**Age, geochemistry, and Sr–Nd–Hf–Pb isotopes of the Caosiyao porphyry Mo deposit in
Inner Mongolia, China**

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ABSTRACT

The giant Caosiyao porphyry Mo deposit (Yinshan area, central Inner

Mongolia) is recently discovered in the northern margin of the North China Craton. The mineralization is newly molybdenite Re–Os dated to be Late Jurassic (ca. 148 Ma). LA-ICP-MS zircon U–Pb dating of the two syenogranite porphyry intrusions in the Caosiyao deposit yielded ca. 148.5 Ma and ca. 140.9–140.1 Ma, respectively, and the Caosiyao monzogranite porphyry yielded ca. 145.0 Ma. These Late Jurassic to Early Cretaceous granitic porphyries are high-K calc-alkaline and featured by high Rb, Th, U, and Zr contents and low TiO₂, P₂O₅, Nb, and La contents, with high K₂O/Na₂O and medium to strong negative Eu anomalies, all resembling post-orogenic granitoids. The Caosiyao granitic porphyries have high whole-rock initial ⁸⁷Sr/⁸⁶Sr (0.710417 to 0.718568), low zircon $\varepsilon_{\text{Hf}}(t)$ (–18.9 to –12.5) and whole-rock $\varepsilon_{\text{Nd}}(t)$ (–17.8 to –13.7), old single-stage and two-stage model ages for zircon Hf (1282–1552 Ma and 1989–2393 Ma, respectively) and for whole-rock Nd (1766–2431 Ma and 2046–2375 Ma, respectively), as well as low K-feldspar ²⁰⁶Pb/²⁰⁴Pb (16.603 to 17.177), ²⁰⁷Pb/²⁰⁴Pb (15.319 to 15.374), and ²⁰⁸Pb/²⁰⁴Pb (36.841 to 37.225) values. We suggest that the Late Jurassic and Early Cretaceous syenogranite porphyry may have been sourced from a highly- and moderately mature lower crust, respectively, whereas the Early Cretaceous monzogranite porphyry may have been sourced from an immature lower crust. The Caosiyao porphyries may have formed during the post-orogenic extension after the Mongol–Okhotsk Ocean closure and coeval with the Paleo-Pacific plate subduction.

Keywords: Caosiyao porphyry Mo deposit; North China Craton; Molybdenite Re–Os dating; Zircon U–Pb dating; Whole-rock and isotope geochemistry; Post-orogenic extension

1. Introduction

The EW-trending Yinshan–Yanshan–Liaoning molybdenum (Mo) belt (YYLMB), (ca. 600 km long and 150 km wide) lies along the northern margin of the North China Craton (NCC). One giant (>0.5Mt Mo at Caosiyao), seven large (0.1–0.5Mt Mo at Dasuji, Jiajiaying, Sadaigoumen, Xiaojiayingzi, Yangjiazhangzi, Lanjiagou, and Gangtun), eleven medium and many small Mo deposits were discovered along the belt (e.g., Dai et al., 2006, 2009; Jiang et al., 2014; Wang et al., 2014; Wu et al., 2014; Pirajno and Zhou, 2015). The YYLMB represents the third largest Mo province in China (Huang et al., 2011), and Mo is the only economic metal in most deposits (including Caosiyao) in the belt (Dai et al., 2006; Han et al., 2009; Jiang et al., 2014; Wang et al., 2014; Wu et al., 2014). In the past, Mo deposits were mainly discovered in the eastern YYLMB (Chen et al., 2003; Dai et al., 2006; Han et al., 2009; Huang et al., 2011; Jiang et al., 2014), yet the recent discoveries of the giant Caosiyao and large Dasuji porphyry Mo deposits demonstrate that the western YYLMB (i.e., Yinshan area) is also highly prospective (Zhang et al., 2009; Li et al., 2012; Nie et al., 2012, 2013; Wang et al., 2014; Wu et al., 2014).

The YYLMB Mo mineralization can be classified into the porphyry, porphyry–skarn, skarn, and vein types; among which the former two are the most important (Huang et al., 1996; Dai et al., 2006; Han et al., 2009; Jiang et al., 2014). Major Mo metallogenic epochs are confined to the Late Triassic and Jurassic (and minor Early Cretaceous) (Huang et al., 1996; Dai et al., 2009; Han et al., 2009; Liu et al., 2012a, b; Nie et al., 2012, 2013; Jiang et al., 2014; Pirajno and Zhou, 2015). Mao et al. (2003) suggested that the North China Plate and its adjacent regions experienced three tectonic evolution stages during the Mesozoic:

Post-collisional orogenesis (ca. 200–160 Ma), transitional tectonics (ca. 140 Ma), and lithospheric stretching and thinning (ca. 130–110 Ma, peaking at 120 Ma). Most Mo deposits in the eastern YYLMB were formed at the transitional stage from an EW-trending tectonic regime to a NNE-trending tectonic regime (ca. 140 Ma).

The giant Caosiyao porphyry Mo deposit is located in the Yinshan area of central Inner Mongolia and is the largest Mo deposit in the YYLMB. Previous studies were mainly focused on the geological characteristics, ore-forming fluid nature, and metallogenic chronology of the deposit (Li et al., 2012; Nie et al., 2013; Wang et al., 2014). Up to now, the age and geochemistry of ore-associated igneous rocks in the Caosiyao deposit have not yet been reported, which limits our understanding of the petrogenesis, tectonic setting, and relationship between the mineralization and these magmatic activities. In this paper, we report the molybdenite Re–Os ages of the Caosiyao deposit and LA-ICP-MS (Laser Ablation Multi-Collector Inductively Coupled Plasma Mass Spectrometry) zircon U–Pb ages, geochemistry, and Sr–Nd–Hf–Pb isotopes of the Caosiyao ore-related granitic porphyries. We aim to determine the mineralization and porphyry formation ages at Caosiyao, as well as to elucidate the magma source composition, petrogenesis, and tectonic setting of the Caosiyao porphyries.

2. Regional geology

The wedge-shaped NCC is bounded by three young orogenic belts: in the north, the Paleozoic–Early Mesozoic Inner Mongolia–Daxing’anling (the eastern Chinese extension of the Central Asian Orogenic Belt); in the south, the Early Mesozoic Qinling–Dabie–Sulu belt;

and in the east, the Mesozoic–Cenozoic Circum-Pacific terrane (Fig. 1a and b). The Precambrian basement of the NCC comprises the Archean to Paleoproterozoic Eastern- and Western blocks and three Paleoproterozoic mobile belts, i.e., the Khondalite Belt, the Trans-North China Orogen (TNCO), and the Jiao–Liao–Ji Belt (JLJB) (Fig. 1b; Zhao et al., 2005). The EW-trending Khondalite Belt was interpreted as a 2.0–1.9 Ga collisional-related belt, along which the Yinshan- and Ordos blocks amalgamated to form the Western Block (Zhao et al., 2005; Wan et al., 2006; Xia et al., 2006; Santosh et al., 2007; Tang et al., 2011). The TNCO was variably suggested to be a ca. 1.85 Ga or ca. 2.5 Ga convergent tectonic zone associated with the collision between the Eastern- and Western blocks (Guo et al., 2005; Zhai and Liu, 2003; Kröner et al., 2005; Zhao et al., 2005; Kusky et al., 2007). The JLJB is located within the Eastern Block and its nature and tectonic setting remain controversial. Some suggested that it was an intra-continental rift that opened and closed in the Paleoproterozoic (Luo et al., 2004; Li and Zhao, 2007), whereas some others suggested it was a Paleoproterozoic accreted island arc (Faure et al., 2004; Lu et al., 2006).

The nearly EW-trending Chifeng–Kaiyuan fault separates the NCC in the south from the Central Asian Orogenic Belt (CAOB) in the north (Fig. 1). The northern margin of the NCC is traditionally divided into an Eastern-, Central-, and Western Segment by the Tan–Lu and Daxing’anling–Taihangshan faults (Chen et al., 2003). The Central–Western segments, where the YYLMB is located, tectonically contain parts of the Longgang block, TNCO, as well as parts of the Yinshan block and Khondalite belt (Fig. 1b).

The basement in the Central–Western segment is composed of Archean granite–greenstone associations and Paleoproterozoic metamorphosed stratigraphic

successions (granulite to amphibolite facies) (Inner Mongolian Autonomous Region Bureau of Geology and Mineral Resource (IBGM), 1991; Zhao et al., 2004a; Wan et al., 2006; Nie et al., 2012). Above that, the Meso–Neoproterozoic cover mainly comprises marine clastics and carbonates, belonging to an aulacogen sedimentary assemblage. The Cambrian and Lower–Middle Ordovician rocks consist mainly of shallow-marine limestone and shale. The Carboniferous–Permian rocks contain mainly terrestrial clastics with minor paralic clastics. The Mesozoic rocks, including the Lower–Middle Jurassic terrestrial clastics and the Upper Jurassic–Lower Cretaceous intermediate–felsic volcanics, are extensively distributed in the study area. The Paleogene–Neogene lithologies contain clastics and dike basalts (IBGM, 1991).

The northern NCC margin is tectonically situated at the junction among the North China-, Siberia-, and Pacific plates, showing complex structural deformation history. Pre-Mesozoic structures include EW-, WNW-, and ENE-trending faults. In the Mesozoic, this area may have undergone intracontinental orogeny, resulting in the reactivation of pre-existing EW- and ENE-trending faults, and formation of the EW- and ENE-trending thrust-nappe structures, ductile shear zones, and metamorphic core complexes (Davis et al., 1998; Zheng et al., 1998; Pirajno and Zhou, 2015). The widespread Mesozoic NE- and NNE-trending faults may have been genetically related to the post-orogenic process following the collision of the Siberia and united North China–Mongolia plates during the closure of the Mongol–Okhotsk Ocean (Davis et al., 1998; Zheng et al., 1998) and/or a NW-dipping subduction of the Paleo-Pacific plate beneath Eurasia (Mao et al., 2003; Zhao et al., 2004b; Chen et al., 2012).

Intrusive rocks, mainly Archean, Proterozoic, Permian, and Mesozoic in age, are widely

exposed in the region. The Archean intrusive rocks contain mainly tonalite–trondhjemite–granodiorite (TTG) and form an Archean granite–greenstone association (IBGM, 1991; Zhao et al., 2005; Santosh et al., 2007; Tang et al., 2011). The Meso–Neoproterozoic intrusive rocks are mainly composed of anorogenic plagiogranite and rapakivi granite with some mafic dyke swarms (IBGM, 1991; Zhai and Liu, 2003). The Permian granitoids contain mainly granodiorite, granite, and monzogranite (Nie et al., 2012). The Mesozoic intrusions include Triassic monzogranite and Jurassic–Cretaceous diorite, quartz diorite, quartz monzonite, granodiorite, and granite porphyry, with minor gabbro, diabase, and rhyolite porphyry (Nie et al., 2012).

3. Local and ore deposit geology

The Caosiyao porphyry Mo deposit is located 4 km southeast of Xinghe County, Inner Mongolia, with geographic coordinates of 113°51'40"–113°54'00" longitude (east) and 40°48'00"–40°49'40" latitude (north). The exposed rocks in the Caosiyao area include mainly Precambrian metamorphic rocks (Xinghe and Jining groups), a Jurassic terrestrial volcano–sedimentary sequence, and Paleogene–Neogene sediments (Fig. 2a). The Xinghe Group was considered Paleoproterozoic (IBGM, 1991; Xu et al., 2008) or Neoarchean (Dong et al., 2012; Jian et al., 2012; Ma et al., 2012) in age, occurs in the southeastern part of the Caosiyao deposit, and is mainly composed of pyroxene granulite, pyroxene plagiogneiss, and amphibolite locally interlayered with diopside–magnetite quartzite. The Jining Group was considered Mesoproterozoic (IBGM, 1991; Xu et al., 2008) or Paleoproterozoic (Xia et al., 2006; Chen et al., 2009a; Dong et al., 2012) in age. The Group, containing mainly

sillimanite–garnet–feldspar gneiss, leptynite, and leucoleptynite locally interlayered with graphite-bearing gneiss and diopside marble, is the major exposed unit at Caosiyao. Middle Jurassic clastic rocks and Upper Jurassic andesite and tuff are distributed in the Datongyao–Yinzihe area. The Paleogene–Neogene sedimentary rocks occur in the Caosiyao deposit and its periphery, and the Neogene dike basalts are mainly exposed in southwestern part of the Caosiyao deposit (Fig. 2a). The two main fault systems at Caosiyao are roughly NE- and NW- trending, with the former being large in scale. Mesozoic intrusions were mainly emplaced at the intersections of these two fault systems (Fig. 2a).

Geological units in the Caosiyao deposit include mainly the Jining Group metamorphic rocks, Yanshanian granite porphyries, and Paleogene–Neogene clastics (Li et al., 2012; Nie et al., 2013) (Fig. 2b). According to the intrusive relationships (and our new ages), the Yanshanian granite porphyries comprise Late Jurassic–Early Cretaceous syenogranite porphyry and Early Cretaceous monzogranite porphyry. The Late Jurassic syenogranite porphyry (six intrusions) (Fig. 2b) contains 15–25% phenocrysts, which include mainly quartz and K-feldspar, minor plagioclase and biotite, and trace zircon, titanite, and apatite (Fig. 3a and b). The groundmass is dominated by cryptocrystalline quartz and feldspar. Most of the rocks are moderately to strongly silicified and sericitized (Fig. 3a and b), with local potassic (K-feldspar and biotite) and muscovite alteration and molybdenite mineralization present. The Late Jurassic syenogranite porphyry has a close temporal-spatial relationship with the Caosiyao Mo deposit. The Early Cretaceous monzogranite porphyry mainly occurs underground (750 m deep) as an apophyse that intruded the Late Jurassic syenogranite porphyry stock. The rocks contain 30–40% phenocrysts (mainly plagioclase, K-feldspar, quartz, and biotite) in a

microcrystalline quartz and feldspar groundmass (Fig. 3c and d). Accessory minerals include zircon, titanite, and apatite. The rocks are largely fresh, implying that they are post-mineralized. The Early Cretaceous syenogranite porphyry (three intrusions) contains 30–40% phenocrysts (mainly quartz and K-feldspar with minor biotite) in a cryptocrystalline quartz and feldspar groundmass (Fig. 3e and f). Accessory minerals are mainly zircon, titanite, and apatite. The rocks are only slightly sericitized and no molybdenite is present, implying that the rocks are also post-mineralized.

The Caosiyao deposit, discovered in 2011, contains reserves of 1,755,579 tonnes Mo (average grade: 0.078%) (No. 2 Geoexploration Party of Henan Bureau of Geoexploration and Mineral Development, 2013; Wang et al., 2014). In cross sections, the Mo orebodies are of asymmetric dumbbell shape (ca. 2000 m long, 1600 m wide, and 400–900 m thick) (Li et al., 2012; Wang et al., 2014) and are mainly hosted by the Jining Group metamorphic rocks and to lesser extent by the Neoproterozoic diabase dikes and Late Jurassic syenogranite porphyry (Fig. 2c).

Ore minerals include mainly molybdenite and pyrite, with minor magnetite, chalcopyrite, and pyrrhotite. Gangue minerals are primarily quartz and sericite, with minor K-feldspar, biotite, muscovite, fluorite, epidote, and scapolite. Ore styles include mainly veinlet- and/or (densely) disseminated types. Major wall rock alteration styles include silicic- and sericite alterations, followed by K-feldspar-, fluorite-, argillic-, and minor biotite-, muscovite- and carbonate alterations. The former three alteration styles are closely related to the Mo mineralization. Details on the mineralization feature and wall-rock alteration are provided in Wang et al. (2016, this issue).

4. Sampling and analytical methods

4.1. Sampling

For the Re–Os dating, six molybdenite samples were collected from Drill Hole No. 1600 (at 205-, 275-, 284-, 367-, 538-, and 694-m deep, respectively) at Caosiyao, in which they mainly occur as dissemination, in veinlets (quartz + molybdenite $\pm$ pyrite $\pm$ chalcopyrite $\pm$ magnetite) or (minor) as massive ores (Fig. 4a and b). Thirteen whole-rock samples were collected from monzogranite porphyry (Drill Hole No. 1600 at 780–825 m deep), together with eight syenogranite porphyry from drill core (Drill Hole No. 807 at 779–800 m deep) (Fig. 2c), and ten syenogranite porphyry from outcrop (ca. 1200 m southeast of Caosiyao village) (Fig. 2b) for major and trace element analyses. Among these samples, one monzogranite porphyry and three syenogranite porphyry were selected for LA-ICP-MS zircon U–Pb dating and Hf isotope analysis. Six monzogranite porphyry and eight syenogranite porphyry were selected for whole-rock Sr–Nd isotope analysis. Eight monzogranite porphyry and seven syenogranite porphyry were selected for K-feldspar Pb isotope analysis.

4.2. Molybdenite Re–Os dating

The molybdenite is mainly flaky and anhedral granular (Fig. 4c), and some are sheaf-like (Fig. 4d). The pyrite is anhedral granular (Fig. 4d); the chalcopyrite is mainly subhedral or anhedral granular (Fig. 4d), and the magnetite is mainly anhedral granular (Fig. 4d). Samples were crushed, separated, and sieved to obtain monomineralic molybdenite (purity >99%), which is fresh (un-oxidized nor contaminated). The sample pretreatment and analysis were conducted at the National Research Center for Geoanalysis (Beijing). The chemical separation and mass spectrometry of Re–Os consists of four steps: sample

decomposition, distillation separation of Os, extraction / separation of Re, and mass spectrometry. The analysis followed the procedures described by Du et al. (1994) and Shirey and Walker (1995). The samples were dissolved in a sealed Carlo Erba tube at 200°C, Os was absorbed through distillation, and Re was extracted with acetone. The Re, ^{187}Re , and ^{187}Os contents were measured with the TJA PQ ExCell ICP-MS (TJA Co, USA). Ordinary Os was computed by measuring $^{192}\text{Os}/^{190}\text{Os}$ based on the abundance of Os with Nier value, and ^{187}Os was the total ^{187}Os isotope. For Re, we chose the mass numbers 185 and 187, and we monitored Os using 190; for Os, we chose the mass numbers 186, 187, 188, 189, 190, and 192, and we monitored Re using 185. The level of confidence was 95%. The Re–Os model age was calculated as $t = 1/\lambda [\ln (1 + ^{187}\text{Os}/^{187}\text{Re})]$, where λ is the decay constant of ^{187}Re , and the adopted value is $\lambda = 1.666 \times 10^{-11} \text{ year}^{-1}$ (Smoliar et al., 1996). Positive and inverse isochrons were computed with the ISOPLOT program (Ludwig, 2003).

4.3. Zircon U–Pb and Hf isotope analyses

Zircons were separated using the conventional heavy liquid and magnetic techniques and purified by handpicking under a binocular microscope at the Langfang Regional Geological Survey, Hebei Province, China. The handpicked zircons were mounted in epoxy and polished to expose the cores of the grains for subsequent cathodoluminescence (CL) imaging and zircon U–Pb analyses. The CL images were obtained at the Institute of Geology, Chinese Academy of Geological Sciences (CAGS). The samples were analyzed at the Institute of Mineral Resources, CAGS using a Finnigan Neptune MC-ICP-MS attached to a New Wave UP 213 laser ablation system with an in-house sample cell. The detailed analytical procedures are similar to those described by Griffin et al. (2004) and Hou et al. (2009). U–Pb fractionation

was corrected using zircon standard GEMOC GJ-1 ($^{207}\text{Pb}/^{206}\text{Pb}$ age of 608.5 ± 1.5 Ma, Jackson et al., 2004), and accuracy was controlled using zircon standard Mud Tank (intercept age of 732 ± 5 Ma, Black and Gulson, 1978). U–Pb ages were calculated from raw signal data using ISOPLOT 3.0 (Ludwig, 2003). Because ^{204}Pb could not be measured due to a low signal and interference from ^{204}Hg in the gas supply, common lead correction was carried out using the EXCEL program ComPbCorr#3 15G (Andersen, 2002). Errors on individual analyses by LA-ICP-MS are quoted at the 1σ level, while errors on pooled ages were quoted at the 95% (2σ) confidence level.

In-situ zircon Hf isotope analysis was carried out at the Institute of Mineral Resources, CAGS using a Neptune MC-ICP-MS with an ArF excimer laser ablation system (193 nm). Instrumental conditions and data acquisition were as described by Yuan et al. (2004). During analyses, the spot size of $44\mu\text{m}$ and a laser repetition rate of 10 Hz with 100 mJ were used. The $^{176}\text{Hf}/^{177}\text{Hf}$ for the standard zircon Mud, obtained during our analyses, is 0.282500 ± 0.000030 for the standard. Measured $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{176}\text{Lu}/^{177}\text{Hf}$ were used to calculate initial $^{176}\text{Hf}/^{177}\text{Hf}$, taking the decay constant for ^{176}Lu as $1.867 \times 10^{-11} \text{ year}^{-1}$ (Söderlund et al., 2004). The present-day chondritic ratios of $^{176}\text{Hf}/^{177}\text{Hf} = 0.282772$ and $^{176}\text{Lu}/^{177}\text{Hf} = 0.0332$ (Blichert-Toft and Albarède, 1997) were adopted to calculate $\varepsilon_{\text{Hf}}(t)$ values. Hf model ages were calculated using present-day values for depleted mantle: $^{176}\text{Hf}/^{177}\text{Hf} = 0.28325$ and $^{176}\text{Lu}/^{177}\text{Hf} = 0.0384$ (Blichert-Toft and Albarède, 1997); and average upper continental crust: $^{176}\text{Lu}/^{177}\text{Hf} = 0.0093$ (Vervoort and Blichert-Toft, 1999). The detailed calculation process was described by Nowell et al. (1998), Amelin et al. (2000), and Griffin et al. (2000).

4.4. Major and trace element analyses

Major and trace element compositions were determined at the Laboratory of Beijing Research Institute of Uranium Geology. For major element analysis, a Leeman Prodigy inductively coupled plasma-optical emission spectrometry (ICP-OES) system with high dispersion Echelle optics was used. The analytical uncertainties, based on the US Geological Survey rock standards BCR-1 and AVG-2, and the Chinese national rock standard GSR-3, were generally better than 1% for many oxides (except for TiO_2 (ca. 1.5%) and P_2O_5 (ca. 2.0%)). Trace elements were analyzed by using an Agilent-7500a ICP-MS. Data quality was monitored by analyses of two US Geological Survey rock reference materials BCR-1 and BHVO-1. Analytical precision for most trace elements is better than 5%.

4.5. Sr–Nd isotope analyses

The Rb, Sr, Sm, and Nd isotopic compositions were determined at the Laboratory of Beijing Research Institute of Uranium Geology on an ISOPROBE-T thermal ionization mass spectrometer (TIMS), operating in static mode, using the procedures described by Chen et al. (2000a). Total procedure blanks were 0.2 ng for Rb and Sr and <0.05 ng for Sm and Nd. The precision for Rb, Sr, Sm, Nd, $^{87}\text{Rb}/^{86}\text{Sr}$, and $^{147}\text{Sm}/^{144}\text{Nd}$ was $\pm 0.2\%$ (2σ), and the precision for $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ (2σ) was shown in Table 4. The mass fractionation correction for $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ were normalized against $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ and $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$, respectively, whereas the reported $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ were adjusted relative to the NBS-987 standard $^{87}\text{Sr}/^{86}\text{Sr} = 0.710250 \pm 0.000007$ (2σ) and the JMC standard $^{143}\text{Nd}/^{144}\text{Nd} = 0.512109 \pm 0.000003$ (2σ). Measured $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ were used to calculate initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, taking the decay constant for ^{87}Rb as $1.42 \times 10^{-11} \text{ year}^{-1}$ (Steiger and Jager,

1977), and the measured $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ were used to calculate initial $^{143}\text{Nd}/^{144}\text{Nd}$, taking the decay constant for ^{147}Sm as $6.54 \times 10^{-12} \text{ year}^{-1}$ (Lugmair and Marti, 1978). $\varepsilon_{\text{Nd}}(t)$, $T_{\text{DM1}}(\text{Nd})$, and $T_{\text{DM2}}(\text{Nd})$ were calculated using present-day values for chondritic uniform reservoir (CHUR): $^{143}\text{Nd}/^{144}\text{Nd} = 0.512638$ (Goldstein et al., 1984) and $^{147}\text{Sm}/^{144}\text{Nd} = 0.1967$ (Jacobsen and Wasserburg, 1980); and for depleted mantle (DM): $^{143}\text{Nd}/^{144}\text{Nd} = 0.513151$ and $^{147}\text{Sm}/^{144}\text{Nd} = 0.2137$ (Liew and Hofmann, 1988).

4.6. Pb isotope analyses

Lead isotope analysis was conducted at the Laboratory of the Beijing Research Institute of Uranium Geology. The lead isotopic composition was measured using a GV IsoProbe-T MC-TIMS. The $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios had a precision better than 0.005% (2σ). The Pb-isotopic analyses were reported with respect to Pb standard reference NBS-981 values (Todt et al., 1993): $^{206}\text{Pb}/^{204}\text{Pb} = 16.934 \pm 0.007$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.486 \pm 0.012$, and $^{208}\text{Pb}/^{204}\text{Pb} = 36.673 \pm 0.033$, respectively.

5. Analytical results

5.1. Molybdenite Re–Os age

The molybdenite Re–Os dating results are presented in Table 1. The Re content of the molybdenite is of 1.296 ppm to 14.37 ppm, with the Re–Os model ages being ca. 147.4–150.1 Ma. The Re–Os isochron age is $148.3 \pm 1.3 \text{ Ma}$ (2σ), with the initial $^{187}\text{Os} = 0.015 \pm 0.045$ ppb and MSWD = 1.50 (Fig. 5a). The model age-weighted average is $148.5 \pm 1.1 \text{ Ma}$ (MSWD = 1.00) (Fig. 5b). The isochron- and weighted average ages are consistent within the error range, indicating that the mineralization occurred at ca. 148 Ma.

5.2. Zircon U–Pb age

Most of the zircons analyzed are colorless to light yellow in color and contain fine oscillatory zoning in CL images (Fig. 6). The zircons have high Th/U values (0.40–3.05), indicative of a magmatic origin (Pupin, 1980; Koschek, 1993).

5.2.1. Sample CM38 (monzogranite porphyry)

The zircons from sample CM38 are mainly pyramidal or bipyramidal in shape with length/width ratios of 2 to 4 (Fig. 6a). A total of 11 spots were analyzed from 11 grains, and the results are presented in Table 2. Except for one analysis (spot CM38-3.1) presenting a slightly older $^{206}\text{Pb}/^{238}\text{U}$ age (150.9 ± 1.2 Ma), the remaining ten analytical spots show a tight, concordant grouping defining a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 145.0 ± 1.0 Ma with an MSWD value of 0.97 (Fig. 7a). We conclude that the age of 145.0 Ma represents the crystallization age of the monzogranite porphyry and that the age of 150.9 Ma represents the crystallization age of captured zircon entrained by the monzogranite porphyry.

5.2.2. Sample CM41 (syenogranite porphyry)

Sample CM41 contains a population of euhedral pyramidal or bipyramidal zircon crystals with a length/width ratio of 1–3 (Fig. 6b). A total of nine spots were analyzed from eight grains; the results are shown in Table 2. The nine analyzed spots yielded a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 148.5 ± 0.9 Ma with an MSWD value of 1.20 (Fig. 7b). We interpret this mean age as the crystallization age of the syenogranite porphyry.

5.2.3. Sample CM95 (syenogranite porphyry)

This sample contains a population of euhedral–subhedral pyramidal, bipyramidal, or lath-shaped zircon crystals with a length/width ratio of 1–4 (Fig. 6c). A total of nine spots were

analyzed from nine grains. These zircons yielded two groups of $^{206}\text{Pb}/^{238}\text{U}$ concordia ages: 140.1 ± 1.7 Ma (MSWD = 0.36, n = 6) and 151.8 ± 2.2 Ma (MSWD = 0.19, n = 3) (Table 2; Fig. 7c). The former represents the crystallization age of the syenogranite porphyry, and the latter represents the crystallization age of captured zircons entrained by the syenogranite porphyry.

5.2.4. Sample CM100 (syenogranite porphyry)

This sample contains a population of euhedral pyramidal or bipyramidal zircon crystals with length/width ratios of 1 to 2 and even 3 in some cases (Fig. 6d). A total of ten spots were analyzed from nine grains. These zircons also yielded two groups of $^{206}\text{Pb}/^{238}\text{U}$ concordia ages: 140.9 ± 1.6 Ma (MSWD = 0.15, n = 5) and 149.9 ± 2.2 Ma (MSWD = 0.78, n = 5) (Table 2; Fig. 7d). The former represents the crystallization age of the syenogranite porphyry, and the latter represents the crystallization age of captured zircons entrained by the syenogranite porphyry.

5.3. Whole-rock geochemistry

5.3.1. Late Jurassic syenogranite porphyry

Eight samples (Samples CM39–CM46) from the syenogranite porphyry contain $\text{SiO}_2 = 72.81\text{--}74.98\%$, $\text{Al}_2\text{O}_3 = 12.26\text{--}12.97\%$, $\text{Fe}_2\text{O}_3 = 0.33\text{--}3.07\%$, $\text{CaO} = 0.18\text{--}1.21\%$, $\text{Na}_2\text{O} = 0.14\text{--}1.07\%$, and $\text{K}_2\text{O} = 4.01\text{--}7.20\%$ (Table 3). Their $\text{Na}_2\text{O}/\text{K}_2\text{O}$, A/CNK (defined as molecular ratio of $\text{Al}_2\text{O}_3/(\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})$), and $\text{Mg}^\#$ (defined as atomic ratio of $100 \times \text{Mg}^{2+}/(\text{Mg}^{2+} + \text{Fe}^{2+})$) are of 0.02 to 0.15 (averaging 0.05), 1.13 to 2.57 (averaging 1.67), and 10 to 25 (averaging 18), respectively. These rocks are characterized by high SiO_2 , very high K_2O , very low Na_2O , very high A/CNK, very low $\text{Na}_2\text{O}/\text{K}_2\text{O}$, and low $\text{Mg}^\#$ values (see Table

3). In addition, all of eight samples have a great loss on ignition (2.03–3.28%, averaging 2.60%), which was caused by sericitization taken place during the Mo mineralization. In the R1 versus R2 diagram (Dela Roche et al., 1980), these samples plot mainly in the syenogranite field and minor in-between the monzogranite, syenogranite, and alkali granite fields (Fig. 8a). In the A/CNK versus A/NK diagram (Maniar and Piccoli, 1989), all the Caosiyao rocks are peraluminous (Fig. 8b). In the SiO₂ versus K₂O diagram of Peccerillo and Taylor (1976), all the Caosiyao rocks are high-K calc-alkaline (Fig. 8c).

The Late Jurassic syenogranite porphyry has relatively high total rare earth elements (REEs) contents (212–367 ppm, averaging 269 ppm). They are characterized by high Yb (1.57–2.93 ppm, averaging 2.01), strongly negative Eu anomalies ($Eu/Eu^* = 0.18–0.34$, averaging 0.23), and marked fractionation between light REE (LREE) and heavy REE (HREE) with $(La/Yb)_N$ values varying from 14.8 to 24.0 (averaging 19.8). Chondrite-normalized REE patterns are characterized by LREE-enrichment and HREE-depletion, and strong LREE fractionation and weaker HREE fractionation (Fig. 9a).

A primitive mantle-normalized multi-element diagram indicates that these rocks are obvious enrichments in Rb, Th, U, K, La, Ce, Nd, Sm, Gd, and Tb, remarkable depletions in Ba, Sr, P, Eu, and Ti, and weak depletions in Nb, Ta, Zr, and Hf relative to the neighboring elements (Fig. 9b). In addition, these rocks have low Sr (19.0–95.2 ppm, averaging 58.4 ppm) and high Y (16.0–28.9 ppm, averaging 20.1 ppm) contents.

5.3.2. Early Cretaceous monzogranite porphyry

Thirteen samples (Samples CM26–CM38) have a narrow range of SiO₂ (75.14–79.62%), Al₂O₃ (10.40–12.72%), Fe₂O₃ (0.03–0.39%), FeO (0.45–0.85%), CaO

(0.69–0.96%), Na₂O (2.67–3.37%), and K₂O (4.18–5.35%). They are characterized by high SiO₂, low Na₂O/K₂O (0.55–0.79, averaging 0.67), and high Mg[#] (43–54, averaging 46), with A/CNK being 0.96–1.02 (averaging 1.00) (Table 3). In the R1 versus R2 diagram, all samples fall in the syenogranite field (Fig. 8a). In the A/CNK versus A/NK diagram, the rocks fall in the metaluminous–peraluminous transitional field (Fig. 8b). In the SiO₂ versus K₂O diagram, all the samples are classified as high-K calc-alkaline (Fig. 8c).

The monzogranite porphyry has the lowest total REEs contents (109–199 ppm, averaging 141 ppm) among the Mesozoic Caosiyao porphyries. They are characterized by high Yb (1.87–2.45 ppm, averaging 2.19), obviously negative Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.38\text{--}0.53$, averaging 0.45), and moderate LREE/HREE fractionation ($(\text{La}/\text{Yb})_N = 7.84\text{ to }13.7$, averaging 10.4). Chondrite-normalized REE patterns are characterized by LREE enrichment, HREE depletion, and strong LREE fractionation but little HREE fractionation (Fig. 9c).

In a primitive mantle-normalized multi-element diagram (Fig. 9d), all samples show obvious enrichments in Rb, Th, U, K, Ta, La, Ce, Nd, and Sm, marked depletions in Ba, Nb, Sr, P, Eu, and Ti, and weak depletions in Zr and Hf relative to the neighboring elements. In addition, these rocks have low Sr (63.0–148 ppm, averaging 88.7 ppm) and Y (14.5–20.4 ppm, averaging 16.6 ppm) contents.

5.3.3. Early Cretaceous syenogranite porphyry

Ten samples (Samples CM94–CM103) have a relatively narrow range of SiO₂ (70.85–76.20%), Al₂O₃ (12.22–14.24%), CaO (0.08–0.13%), and K₂O (7.75–9.11%), but wider range of Fe₂O₃ (0.15–2.74%), FeO (0.15–0.75%), and Na₂O (0.11–1.70%). These rocks are characterized by high SiO₂ and very high K₂O, low Na₂O and MnO, as well as high

A/CNK (1.14–1.53, averaging 1.27), very low $\text{Na}_2\text{O}/\text{K}_2\text{O}$ (0.01–0.22, averaging 0.08), and moderate $\text{Mg}^\#$ (17–52, averaging 35) (Table 3). In the R1 versus R2 diagram, most samples plot in the transitional field of syenogranite and alkali granite (Fig. 8a). In the A/CNK versus A/NK diagram, all samples are peraluminous (Fig. 8b). In the SiO_2 versus K_2O diagram, all the samples are classified as high-K calc-alkaline (Fig. 8c).

The Early Cretaceous syenogranite porphyry has total REE contents of 141–286 ppm (averaging 229 ppm). The intrusion is characterized by low Yb (1.10–1.53 ppm, averaging 1.33), moderately negative Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.48\text{--}0.72$, averaging 0.61), and very strong LREE/HREE fractionation ($(\text{La}/\text{Yb})_N = 18.9\text{--}34.0$, averaging 28.5). Chondrite-normalized REE patterns are characterized by LREEs enrichment, HREEs depletion, and strong LREEs fractionation but no HREEs fractionation (Fig. 9e).

A primitive mantle-normalized multi-element diagram indicates that these rocks are enriched in Rb, Th, K, Ta, La, Ce, Nd, Sm, Gd, and Tb and depleted in Ba, U, Nb, Sr, P, Zr, Hf, and Ti relative to the neighboring elements (Fig. 9f). Compared with the above-mentioned two porphyry types, the Early Cretaceous syenogranite porphyry contains the highest Sr (192–331 ppm, averaging 254 ppm) and lowest Y (9.45–15.9 ppm, averaging 12.0 ppm) contents (Fig. 9f).

5.4. In-situ zircon Hf isotope

5.4.1. Late Jurassic syenogranite porphyry

The initial $^{176}\text{Hf}/^{177}\text{Hf}$ (Sample CM41, $n = 9$) is 0.282186 to 0.282272 (mean = 0.282235), with the $\varepsilon_{\text{Hf}}(t)$, Hf single-stage ($T_{\text{DM1}}(\text{Hf})$) and two-stage model ($T_{\text{DM2}}(\text{Hf})$) ages being -17.5 to -14.4 (averaging -15.7), 1376–1487 Ma (averaging 1426 Ma), and

2116–2308 Ma (averaging 2199 Ma), respectively (Table 4).

5.4.2. Early Cretaceous monzogranite porphyry

The initial $^{176}\text{Hf}/^{177}\text{Hf}$ (Sample CM38, $n = 11$) is 0.282152 to 0.282282 (mean = 0.282218), with the $\varepsilon_{\text{Hf}}(t)$, $T_{\text{DM1}}(\text{Hf})$, and $T_{\text{DM2}}(\text{Hf})$ being –18.8 to –14.2 (averaging –16.4), 1363–1552 Ma (averaging 1477 Ma), and 2095–2385 Ma (averaging 2239 Ma), respectively (Table 4).

5.4.3. Early Cretaceous syenogranite porphyry

The zircons (from Samples CM95 and CM100) yielded two concordant age groups: 140–141 Ma and 150–152 Ma. The initial $^{176}\text{Hf}/^{177}\text{Hf}$ (for the 140–141 Ma zircons) is 0.282150 to 0.282331 (averaging 0.282257), with the $\varepsilon_{\text{Hf}}(t)$, $T_{\text{DM1}}(\text{Hf})$, and $T_{\text{DM2}}(\text{Hf})$ being –18.9 to –12.5 (averaging –15.1), 1282–1551 Ma (averaging 1392 Ma), and 1989–2393 Ma (averaging 2154 Ma), respectively (Table 4). The initial $^{176}\text{Hf}/^{177}\text{Hf}$ (for the 150–152 Ma zircons) is 0.282116 to 0.282329 (averaging 0.282239), with $\varepsilon_{\text{Hf}}(t)$, $T_{\text{DM1}}(\text{Hf})$, and $T_{\text{DM2}}(\text{Hf})$ being –19.9 to –12.3 (averaging –15.6), 1271–1624 Ma (averaging 1422 Ma), and 1986–2462 Ma (averaging 2188 Ma), respectively (Table 4).

5.5. Sr–Nd isotopes

5.5.1. Late Jurassic syenogranite porphyry

The initial $^{87}\text{Sr}/^{86}\text{Sr}$ (Samples CM40, CM41, and CM46) is 0.712611–0.717957 (averaging 0.715478), with the $\varepsilon_{\text{Nd}}(t)$, depleted mantle Nd single-stage ($T_{\text{DM1}}(\text{Nd})$), and two-stage model ($T_{\text{DM2}}(\text{Nd})$) ages being –14.8 to –13.7 (averaging –14.4), 2117–2431 Ma (averaging 2207 Ma), and 2046–2137 Ma (averaging 2104 Ma), respectively (Table 5).

5.5.2. Early Cretaceous monzogranite porphyry

The initial $^{87}\text{Sr}/^{86}\text{Sr}$ (Samples CM27, CM28, CM30, CM32, CM36, and CM38) is 0.710417 to 0.718568 (averaging 0.713671), with the $\varepsilon_{\text{Nd}}(t)$, $T_{\text{DM1}}(\text{Nd})$, and $T_{\text{DM2}}(\text{Nd})$ being -17.8 to -15.9 (averaging -16.8), 1860–2111 Ma (averaging 1972 Ma), and 2221–2375 Ma (averaging 2295 Ma), respectively (Table 5).

5.5.3. Early Cretaceous syenogranite porphyry

The initial $^{87}\text{Sr}/^{86}\text{Sr}$ (Samples CM94, CM96, CM99, CM102, and CM103) is 0.712198 to 0.712641 (averaging 0.712362), with the $\varepsilon_{\text{Nd}}(t)$, $T_{\text{DM1}}(\text{Nd})$, and $T_{\text{DM2}}(\text{Nd})$ being -16.7 to -15.5 (averaging -16.1), 1766–1901 Ma (averaging 1837 Ma), and 2185–2285 Ma (averaging 2238 Ma), respectively (Table 5).

5.6. Lead isotopic compositions

The $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ for the Late Jurassic syenogranite porphyry (Samples CM40 and CM43) are 16.630 and 16.705, 15.319 and 15.336, and 36.841 and 36.980, respectively (Table 6). Those for the Early Cretaceous monzogranite porphyry (Samples CM26–CM30, CM32, CM36, and CM38) are of 16.813–17.177, 15.349–15.373, and 37.080–37.225, respectively (Table 6). The $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ for the Early Cretaceous syenogranite porphyry (Samples CM94, CM96, CM99, CM102, and CM103) are of 16.791–16.820, 15.346–15.374, and 37.079–37.168, respectively (Table 6). In the $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{207}\text{Pb}/^{204}\text{Pb}$ diagram (Zartman and Doe, 1981), the Caosiyao samples fall in the area between the lower crust and the mantle evolution line (Fig. 10a). In the $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$ diagram, the Caosiyao samples fall between the orogenic belt and the lower crust (Fig. 10b).

6. Discussion

6.1. Magmatic and mineralization ages at Caosiyao

Nie et al. (2013) reported a weighted mean Re–Os age of 130.4 ± 2.4 Ma for four molybdenite samples from the Caosiyao Mo deposit and deduced that the deposit was formed during the Early Cretaceous. We obtained a Re–Os isochron age of 148.3 ± 1.3 Ma and a weighted mean Re–Os age of 148.5 ± 1.1 Ma in this study. Our new molybdenite Re–Os dating data indicate that the Caosiyao Mo mineralization occurred at ca. 148 Ma ago.

In this study, we also obtained LA-ICP-MS zircon U–Pb ages of 148.5 ± 0.9 Ma for sample CM41 from one syenogranite porphyry, 145.0 ± 1.0 Ma for sample CM38 from the monzogranite porphyry, and 140.1 ± 1.7 and 140.9 ± 1.6 Ma for samples CM95 and CM100 from the other syenogranite porphyry in the Caosiyao deposit, respectively. These dating results indicate that the two Caosiyao syenogranite porphyry intrusions were emplaced at ca. 148.5 and 140.5 Ma, and the monzogranite porphyry at ca. 145.0 Ma. Most of the Late Jurassic syenogranite porphyry reveals moderate to strong hydrothermal alteration, with local molybdenite mineralization. The Early Cretaceous monzogranite porphyry intruded both the Late Jurassic syenogranite porphyry and the Mo orebodies. The Early Cretaceous syenogranite porphyry is only slightly sericitized and no molybdenite is present. Both the above field geological evidence and the molybdenite Re–Os and zircon U–Pb dating results obtained by us suggest that the older Caosiyao syenogranite porphyry is syn-mineralized, whereas the younger Caosiyao syenogranite porphyry and monzogranite porphyry are both post-mineralized. As for the molybdenite Re–Os age of 130.4 ± 2.4 Ma reported by Nie et al. (2013), we deduce that it may represent a later Mo mineralization event.

Published molybdenite Re–Os ages compiled for the YYLMB indicates three regional Mo mineralization epochs (Table 7): (1) Late Triassic (ca. 237–223 Ma), (2) Early–Middle Jurassic (ca. 191–166 Ma), and (3) Late Jurassic–Early Cretaceous (ca. 148–134 Ma). The Late Triassic epoch had generated mainly porphyry deposits (e.g., Dasuji and Sadaigoumen) and minor porphyry–skarn deposits (e.g., Hekanzi) (Zhang et al., 2009; Liu et al., 2012a; Jiang et al., 2014; Wu et al., 2014) in the central–western YYLMB. The Early–Middle Jurassic epoch had generated mainly skarn deposits (e.g., Xiaojiayingzi and Yangjiazhangzi) and minor porphyry deposits (e.g., Lanjiagou) (Huang et al., 1996; Dai et al., 2009; Han et al., 2009) in the eastern YYLMB. The Late Jurassic–Early Cretaceous epoch is the most significant, with the main deposit types being porphyry (e.g., Caosiyao; as newly dated in this study) and porphyry–skarn (e.g., Xiaosigou and Shouwangfen), and minor deposit types being quartz vein type (e.g., Dacao ping) and explosion breccia type (e.g., Dazhuangke) (Huang et al., 1996; Duan et al., 2007; Liu et al., 2012b; Jiang et al., 2014). The deposits are mainly distributed in the northern Hebei–central Inner Mongolia region.

6.2. Petrogenesis of the Caosiyao granitic porphyries

The Late Jurassic–Early Cretaceous Caosiyao granitic porphyries contain high SiO_2 , K_2O and total alkali contents, and medium to very high $\text{K}_2\text{O}/\text{Na}_2\text{O}$ and A/CNK, all suggesting a continental crustal origin. Compared with the Early Cretaceous monzogranite porphyry, these Late Jurassic–Early Cretaceous syenogranite porphyries have higher $\text{K}_2\text{O}/\text{Na}_2\text{O}$ and A/CNK (Table 3), implying that these syenogranite porphyries may have experienced stronger alteration. In the $(\text{Zr}+\text{Nb}+\text{Ce}+\text{Y})$ versus $(\text{K}_2\text{O}+\text{Na}_2\text{O})/\text{CaO}$ diagram (Whalen et al., 1987) (Fig. 11a), most Late Jurassic syenogranite porphyry samples fall into the

fractionated granite (FG) field, whereas the Early Cretaceous monzogranite porphyry samples fall mainly in the transitional area between the FG and typical M-, I-, and S-type granites (OGT). All the Early Cretaceous syenogranite porphyry samples fall into the A-type granite field. In the (Zr+Nb+Ce+Y) versus TFeO/MgO diagram (Whalen et al., 1987) (Fig. 11b), almost all the Late Jurassic syenogranite porphyry samples fall within the FG field, all the Early Cretaceous monzogranite porphyry samples fall within the OGT field, and the Early Cretaceous syenogranite porphyry samples plot mainly in the OGT field and minor in the FG field. These discrimination diagrams for types of granites indicate that the Late Jurassic–Early Cretaceous syenogranite porphyries belong to highly fractionated granites and that the Early Cretaceous monzogranite porphyry belongs to unfractionated I-type granites. Wu et al. (2007) pointed out that fractional crystallization can increase A/CNK, making granite type discrimination difficult. Mesozoic granites in North China are mainly I-type, and some previously classified to be “S-type granites” may have been highly fractionated I-type granites (Wu et al., 2007). Therefore, we conclude that both the Late Jurassic and Early Cretaceous syenogranite porphyry are most likely highly fractionated I-type granites.

These Late Jurassic–Early Cretaceous granitic porphyries have high Rb (averaging 296 ppm), Th (averaging 25.2 ppm), U (averaging 6.92 ppm), K (averaging 51879 ppm), and Zr (averaging 97.3 ppm) contents, but low Cr (averaging 5.05 ppm) and Ni (averaging 1.24 ppm) contents, indicative of a crust-derived magma. However, Rb (averaging 352 ppm) and K (averaging 61611 ppm) contents and Rb/Nb (averaging 12.3) and K/Nb (averaging 2165) ratios of these Late Jurassic–Early Cretaceous syenogranite porphyries are obviously higher than those of the monzogranite porphyry (Table 3), implying that these syenogranite

porphyries experienced stronger alteration and/or more strongly fractional crystallization than the monzogranite porphyry. The Late Jurassic–Early Cretaceous syenogranite porphyries have high La/Nb (averaging 1.98), Th/Nb (averaging 0.80), Th/La (averaging 0.41), and Th/U (averaging 5.76) ratios, but low Nb/U (averaging 8.04), Nb/Pb (averaging 1.68), and Ce/Pb (averaging 6.27) ratios, which are roughly consistent with those of the continental crust (e.g., La/Nb = 2.20, Th/Nb = 0.44, Th/La = 0.20, Th/U = 6.00, Nb/U = 8.00–9.70, Nb/Pb = 1.60, and Ce/Pb = 4.00; Taylor and McLennan, 1985). Except for showing similar geochemical characteristics to the syenogranite porphyries such as high Th/Nb and Th/La ratios and low Nb/U, Nb/Pb, and Ce/Pb ratios, the Early Cretaceous monzogranite porphyry also reveals low La/Nb (averaging 0.87) and Th/U (averaging 2.70) ratios, which are approximately consistent with those of the primary mantle (PM), mid-ocean ridge basalt (MORB), and oceanic-island basalt (OIB) (e.g., La/Nb = 0.66–1.19 and Th/U = 1.20–4.05; Wood et al., 1979a, b; Taylor and McLennan, 1985; Galer et al., 1989; McDonough et al., 1992). These geochemical characteristics suggest that the Caosiyao granitic porphyries were most likely formed by partial melting of a continental crust. Lower La/Nb and Th/U of the monzogranite porphyry (cf. the syenogranite porphyries) imply that its magma source may have been more mafic.

The Late Jurassic–Early Cretaceous granitic porphyries are characterized by negative $\varepsilon_{\text{Hf}}(t)$ values and very old Hf single-stage and two-stage model ages. In the $\varepsilon_{\text{Hf}}(t)$ versus age diagram (Fig. 12), all Caosiyao samples fall into the Yanshan Fold and Thrust Belt (YFTB) field proposed by Yan et al. (2006), but away from the eastern CAOB field proposed by Xiao et al. (2004) and Chen et al. (2009b). Moreover, all these data points are confined to the field of the Paleoproterozoic crust Hf isotope evolution. Similar to the above Hf isotopic compositions,

the rocks also show negative $\varepsilon_{\text{Nd}}(t)$, very high initial $^{87}\text{Sr}/^{86}\text{Sr}$, and very old Nd single-stage and two-stage model ages. In the $\varepsilon_{\text{Nd}}(t)$ versus $(^{87}\text{Sr}/^{86}\text{Sr})_i$ diagram (Fig. 13), all samples fall into the second quadrant but away from the mantle array. Recently, many Paleoproterozoic ages were obtained by zircon SHRIMP, LA-ICP-MS, and CAMECA U–Pb dating for the Precambrian metamorphic rocks in the NCC (Dong et al., 2012; Liu et al., 2013; Wan et al., 2013; Li et al., 2015). In the northern NCC margin, Dong et al. (2012) and Wan et al. (2013) obtained zircon SHRIMP U–Pb ages of 2450–2370 Ma, 1970–1920 Ma, and 1850 Ma for the mafic granulite from the Daqingshan–Wulashan metamorphic complex in the central Khondalite belt, Liu et al. (2013) reported zircon LA-ICP-MS U–Pb ages of 2450–1930 Ma for the mafic granulite occurring in the Daqingshan–Wulashan area. The protolith of the mafic granulites is composed of basic volcanics, gabbro, and diabase (Liu et al., 2013; Wan et al., 2013), belongs to the tholeiite series, and was formed in an island-arc setting (Liu et al., 2013). In the southern NCC margin, Li et al. (2015) reported zircon SHRIMP U–Pb ages of 2550–2300 Ma for the biotite plagioclase paragneiss from the Dangzehe Group and a zircon CAMECA U–Pb age of 2178 Ma for a metagabbro occurring in the Longmendian area. The zircons from the biotite plagioclase paragneiss and the metagabbro are both typical of a magmatic origin. The above ages indicate that Paleoproterozoic was also an important crustal growth period for both the northern and southern NCC margins. Considering the Sr–Nd–Hf isotopic compositions obtained in this study and the Paleoproterozoic crustal growth events, we concluded that the Late Jurassic–Early Cretaceous granitic porphyries may have resulted from partial melting of the Paleoproterozoic continental crust.

The Late Jurassic–Early Cretaceous granitic porphyries have low radiogenic Pb

isotope and medium μ (averaging 9.2, which are lower than 9.6 in the upper crust, but obviously higher than the range of 8–9 in the mantle; Doe and Zartman, 1979). In the $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{207}\text{Pb}/^{204}\text{Pb}$ diagram (Fig. 10a), the Late Jurassic syenogranite porphyry samples fall into the crust-type high-grade lower crust (CHLC) field proposed by Zhang (1995). The Early Cretaceous monzogranite porphyry samples fall inside the transitional area between the CHLC and the low-grade lower crust (LLC) proposed by Zhang (1995), whereas the Early Cretaceous syenogranite porphyry samples fall into the CHLC field. In the $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$ diagram (Fig. 10b), the Late Jurassic syenogranite porphyry samples fall in the transitional field between the mantle-type high-grade lower crust (MHLC) and CHLC proposed by Zhang (1995). Most of the Early Cretaceous monzogranite porphyry samples fall into the LLC field, whereas the Early Cretaceous syenogranite porphyry samples fall in the transitional field between the CHLC and LLC. These Pb isotopic compositions imply that the Late Jurassic syenogranite porphyry may have been sourced from a higher mature lower crust, the Early Cretaceous monzogranite porphyry from an immature lower crust, and the Early Cretaceous syenogranite porphyry from a moderately mature lower crust. This is also supported by their different $\text{Mg}^\#$ values: Averaging 18 for the Late Jurassic syenogranite porphyry, 46 for the Early Cretaceous monzogranite porphyry, and 35 for the Early Cretaceous syenogranite porphyry.

In summary, the Caosiyao granitic porphyries were interpreted to have formed by the partial melting of the continental crust: The Late Jurassic syenogranite porphyry and Early Cretaceous syenogranite porphyry may have been sourced from a highly- and moderately mature Paleoproterozoic lower crust, respectively, whereas the Early Cretaceous

monzogranite porphyry may have been sourced from an immature Paleoproterozoic lower crust.

6.3. Tectonic setting of the Caosiyao granitic porphyries

There is still considerable debate concerning the Late Jurassic–Early Cretaceous tectonic setting of the northern NCC margin. Five major hypotheses include: (1) NW-dipping subduction of the Paleo-Pacific plate beneath Eurasia (Mao et al., 2003; Zhao et al., 2004b; Ge et al., 2007; Xu et al., 2013a, b); (2) S- to SE-dipping subduction of the Mongol–Okhotsk Ocean plate beneath the united North China–Mongolia plate (Chen et al., 2016, this issue); (3) Post-orogenic extension environment that resulted from the orogenic belt collapse following the collision of the Siberia and united North China–Mongolia plates during the Mesozoic closure of the Mongol–Okhotsk Ocean (Davis et al., 1998; Zheng et al., 1998); (4) Tectonic transition from an EW-trending compression to a NNE-trending extension (Zhai et al., 2002, 2004; Mao et al., 2011; Chen et al., 2012); and (5) Intraplate anorogenic environment (Pirajno et al., 2009; Pirajno and Zhou, 2015). Moreover, various workers had studied a series of porphyry–(skarn) mineral systems in the East Qinling Mo ore belt (southern NCC margin), and concluded that the Late Jurassic–Early Cretaceous porphyry-related Mo deposits were formed under a compressive–extensional transition tectonic regime (e.g., Chen and Fu, 1992; Chen et al., 2000b; and Li et al., 2007).

The Late Jurassic–Early Cretaceous Caosiyao syenogranite- and monzogranite porphyries are high-K calc-alkaline. In the SiO_2 versus Al_2O_3 diagram (Maniar and Piccoli, 1989), all the Late Jurassic and Early Cretaceous syenogranite porphyry samples and most of the Early Cretaceous monzogranite porphyry samples lie within the post-orogenic granitoid

(POG)field(Fig. 14a).In the MgO versus TFeO diagram (Maniar and Piccoli, 1989), most of the Late Jurassic and Early Cretaceous syenogranite porphyry samples plot in the POG field, and all of the Early Cretaceous monzogranite porphyry samples plot in the POG–(island-arc granitoid(IAG)+continental arc granitoid (CAG)+continental collision grantoid (CCG))transitional field (closer to the POG field) (Fig. 14b). In the (Y+Nb) versus Rb diagram (Pearce, 1996), most of the Caosiyao porphyriesfall within the post-collisional granite (post-COLG) field (Fig. 14c). Inthe R1 versus R2 diagram (Batchelor and Bowden, 1985), the Caosiyao porphyries fall mainly in the domains of the post-orogenic granite (VII) and the anorogenic granite (V) (Fig. 14d). These tectonic setting discrimination diagrams suggest that the Late Jurassic–Early Cretaceous Caosiyao porphyriesmay have formed in a post-collisional or post-orogenic setting.

Kravchinsky et al. (2002) proposedthat the Mongol–Okhotsk Ocean may have closed gradually from west to east during the Permian–Early Cretaceous. The continent-continent collision between the Siberia andunited North China–Mongoliaplates in NE-and North Chinamay have taken place in the middle Jurassic (Li et al., 1999; Meng, 2003). TheYanshan Orogen, located in the northern NCC margin, may have been resulted from the Mesozoic closure of the Mongol–Okhotsk Oceanand the subsequent collision of the Siberia and united North China–Mongolia plates(Davis et al., 1998). The evidence implies that the Late Jurassic–Early Cretaceous magmatism in NE- and North China may have been genetically related to the Mongol–Okhotsk orogenic event,whereas the coevalNE- or NNE-trending magmatism in eastern China may have been related to the Paleo-Pacific platesubduction, as supported by theroughly parallel magmatic trend to the subduction front.

To summarize, the Late Jurassic–Early Cretaceous Caosiyao granitic porphyries were most likely to form in a post-orogenic setting, which may have resulted from a combined influence of the post-orogenic gravitational collapse and the Paleo-Pacific plate subduction.

7. Conclusions

(1) The giant Caosiyao porphyry Mo deposit is newly molybdenite Re–Os dated to be Late Jurassic (ca. 148 Ma).

(2) The syenogranite porphyry is newly dated to be Late Jurassic (ca. 148.5 Ma) and Early Cretaceous (ca. 140.9–140.1 Ma), whereas the monzogranite porphyry is dated to be Early Cretaceous (ca. 145.0 Ma).

(3) The Late Jurassic syenogranite porphyry, Early Cretaceous monzogranite porphyry, and Early Cretaceous syenogranite porphyry may have formed by the partial melting of a highly mature-, immature- and moderately mature Paleoproterozoic lower crust, respectively.

(4) The Caosiyao granitic porphyries may have formed in a post-orogenic setting after the Mongol–Okhotsk ocean closure and coeval to the subduction of the Paleo-Pacific plate..

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Figure Captions

Fig. 1. (a) Location map of the NCC; (b) tectonic subdivision of the Archean to Paleoproterozoic basement of the NCC (after Zhao et al., 2005); (c) sketch geological map of the northern margin of the NCC, showing locations of major Mo deposits (modified after Xu

et al., 2008).

Names of numbered faults: F₁, Chifeng–Kaiyuan fault; F₂, Daxing’anling–Taihangshan fault.

Names of numbered deposits: 1, Dasuji porphyry Mo deposit; 2, Caosiyao porphyry Mo deposit; 3, Sanyizhuang porphyry–skarn Mo deposit; 4, Jiajiaying porphyry–skarn Mo deposit; 5, Dazhuangke explosion breccia-type Mo deposit; 6, Dongsancha skarn Mo deposit; 7, Shihuyu porphyry Mo deposit; 8, Dacaopingquartz-vein-type Mo deposit; 9, Sadaigoumen porphyry Mo deposit; 10, Shouwangfen porphyry–skarn Cu (Mo) deposit; 11, Moguyuskarn Cu (Mo) deposit; 12, Xiaosigou porphyry–skarn Cu (Mo) deposit; 13, Hekanzi porphyry–skarn Mo deposit; 14, Xiaojiayingzi skarn Mo deposit; 15, Laohugou porphyry Mo deposit; 16, Beisongshumao porphyry–skarn Mo deposit; 17, Yangjiazhangzi skarn Mo deposit; 18, Xintaimeng porphyry Mo deposit; 19, Lanjiagou porphyry Mo deposit; 20, Gangtun porphyry Mo deposit; 21, Laohudong skarn Mo (Zn) deposit.

Fig. 2. Regional geological map (a), ore deposit geological map (b), and geological cross section along the exploration line No. 8 (c) of the Caosiyao deposit, showing locations of orebody and mineralized body (modified after No. 2 Geoexploration Party of Henan Bureau of Geoexploration and Mineral Development, 2013).

Fig. 3. Representative photomicrographs for intrusive rocks of the Caosiyao deposit: (a) and (b) monzogranite porphyry, mainly comprising plagioclase (Pl), quartz (Q), potassium feldspar (Kf), and biotite (Bi) phenocrysts and felsic matrix with a microgranitic texture, polarized light; (c) and (d) syenogranite porphyry, mainly consisting of potassium feldspar

(Kf), quartz (Q), plagioclase (Pl), and biotite (Bi) phenocrysts and felsic matrix, developing a porphyritic texture, and these rocks reveal moderate sericitization and muscovitization, polarized light; (e) and (f) syenoporphyry, mainly consisting of quartz (Q), potassium feldspar (Kf), and biotite (Bi) phenocrysts and felsic matrix, developing a porphyritic texture, and these rocks show slight sericitization and muscovitization, polarized light.

Fig. 4. Representative photos of ores from the Caosiyao deposit: (a) disseminated, veinlet ore, occurring within biotite–plagioclase gneiss; (b) dense disseminated or bulk ore, occurring within K-feldspar pegmatite; (c) molybdenite in quartz–molybdenite vein showing schistose or anhedral granular texture under reflected light; (d) paragenesis of anhedral granular pyrite, subhedral to anhedral granular chalcopyrite, anhedral granular magnetite, and anhedral granular or sheaflike molybdenite in quartz–pyrite–chalcopyrite–magnetite–molybdenite vein under reflected light. Cp, chalcopyrite; Mo, molybdenite; Mt, magnetite; Py, pyrite.

Fig. 5. Re–Os isochron age (a) and weighted mean model age (b) of molybdenites from the Caosiyao deposit.

Fig. 6. Representative cathodoluminescence (CL) images of zircons from one monzogranite porphyry sample CM38 (a), one syenogranite porphyry sample CM41 (b), and the other syenogranite porphyry samples CM95 and CM100 (c and d) in the Caosiyao deposit, respectively, showing U–Pb analytical spots and corresponding ages.

Fig. 7. Zircon U–Pb concordia diagrams for monzogranite porphyry sample CM38 (a), syenogranite porphyry sample CM41, and syenogranite porphyry samples CM95 (c) and CM100 (d) from the Caosiyao deposit.

Fig. 8. Diagrams of R1 verses R2 (a), A/CNK versus A/NK (b), and SiO₂ versus K₂O (c) for the Mesozoic granitic porphyries in the Caosiyao deposit. The boundary lines in the R1 verses R2, A/CNK versus A/NK, and SiO₂ versus K₂O diagrams are from De la Roche et al. (1980), Maniar and Piccoli (1989), and Peccerillo and Taylor (1976), respectively.

Fig. 9. Chondrite-normalized rare earth element patterns (a, c, and e), and primitive mantle-normalized trace element spidergrams (b, d, and f) for the Mesozoic granitic porphyries in the Caosiyao deposit. Chondrite and primitive-mantle values are from Boynton (1984) and McDonough et al. (1992), respectively.

Fig. 10. Diagram of lead isotopic compositions of the Mesozoic granitic porphyries in the Caosiyao deposit (base map from Zartman and Doe, 1981). CHLC, LLC, LUC, and MHLC are crust endmembers of the NCC defined by Zhang (1995). CHLC, crust-type high-grade lower crust; LLC, low-grade lower crust; LUC, low-grade upper crust; MHLC, mantle-type high-grade lower crust.

Fig. 11. Zr+Nb+Ce+Y versus (K₂O+Na₂O)/CaO (a) and Zr+Nb+Ce+Y versus TFeO/MgO (b) discrimination diagrams for types of granites (after Whalen et al., 1987). FG, fractionated

granite; OGT, unfractionated M-, I-, and S-type granites.

Fig. 12. Correlation diagrams between Hf isotopic compositions and ages of zircons from the Mesozoic graniticporphyries in the Caosiyao deposit. Fields of East CAOB and YFTB are from Xiao et al. (2004), Chen et al. (2009b), and Yang et al. (2006), respectively. CAOB, the Central Asian Orogenic Belt; YFTB, the Yanshan Fold and Thrust Belt.

Fig. 13. $\epsilon_{\text{Nd}}(t)$ versus $(^{87}\text{Sr}/^{86}\text{Sr})_i$ plot for the Mesozoic graniticporphyries in the Caosiyao deposit. DM, EM I, EMII, HIMU, and PM are mantle endmembers defined by Hart (1984) and Zindler and Hart (1986), and ancient mafic lower crust and TTG of the NCC were defined by Zhang et al. (2001). DM, depleted mantle; EMI, I-type enriched mantle; EMII, II-type enriched mantle; HIMU, high- μ mantle; PM, primary mantle.

Fig. 14. Tectonic discrimination diagrams of the Mesozoic graniticporphyries in the Caosiyao deposit. (a) SiO_2 versus Al_2O_3 diagram (after Maniar and Piccoli, 1989); (b) MgO versus TFeO diagram (after Maniar and Piccoli, 1989); (c) $\text{Y}+\text{Nb}$ versus Rb diagram (after Pearce, 1996); (d) R1 versus R2 diagram (after Batchelor and Bowden, 1985). CAG, continental arc granitoids; CCG, continental collision granitoids; CEUG, continental epeirogenic uplift granitoids; IAG, island-arc granitoids; ORG, oceanic ridge granites; POG, post-orogenic granitoids; post-COLG, post-collisional granites; RRG, rift-related granitoids; syn-COLG, syn-collisional granites; VAG, volcanic arc granites; WPG, within-plate granites; I, mantle differentiated granites; II, pre-collisional granites; III, post-collisional uplifting granites; IV,

1070 late-orogenic granites; V, anorogenic granites; VI, syn-collisional granites; VII, post-orogenic
1071 granites.

1072 **Tables**

1073 Table 1 Re–Os analytical results of molybdenite from the CaosiyaoMo deposit.

1074
1075 Table 2 Zircon LA-ICP-MS U–Pb dating data for the monzogranite porphyry sample CM38
1076 and syenogranite porphyry samples CM41, and the other syenogranite porphyry samples
1077 CM95 and CM100 from the Caosiyao deposit.

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1079 Table 3Major (wt %) and trace elements (ppm) analytical results for the Mesozoic granitic
1080 porphyriesin the Caosiyao deposit.

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1082 Table 3(*continued*)

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1084 Table 3(*continued*)

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1086 Table 4Lu–Hf isotopic data for the Mesozoic granitic porphyriesin the Caosiyao deposit
1087 (zircons from samples CM38, CM41, CM95, and CM100).

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1089 Table 5Sr–Nd isotopic compositions for the Mesozoic granitic porphyriesin the Caosiyao
1090 deposit.

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1092 Table 6 Lead isotopic compositions of K-feldspar from the Mesozoic granitic porphyries of the
1093 Caosiyao deposit.

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1095 Table 7 Molybdenite Re–Os age of the major Mo deposits in the Yinshan–Yanshan–Liaoning
1096 Mo ore belt.

Figure 1 Tectonic units and regional geological map

Figure 2 Geological map and geological cross section

Figure 3 Representative photomicrographs of the intrusive rocks

Figure 4 Representative photos of ores from the Caosiyao deposit

Figure 5 Molybdenite Re-Os age

Figure 6 Representative CL images of zircon from intrusive rocks

Figure 7 Zircon U-Pb age of the Caosiyao intrusive rocks

Figure 8 Classification diagrams of the Caosiyao intrusive rocks

Figure 9 REE patterns and trace element spidergrams

Figure 10 Pb isotope diagram of K-feldspar from intrusive rocks

Figure 11 Discrimination diagrams for types of granites

Figure 12 Hf isotope diagram of zircon from the intrusive rocks

Figure 13 Nd isotope diagram of the intrusive rocks

Figure 14 Tectonic discrimination diagrams of intrusive rocks

Table 1 Molybdenite Re-Os isotope data

Table 1 Re–Os analytical results of molybdenite from the Caosiyao Mo deposit.

Sample No.	Weight (g)	Re (ppm)		Os (ppb)		¹⁸⁷ Re (ppm)		¹⁸⁷ Os (ppb)		Modal age (Ma)	
		Re	2σ	Os	2σ	¹⁸⁷ Re	2σ	¹⁸⁷ Os	2σ	Age	2σ
CM50	0.04995	8.501	0.127	0.113	0.010	5.343	0.080	13.15	0.10	147.5	2.8
CM58	0.05000	14.37	0.120	0.003	0.011	9.030	0.078	22.61	0.20	150.1	2.2
CM59	0.05002	8.591	0.151	0.016	0.039	5.400	0.095	13.33	0.13	148.0	3.2
CM66	0.19816	1.296	0.010	0.033	0.005	0.814	0.007	2.039	0.03	150.1	3.0
CM86	0.04987	4.432	0.047	0.009	0.013	2.786	0.029	6.859	0.06	147.6	2.3
CM92	0.05025	4.926	0.061	0.004	0.012	3.096	0.038	7.615	0.08	147.4	2.7

Table 2 Zircon LA-ICP-MS U–Pb dating data for the monzogranite porphyry sample CM38 and syenogranite porphyry samples CM41, and the other syenogranite porphyry samples CM95 and CM100 from the Caosiyao deposit.

Spot no.	Pb (ppm)	Th (ppm)	U (ppm)	Th/U	Isotopic ratios						Ages (Ma)					
					$^{207}\text{Pb}/^{206}\text{Pb}$		$^{207}\text{Pb}/^{235}\text{U}$		$^{206}\text{Pb}/^{238}\text{U}$		$^{207}\text{Pb}/^{206}\text{Pb}$		$^{207}\text{Pb}/^{235}\text{U}$		$^{206}\text{Pb}/^{238}\text{U}$	
					Ratio	1 σ	Ratio	1 σ	Ratio	1 σ	Age	1 σ	Age	1 σ	Age	1 σ
CM38-1.1	20.5	73.8	40.9	1.80	0.04955	0.00151	0.15325	0.00412	0.02250	0.00021	172.3	70	144.8	3.6	143.5	1.3
CM38-2.1	27.4	116	50.4	2.30	0.04994	0.00110	0.15947	0.00364	0.02318	0.00023	190.8	52	150.2	3.2	147.7	1.4
CM38-3.1	232	757	760	1.00	0.04941	0.00087	0.16139	0.00290	0.02368	0.00018	168.6	43	151.9	2.5	150.9	1.2
CM38-4.1	54.8	244	222	1.10	0.05044	0.00073	0.15899	0.00122	0.02287	0.00047	216.7	33	149.8	1.1	145.8	3.0
CM38-5.1	76.5	276	345	0.80	0.04898	0.00040	0.15347	0.00155	0.02273	0.00016	146.4	19	145.0	1.4	144.9	1.0
CM38-6.1	117	371	455	0.82	0.04940	0.00089	0.15727	0.00353	0.02310	0.00045	164.9	43	148.3	3.1	147.2	2.9
CM38-7.1	99.5	388	476	0.82	0.04909	0.00106	0.15568	0.00344	0.02301	0.00038	153.8	55	146.9	3.0	146.6	2.4
CM38-8.1	0.32	25.5	32.7	0.78	0.04924	0.00334	0.15719	0.01160	0.02314	0.00055	166.8	143	148.2	10	147.5	3.5
CM38-9.1	23.5	84.0	51.6	1.63	0.04917	0.00152	0.15513	0.00508	0.02291	0.00038	166.8	75	146.4	4.5	146.0	2.4
CM38-10.1	122	297	577	0.52	0.05211	0.00034	0.16203	0.00150	0.02255	0.00015	300.1	15	152.5	1.3	143.7	0.9
CM38-11.1	35.0	70.8	33.0	2.15	0.04980	0.00454	0.15656	0.01228	0.02285	0.00034	187.1	200	147.7	11	145.6	2.2
CM41-1.1	28.8	50.1	48.9	1.03	0.04966	0.00140	0.15703	0.00393	0.02303	0.00022	189.0	60	148.1	3.5	146.8	1.4
CM41-2.1	31.3	99.9	63.8	1.57	0.04910	0.00153	0.16013	0.00603	0.02363	0.00042	153.8	79	150.8	5.3	150.5	2.7
CM41-3.1	72.2	142	113	1.25	0.04927	0.00047	0.15679	0.00196	0.02308	0.00021	161.2	22	147.9	1.7	147.1	1.3
CM41-3.2	16.9	43.5	44.0	0.99	0.04954	0.00224	0.15899	0.00650	0.02341	0.00033	172.3	106	149.8	5.7	149.1	2.1
CM41-4.1	396	895	827	1.08	0.04996	0.00021	0.16377	0.00299	0.02380	0.00044	194.5	14	154.0	2.6	151.6	2.7
CM41-5.1	55.8	129	150	0.86	0.04953	0.00066	0.16078	0.00250	0.02353	0.00016	172.3	34	151.4	2.2	149.9	1.0
CM41-6.1	11.0	54.9	35.6	1.54	0.04940	0.00250	0.15897	0.00794	0.02336	0.00019	164.9	119	149.8	7.0	148.9	1.2
CM41-7.1	83.5	60.9	116	0.53	0.04992	0.00136	0.16227	0.00440	0.02359	0.00026	190.8	63	152.7	3.8	150.3	1.7
CM41-8.1	153	257	256	1.00	0.04931	0.00033	0.15699	0.00144	0.02309	0.00016	161.2	21	148.1	1.3	147.2	1.0
CM95-1.1	98.3	34.0	20.7	1.64	0.04936	0.00119	0.14677	0.00349	0.02170	0.00026	164.9	57	139.1	3.1	138.4	1.7
CM95-2.1	133	157	51.5	3.05	0.04944	0.00078	0.14948	0.00282	0.02199	0.00028	168.6	37	141.5	2.5	140.2	1.8
CM95-3.1	80.9	51.4	20.0	2.57	0.04916	0.00127	0.14966	0.00444	0.02212	0.00033	153.8	56	141.6	3.9	141.1	2.1
CM95-4.1	87.6	46.0	26.4	1.74	0.04926	0.00333	0.14981	0.00941	0.02221	0.00044	166.8	143	141.7	8.3	141.6	2.7
CM95-5.1	56.9	47.1	109	0.43	0.04935	0.00060	0.16097	0.00283	0.02373	0.00037	164.9	4.6	151.6	2.5	151.2	2.3
CM95-6.1	72.4	57.1	64.1	0.89	0.04931	0.00070	0.16227	0.00257	0.02389	0.00020	161.2	33	152.7	2.2	152.2	1.3
CM95-7.1	38.4	5.50	9.28	0.59	0.04939	0.00468	0.16097	0.01549	0.02355	0.00061	164.9	211	151.6	14	150.0	3.8
CM95-8.1	47.3	12.6	31.8	0.40	0.04964	0.00305	0.15145	0.01028	0.02206	0.00043	189.0	144	143.2	9.1	140.7	2.7
CM95-9.1	90.8	119	55.7	2.14	0.05008	0.00152	0.15207	0.00466	0.02213	0.00042	198.2	103	143.7	4.1	141.1	2.6
CM100-1.1	61.9	79.2	76.6	1.03	0.05019	0.00070	0.16155	0.00379	0.02343	0.00050	211.2	31	152.1	3.3	149.3	3.2
CM100-1.2	109	181	84.7	2.14	0.05016	0.00158	0.15233	0.00671	0.02206	0.00079	211.2	72	144.0	5.9	140.7	5.0
CM100-2.1	135	53.2	53.2	1.00	0.04926	0.00258	0.15052	0.01227	0.02195	0.00087	166.8	124	142.4	11	140.0	5.5
CM100-3.1	33.0	47.8	45.9	1.04	0.04911	0.00361	0.14672	0.01044	0.02172	0.00053	153.8	163	139.0	9.2	138.5	3.3
CM100-4.1	103	74.1	43.0	1.73	0.05020	0.00612	0.15312	0.01869	0.02212	0.00014	211.2	254	144.7	16	141.0	0.9
CM100-5.1	125	24.9	34.8	0.72	0.05025	0.00226	0.15355	0.00755	0.02220	0.00061	205.6	106	145.0	6.6	141.6	3.8
CM100-6.1	87.8	65.2	96.3	0.68	0.04957	0.00108	0.15948	0.00454	0.02333	0.00038	176.0	55	150.2	4.0	148.6	2.4
CM100-7.1	184	161	207	0.78	0.05097	0.00094	0.16294	0.00326	0.02318	0.00036	239.0	44	153.3	2.8	147.8	2.2
CM100-8.1	226	347	167	2.09	0.05008	0.00091	0.16551	0.00431	0.02395	0.00030	198.2	36	155.5	3.8	152.5	1.9
CM100-9.1	38.0	31.5	19.4	1.62	0.04985	0.00292	0.16268	0.01228	0.02352	0.00057	187.1	131	153.0	11	149.9	3.6

Table 3 Major (wt %) and trace elements (ppm) analytical results for the Mesozoic granitic porphyries in the Caosiyao deposit.

Sample	CM26	CM27	CM28	CM29	CM30	CM31	CM32	CM33	CM34	CM35	CM36
SiO ₂	77.43	79.62	77.17	76.94	78.03	77.68	75.49	76.59	77.79	77.81	77.69
TiO ₂	0.21	0.18	0.21	0.23	0.20	0.18	0.18	0.17	0.17	0.16	0.16
Al ₂ O ₃	11.45	10.40	11.57	11.62	10.98	11.24	12.49	11.90	11.26	11.36	11.34
Fe ₂ O ₃	0.27	0.34	0.15	0.39	0.36	0.03	0.10	0.08	0.15	0.17	0.05
FeO	0.70	0.50	0.85	0.65	0.55	0.75	0.65	0.60	0.60	0.60	0.50
MnO	0.04	0.04	0.04	0.04	0.03	0.03	0.02	0.03	0.04	0.03	0.02
MgO	0.41	0.40	0.43	0.43	0.39	0.36	0.32	0.37	0.35	0.37	0.36
CaO	0.80	0.71	0.90	0.91	0.96	0.89	0.88	0.77	0.78	0.78	0.69
Na ₂ O	2.96	2.67	3.36	3.37	2.97	2.99	3.07	3.24	3.07	3.06	2.76
K ₂ O	4.52	4.18	4.25	4.40	4.20	4.30	5.33	4.99	4.49	4.57	5.03
P ₂ O ₅	0.07	0.07	0.07	0.07	0.07	0.06	0.05	0.06	0.06	0.06	0.05
LOI	1.03	0.83	0.85	0.83	1.15	1.35	1.31	1.01	1.06	0.92	1.23
Total	99.89	99.94	99.85	99.88	99.89	99.86	99.89	99.81	99.821	99.89	99.88
Na ₂ O+ K ₂ O	7.48	6.85	7.61	7.77	7.17	7.29	8.40	8.23	7.56	7.63	7.79
K ₂ O/Na ₂ O	1.53	1.57	1.26	1.31	1.41	1.44	1.74	1.54	1.46	1.49	1.82
A/CNK	1.02	1.02	0.98	0.97	0.98	1.00	1.01	0.98	0.99	1.00	1.01
A/NK	1.17	1.17	1.14	1.13	1.16	1.17	1.15	1.11	1.14	1.14	1.14
Mg [#]	44	47	44	43	44	45	43	49	46	47	54
La	49.7	38.8	31.7	29.0	37.7	25.7	25.1	32.4	35.2	29.9	28.2
Ce	91.0	73.4	61.1	58.2	70.0	50.1	47.4	60.4	65.5	56.1	53.0
Pr	9.81	7.90	6.85	6.69	7.55	5.71	5.30	6.54	7.01	6.17	5.86
Nd	30.3	25.6	23.2	23.2	24.8	19.9	18.2	21.1	22.6	20.1	19.5
Sm	4.64	4.15	4.03	4.07	4.03	3.64	3.17	3.39	3.55	3.32	3.27
Eu	0.53	0.47	0.52	0.51	0.50	0.48	0.50	0.48	0.41	0.43	0.51
Gd	3.56	3.08	2.98	3.16	3.03	2.82	2.44	2.45	2.48	2.46	2.46
Tb	0.68	0.58	0.58	0.61	0.59	0.56	0.49	0.48	0.49	0.49	0.49
Dy	3.24	2.87	2.96	3.07	2.82	2.92	2.55	2.35	2.34	2.40	2.53
Ho	0.60	0.52	0.55	0.56	0.52	0.54	0.46	0.44	0.43	0.46	0.47
Er	1.96	1.71	1.78	1.81	1.67	1.68	1.48	1.47	1.46	1.55	1.55
Tm	0.34	0.30	0.33	0.34	0.30	0.31	0.21	0.28	0.27	0.30	0.30
Yb	2.45	2.13	2.39	2.39	2.14	2.21	1.87	2.17	2.04	2.22	2.15
Lu	0.39	0.34	0.39	0.39	0.34	0.36	0.30	0.36	0.34	0.38	0.36
ΣREE	199	162	139	134	156	117	109	134	144	126	121
Eu/Eu [*]	0.38	0.39	0.44	0.42	0.42	0.45	0.53	0.49	0.41	0.44	0.53
(La/Yb) _N	13.7	12.3	8.94	8.18	11.9	7.84	9.05	10.1	11.6	9.08	8.84
Sr	80.4	69.3	86.6	83.5	105	101	148	72.4	63.0	73.2	82.3
Rb	221	219	215	212	182	210	193	250	234	231	228
Ba	171	149	131	135	205	235	391	160	150	136	200
Th	28.7	27.3	28.7	27.2	26.2	25.8	22.8	32.1	30.8	29.9	28.5
Nb	40.7	36.3	39.9	39.8	35.1	37.0	32.8	41.2	43.0	42.1	36.8
Zr	75.8	77.7	83.4	80.4	71.8	75.2	66.9	98.1	92.7	88.4	82.6
Cs	1.61	1.65	2.04	1.90	1.21	1.48	0.99	2.17	2.76	1.49	1.42
Ga	21.2	19.8	22.3	21.2	19.7	19.8	19.7	23.1	20.9	22.1	20.1
Hf	2.97	2.71	3.31	3.10	2.79	2.91	2.60	3.79	3.47	3.43	3.34
Sc	5.97	5.45	6.38	6.08	5.27	4.77	4.39	6.01	6.11	6.02	5.64
Cr	4.81	5.35	5.33	4.61	4.11	3.46	3.45	3.69	3.22	3.18	4.35
V	9.41	8.27	9.57	9.60	12.5	10.6	9.87	5.79	5.96	5.76	6.39
Ni	1.73	1.72	1.71	1.68	2.24	2.17	1.89	2.59	1.45	1.30	1.99
Pb	16.2	16.3	18.6	16.5	13.1	12.1	16.7	18.6	17.6	17.8	15.9
U	11.5	11.4	12.6	11.2	10.0	11.0	8.59	7.45	11.1	10.7	8.89

Y	20.4	17.7	18.7	19.2	17.1	17.2	15.4	14.5	14.6	15.7	15.7
Ta	2.84	2.51	2.97	2.78	3.10	3.22	3.26	3.40	3.31	3.28	3.19
Rb/Nb	5.43	6.03	5.39	5.33	5.19	5.68	5.88	6.07	5.44	5.49	6.20
K/Nb	922	956	884	918	993	965	1349	1005	867	901	1135
La/Nb	1.22	1.07	0.79	0.73	1.07	0.69	0.77	0.79	0.82	0.71	0.77
Th/Nb	0.71	0.75	0.72	0.68	0.75	0.70	0.70	0.78	0.72	0.71	0.77
Th/La	0.58	0.70	0.91	0.94	0.69	1.00	0.91	0.99	0.88	1.00	1.01
Nb/U	3.54	3.18	3.17	3.55	3.51	3.36	3.82	5.53	3.87	3.93	4.14
Nb/Pb	2.51	2.23	2.15	2.41	2.68	3.06	1.96	2.22	2.44	2.37	2.31
Ce/Pb	5.62	4.50	3.28	3.53	5.34	4.14	2.84	3.25	3.72	3.15	3.33
Th/U	2.50	2.39	2.28	2.43	2.62	2.35	2.65	4.31	2.77	2.79	3.21

Table 3 (*continued*)

Sample	CM37	CM38	CM39	CM40	CM41	CM42	CM43	CM44	CM45	CM46
SiO ₂	75.14	76.96	74.68	72.81	72.84	73.53	73.26	74.98	74.27	74.50
TiO ₂	0.16	0.17	0.18	0.19	0.17	0.18	0.17	0.19	0.19	0.12
Al ₂ O ₃	12.72	11.54	12.89	12.92	12.79	12.61	12.82	12.64	12.97	12.26
Fe ₂ O ₃	0.25	0.12	0.91	0.39	0.33	0.89	1.01	1.01	0.95	3.07
FeO	0.45	0.60	0.95	1.25	2.75	1.70	1.10	1.35	2.85	2.10
MnO	0.03	0.03	0.04	0.05	0.04	0.05	0.04	0.05	0.09	0.35
MgO	0.31	0.36	0.33	0.30	0.25	0.30	0.29	0.30	0.43	0.30
CaO	0.77	0.92	0.44	1.19	0.18	0.66	1.21	0.34	0.25	0.18
Na ₂ O	3.20	3.28	0.17	1.07	0.28	0.20	0.18	0.14	0.15	0.16
K ₂ O	5.35	4.53	6.79	6.94	7.20	6.51	7.03	6.78	4.01	4.34
P ₂ O ₅	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.04	0.02
LOI	1.51	1.24	2.33	2.52	2.65	3.02	2.63	2.03	3.28	2.35
Total	99.94	99.80	99.76	99.68	99.53	99.70	99.79	99.86	99.48	99.75
Na ₂ O+K ₂ O	8.55	7.81	6.96	8.01	7.48	6.71	7.21	6.92	4.16	4.50
K ₂ O/Na ₂ O	1.67	1.38	39.9	6.49	25.7	32.6	39.1	48.4	25.7	27.1
A/CNK	1.02	0.96	1.53	1.13	1.49	1.47	1.27	1.55	2.57	2.32
A/NK	1.15	1.12	1.69	1.39	1.55	1.71	1.62	1.67	2.83	2.47
Mg [#]	45	48	25	25	13	18	20	19	17	10
La	40.7	32.3	51.8	59.4	57.5	59.9	78.7	57.2	55.8	43.8
Ce	71.5	59.6	103	120	114	119	159	115	112	89.3
Pr	7.33	6.39	12.7	14.6	13.9	14.5	19.4	14.1	13.8	11.3
Nd	22.7	20.8	45.0	52.3	49.4	51.7	69.4	49.8	49.3	41.3
Sm	3.35	3.36	8.89	10.2	9.83	10.1	14.0	9.70	9.62	8.94
Eu	0.44	0.48	0.53	0.51	0.61	0.52	0.76	0.51	0.82	0.87
Gd	2.39	2.55	5.72	6.81	6.83	6.53	9.55	6.08	6.34	6.02
Tb	0.47	0.49	0.99	1.20	1.18	1.07	1.64	1.05	1.11	1.01
Dy	2.29	2.45	3.78	5.02	5.05	3.98	6.56	3.90	5.14	4.07
Ho	0.43	0.46	0.57	0.78	0.80	0.59	1.00	0.58	0.64	0.63
Er	1.46	1.55	1.68	2.29	2.36	1.81	2.99	1.75	2.41	1.88
Tm	0.27	0.30	0.23	0.33	0.34	0.25	0.43	0.24	0.27	0.29
Yb	2.05	2.24	1.57	2.17	2.23	1.68	2.93	1.65	1.88	2.00
Lu	0.35	0.38	0.24	0.32	0.32	0.25	0.44	0.25	0.29	0.30
ΣREE	156	133	237	276	264	272	367	262	259	212
Eu/Eu*	0.46	0.49	0.21	0.18	0.22	0.18	0.19	0.19	0.30	0.34
(La/Yb) _N	13.4	9.72	22.2	18.5	17.4	24.0	18.1	23.4	20.0	14.8
Sr	96.1	91.9	60.9	78.0	95.2	50.9	94.9	53.0	19.0	15.3
Rb	221	216	427	372	386	359	552	379	305	304
Ba	224	198	417	374	363	326	525	339	95.6	87.8
Th	29.5	30.1	26.7	30.3	29.0	30.2	42.5	29.1	30.1	27.9

Nb	38.4	41.6	25.2	28.4	27.6	28.0	38.3	26.0	28.6	27.7
Zr	79.0	93.4	130	126	127	111	167	111	122	102
Cs	1.30	1.93	3.92	2.99	3.65	3.84	5.47	4.14	1.97	1.70
Ga	21.9	22.1	21.4	22.0	21.6	21.8	31.7	20.8	25.3	22.9
Hf	3.06	3.64	4.14	4.02	3.96	3.81	5.49	3.65	3.78	3.65
Sc	5.35	5.90	5.49	6.11	5.69	5.79	8.49	5.52	5.84	5.46
Cr	4.36	4.27	4.67	4.35	4.29	4.78	6.36	4.38	6.52	3.64
V	6.26	6.16	7.16	7.04	6.33	6.81	10.1	6.93	6.90	3.57
Ni	1.24	1.80	0.50	1.00	0.35	0.65	1.78	0.50	0.47	0.26
Pb	17.2	16.8	15.4	24.8	21.0	36.5	25.4	18.7	6.77	7.69
U	12.6	12.1	5.06	5.69	5.77	5.78	8.13	7.71	4.50	4.99
Y	14.5	15.5	16.0	22.2	21.3	16.0	28.9	16.0	22.7	17.7
Ta	3.18	3.32	1.75	2.02	1.95	1.99	2.90	1.92	2.01	2.10
Rb/Nb	5.76	5.19	16.9	13.1	14.0	12.8	14.4	14.6	10.7	11.0
K/Nb	1157	904	2237	2029	2166	1930	1524	2165	1164	1301
La/Nb	1.06	0.78	2.06	2.09	2.08	2.14	2.05	2.20	1.95	1.58
Th/Nb	0.77	0.72	1.06	1.07	1.05	1.08	1.11	1.12	1.05	1.01
Th/La	0.72	0.93	0.52	0.51	0.50	0.50	0.54	0.51	0.54	0.64
Nb/U	3.05	3.44	4.98	4.99	4.78	4.84	4.71	3.37	6.36	5.55
Nb/Pb	2.23	2.48	1.64	1.15	1.31	0.77	1.51	1.39	4.22	3.60
Ce/Pb	4.16	3.55	6.69	4.84	5.43	3.26	6.26	6.15	16.5	11.6
Th/U	2.34	2.49	5.28	5.33	5.03	5.22	5.23	3.77	6.69	5.59

Table 3 (continued)

Sample	CM94	CM95	CM96	CM97	CM98	CM99	CM100	CM101	CM102	CM103
SiO ₂	75.28	72.49	73.13	74.40	76.20	73.02	74.49	72.82	70.85	74.24
TiO ₂	0.31	0.31	0.34	0.35	0.38	0.32	0.33	0.34	0.30	0.33
Al ₂ O ₃	12.80	13.21	13.11	13.11	12.22	14.24	12.55	12.55	13.23	13.57
Fe ₂ O ₃	0.95	1.16	1.32	0.54	0.15	0.24	0.22	2.12	2.74	0.46
FeO	0.15	0.40	0.50	0.40	0.35	0.50	0.75	0.15	0.30	0.30
MnO	0.003	0.003	0.003	0.002	0.002	0.003	0.004	0.002	0.002	0.001
MgO	0.33	0.45	0.42	0.27	0.29	0.31	0.31	0.30	0.32	0.33
CaO	0.11	0.12	0.09	0.09	0.11	0.12	0.10	0.08	0.10	0.13
Na ₂ O	0.71	1.70	0.42	0.50	0.49	1.05	0.49	0.41	0.57	0.11
K ₂ O	7.75	7.92	8.30	9.11	8.16	8.53	8.77	8.65	8.98	7.82
P ₂ O ₅	0.05	0.06	0.07	0.06	0.06	0.05	0.07	0.12	0.13	0.05
LOI	1.51	2.14	1.93	1.08	1.36	1.53	1.65	2.33	2.41	1.62
Total	99.95	99.96	99.63	99.91	99.77	99.91	99.73	99.87	99.93	98.96
Na ₂ O+K ₂ O	8.46	9.62	8.72	9.61	8.65	9.58	9.26	9.06	9.55	7.93
K ₂ O/Na ₂ O	10.9	4.66	19.8	18.2	16.7	8.12	17.9	21.1	15.8	71.1
A/CNK	1.31	1.14	1.33	1.21	1.24	1.27	1.20	1.23	1.22	1.53
A/NK	1.34	1.16	1.36	1.23	1.27	1.30	1.22	1.25	1.24	1.57
Mg [#]	37	36	31	35	52	43	37	21	17	45
La	54.8	49.9	48.2	66.6	65.0	62.5	68.9	68.9	33.3	43.4
Ce	101	90.3	88.5	124	121	114	129	127	61.7	79.3
Pr	11.5	10.3	10.2	13.8	14.1	13.1	15.0	14.6	7.21	8.97
Nd	39.0	34.7	34.5	46.8	49.5	44.3	51.0	49.7	25.6	31.2
Sm	6.08	5.40	5.48	7.47	8.10	6.83	7.99	7.54	4.19	4.91
Eu	1.02	1.01	0.87	1.08	1.48	1.27	1.06	1.01	0.87	1.00
Gd	3.60	3.49	3.54	4.63	4.99	4.24	4.85	4.78	2.89	3.25
Tb	0.65	0.62	0.64	0.81	0.87	0.75	0.85	0.83	0.50	0.59
Dy	2.20	2.30	2.37	2.78	3.10	2.55	3.00	2.91	2.01	2.30
Ho	0.32	0.37	0.38	0.42	0.47	0.38	0.47	0.46	0.33	0.38

Er	1.09	1.20	1.23	1.37	1.53	1.26	1.56	1.54	1.06	1.24
Tm	0.15	0.18	0.18	0.19	0.22	0.17	0.22	0.22	0.17	0.20
Yb	1.10	1.23	1.25	1.32	1.53	1.26	1.50	1.52	1.19	1.38
Lu	0.17	0.19	0.20	0.20	0.24	0.20	0.23	0.23	0.19	0.22
Σ REE	223	201	198	271	262	253	286	281	141	178
Eu/Eu [*]	0.62	0.67	0.56	0.52	0.66	0.67	0.48	0.48	0.72	0.72
(La/Yb) _N	33.6	27.4	26.0	34.0	28.6	33.4	31.0	30.6	18.9	21.2
Sr	221	192	213	268	331	271	262	276	244	258
Rb	304	340	329	350	309	341	307	326	334	307
Ba	966	989	1172	1097	1258	1206	1155	1050	1202	1085
Th	15.3	14.9	14.6	17.9	19.5	16.2	18.9	19.0	17.2	15.6
Nb	25.8	25.6	27.0	28.0	35.3	30.2	28.7	31.3	25.4	30.8
Zr	88.4	85.2	91.4	98.1	108	94.1	98.0	99.9	87.4	105
Cs	0.89	0.75	0.60	0.75	1.43	0.96	0.72	0.61	0.69	1.17
Ga	20.3	19.6	26.4	18.8	21.7	23.6	20.4	18.5	19.4	22.1
Hf	2.86	2.65	2.85	3.04	3.49	3.13	3.08	3.03	2.72	3.34
Sc	4.59	4.91	5.42	4.33	4.35	4.68	4.36	5.23	4.78	4.74
Cr	6.89	5.77	5.94	6.06	6.25	5.77	6.07	9.13	5.82	5.79
V	21.9	24.5	27.4	21.7	23.7	25.4	23.6	26.5	26.0	24.2
Ni	0.73	1.75	1.30	0.80	0.55	0.85	0.73	0.51	1.50	0.61
Pb	19.7	15.3	17.2	19.3	19.8	19.8	26.7	20.9	19.4	21.9
U	2.25	2.67	2.47	3.09	3.13	2.75	2.55	2.89	3.32	2.55
Y	9.45	11.1	11.4	12.5	14.0	11.0	13.7	15.9	9.94	11.3
Ta	2.36	2.31	2.53	2.55	3.25	2.71	2.62	2.87	2.28	2.78
Rb/Nb	11.8	13.3	12.2	12.5	8.75	11.3	10.7	10.4	13.1	9.97
K/Nb	2494	2568	2552	2701	1919	2345	2537	2294	2935	2108
La/Nb	2.12	1.95	1.79	2.38	1.84	2.07	2.40	2.20	1.31	1.41
Th/Nb	0.59	0.58	0.54	0.64	0.55	0.54	0.66	0.61	0.68	0.51
Th/La	0.28	0.30	0.30	0.27	0.30	0.26	0.27	0.28	0.52	0.36
Nb/U	11.5	9.59	10.9	9.06	11.3	11.0	11.3	10.8	7.65	12.1
Nb/Pb	1.31	1.67	1.57	1.45	1.78	1.53	1.07	1.50	1.31	1.41
Ce/Pb	5.13	5.90	5.15	6.42	6.11	5.76	4.83	6.08	3.18	3.62
Th/U	6.80	5.58	5.91	5.79	6.23	5.89	7.41	6.57	5.18	6.12

Table 4 Lu–Hf isotopic data for the Mesozoic granitic porphyries in the Caosiyao deposit (zircons from samples CM38, CM41, CM95, and CM100).

Spot no.	t (Ma)	$^{176}\text{Yb}/^{177}\text{Hf}$	$^{176}\text{Lu}/^{177}\text{Hf}$	$^{176}\text{Hf}/^{177}\text{Hf}$	$^{176}\text{Hf}/^{177}\text{Hf}$ (corr)	$2\sigma_m$	$\varepsilon_{\text{Hf}}(0)$	$\varepsilon_{\text{Hf}}(t)$	2σ	$T_{\text{DM1}}(\text{Hf})$ (Ma)	$T_{\text{DM2}}(\text{Hf})$ (Ma)	$f_{\text{Lu/Hf}}$
CM38-1.1	145	0.046926	0.000948	0.282285	0.282282	0.000023	-17.2	-14.2	0.8	1363	2095	-0.97
CM38-2.1	145	0.060589	0.001159	0.282155	0.282152	0.000027	-21.8	-18.8	0.9	1552	2385	-0.97
CM38-3.1	145	0.087600	0.001796	0.282263	0.282259	0.000023	-18.0	-15.0	0.8	1425	2147	-0.95
CM38-4.1	145	0.131389	0.002353	0.282226	0.282219	0.000034	-19.3	-16.4	1.2	1501	2234	-0.93
CM38-5.1	145	0.064132	0.001245	0.282194	0.282191	0.000026	-20.4	-17.4	0.9	1500	2298	-0.96
CM38-6.1	145	0.081276	0.001982	0.282233	0.282227	0.000020	-19.1	-16.1	0.7	1476	2217	-0.94
CM38-7.1	145	0.085226	0.001795	0.282209	0.282204	0.000028	-19.9	-16.9	1.0	1502	2269	-0.95
CM38-8.1	145	0.030575	0.000621	0.282249	0.282247	0.000032	-18.5	-15.4	1.1	1401	2173	-0.98
CM38-9.1	145	0.094559	0.002101	0.282233	0.282227	0.000023	-19.1	-16.1	0.8	1480	2217	-0.94
CM38-10.1	145	0.062112	0.001470	0.282196	0.282192	0.000025	-20.4	-17.3	0.9	1507	2296	-0.96
CM38-11.1	145	0.117764	0.002383	0.282199	0.282193	0.000029	-20.3	-17.3	1.0	1541	2294	-0.93
CM41-1.1	149	0.034442	0.000647	0.282240	0.282238	0.000020	-18.8	-15.6	0.7	1414	2190	-0.98
CM41-2.1	149	0.066839	0.001228	0.282245	0.282242	0.000020	-18.6	-15.5	0.7	1429	2183	-0.96
CM41-3.1	149	0.035042	0.000664	0.282231	0.282230	0.000021	-19.1	-15.9	0.7	1427	2210	-0.98
CM41-3.2	149	0.022922	0.000443	0.282254	0.282253	0.000018	-18.3	-15.1	0.6	1387	2158	-0.99
CM41-4.1	149	0.057716	0.001068	0.282217	0.282214	0.000021	-19.6	-16.5	0.7	1462	2245	-0.97
CM41-5.1	149	0.034626	0.000653	0.282188	0.282186	0.000021	-20.7	-17.5	0.7	1487	2308	-0.98
CM41-6.1	149	0.046530	0.000844	0.282273	0.282271	0.000026	-17.6	-14.5	0.9	1376	2119	-0.98
CM41-7.1	149	0.049679	0.000910	0.282209	0.282207	0.000027	-19.9	-16.7	0.9	1467	2261	-0.97
CM41-8.1	149	0.063418	0.001184	0.282275	0.282272	0.000025	-17.6	-14.4	0.9	1385	2116	-0.96
CM95-1.1	140	0.028889	0.000429	0.282314	0.282312	0.000019	-16.2	-13.2	0.7	1305	2031	-0.99
CM95-2.1	140	0.117809	0.001589	0.282244	0.282240	0.000029	-18.7	-15.7	1.0	1444	2192	-0.95
CM95-3.1	140	0.057864	0.000810	0.282304	0.282302	0.000023	-16.6	-13.6	0.8	1331	2054	-0.98
CM95-4.1	140	0.038632	0.000532	0.282332	0.282331	0.000023	-15.5	-12.5	0.8	1282	1989	-0.98
CM95-5.1	152	0.072565	0.000962	0.282236	0.282233	0.000021	-18.9	-15.7	0.7	1431	2199	-0.97
CM95-6.1	152	0.068864	0.000902	0.282286	0.282283	0.000024	-17.2	-13.9	0.9	1360	2088	-0.97
CM95-7.1	152	0.004543	0.000055	0.282329	0.282329	0.000063	-15.6	-12.3	2.2	1271	1986	-0.99
CM95-8.1	140	0.061954	0.000869	0.282250	0.282248	0.000018	-18.5	-15.5	0.6	1409	2175	-0.97
CM100-1.1	150	0.046558	0.000859	0.282235	0.282232	0.000023	-19.0	-15.8	0.8	1429	2203	-0.97
CM100-1.2	141	0.055868	0.001050	0.282152	0.282150	0.000023	-21.9	-18.9	0.8	1551	2393	-0.97
CM100-2.1	141	0.032015	0.000616	0.282225	0.282223	0.000022	-19.3	-16.3	0.8	1434	2229	-0.98
CM100-3.1	141	0.024304	0.000483	0.282256	0.282255	0.000025	-18.2	-15.2	0.9	1386	2159	-0.99
CM100-4.1	141	0.037155	0.000709	0.282231	0.282230	0.000025	-19.1	-16.1	0.9	1428	2215	-0.98
CM100-5.1	141	0.027791	0.000523	0.282282	0.282280	0.000027	-17.3	-14.3	1.0	1352	2102	-0.98
CM100-6.1	150	0.043784	0.000904	0.282274	0.282271	0.000023	-17.6	-14.4	0.8	1376	2116	-0.97
CM100-7.1	150	0.089660	0.001711	0.282120	0.282116	0.000027	-23.0	-19.9	1.0	1624	2462	-0.95
CM100-8.1	150	0.055048	0.000985	0.282222	0.282219	0.000031	-19.4	-16.3	1.1	1452	2232	-0.97
CM100-9.1	150	0.030077	0.000562	0.282226	0.282225	0.000031	-19.3	-16.1	1.1	1430	2220	-0.98

Table 5 Whole rock Sr-Nd isotopes of the intrusive rocks

Table 5 Sr–Nd isotopic compositions for the Mesozoic granitic porphyries in the Caosiyao deposit.

Sample	<i>t</i>	Rb	Sr	⁸⁷ Rb/ ⁸⁶ Sr	⁸⁷ Sr/ ⁸⁶ Sr	2σ	(⁸⁷ Sr/ ⁸⁶ Sr) _i	Sm	Nd	¹⁴⁷ Sm/ ¹⁴⁴ Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	2σ	(¹⁴³ Nd/ ¹⁴⁴ Nd) _i	ε _{Nd} (<i>t</i>)	ε _{Nd} (0)	<i>T</i> _{DM1} (Nd)	<i>T</i> _{DM2} (Nd)	<i>f</i> _{Sm/Nd}
No.	(Ma)	(ppm)	(ppm)					(ppm)	(ppm)							(Ma)	(Ma)	
CM27	145	232	64.0	10.493	0.732920	0.000011	0.711293	3.82	24.1	0.0959	0.511703	0.000008	0.511612	−16.4	−18.2	1867	2262	−0.51
CM28	145	218	80.0	7.8703	0.728517	0.000012	0.712295	3.76	21.8	0.1042	0.511737	0.000007	0.511638	−15.9	−17.6	1960	2221	−0.47
CM30	145	187	97.3	5.5452	0.725503	0.000012	0.714074	3.40	20.8	0.0992	0.511675	0.000008	0.511581	−17.0	−18.8	1957	2311	−0.50
CM32	145	203	136	4.3064	0.719293	0.000012	0.710417	2.88	16.5	0.1058	0.511650	0.000008	0.511550	−17.6	−19.3	2111	2360	−0.46
CM36	145	227	73.3	8.9669	0.737050	0.000015	0.718568	3.08	18.1	0.1030	0.511638	0.000010	0.511540	−17.8	−19.5	2074	2375	−0.48
CM38	145	223	84.6	7.6390	0.731126	0.000015	0.715381	3.12	19.6	0.0965	0.511716	0.000007	0.511624	−16.1	−18.0	1860	2242	−0.51
CM40	149	384	73.9	15.0372	0.747716	0.000010	0.715867	9.94	51.4	0.1170	0.511802	0.000007	0.511688	−14.8	−16.3	2117	2137	−0.41
CM41	149	386	89.2	12.5222	0.744480	0.000012	0.717957	9.08	46.0	0.1193	0.511862	0.000006	0.511746	−13.7	−15.1	2072	2046	−0.39
CM46	149	346	15.4	64.8995	0.850071	0.000012	0.712611	8.69	40.2	0.1307	0.511820	0.000007	0.511693	−14.7	−16.0	2431	2130	−0.34
CM94	141	339	213	4.6134	0.721822	0.000013	0.712641	5.75	36.6	0.0950	0.511688	0.000007	0.511601	−16.7	−18.5	1872	2285	−0.52
CM96	141	349	195	5.1840	0.722549	0.000012	0.712233	4.90	31.2	0.0951	0.511730	0.000006	0.511643	−15.9	−17.7	1820	2219	−0.52
CM99	141	358	253	4.0836	0.720333	0.000007	0.712207	6.24	40.4	0.0932	0.511750	0.000006	0.511665	−15.5	−17.3	1766	2185	−0.53
CM102	141	363	230	4.5580	0.721268	0.000013	0.712198	3.83	23.6	0.0981	0.511704	0.000008	0.511614	−16.5	−18.2	1901	2264	−0.50
CM103	141	328	253	3.7438	0.719981	0.000009	0.712531	4.83	30.8	0.0947	0.511719	0.000014	0.511632	−16.1	−17.9	1828	2236	−0.52

Table 6 Lead isotopic compositions of K-feldspar from the Mesozoic granitic porphyries of the Caosiyao deposit.

Sample No.	Lithology	Mineral	Age (Ma)	$^{206}\text{Pb}/^{204}\text{Pb}$ (2 σ)	$^{207}\text{Pb}/^{204}\text{Pb}$ (2 σ)	$^{208}\text{Pb}/^{204}\text{Pb}$ (2 σ)	μ	ω
CM26	Monzogranite	K-feldspar	145	16.986 $\pm$ 0.002	15.362 $\pm$ 0.002	37.174 $\pm$ 0.005	9.2	37.1
CM27	Monzogranite	K-feldspar	145	17.177 $\pm$ 0.001	15.358 $\pm$ 0.001	37.225 $\pm$ 0.002	9.2	36.1
CM28	Monzogranite	K-feldspar	145	16.946 $\pm$ 0.001	15.351 $\pm$ 0.001	37.091 $\pm$ 0.003	9.2	36.9
CM29	Monzogranite	K-feldspar	145	17.147 $\pm$ 0.001	15.372 $\pm$ 0.001	37.222 $\pm$ 0.002	9.2	36.4
CM30	Monzogranite	K-feldspar	145	16.857 $\pm$ 0.001	15.349 $\pm$ 0.001	37.082 $\pm$ 0.003	9.2	37.4
CM32	Monzogranite	K-feldspar	145	16.813 $\pm$ 0.002	15.354 $\pm$ 0.001	37.080 $\pm$ 0.004	9.2	37.8
CM36	Monzogranite	K-feldspar	145	17.087 $\pm$ 0.002	15.373 $\pm$ 0.001	37.208 $\pm$ 0.003	9.2	36.7
CM38	Monzogranite	K-feldspar	145	16.972 $\pm$ 0.001	15.362 $\pm$ 0.001	37.126 $\pm$ 0.002	9.2	37.0
CM40	syenogranite	K-feldspar	149	16.630 $\pm$ 0.002	15.319 $\pm$ 0.002	36.841 $\pm$ 0.005	9.2	37.5
CM43	syenogranite	K-feldspar	149	16.705 $\pm$ 0.001	15.336 $\pm$ 0.001	36.980 $\pm$ 0.004	9.2	37.8
CM94	syenogranite	K-feldspar	141	16.791 $\pm$ 0.001	15.350 $\pm$ 0.001	37.079 $\pm$ 0.003	9.2	37.9
CM96	syenogranite	K-feldspar	141	16.820 $\pm$ 0.001	15.346 $\pm$ 0.001	37.084 $\pm$ 0.003	9.2	37.7
CM99	syenogranite	K-feldspar	141	16.791 $\pm$ 0.001	15.369 $\pm$ 0.001	37.129 $\pm$ 0.002	9.3	38.3
CM102	syenogranite	K-feldspar	141	16.799 $\pm$ 0.001	15.374 $\pm$ 0.001	37.168 $\pm$ 0.002	9.3	38.5
CM103	syenogranite	K-feldspar	141	16.819 $\pm$ 0.001	15.362 $\pm$ 0.001	37.127 $\pm$ 0.004	9.2	38.0

$\mu = ^{238}\text{U}/^{204}\text{Pb}$, $\omega = ^{232}\text{Th}/^{204}\text{Pb}$.

Table 7 Molybdenite Re–Os age of the major Mo deposits in the Yinshan–Yanshan–Liaoning Mo ore belt.

Deposit	Deposit type	Number	Model age ($\pm 2\sigma$) (Ma)	Ore-forming age (Ma)	Source of data
Sadaigoumen	Porphyry	6	234.0 $\pm$ 4.1–238.9 $\pm$ 3.5	236.5 $\pm$ 2.2	Jiang et al., 2014
Dasuji	Porphyry	4	222.1 $\pm$ 3.2–224.6 $\pm$ 3.4	222.5 $\pm$ 3.2	Zhang et al., 2009
		5	223.6 $\pm$ 3.1–224.2 $\pm$ 3.4	223.5 $\pm$ 5.5	Wu et al., 2014
Hekanzi	Porphyry–skarn	6	221.5 $\pm$ 3.2–225.3 $\pm$ 3.3	222.8 $\pm$ 3.2	Liu et al., 2012a
Yangjiazhangzi	Skarn	3	187 $\pm$ 2–191 $\pm$ 6	190–191	Huang et al., 1996
Lanjiagou	Porphyry	5	185 $\pm$ 4–192 $\pm$ 5	186.5 $\pm$ 0.7	Huang et al., 1996
		11	182.3 $\pm$ 2.9–184.3 $\pm$ 2.5	182.0 $\pm$ 6.5	Han et al., 2009
Xiaojiayingzi	Skarn	1	177 $\pm$ 5	177 $\pm$ 5	Huang et al., 1996
		6	159.1 $\pm$ 2.6–165.8 $\pm$ 2.8	165.6 $\pm$ 4.6	Dai et al., 2009
Caosiyao	Porphyry	6	147.4 $\pm$ 2.7–150.1 $\pm$ 3.0	148.3 $\pm$ 1.3	This study
Shouwangfan	Porphyry–skarn	1	148 $\pm$ 4	148	Huang et al., 1996
Dazhuangke	Explosion breccia	3	145 $\pm$ 11–147 $\pm$ 7	145–147	Huang et al., 1996
		5	136.0 $\pm$ 1.9–137.3 $\pm$ 1.9	136.8 $\pm$ 2.6	Liu et al., 2012b
Dacaoping	Quartz vein	5	138.9 $\pm$ 2.0–140.2 $\pm$ 2.5	140.1 $\pm$ 3.4	Jiang et al., 2014
Xiaosigou	Porphyry–skarn	1	134 $\pm$ 3	134	Huang et al., 1996