relatively high Mo content of the fluid in Stage II (compared to the fluid in Stage III) and lower temperature (compared to Stage I), caused the fluid to be highly oversaturated with respect to molybdenite, and explains why molybdenite was deposited mainly in Stage II. This leads to the conclusion that the absolute content of metal in the ore fluid was not the key factor controlling metallic mineral deposition, and that molybdenite saturation was controlled by the system temperature. Another important conclusion of the study is that magmas that were unusually enriched in Mo due to crustal contamination, and crystallized the syn-ore intrusions, were the most plausible source of Mo for the Chalukou deposit. This shows, contrary to previous studies, that magma fertility (enrichment in Mo) may play an essential role in generating large porphyry Mo deposits. Finally, the study highlights the importance of in situ compositional analyses (including S and Pb isotopes and trace elements) of ore.
sulfides as tools for constraining the origin and chemical evolution of ore fluids that should find widespread application well beyond porphyry Mo ore genesis.

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REFERENCES CITED


Kang, Y.J. (2015) The Ore-forming processes and mineralization of Badaguan...


——— (2015a) Geochemical signature of the granitoids in the Chalukou giant porphyry Mo deposit in the Heilongjiang Province, NE China. Ore Geology Reviews, 64, 35–52.


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Figure captions

Fig. 1. (A) A schematic map of the Central Asian orogenic belt (CAOB; modified
from Shu et al. 2016; Zhai et al. 2019); (B) A geological map of the northern Great Hinggan Range showing the locations of major ore deposits (modified from Chen et al. 2017).

Fig. 2. (A) A geological map of the Chalukou porphyry Mo deposit (modified from Xiong et al. 2015); (B) A representative cross-section showing the local intrusions, dikes and hydrothermal breccias (modified from Li et al. 2014); (C) A representative cross-section showing the vertical distribution of different hydrothermal alteration zones, and (D) A representative cross-section showing the vertical distribution of Mo-bearing orebodies (modified from Li et al. 2019).

Fig. 3 Field and hand-specimen photographs of alteration in the Chalukou deposit. (A and B) Field and hand-specimen photographs of silicic alteration; (C and D) Molybdenite-quartz veins associated with potassic alteration; (E) Phyllic alteration overprinting the earlier potassic alteration.

Fig. 4. (A) A photograph showing the stockwork ores; (B and C) The mode of occurrence of molybdenite-pyrite-quartz-fluorite veins; (D) Martite after magnetite; (E) Magnetite replaced by hematite; (F) Molybdenite (Mol-II) cross-cutting early-formed pyrite (Py-I); (G) An early-formed pyrite (Py-I) vein; (H) Molybdenite (Mol-II) cut by a pyrite (Py-II) vein; (I) Sphalerite intergrown with galena, pyrrhotite and pyrite; (J) Pyrite (Py-III) associated with galena and sphalerite; (K) The occurrence of molybdenite (Mol-III) in pyrite interstices.

Fig. 5. (A) A hand specimen showing two generations of molybdenite; (B)
Molybdenite (Mol-I) associated with pyrite (Py-I); (C) A molybdenite-quartz vein; (D) an occurrence of molybdenite (Mol-II) as fine-grained aggregates; (E, F, G) An occurrence of molybdenite (Mol-II) as wispy veinlets.

Fig. 6. Box and whisker plots showing the concentrations of trace elements in different molybdenite generations analyzed by LA-ICP-MS.

Fig. 7. Binary plots of (A) Fe vs. Ti, (B) Fe vs. Cu, (C) Bi vs. Pb, (D) Bi vs. Ag, (E) W vs. As and (F) Sb vs. Au for different molybdenite generations. Two samples show anomalously high Ti contents (dashed ellipse), due probably to the presence of mineral inclusions (e.g., ilmenite and rutile).

Fig. 8. Box and whisker plots showing the concentrations of trace elements in different pyrite generations analyzed by LA-ICP-MS.

Fig. 9. Binary plots of (A) Pb vs. Ag, (B) Bi vs. Pb, (C) Mn vs. Zn, (D) Ti vs. Zn, (E) Ni vs. Co and (F) Mo vs. Cu for different pyrite generations. See text for additional explanation.

Fig. 10. Representative pyrite samples selected for in situ trace element analyses. (A) Pyrite (Py-II) from stage II (A1 A hand specimen photo of Py-II bearing mineralization; A2 A reflected light image of pyrite showing the spots of a LA-ICP-MS analytical profile; A3 Time-resolved depth profiles of selected elements for the spot shown in A2; A4 Concentrations of selected trace elements along the profile shown in A2); (B) Pyrite (Py-III) from stage III (B1 A hand specimen photograph of Py-III bearing mineralization; B2 A reflected light image of pyrite
showing the spots of a LA-ICP-MS analytical profile; B3 Time-resolved depth profiles of selected elements for the spot shown in B2; B4 Concentrations of selected trace elements along the profile shown in B2).

Fig. 11. (A) A histogram of sulfur isotopic compositions ($\delta^{34}$S$_{V-CDT}$) for sulfides from the Chalukou porphyry Mo deposit; (B) A comparison of the sulfur isotopic compositions ($\delta^{34}$S$_{H2S}$) of sulfide minerals from deposits in the Derbugan and Duobaoshan ore fields (data from Ma 1984; Chen et al. 2011; Fu et al. 2014; Hou 2014; Hu et al. 2014; Kang 2015; Liu et al. 2015b; Zhang et al. 2016; Zhao et al. 2016; Gao et al. 2017; Mi et al. 2017; Yuan et al. 2018).

Fig. 12. Lead isotope compositions of sulfides from the Chalukou porphyry Mo deposit compared to local early Paleozoic volcano-sedimentary rocks, Mesozoic granite, basalt and trachyte, and local early Paleozoic to Mesozoic ore deposits (data from Guo et al. 2010; Chu et al. 2012; Hu et al. 2014; Liu et al. 2015b; Zhao et al. 2016; Gao et al. 2017; Mi et al. 2017; Deng et al. 2018; Yuan et al. 2018). (A) $^{206}$Pb/$^{204}$Pb vs. $^{208}$Pb/$^{204}$Pb plots; (B) $^{206}$Pb/$^{204}$Pb vs. $^{207}$Pb/$^{204}$Pb plots. The arrows in the inset figures show that Moly-I, Moly-II and Py-II have more radiogenic Pb isotope compositions than those of the Stage III sulfides. The Pb isotope curves for the mantle, orogen, and crust were taken from Zartman and Doe (1981).

Fig. 13. A summary plot showing bulk igneous rock Mo concentrations as well as Mo concentrations in different pyrite generations; The Mo contents of local intrusions are from Li et al. (2014) and Liu et al. (2015a) and the Mo contents of the sulfides are
from this study. Spot with anomaly high element content (pink dotted line) is excluded.

Table 1. In situ trace element compositions of sulfides from the Chalukou porphyry Mo deposit

Table 2. In situ sulfur isotopic compositions of sulfides from the Chalukou porphyry Mo deposit

Table 3. In situ lead isotopic compositions of sulfides from the Chalukou porphyry Mo deposit

Table 4. Whole rock lead isotopic compositions of intrusions from the Chalukou porphyry Mo deposit

Appendix Table 1A. S isotope data of sulfides from ore deposits in NE China

Appendix Table 2A. Pb isotope data of sulfides from local ore deposits, Mesozoic granite, basalt, tracyte, and Duobaoshan Formation volcano-sedimentary rocks in NE China
Table 1. In situ trace element compositions of sulfides from the Chalukou porphyry Mo deposit

<table>
<thead>
<tr>
<th>Element (ppm)</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>As</th>
<th>Se</th>
<th>Ag</th>
<th>Cd</th>
<th>Sn</th>
<th>Sb</th>
<th>W</th>
<th>Pb</th>
<th>Bi</th>
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<tbody>
<tr>
<td><strong>Mol-I (n=6)</strong></td>
<td></td>
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<td>Max</td>
<td>152</td>
<td>31.8</td>
<td>88</td>
<td>296</td>
<td>4555</td>
<td>0.3</td>
<td>6.8</td>
<td>40.9</td>
<td>1250</td>
<td>6.6</td>
<td>70</td>
<td>22.5</td>
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<td>20.6</td>
<td>3.2</td>
<td>207</td>
<td>424</td>
<td>106</td>
<td></td>
</tr>
<tr>
<td>Min</td>
<td>85</td>
<td>3.3</td>
<td>26.2</td>
<td>16</td>
<td>517</td>
<td>0.1</td>
<td>1.0</td>
<td>2.9</td>
<td>2.8</td>
<td>1.4</td>
<td>55</td>
<td>0.6</td>
<td>48.7</td>
<td>11.2</td>
<td>0.3</td>
<td>1.7</td>
<td>45</td>
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<tr>
<td>Mean</td>
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<td>101</td>
<td>1570</td>
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<td>3.8</td>
<td>18.1</td>
<td>217.1</td>
<td>3.4</td>
<td>63</td>
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<td>Median</td>
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<td>2.2</td>
<td>3.6</td>
<td>1.3</td>
<td>85.6</td>
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<tr>
<td><strong>Mol-II (n=7)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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Abbreviations: Fl = fluorite, Gn = galena, Mol = molybdenite, Py = pyrite, Qz = quartz, Sp = sphalerite.
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Abbreviations: Fl = fluorite, Gn = galena, Mol = molybdenite, Py = pyrite, Qz = quartz, Sp = sphalerite.
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Fig. 5
Fig. 7

A. Fe (ppm) vs. Ti (ppm)
B. Fe (ppm) vs. Cu (ppm)
C. Bi (ppm) vs. Pb (ppm)
D. Bi (ppm) vs. Ag (ppm)
E. W (ppm) vs. As (ppm)
F. Sb (ppm) vs. Au (ppm)