1 **Geochronology and zircon Hf isotope geochemistry of**
2 **granites in the giant Chalukou Mo deposit, NE China:**
3 **Implications for tectonic setting**

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Abstract

In this contribution, the largest porphyry Mo deposit in NE China, Chalukou, is selected to provide insights into the tectonic evolution of NE China. The deposit was considered to be rift-related (or Climax-type) porphyry Mo deposit developed in an extensional setting, while other researchers attributed its formation to the subduction of the Paleo-Pacific Ocean. In view of different granite petrogenesis between rift-type and subduction-type porphyry Mo deposits, geochronological and zircon Lu–Hf isotope studies have been carried out on granitic rocks associated with the Chalukou deposit. Zircon grains from the ore-host monzogranite and ore-causative granite porphyry yield weighted mean $^{206}\text{Pb}/^{238}\text{U}$ ages of 166 ± 2 Ma and 152 ± 2 Ma, with molybdenite samples yielding a Re–Os isochron age of 150 ± 2 Ma, indicating a Jurassic age for both granitic intrusion and Mo mineralization. Zircon $\varepsilon\text{Hf}(t)$ values of monzogranite and granite porphyry range from 0.9 to 3.0 and from -1.4 to 0.5, respectively. When integrated with published zircon Lu–Hf isotopic data, our data suggest that the barren granites (both pre- and post-ore) were mainly derived from mantle-derived juvenile rocks, whereas the syn-ore granite requires additional involvement of old continental crust. Thus, a contribution of continental crust to Mo mineralization is suggested. The petrogenesis and geochemical data reveal that the Chalukou deposit is a subduction-related porphyry Mo deposits and not rift-related. Integrated evidence links its formation to the southeastward subduction of the Mongol–Okhotsk Ocean, instead of the westward subduction of the Paleo–Pacific Ocean.

Keywords

Zircon U–Pb age; Hf isotope; molybdenite Re–Os age; porphyry Mo deposit; Chalukou; the Great Hingan Range

1. Introduction

Mineral systems are the products of a complex combination of tectono-thermal processes that result in anomalous metals concentration. They are not randomly distributed in time and/or in space, but form in through a series of events involving various combinations of tectono-magmatic, metamorphism, and hydrothermal processes ([Chen et al., 2008](#); [Pirajno and Zhou, 2015](#)). Since the advent of the plate tectonic theory, economic geologists attempted to understand the relationships between mineral systems and geodynamic settings. For instance, [Sillitoe \(1972\)](#) outlined a plate tectonic model to account for the genesis and distribution of porphyry Cu deposits. [Meyer \(1981\)](#), [Mitchell and Garson \(1981\)](#) and [Sawkins \(1984, 1990\)](#) convincingly demonstrated how deposits of diamonds formed in anorogenic continental hot spots, deposits of salt and limestone-hosted Pb–Zn formed on passive margin, sandstone-hosted U and Cu developed within intracontinental basins. Subsequently, considerable progress was made in connecting the formation of ore deposits to global tectonics, and several classification schemes for ore deposits based on tectonic setting have been proposed (e.g. [Kerrick et al., 2000](#); [Meyer, 1988](#); [Pirajno, 2009, 2016](#)). For instance, porphyry Mo deposits can be classified into three types, rift-related (e.g. Climax, high-fluorine type), subduction-related (e. g Endako, low-fluorine type) and collision-related

(Dabie type) (Chen et al., 2016a; Li et al., 2012a, 2013; Mi et al., 2015; Wang et al., 2016b; Yang et al., 2015a, 2016).

The Chalukou porphyry Mo deposit, located in the northern Great Hingan Range (Fig. 1), is the largest Mo deposit in NE China, with a proven reserve of 2.46 Mt Mo metal at an average grade of 0.11%, plus 0.37 Mt Pb and Zn at an average grade of 1.27% (Li et al., 2014; Nie et al., 2011). This deposit was once considered to be a porphyry Mo deposit linked to continental rifting (Li et al., 2014; Nie et al., 2013), which, in turn, constrains its formation to an extensional tectonic regime. Other researchers, however, argued that its formation resulted from the subduction of the Paleo-Pacific oceanic plate (Liu et al., 2014; Xiong et al., 2015). Considering the fact that the ore-causative granitoids responsible for either rifting or subduction-related porphyry Mo deposits have different geochemical signatures and magmatic sources (Ludington and Plumlee, 2009; Taylor et al., 2012), detailed geochronological and isotopic studies (including molybdenite Re–Os dating, zircon U–Pb dating and Lu–Hf analysis) were employed to constrain the emplacement/mineralization ages and granite petrogenesis. Our results show that, the Jurassic granitoids in the Chalukou deposit originated from partial melting of juvenile crust. Therefore, this deposit shares similar geological and geochemical features with porphyry Mo deposits developed in continental arc settings. When taking into consideration the spatio-temporal distribution and geochemical features of porphyry Mo deposits in NE China, it is proposed that the Chalukou deposit was formed in a continental arc setting, caused by the southeastward subduction of the Mongol–Okhotsk Ocean.

2. Geological setting

As the eastern segment of the CAOBS, the Great Hinggan Range (GHR) is bounded by the Mongol–Okhotsk Suture to the north, the Kangbao–Chifeng Fault to the south, the Nenjiang Fault to the east (Fig. 1B). The giant Chalukou Mo deposit is located in the northern part of the GHR, which includes two tectonic units named Erguna Massif and Hinggan Massif (Fig. 1B; Chen et al., 2012; Qi et al., 2005). The Erguna Massif is considered as the eastern extension of the Central Mongolian microcontinent (Wu et al., 2011). It is mainly composed of voluminous Paleozoic and Mesozoic granitoids, and Mesozoic volcanic rocks. The basement discontinuously occurs in restricted areas and is composed of Precambrian metamorphic supracrustal rocks and associated granitic complexes (Fig. 1C). The metamorphic rocks included upper greenschist- to lower amphibolite-facies rocks, such as amphibolites, gneisses, schists, leptynites, leucoleptynites, and marbles. These are conventionally subdivided into the Xinghuadukou, Luomahu and Jiageda groups (HBGMR, 1993). They were previously regarded as Archean or Paleoproterozoic in age (Biao et al., 1999; HBGMR, 1993), but recent zircon U–Pb dating revealed Neoproterozoic ages (Ge et al., 2015; Miao et al., 2007; Wu et al., 2012). Traditionally, granitoids in the Erguna Massif were assigned to the Paleozoic in the eastern part and the Proterozoic–Paleozoic in the western part (HBGMR, 1993). Recently obtained geochronological data indicate multiple episodes of granitic magmatism, with the majority formed in the Cretaceous (118–132 Ma), Jurassic to Triassic (182–220 Ma) and Devonian to Cambrian (416–517 Ma), and less in the Triassic to Carboniferous (244–336 Ma) and Neoproterozoic (792–927 Ma) (Wu et al., 2011). Mesozoic volcanism is widespread and is subdivided into the Tamulangou, Jixiangfeng,

Shangkuli and Yiliegede formations from old to young (HBGMR, 1993). Detailed geochronological data indicate a Jurassic–Cretaceous depositional age (Wang et al., 2006; Xu et al., 2013).

The Hingan Massif is characterized by voluminous Mesozoic granites and volcanic rocks (Fig. 1C; Zhang et al., 2010; Zhou and Wilde, 2013). Precambrian basement units may be present locally, but no reliable evidence is available. The metamorphic rocks that were assumed to be Proterozoic in age (HBGMR, 1993; IMBGMR, 1991) are actually Paleozoic and/or Mesozoic in age as constrained by more recent zircon U–Pb dating (Miao et al., 2007; Sun et al., 2014; Xu et al., 2013). The Paleozoic strata (mainly marine volcano–clastic rocks) are well developed, especially in the middle and eastern part, and locally outcrop as roof pendants in granite. Contemporaneous granitoids were metamorphosed and deformed (Han et al., 2011). Late Mesozoic granitoids, however, are undeformed and widespread throughout the region (Wu et al., 2003; Zhou and Wilde, 2013). The Mesozoic to Cenozoic sedimentary and volcanic rocks are volumetrically important, accounting for about 70% of all exposed rocks (Fig. 1C).

3. Local and ore geology

The Chalukou porphyry Mo deposit is located 64 km northwest of Xiaoyangqi Town, Heilongjiang Province (E: 123°49'15"–123°56'30", N: 51°08'15"–51°11'00") (Fig. 2). The mineralized area is 8 km long and 5 km wide, and is divided into east and west sections by the Duobukuer River (Fig. 2). Compared to the western section, the eastern one is explored and studied in more detail.

3.1 Lithologies and structures

Rocks in the Chalukou area include the Dawangzi Formation and Baiyingaolao Formation (Fig. 3A). The Dawangzi Formation is a suite of low-grade meta-volcanic and meta-sedimentary rocks that are composed of quartz-chlorite schists, quartz-biotite schists and minor marble. This formation locally occurs to the southeast and northwest part of the deposit and was traditionally considered to be Neoproterozoic–Early Cambrian in age (HBGMR, 1993). Zircon U–Pb data, however, constraint its formation to the Silurian–Cambrian (Miao et al., 2007; Sun et al., 2014). The Jurassic Baiyingaolao Formation is widely distributed, and is mainly composed of rhyolites, dacites, andesites and intermediate–felsic tuffs (Lv et al., 2010). These rocks are one of the main ore-host and as such are hydrothermally altered (see below).

NE- and NW-trending faults and volcanic ring fractures are dominant in the deposit area (Fig. 2). They were formed prior to or simultaneously with Mo mineralization, and controlled the distribution of both intrusions and orebodies. The thick, high-grade and continuous orebodies are preferentially located at the intersections between NE- and NW-trending faults. Explosive breccias pipes, lenses and veins are also well developed in the mineralized zone (Fig. 3A and 4C).

3.2 Intrusive rocks

Multiple episodes of igneous activity are recognized in the mining area. The Late Paleozoic quartz diorite in the southwestern corner intruded into Silurian–Cambrian metamorphic rocks, and was crosscut by later intrusions (Fig. 3A). The Jurassic monzogranite,

which underlies the western part of the deposit is one of the main host rock to Mo mineralization in the Chalukou area. It intruded into the Late Paleozoic quartz diorite and is overlain by Jurassic volcanic–sedimentary rocks (Fig. 3A, B). The Late Jurassic granitoids record a complex history that includes emplacement, solidification, locally intense veining, dyke intrusion, hydrothermal alteration and Mo mineralization. They display a range of compositions from granite porphyry, quartz porphyry, aplite porphyry and granite. Some post-ore intrusions and extrusions, such as diorite porphyry, quartz monzonite porphyry, rhyolite porphyry or diorite porphyry, intruded or covered early granitoids and Mo orebodies (Fig. 2 and 3).

3.3 Mineralization

Both Mo and Pb–Zn mineralization can be identified in the Chalukou deposit. Mo mineralization mainly occurs as quartz-sulfide veinlets in the central part, whereas the Pb–Zn mineralization is hosted by NW-dipping veins with dip angles of 30–50° in distal zones (Liu et al., 2014a).

The Mo orebodies are generally hosted by the monzogranite, granite porphyry, breccia pipes and Jurassic volcanic–sedimentary rocks (Fig. 3B). The largest Mo orebody is 1,800 m long, 200–1,000 m wide and 815 m thick (Nie et al., 2011). A vertical variation can be recognized (Liu et al., 2011; Nie et al., 2011): (1) at the top, the Mo orebodies occur as thin layers and veins in the felsic volcanic rocks, and are characterized by low grade (with an average of 0.06%), small scale (several to dozens of meters thick) and are discontinuous; (2) in the middle part, the Mo orebodies are very thick and lenticular, mainly hosted by felsic

volcanic rocks and granite porphyry, and characterized by high grade (0.06% to 0.26%), large scale (with thickness of over 100 m) and good continuity; (3) at the base, the Mo orebodies are located in granite porphyry and breccia pipes, with thickness of nearly 100 m and Mo grades of 0.08% to 0.53%.

Molybdenite can occur: (a) as blades or films filling fractures of granite porphyry, monzogranite, Jurassic volcanic–sedimentary rocks and pre-Mesozoic metamorphic rocks (Fig. 4F); (b) as disseminations in quartz-dominated veinlets (Fig. 4G); or (c) as matrix in breccias that cements clasts of granite porphyry and Jurassic volcanic–sedimentary rocks (Fig. 4H). Other ore minerals include pyrite, sphalerite and galena, with minor chalcopyrite, pyrrhotite and magnetite. Gangue minerals are mainly K-feldspar, quartz, plagioclase, sericite, calcite, chlorite and fluorite.

3.4 Hydrothermal alteration

Four alteration zones can be recognized from the center of the porphyry stock outwards, i.e. potassic, phyllic, argillic and propylitic, though their boundaries are transitional and therefore not sharply defined. Mo mineralization is associated with potassic and phyllic alteration (Fig. 4K–O), while Pb–Zn mineralization is closely associated with propylitic alteration (Liu et al., 2011; Nie et al., 2011, 2013).

The potassic alteration occurs mainly in the granite porphyry and the wall rocks (Fig. 3A). It is characterized by an assemblage of K-feldspar + quartz ± biotite with rare sericite and anhydrite. Hydrothermal quartz and K-feldspar usually replace magmatic quartz and feldspar within the intrusion, or occur as veins and veinlets (Fig. 4I). The phyllic alteration

zone is represented by the mineral assemblage of quartz + sericite + hydromuscovite + pyrite $\pm$ kaolinite $\pm$ calcite (Fig. 4J), and mainly is developed in the Jurassic volcanic–sedimentary rocks, monzogranite and some granite porphyry (Fig. 3A). Abundant sericite and/or hydromuscovite either occur as veins or replacement of magmatic minerals, such as plagioclase, K-feldspar and biotite in the intrusion. The argillic alteration zone is observed mainly in the Jurassic volcanic–sedimentary rocks (Fig. 3A), with a characteristic assemblage of quartz + kaolinite + chlorite + calcite $\pm$ fluorite $\pm$ pyrite (Fig. 4L). Propylitic alteration is manifested as extensive replacement of feldspar, biotite and muscovite by epidote, chlorite and calcite (Fig. 4M), and is well developed in the monzogranite, the Jurassic volcanic–sedimentary rocks and Silurian–Cambrian metamorphic rocks (Fig. 3A). Propylitic alteration overprints early alteration types at all scales.

4. Sampling and methodology

4.1 Sampling

Seven molybdenite samples for Re–Os analyses were collected from different depth of drill core ZKHD903 in the eastern section (Fig. 3A). They include both molybdenite-only (CLK-03, 04, 05, 06, 07) and quartz–molybdenite veins (CLK-10, 11) (Fig. 4F, N, O).

Two samples were selected for zircon U–Pb dating and Lu–Hf analysis (Fig. 3A). Sample CLKY-01 is a reddish medium to coarse-grained monzogranite collected from 1225 m depth of drill core GK-02. It is composed of 35 to 40 vol.% plagioclase, 30 to 35 vol.% K-feldspar, 25 to 30 vol.% quartz and 2 to 5 vol.% biotite (Fig. 4A, D). Plagioclase with polysynthetic twins is subhedral or euhedral and partially altered to sericite (Fig. 4D).

K-feldspar is subhedral or anhedral and commonly replaced by kaolinite. Quartz is mostly subhedral or anhedral, showing myrmekitic texture and undulating extinction. Biotite is partially altered to chlorite, generating fine-grained opaque minerals. The major accessory minerals are zircon, sphene and magnetite.

Sample CLKY-07 is granite porphyry collected from 1018 m depth of drill core ZKHD903. It is strongly altered, with minor sulfide mineralization (Fig. 4B). It is reddish, massive and porphyritic. Phenocrysts with sizes of 0.5–5 mm account for about 10 vol.% of the whole rock and consist mainly of quartz (~ 3 vol.%), K-feldspar (~ 4 vol.%), plagioclase (~ 3 vol.%), and lesser amount of biotite (< 1 vol.%) (Fig. 4E). Plagioclase phenocrysts are subhedral–euhedral with obvious sericite alteration. K-feldspar phenocrysts are subhedral–anhedral and altered to kaolinite. Sometimes the anhedral quartz phenocrysts are partly eroded with embayed boundaries. The matrix is composed of quartz, K-feldspar, plagioclase and mafic minerals, with accessory apatite, zircon, sphene and magnetite (Fig. 4E).

4.2 Re–Os analyses

Molybdenite separates were obtained by crushing the ore samples to 100 mesh in a porcelain mill, gravity sorting, electromagnetic separation, and finally handpicked to a purity of more than 98% under a binocular microscope. Re–Os isotopes were performed and analyzed by a TJA X-series ICP-MS at the Re–Os Laboratory, National Research Center of Geoanalysis, Chinese Academy of Geological Sciences (CAGS). The uncertainty in each individual age determination is about 1.5%, including the uncertainty of the decay constant of

¹⁸⁷Re, uncertainty of the isotope ratio measurement, and the spike calibration. The details of the chemical procedure have been described by [Du et al. \(2004\)](#), [Markey et al. \(1998\)](#) and [Stein et al. \(1998\)](#).

4.3 Zircon U–Pb dating and Lu–Hf isotope analyses

Zircon separates were mounted in epoxy resin together with several reference crystals, including 91500 and GJ-1. Then the mount was polished and coated with gold. Cathodoluminescence (CL) images were obtained using a CAMECA SX50 microprobe at the Institute of Geology and Geophysics, Chinese Academy of Sciences, in order to identify internal textures and choose potential analysis sites. These zircons were first analyzed for their U–Pb isotopic composition, followed by Hf isotope analysis on the same domains, in order to get coupled U–Pb–Hf isotope data.

U–Pb dating of zircons was conducted by LA-ICP-MS at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan. Detailed operating conditions for the laser ablation system and the ICP-MS instrument and data reduction are the same as description by [Liu et al. \(2010\)](#). Laser sampling was performed using a GeoLas 2005. An Agilent 7500a ICP-MS instrument was used to acquire ion-signal intensities. Helium was applied as a carrier gas. Argon was used as the make-up gas and mixed with the carrier gas via a T-connector before entering the ICP. Nitrogen was added into the central gas flow (Ar + He) of the Ar plasma to decrease the detection limit and improve precision ([Hu et al., 2012](#)). Each analysis incorporated a background acquisition of approximately 20–30 s (gas blank) followed by 50 s data acquisition from the sample. The

Agilent Chemstation was utilized for the acquisition of each individual analysis. Off-line selection and integration of background and analyses signals, and time-drift correction and quantitative calibration for U–Pb dating were performed by ICPMSDataCal (Liu et al., 2010).

Zircon 91500 was used as external standard for U–Pb dating, and was analyzed twice every 5 analyses. Time-dependent drift of U–Th–Pb isotopic ratios was corrected using a linear interpolation (with time) for every five analyses according to the variations of 91500 (Liu et al., 2010). Preferred U–Th–Pb isotopic ratios used for 91500 are from Wiedenbeck et al. (1995). Uncertainty of preferred values for the external standard 91500 was propagated to the final results of the samples. Common Pb was corrected according to the method proposed by Anderson (2002). Concordia diagrams and weighted mean calculations were made using Isoplot/Ex_ver3 (Ludwig, 2003).

Lu–Hf isotope analysis was conducted using a Neptune Plus MC-ICP-MS (Thermo Fisher Scientific, Germany) in combination with a GeoLas 2005 excimer ArF laser ablation system (Lambda Physik, Göttingen, Germany) that was hosted at the state Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences in Wuhan. The energy density of laser ablation that was used in this study was $5.3 \text{ J} \cdot \text{cm}^{-2}$. Helium was used as the carrier gas within the ablation cell and was merged with argon (makeup gas) after the ablation cell. All data were acquired on zircon in single spot ablation mode at a spot size of 44 μm . Each measurement consisted of 20 s of acquisition of the background signal followed by 50 s of ablation signal acquisition. Detailed operating conditions for the laser ablation system and the MC-ICP-MS instrument and analytical method are the same as described by Hu et al. (2012). The major limitation to accurate in situ zircon Hf isotope

determination by LA-MC-ICP-MS is the very large isobaric interference from ^{176}Yb and, to a lesser extent ^{176}Lu on ^{176}Hf . We applied the directly obtained β_{Yb} value from the zircon sample itself in real-time in this study. The $^{179}\text{Hf}/^{177}\text{Hf}$ and $^{173}\text{Yb}/^{171}\text{Yb}$ ratios were used to calculate the mass bias of Hf (β_{Hf}) and Yb (β_{Yb}), which were normalised to $^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$ and $^{173}\text{Yb}/^{171}\text{Yb} = 1.13017$ (Segal et al., 2003) using an exponential correction for mass bias. The interference of ^{176}Yb on ^{176}Hf was corrected by measuring the interference-free ^{173}Yb isotope and using $^{176}\text{Yb}/^{173}\text{Yb} = 0.79381$ (Segal et al., 2003) to calculate $^{176}\text{Yb}/^{177}\text{Hf}$. Similarly, the relatively minor interference of ^{176}Lu on ^{176}Hf was corrected by measuring the intensity of the interference-free ^{175}Lu isotope and using the recommended value of $^{176}\text{Lu}/^{175}\text{Lu} = 0.02656$ (Blichert-Toft and Albarede, 1997) to calculate $^{176}\text{Lu}/^{177}\text{Hf}$. We used the mass bias of Yb (β_{Yb}) to calculate the mass fractionation of Lu because of their similar physicochemical properties. Off-line selection and integration of analyte signals, and mass bias calibrations were performed using ICPMSDataCal (Liu et al., 2010). Zircon GJ-1 was used as the reference standard, with a weighted mean $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of 0.282010 ± 15 (1σ) during our routine analyses, which is in good agreement with the recommended ratios 0.282015 ± 19 (2σ) for GJ-1 (Elhlou et al., 2006).

Analytical ratios of $^{176}\text{Yb}/^{177}\text{Hf}$, $^{176}\text{Lu}/^{177}\text{Hf}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ are reported with 2σ error. Initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratio, i.e. $\varepsilon_{\text{Hf}}(t)$, is calculated referring to chondrite at the time of zircon growth from magma. The decay constant of $1.867 \times 10^{-11} \text{ year}^{-1}$ for ^{176}Lu (Söderlund et al., 2004) and the chondritic ratios of $^{176}\text{Hf}/^{177}\text{Hf}$ (0.282772) and $^{176}\text{Lu}/^{177}\text{Hf}$ (0.0332) introduced by Blichert-Toft and Albarede (1997) were adopted in calculations. Single-stage Hf model ages (T_{DMI}) are calculated relative to the depleted mantle with a present day $^{176}\text{Hf}/^{177}\text{Hf}$ ratios

of 0.28325 and $^{176}\text{Lu}/^{177}\text{Hf}$ of 0.0384 (Griffin et al., 2000). Two-stage Hf model ages (T_{DM2}) are calculated by referring to the $f_{\text{Lu/Hf}}$ value of -0.55 for the average continental crust (Griffin et al., 2002). The $f_{\text{Lu/Hf}}$ ratio equals to $(^{176}\text{Lu}/^{177}\text{Hf})_{\text{s}}/(^{176}\text{Lu}/^{177}\text{Hf})_{\text{CHUR}} - 1$, where the $(^{176}\text{Lu}/^{177}\text{Hf})_{\text{CHUR}} = 0.0332$, and the $(^{176}\text{Lu}/^{177}\text{Hf})_{\text{s}}$ value is obtained from sample analysis.

5. Analytical results

5.1 Re–Os geochronology

The Re–Os isotope data of seven molybdenite samples are listed in Table 1 with 2σ errors. The samples have a relatively wide range of Re and ^{187}Os contents (i.e. 3.14–19.49 ppm and 4.74–30.55 ppb, respectively), but the positive correlation between Re and Os is clear. The Re–Os model ages are consistent, ranging from 146 Ma to 150 Ma with a weighted mean age of 148 ± 1 Ma (Table 1). Using Isoplot/Ex_ver3 (Ludwig, 2003), the data yield an isochron age of (150 ± 2) Ma with MSWD = 1.9 and an initial ^{187}Os of -0.42 ± 0.28 ppb (Fig. 5).

5.2 Zircon morphology and U–Pb dating

Zircon grains collected from sample CLKY-01 are euhedral and have sharp facets and pointed tips. They are mainly colorless and transparent, with lengths ranging from 100 to 200 μm and length/width ratios from 2:1 to 4:1. Oscillatory zoning is well developed (Fig. 6). Obtained Th/U values range from 0.45 to 1.09 (Table 1), indicating a typically magmatic genesis (Wu and Zheng, 2004). All of the eighteen analyses are concordant, and the $^{206}\text{Pb}/^{238}\text{U}$

ages scatter between 161 ± 2 and 171 ± 2 Ma (Table 1), averaging at 166.2 ± 1.5 Ma (95% confidence level, MSWD = 1.8, n = 18; Fig. 7).

Zircon crystals collected from sample CLKY-07 are colorless and transparent, showing sub- to euhedral prismatic shapes with sharp facets and pointed tips (Fig. 6). They range in size from 80 to 150 μm in length with length/width ratios of about 1.5:1–3:1. Some zircons are cracked, have inclusions and/or have been partially dissolved in the host magmas (CLKY-07-01, 02, 13; Fig. 6). The CL images reveal a variety of internal textures ranging from irregular patchy to fine-scale oscillatory zoning. LA-ICP-MS analyses were performed on sixteen spots (Fig. 6, Table 2). Their Th/U ratios are relatively high (0.52–1.02; Table 2), consistent with the features of magmatic zircons (Wu and Zheng, 2004). The data yield $^{206}\text{Pb}/^{238}\text{U}$ ages of 149–157 Ma (Table 2), with a weighted mean age of 152 ± 2 Ma (95% confidence level, MSWD = 1.3, n = 16; Fig. 7).

5.3 Zircon Hf isotopes

The results of zircon Lu–Hf isotopic analyses are listed in Table 3 and shown in Fig. 8. Hf isotopic data, expressed as values of epsilon Hf at the time of formation ($\epsilon\text{Hf}(t)$), from the ore-host monzogranite porphyry and ore-causative granite porphyry as well as other phases making up the Chalukou granitoids are plotted versus time in Fig. 8.

The $^{176}\text{Lu}/^{177}\text{Hf}$ ratios are very low (0.000575–0.001652 for sample CLKY-01 and 0.000817–0.001587 for sample CLKY-07, respectively), indicating very little radiogenic Hf. Thus, the measured $^{176}\text{Hf}/^{177}\text{Hf}$ ratios can approximately represent initial Hf isotopic composition.

The obtained $^{176}\text{Hf}/^{177}\text{Hf}$ ratios of eighteen spots from sample CLKY-01 have limited variation, ranging from 0.282701 ± 0.000007 to 0.282761 ± 0.000012 with a weighted average of 0.282721 ± 0.000009 (1σ , $n = 18$). Calculated $\varepsilon\text{Hf}(t)$ values vary from 0.9 to 3.0, with an average of 1.7 ± 0.6 (1σ , $n = 18$). Corresponding two-stage Hf model ages ($T_{\text{DM}2}$) range from 1016 to 1232 Ma, with a weighted mean of 1116 Ma (Table 3).

Sixteen zircons from Sample CLKY-07 display variable $^{176}\text{Hf}/^{177}\text{Hf}$ ratios of 0.282644 ± 0.000006 to 0.282689 ± 0.000017 with a weighted average of 0.282667 ± 0.000012 (1σ , $n = 16$) (Table 3). Obtained $\varepsilon\text{Hf}(t)$ values are -1.4 to 0.5, with an average of -0.4 ± 0.7 (1σ , $n = 16$). Two-stage Hf model ages ($T_{\text{DM}2}$) range from 1174 to 1284 Ma, with a weighted mean of 1228 Ma (Table 3).

6. Discussion

6.1 Timing of magmatism and mineralization

Available data show that the duration of magmatic activity responsible for hydrothermal mineralization varies significantly, from less than one million years to more than tens of million years (see Li et al., 2013 and references therein). The Chalukou deposit is a typical porphyry Mo deposit characterized by large tonnage, but low-grade stockwork and breccia-hosted ores, as well as large-scale hydrothermal alteration and spatial and a genetic association with granite porphyry. A combination of zircon U–Pb and molybdenite Re–Os ages obtained by Li et al. (2014), Liu et al. (2014a), Nie et al. (2011) and from this study allow us to construct the time framework and to evaluate the duration of the magmatic

activity and deposit formation. We suggest a long-lived magmatic system with a short-lived mineralization event for the Chalukou deposit as follows (Fig. 9).

The monzogranite from the neighboring district of the Chalukou deposit is the oldest Mesozoic intrusion. It is barren and poorly altered, with a zircon U–Pb age of 172.4 ± 1.6 Ma (Li et al., 2014). Following its intrusion, another phase of monzogranite was emplaced in the northwest and southeast part of the ore district. New U–Pb zircon ages (Li et al., 2014; Liu et al., 2014a; this paper) suggested that its emplacement took place between 166 and 162 Ma. This phase, however, is still ore-barren but serves as important host rock to Mo mineralization. Afterward, several porphyritic phases, including aplite porphyry, granite porphyry and quartz porphyry, intruded at ca. 148 Ma (Li et al., 2014; Liu et al., 2014a; this paper). These porphyry intrusions are considered as the main contributor that resulted in extensive and intensive Mo mineralization. New molybdenite Re–Os isochron method places a robust mineralization age of 150 ± 2 Ma, verifying their co-occurrence. Subsequently, post-ore intrusive (such as diorite porphyry and quartz monzonite porphyry) and extrusive (such as andesite porphyry and rhyolite porphyry) rocks were emplaced and destroyed or covered the Mo orebodies. These rocks yield crystallization ages ranging from 142 Ma to 128 Ma (Li et al., 2014; Liu et al., 2014a). Hence, it is concluded that the magmatic event at the Chalukou deposit span ca. 45 Ma (from 172 to 128 Ma). Related Mo mineralization, however, is short-lived, as constrained to 150–147 Ma by molybdenite Re–Os dating (Liu et al., 2014a; Nie et al., 2011; this paper).

6.2 Contribution of continental crust to the ore-causative granitoids

Zircon can effectively record the primary Lu–Hf isotopic characteristics, due to its low concentration of initial Lu and consequently negligible radiogenic Hf within it (Amelin et al., 2000; Griffin et al., 2002). Since Hf is partitioned more strongly into melts than Lu during partial melting, the crust generally has lower $^{176}\text{Lu}/^{177}\text{Hf}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios than the mantle. Accordingly, granitoids with positive $\epsilon\text{Hf}(t)$ values are considered to be sourced from the partial melting of juvenile crustal materials, while the negative $\epsilon\text{Hf}(t)$ values indicate a source of old crust (Sui et al., 2007; Sun et al., 2005). As shown in Fig. 8 and Table 3, the monzogranite and granite porphyry of the Chalukou Mo deposit display different zircon Hf isotopic compositions, indicating discrepant sources of magma. The positive $\epsilon\text{Hf}(t)$ values of the monzogranite (0.9–3.0) indicate a predominantly juvenile protolith. However, the granite porphyry has much lower $\epsilon\text{Hf}(t)$ values (-1.4–0.5) than those of monzogranite, although they have similar two-stage Hf model ages (1174–1284 Ma and 1016–1232 Ma).

When integrated with published zircon Lu–Hf isotopic data (Li et al., 2014; Liu et al., 2014), our data allow us to address the question of whether there are fundamental differences in magma sources of barren versus mineralized granite. From Fig. 8 we can see that both the pre- and post-ore, barren granites are characterized by limited and positive $\epsilon\text{Hf}(t)$ values, indicating their juvenile character and suggesting their derivation from source rock or magmas separated shortly from the upper mantle. By contrast, the syn-ore rocks, including granite porphyry, quartz porphyry, granite and apalite porphyry, are characterized by more heterogeneous $\epsilon\text{Hf}(t)$ values (-4.2 to 10.2) than the barren rocks. Their positive $\epsilon\text{Hf}(t)$ values are comparable with those of barren rocks, although zircon grains with negative $\epsilon\text{Hf}(t)$ values

also exist, reflecting the contamination of older, evolved continental crust in the magma generation processes. Thus it is concluded that the contribution of old continental crust is critical to Mo mineralization (Chen et al., 2012, 2016b; Zhang and Li, 2014). Actually, this conclusion is verified by the prominent spatial relationship between porphyry Mo deposits and continental crust: the majority of porphyry Mo deposits are underlain by continental crust in tectonic settings such as continental arc, back-arc rift or continental orogeny, whereas in island arc where no continental crustal sources are inferred, porphyry Mo deposits are limited (Misra, 2000; Sillitoe, 1980, 2010).

6.3 Granitoid petrogenesis as a constraint to the genetic type of the deposit

Three subtypes of porphyry Mo deposits are distinguished in the context of their intricate processes of ore formation, namely rift-related, subduction-related and collision-related (Table 4). The Chalukou deposit was at first assigned to rifting processes by Nie et al. (2013) based on evidences such as: the A-type affinity of the main ore-causative rocks, the inverted-cup-shape of the ore-body, the hydrothermal alteration, as well as the P–T condition of the ore-forming fluids. However, the argillic alteration, which is widespread in the Chalukou deposit is actually not well-developed in rift-related Mo deposits. The shape of the orebody and the P–T condition of ore-forming fluids cannot be regarded as reliable criteria for assessing the tectonic regime under which the deposit may have formed (Chen et al., 2016a; Li et al., 2012a, 2013; Ludington and Plumlee, 2009; Taylor et al., 2012).

Another important evidence disputing the rift- affinity of the Chalukou deposit lies on the petrogenesis of granitoids. Typical rift-related porphyry Mo deposits are invariably

associated with A-type granites. The classic view interpreted the dominant parental melt to be derived from evolved lower continental crust instead of juvenile crust. Such arguments are based mainly on the per-aluminous character of the most evolved magmas, the variably negative $\epsilon\text{Nd}(t)$, moderately radiogenic Sr and non-radiogenic Pb isotope ratios (Farmer and Depaolo, 1984; Pettke et al., 2010; Stein, 1985; Zartman, 1974). For instance, 3 samples from Henderson yield $\epsilon\text{Nd}(t)$ values ranging from -9.5 to -9.9 that are indistinguishable from the high end ϵNd of Precambrian (1.6 to 1.8 Ga) basement rocks (Farmer and Depaolo, 1984). Hence, the granitic magmas were considered to be derived mainly from mid-Proterozoic crust. The Pine Grove topaz rhyolite that is associated with a Climax-type porphyry Mo deposit displays $(^{87}\text{Sr}/^{86}\text{Sr})_i$ values between 0.706 and 0.710, and $\epsilon\text{Nd}(t)$ values between -11 and -9 (Christiansen et al., 2007). All these data emphasize significant contribution of old, highly evolved lower crust (Ludington and Plumlee, 2009; Seedorff et al., 2005).

Biotite is the dominant mafic mineral in the Chalukou ore-causative granitoids, and no mafic alkaline silicates, such as arfvedsonite or riebeckite are observed. Geochemical analysis reveals low proportions of Zr, Nb, Y, La, Ce and Ga, suggesting I-type affinity instead of A-type (Li et al., 2014; Liu et al., 2015). Moreover, the large variation in zircon $\epsilon\text{Hf}(t)$ values from -4.2 to 10.2 indicate variable proportions of older continental crust and juvenile sources. Such a scenario contrasts with a rift- related porphyry Mo deposit, instead it is suggestive of a subduction system in which the production of granite was initiated by extensive basaltic underplating, accompanied by partial melting of a range of lithologic associations. Further, the trace element concentrations in the ore-causative granite are also comparable with subduction-related deposits: with Rb ranging from 141 to 229 ppm (mainly <200 ppm), Sr

from 24 to 387 ppm (mainly <100 ppm), Nb from 9 to 46 ppm (mainly <15 ppm), and Zr from 89 to 285 ppm (mainly >100 ppm) (Table 4). Hence, the petrogenesis of the Chalukou granitoids supports a subduction link. This conclusion is also evidenced by the widespread argillic alteration and the low, if any, contents of CO₂ in the ore-forming fluids (Liu et al., 2014b; Xiong et al., 2015).

6.4 Implications for the geodynamic setting of the Chalukou porphyry Mo deposit

With the Chalukou deposit considered as subduction-related, the question can be posed: which ocean was responsible for the formation of the continental arc? The Paleo-Asian Ocean can be excluded as it had closed in Late Permian–Triassic times (Chen et al., 2007; Zhang and Li, 2014). Hence, only the Paleo-Pacific Ocean or the Mongol–Okhotsk Ocean can be considered to have developed subduction zones or plates, which were ultimately responsible for partial melting and the emplacement of granitic rocks and porphyritic granites, which caused the formation of the Chalukou deposit.

Taking into consideration that: (1) spatially, the Chalukou deposit is located in the northeastern part of the Hingan Massif, which is too far away from the East Asian continental margin to be accounted for the effect of the subduction of the Paleo-Pacific plate (Chen et al., 2007; Li et al., 2007; Qi et al., 2005); (2) temporally, the subduction of the Paleo-Pacific plate beneath the Eurasia continent began in the Early Cretaceous (Chen et al., 2016b; Engebretson et al., 1985; Shao and Tang, 2015; Shao et al., 2013), which is much later than the formation of the Chalukou deposit at ca. 150 Ma; (3) porphyry Mo deposits and related magmatic rocks aged 160–130 Ma have been only reported to the west of the Songliao basin, whereas are

absent to its eastern part (Chen et al., 2012, 2016b), thereby subduction of the Paleo-Pacific plate is not related to the emplacement of granitoids and the Mo mineralization at Chalukou.

On the other hand, abundant evidences indicate that granite emplacement and mineralization at the Chalukou deposit is related to the subduction of the Mongol–Okhotsk Ocean. Extensive studies of the Early Mesozoic granitoids along the Mongol–Okhotsk Suture have revealed that these rocks are dominated by granodiorite, monzogranite, syenogranite, biotite granite, and diorite, and are widely distributed along both sides of the suture (Tang et al., 2014; Wu et al., 2011). Petrologically, the genetic types of granite also show variations, where Jurassic granites are mainly I-type, whereas A-type granites were only emplaced in the Early Cretaceous. Thus, the Jurassic granites formed in an active continental margin related to the bidirectional subduction of the Mongol–Okhotsk Ocean (Tang et al., 2014; Wu et al., 2011; Xu et al., 2013).

Another line of evidence supporting the southeastward subduction of the Mongol–Okhotsk oceanic plate comes from Jurassic porphyry deposits located in the western part of NE China (Fig. 1C). They include, Fe–Cu, Cu–Mo and Mo–(Cu–Pb–Zn) mineral systems, which are commonly observed in continental arc settings. Moreover, the corresponding ore-forming fluids are of high temperature, of high salinity, with little, if any, CO₂ (Li et al., 2012b; Liu et al., 2014b; Wang et al., 2009). These features are commonly observed in porphyry systems formed in subduction-related continental arcs (Chen and Li, 2009). Furthermore, a spatial and temporal distribution can be recognized (Fig. 1C). Spatially, the Cu–(Fe–Mo) deposits are distributed in the northwestern parts of the GHR (mainly in the Erguna Massif), whereas Mo–(Cu–Pb–Zn) deposits occur in the inner parts of GHR (both in

the Erguna Massif and the Xing'an Massif). Temporally, Cu–(Fe–Mo) deposits formed earlier (e.g. the 178 Ma Wunugetushan Cu–Mo deposit, [Chen et al., 2011](#); [Li et al., 2007, 2012b](#); the 176 Ma Sankuangou Fe–Cu deposit, [Chu et al., 2012](#)), whereas Mo–(Cu–Pb–Zn) deposits formed later (from 150 Ma to 129 Ma, [Liu et al., 2014a](#); [Nie et al., 2011](#); [Wang et al., 2009, 2016a](#); [Zhai et al., 2009](#); [Zhang et al., 2013](#) and this paper). Such a spatio-temporal variation is commonly observed in a continental subduction setting and reinforces a southeastward subduction of the Mongol–Okhotsk Ocean.

Additional evidence comes from paleomagnetic studies, which indicated that the Mongol–Okhotsk Ocean was still open in the early Late Jurassic ([Cogne et al., 2005](#); [Enkin et al., 1992](#); [Kravchinsky et al., 2002](#); [Metelkin et al., 2007](#); [Zhao et al., 1996](#)). [Yang et al. \(2015b\)](#) reviewed systematically the Late Jurassic–Early Cretaceous stratigraphic and structural evolution of basins in northern China and Mongolia, and concluded that during Late Jurassic, an oceanic arm several hundred kilometers wide existed between eastern Amuria (including the Great Hingan Range) and Siberia.

Based on the above discussion, it is clear that the Chalukou deposit is a porphyry Mo deposit developed in a continental arc setting, and can be interpreted as a product of the southeastward subduction of the Mongol–Okhotsk Ocean and not of the westward subduction of the Paleo-Pacific Ocean ([Fig. 10](#)). Such a conclusion can also be supported by porphyry molybdenum deposits from the southern segment of the Great Hingan Range ([Chen et al., 2012, 2016b](#); [Wang et al., 2016a](#)).

7. Concluding remarks

(1) The Chalukou deposit is a typical porphyry Mo deposit associated with a multistage porphyry complex, with a zircon U–Pb age of 166 ± 2 Ma for the ore-hosting monzogranite and 152 ± 2 Ma for the ore-causative granite porphyry. Mo mineralization occurred at 150 ± 2 Ma (molybdenite Re–Os isochron age).

(2) The monzogranite and granite porphyry yield zircon $\epsilon_{\text{Hf}}(t)$ values of 0.9–3.0 and –1.4–0.5, respectively. Combined with previous geochemical data, it is suggested that the barren magmas (both pre-ore and post-ore) were originated mainly from partial melting of juvenile crust, whereas the ore-causative granites require additional involvement of old continental crust.

(3) The Chalukou deposit shares similar geological and geochemical features with subduction-related porphyry Mo deposits. Its formation indicates the southeastward subduction of the Mongol–Okhotsk Ocean lasted to at least Late Jurassic in the eastern part.

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Figure Captions

Fig. 1 (A) Schematic map of main tectonic domains of Asia (modified after [Chen et al., 2004, 2007](#)). (B) Tectonic sub-divisions of Northeast China and Far East Russia (modified after [Zhou and Wilde, 2013](#)). (C) Geological map of the northern Great Hingan Range, showing the locations of porphyry Mo-bearing deposits (modified after [Chen et al., 2012](#); [Qi et al., 2005](#)).

Fig. 2 Sketch regional geological map of the Chalukou orefield, showing the locations of the east and west section (modified after [Fu et al., 2011](#)).

Fig. 3 (A) Geological map of the east section of the Chalukou Mo deposit. (B) Geological profile for prospecting line No. 10 (modified after [Liu et al., 2011](#)).

Abbreviation: Q-K: quartz–potassic alteration zone; Q-S: quartz–sericite alteration zone; Agl: argillization zone; Pro: propylitization zone.

Fig. 4 Photographs showing ore petrography of the Chalukou Mo deposit.

(A) monzogranite; (B) granite porphyry with slight alteration and sulfide precipitation; (C) the explosive breccias with clasts of granite porphyry and monzogranite; (D) medium-coarse grained texture of the monzogranite; (E) phenocrysts of K-feldspar, plagioclase and quartz in granite porphyry; (F) bladed molybdenite; (G) quartz-molybdenite-pyrite veinlet; (H) disseminated molybdenite; (I) the potassic alteration where plagioclase is replaced by K-feldspar; (J) the quartz-sericite alteration where sericite coexists with quartz and pyrite; (K) the silicification represented by abundant fine-grained hydrothermal quartz; (L) the argillization, with mineral association of chlorite, kaolinite, fluorite and pyrite; (M) the propylitization as represented by mineral association of epidote and chlorite; (N) quartz-molybdenite vein in the potassic altered granite porphyry; (O) Mo-dominated stockwork.

Abbreviations: Bi: biotite, Chl: chlorite; Ep: epidote; Fl: fluorite; Kao: kaolinite; Kfs: K-feldspar; Mo: molybdenite; Pl: plagioclase; Py: pyrite; Qz: quartz; Srt: sericite.

Fig. 5 Re-Os isochron plot and weighted average age for molybdenite samples from the Chalukou Mo deposit.

Fig. 6 Cathodoluminescence (CL) images of zircons from monzogranite and granite porphyry. Small and big circles represent spots of U-Pb dating and Hf isotopic analyses, respectively.

880 Fig. 7 Zircon U–Pb isotope concordian diagrams and weighted average ages.

881

882 Fig. 8 $\varepsilon\text{Hf}(t)$ vs. U–Pb age plot for zircons from various kinds of magmatic rocks.

883 Data are from this study, [Li et al. \(2014\)](#) and [Liu et al. \(2015\)](#); CHUR: chondrite uniform reservoir.

884

885 Fig. 9 Time framework of the magmatism and mineralization of the Chalukou porphyry Mo deposit.

886 Data are from this study, [Li et al. \(2014\)](#), [Liu et al. \(2014a\)](#) and [Nie et al. \(2011\)](#).

887

888 Fig. 10 Conceptual model showing the tectonic setting of the Chalukou Mo deposit at about 150 Ma.

889

890 **Table Captions**

891 Table 1 Re–Os isotope data for molybdenite from the Chalukou Mo deposit.

892

893 Table 2 LA-ICP-MS zircon U–Pb data for monzogranite and granite porphyry from the Chalukou
894 deposit.

895

896 Table 3 Zircon Lu–Hf data for monzogranite and granite porphyry from the Chalukou deposit.

897

Figure 1

Figure 10
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Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Table 1

Table 1 Re–Os isotope data for molybdenite from the Chalukou Mo deposit.

Sample	Depth (m)	Weight (mg)	Re (ppm)		Common Os (ppb)		¹⁸⁷ Re (ppb)		¹⁸⁷ Os (ppb)		Model age (Ma)	
			Measured	2σ	Measured	2σ	Measured	2σ	Measured	2σ	Measured	2σ
CLK-03	737	50.15	14.92	0.11	0.024	0.009	9379	70	23.13	0.20	148	2
CLK-04	744	50.26	3.14	0.03	0.003	0.009	2039	18	4.74	0.05	146	2
CLK-05	784	50.66	19.49	0.17	0.003	0.009	12450	110	30.55	0.24	150	2
CLK-06	850	50.03	17.86	0.13	0.005	0.024	11270	80	27.96	0.23	149	2
CLK-07	872	50.78	7.65	0.07	0.003	0.012	4809	44	11.49	0.09	146	2
CLK-10	1135	50.18	13.95	0.13	0.045	0.003	8670	82	21.12	0.17	147	2
CLK-11	1283	50.32	11.06	0.10	0.003	0.012	6954	62	16.84	0.14	147	2

Note: Absolute uncertainties are stated at 2σ; Decay constant: $\lambda(^{187}\text{Re}) = 1.666 \times 10^{-11} \text{ year}^{-1}$ ([Smoliar et al., 1996](#)).

Table 2

Table 2 LA-ICP-MS zircon U–Pb data for monzogranite and granite porphyry from the Chalukou deposit

Spot number	Element (ppm)			²³² Th/ ²³⁸ U	Isotope ratio						Age (Ma)					
	Pb*	Th	U		²⁰⁷ Pb/ ²⁰⁶ Pb	1σ	²⁰⁷ Pb/ ²³⁵ U	1σ	²⁰⁶ Pb/ ²³⁸ U	1σ	²⁰⁷ Pb/ ²⁰⁶ Pb	1σ	²⁰⁷ Pb/ ²³⁵ U	1σ	²⁰⁶ Pb/ ²³⁸ U	1σ
CLKY-01-01	167	1413	1901	0.74	0.0490	0.0023	0.1810	0.0083	0.0270	0.0005	146	109	169	7	169	3
CLKY-01-02	174	1568	1962	0.80	0.0537	0.0023	0.1929	0.0085	0.0259	0.0003	367	100	179	7	165	2
CLKY-01-03	237	2215	2190	1.01	0.0477	0.0021	0.1704	0.0073	0.0258	0.0003	87	100	160	6	164	2
CLKY-01-04	175	1546	1838	0.84	0.0502	0.0021	0.1813	0.0077	0.0262	0.0003	211	98	169	7	166	2
CLKY-01-05	68.9	590	902	0.65	0.0515	0.0029	0.1856	0.0099	0.0265	0.0004	261	131	173	8	169	3
CLKY-01-06	215	2126	1951	1.09	0.0489	0.0020	0.1705	0.0067	0.0254	0.0003	143	90	160	6	162	2
CLKY-01-07	96	789	1756	0.45	0.0490	0.0024	0.1741	0.0085	0.0257	0.0003	146	114	163	7	164	2
CLKY-01-08	120	989	1565	0.63	0.0459	0.0025	0.1665	0.0089	0.0265	0.0003	45	93	156	8	168	2
CLKY-01-09	126	988	1523	0.65	0.0516	0.0026	0.1868	0.0095	0.0262	0.0004	265	121	174	8	167	2
CLKY-01-10	140	1103	1680	0.66	0.0490	0.0023	0.1813	0.0086	0.0268	0.0004	150	111	169	7	170	3
CLKY-01-11	161	1358	1960	0.69	0.0506	0.0022	0.1866	0.0081	0.0268	0.0004	220	99	174	7	170	2
CLKY-01-12	198	1670	2263	0.74	0.0505	0.0023	0.1851	0.0081	0.0264	0.0003	217	106	172	7	168	2
CLKY-01-13	87	637	1093	0.58	0.0545	0.0031	0.1940	0.0102	0.0263	0.0004	391	130	180	9	167	3
CLKY-01-14	97	822	1296	0.63	0.0474	0.0025	0.1756	0.0097	0.0267	0.0004	78	117	164	8	170	3
CLKY-01-15	139	1224	1588	0.77	0.0498	0.0024	0.1836	0.0087	0.0268	0.0004	187	108	171	7	171	2
CLKY-01-16	125	1027	1652	0.62	0.0529	0.0025	0.1871	0.0091	0.0258	0.0004	324	109	174	8	164	2
CLKY-01-17	264	2536	2374	1.07	0.0505	0.0023	0.1763	0.0081	0.0253	0.0003	217	106	165	7	161	2
CLKY-01-18	102	821	1171	0.70	0.0547	0.0032	0.1975	0.0112	0.0264	0.0004	398	130	183	10	168	3
CLKY-07-01	81	738	746	0.99	0.0489	0.0024	0.1590	0.0075	0.0234	0.0003	146	110	150	7	149	2
CLKY-07-02	75	590	960	0.62	0.0493	0.0022	0.1674	0.0074	0.0244	0.0003	161	106	157	6	150	2
CLKY-07-03	70	608	596	1.02	0.0497	0.0028	0.1688	0.0082	0.0251	0.0004	183	127	158	7	151	3
CLKY-07-04	57	510	536	0.95	0.0497	0.0027	0.1625	0.0084	0.0238	0.0004	189	125	153	7	150	2
CLKY-07-05	44	326	545	0.60	0.0500	0.0031	0.1720	0.0101	0.0246	0.0004	198	151	161	9	154	3
CLKY-07-06	82	645	649	0.99	0.0525	0.0027	0.1813	0.0092	0.0250	0.0004	306	119	167	8	157	2
CLKY-07-07	75	619	771	0.80	0.0543	0.0034	0.1775	0.0090	0.0244	0.0004	387	141	166	8	156	2
CLKY-07-08	41	328	420	0.78	0.0526	0.0029	0.1787	0.0097	0.0246	0.0004	309	121	167	8	157	3
CLKY-07-09	73	608	757	0.80	0.0512	0.0023	0.1733	0.0079	0.0243	0.0004	250	106	162	7	153	2
CLKY-07-10	58	458	565	0.81	0.0535	0.0027	0.1812	0.0092	0.0244	0.0005	350	115	169	8	155	3
CLKY-07-11	64	522	641	0.81	0.0502	0.0025	0.1683	0.0079	0.0244	0.0004	206	115	158	7	151	3

CLKY-07-12	63	508	720	0.71	0.0473	0.0022	0.1647	0.0077	0.0250	0.0004	65	107	155	7	150	3
CLKY-07-13	53	388	749	0.52	0.0500	0.0025	0.1659	0.0076	0.0242	0.0004	195	119	156	7	154	2
CLKY-07-14	49	406	510	0.80	0.0492	0.0025	0.1679	0.0085	0.0247	0.0004	167	120	158	7	152	3
CLKY-07-15	50	377	486	0.78	0.0526	0.0037	0.1775	0.0102	0.0250	0.0005	309	159	166	9	156	3
CLKY-07-16	69	579	689	0.84	0.0518	0.0050	0.1653	0.0089	0.0245	0.0004	276	220	155	8	149	3

Table 3

Table 3 Zircon Lu–Hf data for monzogranite and granite porphyry from the Chalukou deposit

Rock	Spot number	Age (Ma)	¹⁷⁶ Yb/ ¹⁷⁷ Hf	¹⁷⁶ Lu/ ¹⁷⁷ Hf	¹⁷⁶ Hf/ ¹⁷⁷ Hf	1σ	εHf(0)	εHf(t)	T _{DM1} (Ma)	T _{DM2} (Ma)	f _{Lu/Hf}
monzogranite	CLKY-01-01	169	0.026720	0.001296	0.282753	0.000010	-0.7	2.9	713	1027	-0.96
	CLKY-01-02	165	0.026050	0.001185	0.282732	0.000012	-1.4	2.1	740	1076	-0.96
	CLKY-01-03	164	0.027953	0.001171	0.282713	0.000009	-2.1	1.4	767	1119	-0.96
	CLKY-01-04	166	0.027701	0.001127	0.282701	0.000010	-2.5	1.0	783	1145	-0.97
	CLKY-01-05	169	0.013860	0.000575	0.282723	0.000009	-1.7	1.9	741	1090	-0.98
	CLKY-01-06	162	0.033734	0.001269	0.282761	0.000009	-0.4	3.0	701	1013	-0.96
	CLKY-01-07	164	0.038773	0.001548	0.282714	0.000009	-2.1	1.4	773	1120	-0.95
	CLKY-01-08	168	0.021656	0.000990	0.282736	0.000008	-1.3	2.3	731	1064	-0.97
	CLKY-01-09	167	0.019700	0.000845	0.282706	0.000008	-2.3	1.2	770	1131	-0.97
	CLKY-01-10	170	0.015468	0.000583	0.282726	0.000008	-1.6	2.0	737	1082	-0.98
	CLKY-01-11	170	0.035497	0.001497	0.282709	0.000007	-2.2	1.3	780	1127	-0.95
	CLKY-01-12	168	0.035338	0.001433	0.282724	0.000011	-1.7	1.8	757	1094	-0.96
	CLKY-01-13	167	0.024508	0.001103	0.282721	0.000008	-1.8	1.7	754	1099	-0.97
	CLKY-01-14	170	0.018830	0.000856	0.282725	0.000010	-1.7	2.0	744	1087	-0.97
	CLKY-01-15	171	0.027456	0.001140	0.282712	0.000010	-2.1	1.5	768	1117	-0.97
	CLKY-01-16	164	0.038648	0.001652	0.282702	0.000011	-2.5	0.9	793	1147	-0.95
	CLKY-01-17	161	0.027588	0.001213	0.282705	0.000008	-2.4	1.0	779	1139	-0.96
	CLKY-01-18	168	0.013652	0.000604	0.282714	0.000008	-2.1	1.6	754	1111	-0.98
granite porphyry	CLKY-07-01	149	0.038355	0.001587	0.282685	0.000010	-3.1	0.0	816	1194	-0.95
	CLKY-07-02	150	0.030322	0.001343	0.282644	0.000010	-4.5	-1.4	869	1283	-0.96
	CLKY-07-03	151	0.031465	0.001380	0.282661	0.000012	-3.9	-0.7	845	1245	-0.96
	CLKY-07-04	150	0.023920	0.001089	0.282677	0.000014	-3.4	-0.2	816	1208	-0.97
	CLKY-07-05	154	0.022550	0.001028	0.282653	0.000017	-4.2	-0.9	849	1259	-0.97
	CLKY-07-06	157	0.021628	0.000935	0.282689	0.000008	-2.9	0.4	796	1176	-0.97
	CLKY-07-07	156	0.018212	0.000840	0.282655	0.000012	-4.1	-0.8	842	1252	-0.97
	CLKY-07-08	157	0.024124	0.001077	0.282663	0.000014	-3.9	-0.5	836	1235	-0.97
	CLKY-07-09	153	0.028556	0.001264	0.282648	0.000010	-4.4	-1.2	861	1272	-0.96
	CLKY-07-10	155	0.031722	0.001471	0.282659	0.000013	-4.0	-0.7	850	1248	-0.96
	CLKY-07-11	151	0.017699	0.000817	0.282674	0.000010	-3.5	-0.2	815	1212	-0.98
	CLKY-07-12	150	0.033979	0.001447	0.282653	0.000010	-4.2	-1.1	858	1264	-0.96
	CLKY-07-13	154	0.030519	0.001303	0.282686	0.000012	-3.0	0.2	808	1187	-0.96

CLKY-07-14	152	0.033347	0.001402	0.282681	0.000015	-3.2	0.0	817	1200	-0.96
CLKY-07-15	156	0.027290	0.001159	0.282674	0.000006	-3.5	-0.2	822	1212	-0.97
CLKY-07-16	149	0.026793	0.001252	0.282678	0.000010	-3.3	-0.2	818	1207	-0.96

Note: The following parameters were employed to the calculation: ($^{176}\text{Lu}/^{177}\text{Hf}$)_{CHUR, 0} = 0.0332 and ($^{176}\text{Hf}/^{177}\text{Hf}$)_{CHUR, 0} = 0.282772 (Blichert-Toft and Albarede., 1997); ($^{176}\text{Lu}/^{177}\text{Hf}$)_{DM, 0} = 0.0384 and ($^{176}\text{Hf}/^{177}\text{Hf}$)_{DM, 0} = 0.28325 (Griffin et al., 2000); ^{176}Lu decay constant $\lambda = 1.867 \times 10^{-11}/\text{y}$ (Söderlund et al., 2004).

Table 4

Table 4 Comparison of the Chalukou deposit with the ever-known porphyry Mo deposits sub-types

	Characteristics	Rift- or Climax-type	Subduction- or Endako-type	Collision- or Dabie-type	The Chalukou deposit
Ore-causative intrusion	Rock type	Granite porphyry, rhyolite porphyry	Quartz monzonite, granodiorite, granite porphyry	Multiple or simple intrusions of (K-feldspar) granite, monzogranite	Monzogranite, granite porphyry
	Occurrence	Stock, dyke	Stock, granite batholith	Stock, minor granite batholith	Stock, granite batholith
	Comagmatic extrusion	Yes	Yes	None	Rhyolite, dacite
Petrological geochemistry	F/ppm	400–3185, mostly >1000	Low, 1251 (only one data)	High, mostly >1500	Low
	Rb/ppm	114–857, mostly >300	58–240, mostly <200	60–577, mostly 100–400	141–229 (Li et al., 2014)
	Sr/ppm	2–260, mostly <100	20–653	9–791, mostly 100–700	20.7–92.8 (Li et al., 2014)
	Nb/ppm	14–208, mostly >50	5–18, mostly <15	4–97, mostly 10–70	8.94–46.2 (Li et al., 2014)
	Zr/ppm	76–306, mostly <120	59–166, mostly >120	1–266, mostly 10–230	88.6–289 (Li et al., 2014)
Mineralization	Commodity	Mo-only, Mo–W, Mo–Sn	Mo ± Cu ± Pb ± Zn ± Ag, Mo–W, rare Mo-only	Mo-only, Mo–W, Mo–Fe, Mo ± Pb ± Zn ± Ag	Mo–Pb–Zn
	Orebody shape	Inverted cup, hemispheric	Inverted cup, layered, circular, lenticular, irregular	Sheet-like, lenticular, irregular	Inverted cup, layered, lenticular
	Style	Stockwork veinlets, disseminations	Stockwork veinlets, disseminations and breccias	Stockwork veinlets, minor disseminations and breccias	Stockwork veinlets, disseminations and breccias
	Average Mo ore grade/%	0.1–0.3	0.03–0.20	0.06–0.11	0.11
	Ore-associated mineral	Molybdenite, pyrite, wolframite, cassiterite, stibnite, chalcopyrite, fluorite, topaz, sericite	Molybdenite, pyrite, cassiterite, scheelite, chalcopyrite, sphalerite, galena, magnetite, fluorite, sericite	Molybdenite, pyrite, scheelite, chalcopyrite, sphalerite, galena, wolframite, fluorite, sericite, K-feldspar, carbonates	Molybdenite, sphalerite, galena, pyrite, magnetite, chalcopyrite

Alteration	Hydrothermal alteration	Potassic and phyllic alteration, intense silicified and propylitic alteration	Potassic alteration, , intense propylitic alteration, widespread argillic alteration	Intense potassic alteration, weak phyllic and propylitic alteration, showing unclear zonation	Potassic and phyllic alteration, intense propylitic and argillic alteration
Fluids	Inclusion type	Aqueous, brine, with or without CO ₂ –H ₂ O	Aqueous, rare CO ₂ –H ₂ O, with or without brine	Pure CO ₂ , CO ₂ –H ₂ O, aqueous, lack of brine inclusions	Aqueous, brine without CO ₂ (Liu et al., 2014b)
	Original phase	Low salinity liquid with moderate to low CO ₂	Low to moderate salinity liquid with low CO ₂ or without CO ₂	High to moderate salinity liquid with CO ₂ -rich vapor	Moderate salinity liquid with minor low CO ₂ (Liu et al., 2014b)
	Temperature/°C	300–450	250–450	250–400	234–511 (Liu et al., 2014b)
Metallogenic age		5–50 Ma, mostly 20–35 Ma	8–160 Ma, mostly 50–90 Ma	110–158 Ma, mostly 130–150 Ma	149.7 ± 2.4 Ma
Tectonic setting		Back-arc rift, post-subduction extension	Subduction-related continental arc	Syn- to post-collision tectonic regime	Subduction-related continental arc
Example		Climax (Wallace, 1995); Colorado and Questa (Cline and Bodnar, 1994 ; Klemm et al., 2008); Urad–Henderson (Seedorff and Einaudi, 2004a, b)	Endako (Selby et al., 2000); MAX (Lawley et al., 2010); Zhaiwa (Deng et al., 2013); Luoboling (Zhong et al., 2014); Diyanqin’amu (Wang et al., 2016a)	Yuchiling (Li et al., 2012a, 2013); Qian’echong (Yang et al., 2013 ; Mi et al., 2015); Donggebi (Wu et al., 2014); Yaochong (Wang et al., 2014); Donggou (Yang et al., 2015a)