Molybdenite Re–Os age, H–O–C–S–Pb isotopes, and fluid inclusion study of the Caosiyao porphyry Mo deposit in Inner Mongolia, China

Guorui Wang ^{a, b}, Guang Wu ^{a,*}, Liquan Xu ^c, Xiangzi Li ^d, Tong Zhang ^c, Zhixin Quan ^d, Hao Wu ^e, Tiegang Li ^e, Jun Liu ^a, Yuchuan Chen ^f

^a*MLR Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing 100037, PR China*

^b*Wanbao Mining Ltd., Beijing 100053, PR China*

^c*Inner Mongolia Institute of Geological Survey, Hohhot 010020, PR China*

^d*No. 2 Geoexploration Party of Henan Bureau of Geoexploration and Mineral Development, Xuchang 461000, PR China*

^e*School of Earth Sciences and Resources, China University of Geosciences, Beijing 100083, PR China*

^f*Chinese Academy of Geological Sciences, Beijing 100037, PR China*

*Corresponding author at: MLR Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing 100037, China.

Tel: +86 010 68999857. E-mail address: wuguang65@163.com (G. Wu).

ABSTRACT

The giant Caosiya porphyry Mo deposit, located in the northern margin of the North China Craton, is a newly discovered Mo deposit in the Yan–Liao molybdenum belt. Orebodies of the deposit are mainly hosted in metamorphic rocks of the Mesoarchean Jining Group with a small amount of orebodies in the Late Jurassic syenogranite porphyry. The ore-forming process of the deposit can be divided into three stages: an early quartz–molybdenite±magnetite±pyrite stage, a middle quartz–molybdenite–pyrite±pyrrhotite±chalcopyrite stage, and a late quartz–carbonate–pyrite±fluorite±pyrrhotite stage. Molybdenite Re–Os dating indicates that the Caosiya deposit formed at ca. 150 Ma. Four types of fluid inclusions (FIs) have been distinguished in quartz phenocryst and various quartz veins including liquid-rich, gas-rich, H₂O–CO₂, and daughter mineral-bearing inclusions. The FIs in the quartz phenocrysts of the syenogranite porphyry contain liquid-rich, gas-rich, H₂O–CO₂, and daughter mineral-bearing types; their homogenization temperatures and salinities vary from 385°C to >550°C and 6.5 wt% to 65.0 wt% NaCl eqv., respectively. The FIs in the quartz of the early stage are also mainly liquid-rich, gas-rich, H₂O–CO₂, and daughter mineral-bearing types; their homogenization temperatures and salinities vary from 243°C to 401°C and 6.0 wt% to 39.8 wt% NaCl eqv., respectively. The FIs in the quartz of the middle stage are mainly liquid-rich, H₂O–CO₂, and daughter mineral-bearing types; their homogenization temperatures and salinities vary from 208°C to 336°C and 1.2 wt% to 34.1 wt% NaCl eqv., respectively. The FIs in the quartz of the late stage are only liquid-rich type; their homogenization temperatures and salinities vary from 124°C to 196°C and 3.9 wt% to 13.2 wt% NaCl eqv., respectively. The ore-forming fluids of

the Caosiyao deposit are characterized by moderate–high temperature and great fluctuating salinity, belonging to an $\text{H}_2\text{O}\text{--}\text{NaCl}\text{--}\text{KCl}\text{--}\text{MgCl}_2\text{--}\text{CO}_2\pm\text{CH}_4$ system. The $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ values of the early and middle stages vary from 3.5‰ to 7.4‰ and –96‰ to –77‰, respectively; the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ values of the late stage vary from –2.9‰ to –0.6‰ and –112‰ to –77‰, respectively; indicating that the ore-forming fluids of the early and middle stages mainly consist of magmatic water and that the fluid in late stage is a mixture of magmatic and meteoric water. The $\delta^{13}\text{C}$ values vary from –16.5‰ to –8.8‰ for the early and middle stages and –11.4‰ to –5.3‰ for the late stage, suggesting that the carbon of the early and middle stages consists of a mixture of organic and magmatic sources and that the carbon in the late stage was mainly from a magmatic source. The $\delta^{34}\text{S}$ values range from 4.0‰ to 6.1‰ with an average of 4.8‰. The $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of the metallic minerals are in the ranges of 15.962–17.832, 15.200–15.511, and 35.918–37.927, respectively. Both S and Pb isotopic systems indicate that the ore-forming metals came primarily from Mesozoic intermediate–felsic magma. The multi-stage boiling or immiscibility of the ore-forming fluids was the dominant mechanism for the deposition of ore-forming materials.

Keywords: Molybdenite Re–Os age; H–O–C–S–Pb isotopes; Fluid inclusions; Caosiyao porphyry Mo deposit; Inner Mongolia; Northern margin of the North China Craton.

1. Introduction

The Yanshan–Liaoning molybdenum belt (hereinafter referred to as the Yan–Liao Mo belt), which contains approximately 2.34Mt of Mo reserves, is located in the northern margin

of the North China Craton(Zeng et al., 2013). To date, more than twenty Mo deposits have been explored in northern Hebei and western Liaoning Provinces (Zeng et al., 2012a, 2012b). The Mo deposits in the Yan–Liao Mo belt are classified as porphyry-, skarn-, and quartz vein-types(Dai et al., 2009;Jiang et al., 2014). Recently, prospecting work of the Jining area,Inner Mongolia, which is located in the west segment of the northern margin of the North China Craton, has achieved a great breakthrough, and the large Dasuji (ca. 0.12Mt Mo) and giantCaosiyao (ca. 1.76Mt Mo) Mo deposits have been found at the westest of the Yan–Liao Mo belt (Huang et al., 2011; Nie et al., 2012; Wang et al., 2014; Wu et al., 2014), indicating that the Jining areahas great potential for prospecting of Mo deposits.

Comparison with the central and eastern parts of the Yan–Liao Mo belt, namelynorthern Hebei and western Liaoning Provinces, the researches of Mo depositsinthe Jining area are relatively weak. As for the Dasuji Mo deposit,previous studies mainly involved geological characteristics (Yu et al., 2008; Nie et al., 2012), ore-forming age (Zhang et al., 2009; Wu et al., 2014), and fluid inclusion property (Wu et al., 2014); as forthe Caosiyao Mo deposit, previous researchers mainly focused on geological characteristics of deposit(Li et al., 2012; Nie et al., 2012) and ore-forming age(Nie et al., 2013).The lack of fluid inclusion and isotopic data seriously limits our understanding of the deposit’s genesis type and ore-forming mechanism in the Jining area. In view of the above reasons, we selected the Caosiyao Mo deposit to carry out a systematic study of molybdenite Re–Os dating, fluid inclusions, and H–O–C–S–Pb isotopes. The purpose of this study is to classify the deposit type, determine the mineralization age, reveal the characteristics of the ore-forming fluids and their evolution, and discuss the sources of ore-forming fluids and metals of the CaosiyaoMo deposit.

2. Regional geology

The North China Craton (NCC) is located in the northern part of China and occurs as a wedge in shape (Fig. 1a). Its Precambrian basement can be divided into the Archean to Paleoproterozoic Western Continental Block (WCB), Eastern Continental Block (ECB), and three Paleoproterozoic mobile belts, which include the Khondalite Belt, the Trans-North China Orogen (TNCO), and the Jiao–Liao–Ji Belt (JLJB) (Fig. 1a; Zhao et al., 2005; Tang et al., 2011). The Mo deposits explored so far in the northern margin of the NCC are distributed primarily in the ECB and the TNCO with a small amount of deposits such as the Caosiyao and Dasuji deposits in the Khondalite Belt (Fig. 1b).

The Jining region, located in the eastern part of the Khondalite Belt (Fig. 1b), experienced continuous uplifting from the Late Archean to the Triassic, and the Precambrian metamorphic rocks are widely outcrop in the study area (Inner Mongolia Autonomous Region Bureau of Geology and Mineral Resource (IBGM), 1991; Nie et al., 2012).

The lithologies exposed in the Jining region are the Paleoproterozoic Xinghe Group, Mesoarchean Jining and Wulashan Groups, Lower Permian Zhusiwa Formation, Jurassic, Cretaceous, Paleogene, Neogene, and Quaternary (Fig. 1c). The Xinghe Group, which is distributed in the southeast of Xinghe County, comprises banded hypersthene–plagioclase granulite, two-pyroxene granulite, and diopside–magnetite quartzite. The Jining Group, which is widely distributed in the study area, is composed of sillimanite–garnet–K-feldspar gneiss, biotite–plagioclase gneiss, migmatite, and marble. The Wulashan Group, which is only distributed in the northwestern part of the area, comprises granulite, gneiss, and marble. The Zhusiwa Formation, which is sporadically distributed in the northern part of Fengzhen,

is composed of conglomerate, sandstone, shale with coal seams. The Jurassic strata are mainly distributed in the eastern part of Xinghe County, and the Cretaceous strata are mainly distributed in the southwestern and western parts of the study area. The Mesozoic strata, being composed of the Jurassic and Cretaceous, comprise tuffaceous andesite, tuff, siltstone, sandstone, conglomerate, and marlstone. The Paleogene–Neogene strata, including the Paleogene Wulangechu and Huerjing formations and the Neogene Hannuoba and Baogedawula formations, are widely distributed in the central part of the area. Except for the Hannuoba Formation basalt, these Paleogene–Neogene strata are mainly composed of sandstone, conglomerate, siltstone, mudstone, and shale with local coal seams. The Quaternary sediments are mainly distributed in the southeastern part of this area and consist of eolian sand (IBGM, 1991).

Fault structures are well developed in this area. The faults are mainly EW-, NEE, and NW-trending (Fig. 1c). The EW-trending Guyang–Wuchuan–Shangyi fault was considered as a lithosphere fault, formed at the Neoproterozoic–Paleoproterozoic in age, and the fault is the boundary of the southern Archean–Paleoproterozoic Liangcheng fault-uplift and northern Meso–Neoproterozoic Langshan–Chartaishan–Bayan Obo aulacogen. The NEE-trending Linhe–Baotou–Jining fault, being formed at Mesozoic era, separates the Wulashan and Daqingshan mountains in the north from the Hetuo plain in the south (IBGM, 1991). The NEE-trending Daihai–Huangqihai fault and NW-trending Shangdu–Xinghe–Weixian faults were formed in Mesozoic era and controlled the distribution of the Mesozoic volcanic–intrusive rocks (Nie et al., 2012). The Caosiyao Mo deposit is situated at the intersection part of the NEE-trending Daihai–Huangqihai fault, NW-trending

Shangdu–Xinghe–Weixian fault, and the subordinate structures derived from the two faults (Li et al., 2012; Nie et al., 2013).

Regional magmatism can be divided into the Mesoarchean, Neoproterozoic, Variscan, Mesozoic periods (Fig. 1c; IBGM, 1991). The Mesoarchean intrusive rocks, being mainly composed of tonalite, trondhjemite, and granodiorite (TTG), are widely distributed in the area and occur with greenstone together, forming the Archean granite–greenstone associations (IBGM, 1991; Zhao et al., 2005; Santosh et al., 2007; Tang et al., 2011). The Neoproterozoic intrusive rocks, which are sporadically distributed in the northeastern part of Xinghe County, mainly consist of anorogenic plagiogranite and rapakivi granite with some mafic dyke swarms (IBGM, 1991; Zhai and Liu, 2003). The Variscan granitoids, which are distributed in the northern part of the study area, are dominated by the Permian granodiorite, granite, and monzogranite (Nie et al., 2012). The Mesozoic intrusive rocks include the Indosinian and Yanshanian granitoids. The Indosinian granite is mainly exposed in northwestern part of the area, and the Indosinian granitic porphyries, being composed of granite porphyry, quartz porphyry, and syenogranite porphyry, are exposed in the Dasuji Mo ore district (Zhang et al., 2009). The Yanshanian intrusive rocks, which consist of granite and granite porphyry with small size, are mainly exposed in the south Xinghe County. The Caosiyao Mo deposit is related to the Yanshanian granite porphyry (Li et al., 2012; Nie et al., 2012).

3. Ore deposit geology

The Caosiyao porphyry Mo deposit, discovered by No. 2 Geoexploration Party of Henan

Bureau of Geoexploration and Mineral Development (HBGMD) in 2011, is located 4 km southeast of Xinghe County, Inner Mongolia, with coordinates of $113^{\circ}51'40''$ – $113^{\circ}54'00''$ longitude (east) and $40^{\circ}48'00''$ – $40^{\circ}49'40''$ latitude (north) (Fig. 1c). The deposit is the third largest Mo deposit in China with a reserve of ~ 1.75 Mt Mo and an average grade of 0.078% Mo (No. 2 Geoexploration Party, HBGMD, 2014).

The rocks exposed in the Caosiyao deposit are metamorphic rocks of the Mesoproterozoic Huangtuyao Formation of the Jining Group, sedimentary rocks of the Neogene (Baogedawula Formation) and Paleogene (Wulangechu and Huerjing formations), and the Quaternary sediments (Fig. 2a). The Huangtuyao Formation is composed of garnet-bearing leucogranulite and plagioclase gneiss, which are important ore-hosting rocks. The Paleogene–Neogene rocks are mainly composed of sandstone and conglomerate with minor siltstone and mudstone. There are three main fracture trends: NE, NW, and near SN. In general, the sizes of the fractures in the mine area are small. The NE- and NW-trending structural belts, which control the distribution of ore bodies, consist of cataclasite that is characterized by silicic, chlorite, sericite, ferrite, and pyrite alterations. The near SN-trending fault is filling with quartz veins (Li et al., 2012; Nie et al., 2013). The Yanshanian hypabyssal rocks, which present in the form of stocks and apophyses, consist of the late Jurassic syenogranite porphyry and early Cretaceous monzogranite porphyry and syenogranite porphyry, with zircon U–Pb ages of 148.5 ± 0.9 Ma, 145.0 ± 1.0 Ma, and 140.1 ± 1.7 Ma, respectively (Wu et al., 2016, this issue). There are medium–fine grained porphyritic granites occurring as batholith in the deep-seated drilling. These magmatic rocks are all intruded into the Huangtuyao Formation. It is noteworthy that the Late Jurassic syenogranite porphyry

shows a close spatial, temporal, and genetic relationship with the Mo ore bodies (Wang et al., 2014).

Mo orebodies are hosted in the contact zone of syenograniteporphyry of the Late Jurassic and metamorphic rocks of the Jining Group, and there are no clear boundaries between ore bodies and wall rocks. The orebodies are distributed in a zone that extends ~2000m from east to west and ~1600m from south to north, 400 to 900m in thickness, asymmetric dumbbell-shape in plane and arcuate in cross section (Fig.2b). There are molybdenum oxide belts, which are less than 150m in thickness, above the ore bodies(Li et al., 2012; Nie et al., 2013).

The ore minerals include molybdenite, pyrite, magnetite, chalcopyrite, and pyrrhotite(Fig.3). Molybdenite is the only economic ore mineral at the Caosiyao deposit. The gangue minerals are primarily quartz and sericite, with minor amounts of K-feldspar, muscovite, epidote, fluorite, and scapolite (Fig 4). Molybdenite is mainly of leaf-like (Fig. 3a, c, and d) and anhedral granular textures (Fig. 3b and e); pyrite is mainly of anhedral granular(Fig. 3 c, e, and f), euhedral–subhedral granular(Fig. 3g and h), and poikilitic textures (Fig. 3e); magnetite is mainly of anhedral granular texture (Fig. 3b and c); chalcopyrite is primarily of anhedral granular(Fig. 3f); pyrrhotite is chiefly of anhedral granular texture (Fig. 3f–h) and usually replaces molybdenite, pyrite, and chalcopyrite, developing a metasomatic dissolution texture (Fig. 3f). The ore structure is primarily veinlet, disseminated, and veinlet disseminated structures, with a small amount of densely disseminated structure(Fig 3i–l).

The hydrothermal alteration is well developed, such as silicification, sericitization, K-feldspathization, biotitization, muscovitization, fluoritization, argillization, and carbonation

(Fig. 4). The silicic and sericitic alterations are the predominant alteration of the Caosiyao deposit, and are closely related to the molybdenite mineralization (Fig 4a–e). The potassic alteration could only be observed in the Jurassic syenogranite porphyry (Fig 4b). The silicic and sericitic alterations, which were usually superimposed by the argillic alteration characterized by the kaolinite and montmorillonite, are present at the peripheral of the potassic alteration zone. A small amount of chlorite, epidote, scapolite, and carbonate alterations could only be detected in metamorphic rocks of the Jining Group (Fig. 4f).

On the basis of the mineral assemblages, ore fabrics, and cross-cutting relationships between the veins, the ore-forming process in the Caosiyao deposit can be preliminarily divided into the following three stages: (1) an early quartz–molybdenite±magnetite±pyrite stage; (2) a middle quartz–molybdenite–pyrite±pyrrhotite±chalcopyrite stage; and (3) a late quartz–carbonate–pyrite±fluorite±pyrrhotite stage.

4. Samples and analytical methods

4.1. Molybdenite Re–Os measurements

The five molybdenite samples used for the Re–Os dating were from the early and middle stages, taken at 416.7-m underground in borehole No. 0403, 458.0-, 474.0-, and 494.0-m underground in borehole No. 0808, and 262.5-m underground in borehole No. 1208 of the Caosiyao Mo deposit, respectively. The molybdenite occurs mainly as disseminated or veinlet minerals in quartz with a small amount of densely disseminated or massive ores (Fig. 3i–k).

The crushing of samples and separation and purification of molybdenites were carried

out at the Langfang Regional Geological Survey, Hebei Province, China. The decomposition of the molybdenites, the pretreatment of the purification and separation of Re–Os, and the inductively coupled plasma-mass spectrometry (ICP-MS) analysis of Re–Os content were conducted at the National Research Center for Geoanalysis (Beijing). The Re, ^{187}Re , and ^{187}Os contents were measured with the TJA PQ ExCell ICP-MS (TJA Co, USA). Chemical separation and mass spectrometry of Re–Os followed the procedures described by Du et al. (1994) and Shirey and Walker (1995). Concerning more detailed methods and processes of sample decomposition, distillation separation of Os, extraction separation of Re, and mass spectrometry, the reader is referred to Wu et al. (2016, this issue). The Re–Os model age is 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).

4.2. Fluid inclusion microthermometry and laser Raman spectroscopy

Fifteen samples were selected for fluid inclusion analyses, including syenogranite porphyry and veins of the early, middle, and late stages. Samples CM25, CM34, and CM37, collected from 813.9-m, 779.6-m, and 785.3-m drilling core underground in drill hole No. 1600, respectively, are syenogranite porphyry; samples CM54, CM55, CM56, CM61, CM76, and CM87, collected from 266.2-m, 265.1-m, 271.8-m, 292.0-m, 460.6-m, and 604.0-m drilling core underground in drill hole No. 1600, respectively, are all the early stage veins; samples CM67, CM73, and CM93, collected from 373.2-m, 451.4-m, and 751.9-m drilling core underground in drill hole No. 1600, respectively, are all the middle stage veins; samples CM68, CM80, and CM84, collected from 401.1-m, 476.8-m, and

522.5-mdrilling core underground in drill hole No. 1600, respectively, are all the late stage veins.

Microthermometric measurements were conducted using a Linkam THMSG 600 heating-freezing stage mounted on an Olympus BX-50 microscope at the China University of Geosciences, Beijing. The estimated accuracies of the freezing and heating measurements were $\pm 0.1^{\circ}\text{C}$ from -100°C to 25°C , $\pm 1^{\circ}\text{C}$ from 25°C to 400°C , and $\pm 2^{\circ}\text{C}$ above 400°C , respectively. Heating and freezing rates were generally $0.2\text{--}5^{\circ}\text{C}/\text{min}$, but these were reduced to less than $0.2^{\circ}\text{C}/\text{min}$ near the temperatures of phase transitions. Salinity of aqueous and $\text{H}_2\text{O}\text{--}\text{CO}_2$ fluid inclusions were calculated by using the ice points (Bodnar, 1993) and final melting temperatures of CO_2 clathrate (Collins, 1979), respectively. Salinities of halite-bearing fluid inclusions were calculated by using the dissolution temperatures of daughter minerals (Hall et al., 1988). The densities of aqueous fluid inclusions were calculated with the equation of Liu and Duan (1987); the densities of $\text{H}_2\text{O}\text{--}\text{CO}_2$ fluid inclusions were obtained from the phase diagrams of Shepherd et al. (1985); the densities of halite-bearing fluid inclusions were calculated with the equation of Liu (2001).

Volatile compositions of single fluid inclusions were identified by using a Renishaw in Via laser Raman probe at the Laboratory of Fluid Inclusion, Institute of Mineral Resources, Chinese Academy of Geological Sciences (CAGS). The wavelength of the Ar^+ laser was 514.5nm and the measured spectrum time was 20s. The counting rate was one per centimeter. The spectrum diagram was taken from the wave band of $100\text{--}4000\text{cm}^{-1}$. The spectrum resolution was $\pm 2\text{cm}^{-1}$ with a beam size of $1\mu\text{m}$. Instrumental setting was kept constant during all analyses.

4.3. H–O–C–S–Pb isotopes

Nineteen quartz samples from the early, middle, and late stages were analyzed for O (quartz), H (fluid inclusions), and C (CO₂ in fluid inclusions) isotopes. Of these, samples CM62, CM63, CM64, CM74, CM82, CM83, CM85, CM87, and CM88, collected from 292.0-m, 296.0-m, 294.1-m, 453.1-m, 506.8-m, 508.9-m, 531.3-m, 604.0-m, and 610.5-m drilling core underground in drill hole No. 1600, respectively, are veins of the early stage; samples CM73, CM75, CM77, and CM93, collected from 451.4-m, 456.0-m, 461.9-m, and 751.9-m drilling core underground in drill hole No. 1600, respectively, are veins of the middle stage; samples CM68, CM69, CM70, CM78, CM80, and CM84, collected from the 401.1-m, 413.0-m, 422.3-m, 473.4-m, 476.8-m, and 522.5-m drilling core underground in drill hole No. 1600, respectively, are veins of the late stage. The H–O–C isotope analyses were accomplished with a MAT253 mass spectrometer at the Analytical Laboratory of the Beijing Research Institute of Uranium Geology. The accuracy of the O isotope analysis is better than $\pm 0.2\text{‰}$, that of the H isotope analysis is better than $\pm 2\text{‰}$, and that of the C isotope analysis is typically better than $\pm 0.1\text{‰}$. The amount of O in quartz water ($a_{\text{quartz water}}$) was calculated from the O isotope level of the analyzed quartz by using the fractionation equation $1000 \ln a_{\text{quartz water}} = (3.38 \times 10^6) T^{-2} - 3.40$, where T is the temperature in kelvins (Clayton et al., 1972), and the average fluid inclusion temperature of each stage was used to calculate the $\delta^{18}\text{O}_{\text{water}}$ value.

The S–Pb isotopic tests were conducted for 20 sulfide samples from the early, middle, and late stages, including nine molybdenites and eleven pyrites. Of these, samples CM54, CM55, CM57, CM61, CM65, CM76, CM87, and CM76, collected from 266.2-m, 265.1-m, 275.1-m, 292.0-m, 363.0-m, 460.6-m, 604.0-m, and 460.6-m drilling core underground in drill

hole No. 1600, respectively, are ores of the early stage; samples CM67, CM93, CM49, CM51, CM73, and CM75, collected from 373.2-m, 751.9-m, 202.7-m, 214.3-m, 451.4-m, and 456.0-m drilling core underground in drill hole No. 1600, respectively, are ores of the middle stage; samples CM68, CM71, CM72, CM79, CM89, and CM90, collected from the 401.1-m, 448.3-m, 449.2-m, 469.0-m, 613.7-m, and 623.9-m drilling core underground in drill hole No. 1600, respectively, are pyrite of the late stage. The S and Pb isotopic analyses were undertaken at the Analytical Laboratory of the Beijing Research Institute of Uranium Geology. The S isotopic analyses were performed using a Delta v plus mass spectrometer with an analytical precision of better than $\pm 0.2\%$. GBW-04414 and GBW-04415 silver sulfide standards were used as sulfide references, and the $\delta^{34}\text{S}$ values were $-0.07 \pm 0.13\%$ and $22.15 \pm 0.14\%$, respectively. The Pb isotope was measured using an IsoProbe-T multi-collector thermal ionization mass spectrometer, and the measurement accuracy was better than 0.005% (2σ) for $1\mu\text{g}$ of $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$. The Pb-isotopic analyses are 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 Re–Os isotope results of five molybdenites from the Caosiyao Mo deposit are given in Table 1. The Re content of the molybdenites lies in a range from 9.065 ppm to 13.720 ppm, and the Re–Os model ages are between 150.9 ± 2.2 and 148.6 ± 2.2 Ma. The Re–Os isochron age is $152.5 \pm 5.6\text{Ma}$ (2σ), with an initial ^{187}Os of -0.29 ± 0.61 , and the mean squared weighted

deviation (MSWD) is 0.86(Fig. 5a). The model age weighted average is 149.8 ± 1.0 Ma, which is slightly smaller than the isochron age, and the MSWD is 0.61(Fig. 5b). Because the uncertainty in the isochron age is larger than that of the model age-weighted average, we used the model age-weighted average as the crystallization age of the molybdenite, and therefore the age of Mo mineralization of the Caosiyao deposit is 149.8 ± 1.0 Ma.

5.2. Fluid inclusions

5.2.1. Petrography

Based on phase characteristics at room temperature, phase transitions during heating, and the results of laser Raman spectroscopy, Fls in the Caosiyao deposit are divided into following four major types:

(1)Liquid-rich inclusions (WL type): These are extensively hosted in the tested quartz phenocrysts and various types of quartz veins. The inclusions are oval, polygonal, and irregular, with diameters of 3–29 μ m, mainly 5–20 μ m, and contain gas bubbles which accounting for 5–45% of the total volume. These inclusions can be homogenized to liquid when heated. Inclusions of this type account for approximately 60% of the total number of inclusions and are distributed in groups or alone in quartz phenocryst and quartz crystal at various stages (Fig. 6a, d, and f).

(2)Gas-rich inclusions (WG type): These are mainly hosted in quartz phenocryst and quartz of the early stage with a small amount of WG-type inclusions being hosted in quartz of the middle stage. The inclusions are oval or irregular with sizes of 4–18 μ m, mainly approximately 10 μ m in size, and have bubbles usually accounting for 50–85% of the total

volume. These fluid inclusions were homogenized to vapor when heated. Inclusions of this type comprise approximately 20% of the total number of inclusions and are mainly distributed alone (Fig. 6b and d).

(3)H₂O–CO₂ inclusions (C type): These inclusions are irregular and 3–16μm in size, with a CO₂ content of approximately 25–80% of the total volume of inclusions; when heated, most of C-type inclusions can be homogenized to liquid CO₂ while a small number of inclusions can be homogenized to gaseous CO₂. Inclusions of this type account for less than 10% of the total number of inclusions and are distributed as isolated or in group in quartz phenocryst of the syenogranite porphyry and in quartz of the early and middle stages (Fig.6c).

(4) Daughter mineral-bearing inclusions (S type): These are infrequently hosted in quartz phenocryst and quartz of the early and middle stages. The inclusions are oval or irregular, generally measure 3–13μm in size, and contain bubbles generally accounting for 5–30% of the total volume. These inclusions may contain one, two, or three daughter minerals, which can be halite or metallic minerals (Fig.6d and e). Halite is light blue and cube-shaped; and metallic minerals are opaque. Inclusions of this type account for less than 10% of the total number of inclusions and are distributed alone or coexist with other types of inclusions.

5.2.2. Microthermometry

The microthermometric results and FI parameters are shown in Table 2 and Fig 7.

Fluid inclusions in quartz phenocryst of syenogranite porphyry (samples CM25, CM34, and CM37): The final ice melting temperature of WL-type FIs is –8.8°C to –7.1°C, the salinity is 10.6–12.6 wt% NaCl eqv., the homogenization temperature is 385–436°C, the fluid density is 0.60–0.72 g/cm³, and the eutectic temperature ranges from

–35.4°C to –29.3°C, which is obviously lower than the eutectic temperature of an H₂O–NaCl system (–20.8°C) or an H₂O–NaCl–KCl system (–22.9°C) but close to that of an H₂O–NaCl–KCl–MgCl₂ system, indicating that the fluid roughly belonged to an H₂O–NaCl–KCl–MgCl₂ system. The final ice melting temperature of WG-type FIs is –11.8°C to –7.6°C, the salinity is 11.2–15.8 wt% NaCl eqv., the homogenization temperature ranges from 388°C to 482°C, and the fluid density is 0.56–0.68 g/cm³. The initial melting temperature of C-type FIs is –66.9°C to –60.2°C, the melting temperature of clathrate is 3.8–6.6°C, the salinity is 6.5–10.9 wt% NaCl eqv., the homogenization temperature of the CO₂ phase is 9.6–30.6°C, the homogenization temperature is 471°C, and the fluid density is 0.51–0.97 g/cm³. The bubble-disappearing temperature of S-type FIs ranges from 233°C to >550°C, the disappearing temperature of halite daughter minerals is 304°C to >550°C, the salinity is 38.5–65.0 wt% NaCl eqv., and the fluid density is 1.08–1.21 g/cm³ (Table 2; Fig. 7a and b). For S-type FIs in these quartz phenocrysts, daughter minerals disappeared before and after the disappearance of bubbles, indicating that part of the ore-forming fluids is oversaturated with salt.

Fluid inclusions in quartz of the early stage (samples CM54, CM55, CM56, CM61, CM76, and CM87): The final ice melting temperature of WL-type FIs is –10.8°C to –4.8°C, the salinity is 7.6–14.8 wt% NaCl eqv., the homogenization temperature is 243–395°C, the fluid density is 0.70–0.90 g/cm³, and the eutectic temperature ranges from –33.1°C to –29.1°C, indicating that the ore-forming fluid of the early stage roughly belonged to an H₂O–NaCl–KCl–MgCl₂ system. In WG-type FIs, ice did not noticeably melt in the measurement. There was no measurement of final ice melting temperature, and the

homogenization temperature is 328–401°C. The initial melting temperature of C-type FIs is –65.7°C to –60.7°C, the melting temperature of clathrate is 4.1–6.8°C, the salinity is 6.0–10.3 wt% NaCl eqv., the homogenization temperature of the CO₂ phase is 9.7–30.4°C, the homogenization temperature is 302–365°C, and the fluid density is 0.42–0.94 g/cm³. The bubble-disappearing temperature of S-type FIs is 202–354°C, the disappearing temperature of halite daughter minerals is 236–321°C, the homogenization temperature is 276–354°C, the salinity is 33.8–39.8 wt% NaCl eqv., and the fluid density is 1.02–1.09 g/cm³ (Table 2; Fig. 7c and d). The different disappear types of the daughter minerals within the S-type FIs, before or after the disappearance of bubbles, indicate that some ore-forming fluids are oversaturated salt solutions while the others are nonsaturated.

Fluid inclusions in quartz of the middle stage (samples CM67, CM73, and CM93): The final ice melting temperature of WL-type FIs is –8.9°C to –0.7°C, the salinity is 1.2–12.7 wt% NaCl eqv., the homogenization temperature is 208–336°C, the fluid density is 0.76–0.95 g/cm³, and the eutectic temperature ranges from –35.2°C to –32.3°C, indicating that the ore-forming fluid of the middle stage roughly belonged to an H₂O–NaCl–KCl–MgCl₂ system. In WG-type FIs, because the percentage of bubble volume is >80%, bubbles changed weakly in the measurement, and there was no observable ice melting. Therefore, we didn't obtain final ice melting temperature and homogenization temperature of the WG-type FIs. The initial melting temperature of C-type FIs is –60.9°C to –60.4°C, the melting temperature of clathrate is 6.7–7.7°C, the salinity is 4.5–6.3 wt% NaCl eqv., the homogenization temperature of the CO₂ phase is 29.2–30.8°C, the homogenization temperature is 310°C, and the fluid density is 0.70–0.81 g/cm³. The bubble-disappearing temperature of S-type FIs is 168–292°C, the

disappearing temperature of halite daughter minerals is 132–247°C, the homogenization temperature is 228–292°C, the salinity is 29.0–34.1 wt% NaCl eqv., and the fluid density is 1.06–1.14 g/cm³(Table 2; Fig. 7e and f).

Fluid inclusions in quartz of the late stage(samples CM68, CM80, and CM84): The final ice melting temperature of WL-type FIs is –9.3°C to –2.3°C, the salinity is 3.9–13.2 wt% NaCl eqv., and the homogenization temperature is 124–196°C, the fluid density is 0.93–1.03 g/cm³(Table 2; Fig. 7g and h).The eutectic temperature ranges from –35.3°C to –34.9°C, indicating that the hydrothermal fluid of the late stage also roughly belonged to an H₂O–NaCl–KCl–MgCl₂ system.

5.2.3. Laser Raman spectra analysis

We conducted a laser Raman spectroscopic peak scan of gas phase components for fluid inclusions in quartz phenocrysts of syenograniteporphyry and quartz of the three metallogenic stages of the Caosiyao deposit. The results of representative laser Raman spectroscopic analyses are shown in Fig. 8. The primary gas components of WL-type FIs in quartz phenocrysts of syenograniteporphyry are mainly H₂O and CO₂(Fig. 8a). The main gas components of WG-type FIs in quartz phenocrysts are mainly CO₂ and CH₄(Fig. 8b). The gas components of WL-type FIs in quartz of the early stage are mainly H₂O and CO₂(Fig. 8c). The gas components of C-type FIs in quartz of the early stage are mainly CO₂(Fig. 8d). The gas components of S-type FIs inclusions in quartz of the middle stage and WL-type FIs in quartz of the late stage are both mainly H₂O(Fig. 8e and f). In general, from quartz phenocryst to the early stage, later, to the middle stage, and last, to the late stage, the CO₂ and CH₄ contents of the ore-forming fluids gradually decrease, evolving from an early

H₂O–NaCl–KCl–MgCl₂–CO₂–CH₄ system through a middle H₂O–NaCl–KCl–MgCl₂–CO₂ system into a last H₂O–NaCl system, with ore-forming fluids generally having affinities to an H₂O–NaCl–KCl–MgCl₂±CO₂±CH₄ system.

5.3. Isotopes systematics

5.3.1. Hydrogen and oxygen isotopes

The analytical results for oxygen isotopes in 19 quartz samples and hydrogen isotopes in fluid inclusions of 14 quartz samples from the Caosiyao deposit are shown in Table 3. Of these, the $\delta^{18}\text{O}(\text{‰})$ values of quartz in nine samples from the early stage are 9.3–13.3, and $\delta\text{D}(\text{‰})$ values for seven samples are between –96 and –77, and the calculated $\delta^{18}\text{O}_{\text{water}}(\text{‰})$ values are between 3.5 and 7.4; the $\delta^{18}\text{O}(\text{‰})$ values of quartz in four samples from the middle stage are 12.3–14.2, the $\delta\text{D}(\text{‰})$ value for one sample is –85, and the calculated $\delta^{18}\text{O}_{\text{water}}(\text{‰})$ values are between 4.3 and 6.2; the $\delta^{18}\text{O}(\text{‰})$ values of quartz in the six samples from the late stage are 11.6–14.0, the $\delta\text{D}(\text{‰})$ values are between –112 and –77, and the calculated $\delta^{18}\text{O}_{\text{water}}(\text{‰})$ values are between –2.9 and –0.6. In the H–O isotopic composition diagram (Fig. 9), the early and middle ore-forming stage samples are projected to the region of magmatic water, or its vicinity, whereas the late stage samples are plotted between the magmatic water zone and meteoric water line. The H–O isotopic compositions indicate that the ore-forming hydrothermal fluids of the Caosiyao deposit were mainly magmatic water and were diluted by meteoric water in the late stage.

5.3.2. Carbon isotopes

Carbon isotopic compositions for CO₂ of fluid inclusions in 12 quartz samples from the Caosiyao deposit are shown in Table 3 and Fig. 10.

The $\delta^{13}\text{C}$ (‰) values of CO_2 of fluid inclusions in six samples from the early stage vary from -16.5 to -8.8 , averaging -12.8 . The $\delta^{13}\text{C}$ (‰) value of CO_2 of fluid inclusion in one sample from the middle stage is -9.3 . The $\delta^{13}\text{C}$ (‰) values of CO_2 of fluid inclusions in five samples from the late stage vary from -11.4 to -5.3 , averaging -7.7 . In general, the C isotope of the hydrothermal fluids gradually increases from the early stage to the middle stage, and then to the late stage.

5.3.3. Sulfur isotopes

Sulfur isotopic compositions for nine molybdenite samples and eleven pyrite samples from the Caosiyao deposit are shown in Table 4 and Fig. 11.

The $\delta^{34}\text{S}$ (‰) values are between 4.6 and 6.1 with an average of 5.2 for seven molybdenite samples and 4.6 for one pyrite sample from the early stage; the $\delta^{34}\text{S}$ (‰) values range from 4.9 to 5.3 with an average of 5.1 for two molybdenite samples and 4.2 to 5.4 with an average of 4.9 for four pyrite samples from the middle stage; and the $\delta^{34}\text{S}$ (‰) values range from 4.0 to 5.2 with an average of 4.4 for six pyrite samples from the late stage. In general, the S isotopic composition of sulfides in the Caosiyao deposit is slightly larger than that of mantle and very concentrated, indicating that the S sources of sulfides in the Caosiyao deposit were undiversified and mainly deeply sourced felsic magma sulfur.

5.3.4. Lead isotopes

Lead isotopic compositions for nine molybdenite samples and 11 pyrite samples from the Caosiyao deposit are shown in Table 4 and Fig. 12.

The $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of nine molybdenite samples range from 15.962 to 17.695 , 15.200 to 15.475 , and 35.918 to 37.757 , respectively. The $^{206}\text{Pb}/^{204}\text{Pb}$,

$^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of 11 pyrite samples range from 16.345 to 17.832, 15.308 to 15.511, and 36.464 to 37.927, respectively. In the $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{207}\text{Pb}/^{204}\text{Pb}$ diagram of Zartman and Doe(1981)(Fig. 12a), the Pb isotopic compositions of the Caosiyao deposit are primarily projected in the area between the orogenic belt and lower crust evolution lines; in the $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$ diagram(Fig. 12b), almost all of the projected data points are also located between the orogenic belt and lower crust evolution lines.

6. Discussion

6.1. Mineralization age

Molybdenite Re–Os dating is the only direct method to routinely date a sulfide mineral with a high internal precision (<0.2%) throughout the geologic time scale (Chiaradia et al., 2013). Concerning the formation age of the Caosiyao Mo deposit, previous researchers have reported two sets of molybdenite Re–Os age data: Nie et al. (2013) reported a weighted mean Re–Os age of 130.4 ± 2.4 Ma for four molybdenite samples; Wu et al. (2016, this issue) reported a Re–Os isochron age of 148.3 ± 1.3 Ma and a weighted mean Re–Os age of 148.5 ± 1.1 Ma for six molybdenite samples. However, the two groups of ages are significantly inconsistent; and therefore the ore-forming age of the deposit still needs further study. We obtained a Re–Os isochron age of 152.5 ± 5.6 Ma and a weighted mean Re–Os age of 149.8 ± 1.0 Ma for five molybdenite samples from the Caosiyao Mo deposit in this study. In addition, Wu et al. (2016, this issue) reported a zircon LA-ICP-MS U–Pb age of 148.5 ± 0.9 Ma for a syenogranite porphyry intrusion related to the Mo mineralization of the Caosiyao deposit. Our molybdenite Re–Os age is consistent with those molybdenite Re–Os and zircon U–Pb ages

obtained by Wu et al. (2016, this issue) within the error range, we, therefore, think that the Caosiyao Mo deposit formed in the late Jurassic (~149–150 Ma) rather than the early Cretaceous (~130 Ma) proposed by Nie et al. (2013).

As for the Dasuji porphyry Mo deposit, which is located in the west part of the Jining area, Zhang et al. (2009) obtained a molybdenite Re–Os isochron age of 222.5 ± 3.2 Ma, and Wu et al. (2014) reported a molybdenite Re–Os isochron age of 223.5 ± 5.5 Ma. The molybdenite Re–Os isochron ages indicate that the Dasuji Mo deposit formed in the Indosinian period.

Considering the Re–Os age obtained by us in this study and other geochronological data obtained by other researchers together, we conclude that important porphyry Mo mineralization in the Jining area mainly occurred in two periods: late Triassic and late Jurassic.

6.2. Nature and evolution of the ore-forming fluid

The quartz phenocrysts in syenogranite porphyry contain WL-, WG-, C-types as well as a few S-type fluid inclusions. The ore-forming fluids are characterized by high temperatures (385–550°C, averaging 439°C) and large variation in salinity (6.5–65.0 wt% NaCl eqv.) and contain CO₂. Laser Raman spectroscopy indicated a minor amount of CH₄ in individual fluid inclusions, thus the ore-forming fluid in the quartz phenocrysts is an H₂O–NaCl–KCl–MgCl₂–CO₂–CH₄ system.

The fluid inclusions in the early stage are mainly WL-type, with abundant of WG-, C-, and S-types fluid inclusions. The ore-forming fluids are characterized by moderate–high temperatures (243–401°C, averaging 333°C) and large variation in salinity (6.0–39.8 wt%

NaCl eqv.). Laser Raman spectroscopy identified significant amount of CO₂ in the gaseous phase of WL-type inclusions, thus the ore-forming fluid of the early stage belongs to an H₂O–NaCl–KCl–MgCl₂–CO₂ system.

The fluid inclusions in the middle stage are mainly WL-type inclusions with minor amounts of WG-, C-, and S-types inclusions. The ore-forming fluids are characterized by moderate temperatures (208–336°C, averaging 274°C) and large variation in salinity (1.2–34.1 wt% NaCl eqv.). Laser Raman spectroscopic analyses indicate that the middle stage ore-forming fluid belongs to an H₂O–NaCl–KCl–MgCl₂–CO₂ system.

There are only WL-type aqueous inclusions in the late stage. The ore-forming fluids are characterized by relatively low temperatures (124–196°C, averaging 162°C) and low salinity (3.9–13.2 wt% NaCl eqv.). Laser Raman spectroscopy identified only H₂O in the gaseous phase of WL-type inclusions, indicating that the ore-forming fluid belongs to an H₂O–NaCl–KCl–MgCl₂ system.

In summary, the ore-forming fluids in the Caosiyao deposit were characterized by moderate–high temperature and high salinity magmatic hydrothermal fluids and generally belong to an H₂O–NaCl–KCl–MgCl₂–CO₂±CH₄ system. The temperature and salinity of the hydrothermal fluids gradually decreased from the quartz phenocrysts in syenogranite porphyry, through the early and middle stages, and then to the late stage. The composition of ore-forming fluids from early to late becomes more and more simple.

6.3. Sources of ore-forming fluids and ore-forming materials

6.3.1. Source of ore-forming fluids

The δ¹⁸O values of quartz in the Caosiyao deposit range from 9.3‰ to 14.2‰, with

average 12.4‰(Table 3). This range is largely consistent with the $\delta^{18}\text{O}$ values of crust-remelting type granite (10.0–12.0‰; Chen et al., 2000a), indicating that the formation of hydrothermal quartz in the deposit was associated with the Yanshanian felsic intrusive rocks and was derived from magmatic fluids. The $\delta^{18}\text{D}$ values of the ore-forming fluids of the early and middle stages range from –96‰ to –77‰, and the $\delta^{18}\text{O}_{\text{water}}$ values range from 3.5‰ to 7.4‰; the $\delta^{18}\text{D}$ values of the hydrothermal fluids of the latest stage range from –112‰ to –77‰, and the $\delta^{18}\text{O}_{\text{water}}$ values range from –2.9‰ to –0.6‰. As shown in Fig. 9, the majority of the H–O isotope data of the early and middle stages are plotted in the magmatic domain and its vicinity, and the H–O isotope data of the latest stage are plotted between the magmatic water field and the meteoric water line, indicating that the ore-forming fluid of the Caosiyao deposit was derived from the Yanshanian magmatic hydrothermal fluids and that the hydrothermal fluid of the latest stage was a mixed fluid between meteoric water and magmatic water.

The $\delta^{13}\text{C}$ values of CO_2 in the ore-forming fluids of the early and middle stages of the Caosiyao deposit vary from –16.5‰ to –8.8‰ with an average of –12.3‰, and the $\delta^{13}\text{C}$ values of CO_2 in the hydrothermal fluids of the late stage of the Caosiyao deposit range from –11.4‰ to –5.3‰ with an average of –7.7‰. In general, there are three major carbon reservoirs in the earth: marine carbonate with a $\delta^{13}\text{C}$ mean of 0‰ (Ohmoto, 1986); carbonatite with $\delta^{13}\text{C}$ values varying from –7‰ to –3‰, averaging –5‰ (Taylor et al., 1967; Hoefs, 1987); and organic matter having a $\delta^{13}\text{C}$ mean of –25‰ (Faure, 1986). The $\delta^{13}\text{C}$ values of the early–middle stage ore-forming fluids in the Caosiyao deposit range between the carbonatite carbon and organic matter carbon (Fig. 10a), implying a mixed origin. Klein et al.

(2008), Zoheir et al. (2008), and Tomilenko et al. (2010) pointed out that hydrothermal fluid could mix stratigraphic carbon through reaction: $2C + 2H_2O = CH_4 + CO_2$. Wang (1989; 1994) and Chen et al. (2000b) studies indicated that central Inner Mongolia developed carbon-bearing khondalite series and formed many graphite deposits in the Jining area. The $\delta^{13}C$ values of graphite in the graphite deposits vary from range -29.0‰ to -6.4‰ (Fig. 10b). We, therefore, infer that the carbon of the ore-forming fluids in the Caosiyao deposit was derived from deeply source and was magmatic carbon. The magmatic carbon-bearing hydrothermal fluids developed fluid–rock reactions with carbonaceous strata and/or graphite in ascending process, forming the early and middle stage ore-forming fluids. As for the late stage fluids of the Caosiyao deposit, they are difficult to react with country rocks because of the relatively low fluid temperature. Therefore, the $\delta^{13}C$ values of fluid inclusion CO_2 of the late stage more retain signatures of the original fluid, representing isotope characteristics of a deeply sourced carbon, most likely derived from the late Jurassic felsic magma.

6.3.2. Source of ore-forming materials

Ohmoto (1972) proposed that S isotopic composition of sulfides in a hydrothermal deposit is a function of the total S isotopic composition ($\delta^{34}S_{\Sigma}$) of the ore-forming solution, oxygen fugacity (f_{O_2}), pH, ionic strength, and temperature; that is, the S isotopic composition of hydrothermal sulfides depends not only on the $\delta^{34}S$ value of source materials but also on the physical and chemical evolution of the ore-forming fluid. Therefore, the S sources must be determined based on the total S isotopic signature of the hydrothermal fluids when the sulfides were deposited. However, when the hydrothermal fluids are dominated by H_2S with low oxygen fugacity and low pH values, the relationship $\delta^{34}S_{\Sigma} \approx \delta^{34}S_{H_2S} \approx \delta^{34}S_{pyrite}$ holds in

the equilibrium state (Ohmoto, 1972). Silicification–sericitization is the most important alteration type in the Caosiyao deposit. Except for minor magnetite in the ore-forming early stage, the sulfide assemblage in the Caosiyao deposit is dominated by molybdenite and pyrite with a small amount of chalcopyrite and pyrrhotine, and no sulfate minerals have been detected. Therefore, the hydrothermal system during the ore-forming process in the Caosiyao deposit was dominated by H_2S ; molybdenite, pyrite, chalcopyrite, and pyrrhotine were formed under low- f_{O_2} and low-pH conditions. According to Table 4, the average $\delta^{34}S$ value for nine molybdenite samples from the Caosiyao deposit is 5.2‰, and the average $\delta^{34}S$ value for eleven pyrite samples is 4.6‰. The basic sequence is consistent with the $\delta^{34}S$ enrichment condition of $\delta^{34}S_{Mo} > \delta^{34}S_{Py}$ at isotopic equilibrium, indicating that the mineral S isotopes had reached equilibrium (Ohmoto, 1986). Therefore, the S isotopic compositions of pyrite are similar to the total S isotopic compositions of the hydrothermal system and can be used to trace the S sources. The overall range of the $\delta^{34}S$ values of sulfides in the Caosiyao deposit is narrow, indicating that the S sources of sulfides deposited in the ore-forming hydrothermal fluids were undiversified. The $\delta^{34}S_{Py}$ values are slightly higher than that of the meteorite S but consistent with that of the felsic magma (Ohmoto and Rye, 1979), indicating sulfur in the Caosiyao deposit was mainly derived from the late Jurassic intrusive rocks.

The Pb isotope data are useful geochemical tracers and can indicate crustal evolution, a source of lead, and deposit genesis (Lu et al., 2000). The sulfide minerals of the Caosiyao deposit are characterized by low–medium radiogenic Pb isotope values and medium μ values (between 9.0 and 9.4, which is lower than 9.6 in the upper crust, but obviously higher than the range of 8–9 in the mantle; Doe and Zartman, 1979), implying that Pb was derived from the

lower crust. In the $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{207}\text{Pb}/^{204}\text{Pb}$ diagram (Fig. 12a), the Pb isotopic compositions of the Caosiyao deposit are projected primarily toward the area between the orogenic belt and the lower crust evolution lines; in the $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$ diagram (Fig. 12b), almost all of the data points are also located between the lower crust and orogenic belt evolution lines. In addition, Wu et al. (2016, this issue) reported the Pb isotopic compositions of the K-feldspar from the Late Jurassic syenogranite porphyry in the Caosiyao deposit, and the Pb isotopic data show that the late Jurassic porphyry also has low radiogenic Pb isotope values (varying from 16.630 to 16.705 for $^{206}\text{Pb}/^{204}\text{Pb}$ ratio, 15.319 to 15.336 for $^{207}\text{Pb}/^{204}\text{Pb}$ ratio, and 36.841 to 36.980 for $^{208}\text{Pb}/^{204}\text{Pb}$ ratio, respectively) and medium μ values (averaging 9.2), which are consistent with those of the sulfide minerals of the Caosiyao deposit. Therefore, we deduce that Pb in the Caosiyao deposit was mainly derived from the Late Jurassic magma formed by partial melting of a lower crust.

The Re–Os isotopic system is a powerful tracer of sulfide ore formation and assimilative degree of the material (Lambert et al., 1994; Foster et al., 1996). Mao et al. (1999) and Stein et al. (2001) have summarized the rhenium contents in molybdenite decrease when going from a mantle source, to mixtures between mantle and crust, and then to crust. The Re contents of the five molybdenite samples from the Caosiyao deposit vary from 9.065 ppm to 13.720 ppm, indicating that the ore-forming materials are mainly derived from the earth crust.

In summary, the ore-forming materials of the Caosiyao deposit were mainly derived from the lower crust, and the mineralization was related to the late Jurassic felsic intrusive rocks.

6.4. Mechanism of mineral deposition

The early and middle stage fluids of the Caosiyao Mo deposit, i.e., main ore-forming

period fluids of Mo, are characterized by moderate–high temperature and high salinity magmatic hydrothermal solution. Previous studies (Candela and Holland, 1986; Cline and Bodnar, 1991; Bodnar, 1994; Hedenquist and Lowenstern, 1994; Shinohara and Hedenquist, 1997; Cline, 2003; Heinrich, 2007; Leng et al., 2008) have indicated that there are three possible mechanisms for the formation of high-salinity magmatic fluids: (1) formation at magmatic temperature, in which felsic–intermediate magma in the chamber increases its volatile content to saturated or oversaturated levels through crystallization and separation to a certain extent and further differentiates to independent fluid phases with high salinities (which is commonly called “second boiling”) (Cline, 2003; Heinrich, 2007); (2) formation from hydrothermal fluids with medium–low salinities through liquid immiscibility or decompression boiling, which is often caused by release of pressure related to fracture of caprocks (commonly termed as “first boiling”) (Cline, 2003; Heinrich, 2007); and (3) formation from the exsolution of residual magma late in the crystallization evolution during the magmatic hypabyssal emplacement (Bodnar, 1994; Shinohara and Hedenquist, 1997; Leng et al., 2008).

The quartz phenocrysts in syenograniteporphyry of the Caosiyao deposit consist of WL-, WG-, C-, and S-type FIs that coexist in the same quartz matrix with similar homogenization temperatures except S-type FIs (Fig. 13). These results indicate that the ore-forming fluids were immiscible, implying that they may result from the boiling of an initial fluid. Therefore, we speculate that the initial fluid in the Caosiyao deposit was most likely an high temperature, mediumsalinity, and CO₂- and CH₄-bearing magmatic fluidproduced by second boiling of magma, whereas the fluid in quartz phenocrysts was produced by boiling of the initial fluid at

temperatures $>500^{\circ}\text{C}$. The quartz veins from the early and middle stages of the Caosiyao deposit consist of WL-, WG-, C-, and S-type FIs that coexist in the same quartz matrix (Fig. 6d) with similar homogenization temperatures (Fig. 13), which is a typical feature of fluid immiscibility or boiling (Fan et al., 2011; Lu et al., 2004). This indicates that, during the Mo mineralization, the ore-forming fluids experienced multi-episode boiling, with temperature of fluids approximately between 210°C and 400°C (Figs. 7c, 7e, and 13). The WL-type FIs in the late stage are characterized by low temperature and low salinity (Fig. 13), representing a mixture between magmatic fluid and meteoric water in the late stage of the mineralization.

At $500\text{--}400^{\circ}\text{C}$ and probably also at higher temperature, the $\text{HMoO}_4\cdot\text{Si}(\text{OH})_4^-$ and $\text{NaHMoO}_4\cdot\text{Si}(\text{OH})_4^-$ associates are very important; at $350\text{--}300^{\circ}\text{C}$, molybdenum is predominantly transported as NaHMoO_4 or KHMoO_4 complexes (Candela and Holland, 1984; Wood et al., 1987; Zotov et al., 1995); and below 300°C , the chloride and sulfide complexes of molybdenum are significant in solutions of low NaCl concentrations (Zotov et al., 1995). The Caosiyao deposit is a moderate–high temperature and high salinity porphyry Mo deposit; thus, Mo in the deposit is mainly transported as NaHMoO_4 or KHMoO_4 complexes. Efficient metal precipitation is controlled by a series of factors, such as the hydrolysis of SO_2 in the fluid (Burnham 1979), throttling or rapid changes in pressure that results in fluid immiscibility (Wilkinson, 2001; Redmond et al., 2004; Klemm et al., 2008; Rusk et al., 2008; Wu et al., 2014), and variation in the pressure–temperature–density paths experienced by ascending ore-forming fluid (Redmond et al., 2004; Landtwing et al., 2010; Simon and Ripley, 2011). As above-mentioned, the hydrothermal fluids in the quartz phenocrysts of syenogranite porphyry and the veins of the early and middle stages in the Caosiyao deposit

are all immiscible. We conclude that ascending the initial fluid characterized by high temperature, medium salinity, and CO_2 - and CH_4 -bearing, due to pressure fluctuation, took place boiling, giving rise to fluid immiscibility. Boiling resulted in escape of a large number of volatile components, causing the strong changes of physicochemical condition of hydrothermal fluids (Fan et al., 2000; Pirajno, 2009; 2012). For example, escape of CO_2 component can cause fluid pH value increase and oxygen fugacity decrease. The above changes of physicochemical condition destroyed the stability of the NaHMoO_4 or KHM_4O_4 complexes, leading to the precipitation of metals from the complexes. It should be emphasized that the initial fluid of the Caosiyao deposit experienced at least two ascents, resulting in multi-episode fluid boiling. The fluid boiling occurring in the quartz phenocryst stage of syenogranite porphyry hardly led to the precipitation of economic minerals because of high temperature of the hydrothermal fluid. In the early and middle stages, however, strong boiling of the initial fluid occurred, giving rise to a large amount of precipitation of ore-forming materials. Therefore, fluid boiling is the dominant mechanism for the deposition of ore-forming materials in the Caosiyao Mo deposit.

7. Conclusions

(1) The molybdenite Re–Os dating indicates that the Caosiyao Mo deposit formed approximately 150 Ma ago.

(2) The ore-forming fluids of the Caosiyao deposit are characterized by moderate–high temperature, great fluctuating salinity, and an H_2O – NaCl – KCl – MgCl_2 – CO_2 ± CH_4 composition.

(3) The ore-forming fluids of the early and middle stages in the Caosiyao deposit were mainly magmatic water, and the hydrothermal fluid of the latestage was a mixed fluid between meteoric water and magmatic water. The ore-forming materials were mainly derived from the late Jurassic felsic magma.

(4) The multi-stage boiling or immiscibility of the ore-forming fluid was the dominant mechanism for the deposition of ore-forming materials.

Acknowledgments

We thank Professor Huiyan Zhu from the China University of Geosciences, Beijing and Dr. Wei Yuan from the Guiyang Institute of Geochemistry, Chinese Academy of Sciences for their help during fluid inclusion analyses. We also thank Senior Engineer Mu Liu from the Beijing Research Institute of Uranium Geology for her help during C–H–O–S–Pb isotope analyses. Professors Hongrui Fan and Weidong Sun are thanked for their useful suggestions. The work was financially supported by the National Science Foundation of China (grant no. 41572061), the Major State Basic Research Program of the People's Republic of China (also referred to as the Chinese National 973 Program) (grant no. 2013CB429805), the Inner Mongolia Geological Exploration Foundation (grant no. 201203YS01), and the Science and Technology Basic Work Specific Project of the Ministry of Science and Technology of the People's Republic of China (grant no. 2014FY121000).

References

Bodnar, R.J., 1983. A method of calculating fluid inclusion volumes based on vapor bubble diameters and PVTX properties of inclusion fluids. *Economic Geology* 78, 535–542.

696 Bodnar, R.J., 1993. Revised equation and table for determining the freezing point depression
697 of H₂O–NaCl solutions. *Geochimica et Cosmochimica Acta* 57, 683–684.

698 Bodnar, R.J., 1994. Synthetic fluid inclusions: XII. The system H₂O–NaCl: experimental
699 determination of the halite liquidus and isochores for a 40 wt% NaCl solution.
700 *Geochimica et Cosmochimica Acta* 58, 1053–1063.

701 Burnham, C.W., 1979. Magmas and hydrothermal fluids. In: Barnes, H.L., (Ed.),
702 *Geochemistry of Hydrothermal Ore Deposits*. John Wiley, New York, pp. 71–136.

703 Candela, P.A., Holland, H.D., 1984. The partitioning of copper and molybdenum between
704 silicate melts and aqueous fluids. *Geochimica et Cosmochimica Acta* 48, 373–380.

705 Candela, P.A., Holland, H.D., 1986. A mass transfer model for copper and molybdenum in
706 magmatic hydrothermal system: the origin of porphyry-type ore deposits. *Economic*
707 *Geology* 81, 1–19.

708 Chen, Y.J., Li, C., Zhang, J., Li, Z., Wang, H.H., 2000a. Sr and O isotopic characteristics of
709 porphyries in the Qinling molybdenum deposit belt and their implication to genetic
710 mechanism and type. *Science in China (Series D): Earth Sciences* 43, 82–94.

711 Chen, Y.J., Liu, C.Q., Chen, H.Y., Zhang, Z.J., Li, C., 2000b. Carbon isotope geochemistry of
712 graphite deposits and ore-bearing khondalite series in North China: implications for
713 several geoscientific problems. *Acta Petrologica Sinica* 16,233–244 (in Chinese with
714 English abstract).

715 Chiaradia, M., Schaltegger, U., Spikings, R.A., Wotzlaw, J.F., Ovtcharova, M., 2013. How
716 accurately can we date the duration of magmatic-hydrothermal events in porphyry
717 systems? *Economic Geology* 108, 565–584.

718 Clayton, R.N., O'Neil, J.R., Mayeda, T.K., 1972. Oxygen isotope exchange between
719 quartz and water. *Journal of Geophysical Research* 77, 3057–3067.

720 Cline, J.S., 2003. How to concentrate copper. *Science* 302, 2075–2076.

721 Cline, J.S., Bodnar, R.J., 1991. Can economic porphyry copper mineralization be generated
722 by a typical calc-alkaline melt? *Journal of Geophysical Research* 96, 8113–8126.

723 Collins, P.L.F., 1979. Gas hydrates in CO₂-bearing fluid inclusions and the use of freezing
724 data for estimation of salinity. *Economic Geology* 74, 1435–1444.

725 Dai, J.Z., Mao, J.W., Yang, F.Q., Ye, H.S., Zhao, C.S., Xie, G.Q., Zhang, C.Q., 2006.
726 Geological characteristics and geodynamic background of molybdenum (copper)
727 deposits along Yanshan–Liaoning metallogenic belt on northern margin of North China
728 block. *Mineral Deposits* 25, 598–612 (in Chinese with English abstract).

729 Dai, J.Z., Mao, J.W., Zhao, C.S., Xie, G.Q., Yang, F.Q., Wang, Y.T., 2009. New U–Pb and
730 Re–Os age data and the geodynamic setting of the Xiaojiayingzi Mo (Fe) deposit,
731 western Liaoning province, Northeastern China. *Ore Geology Reviews* 35, 235–244.

732 Doe, B.R., Zartman, R.E., 1979. Plumbotectonics of the Phanerozoic. In: Barnes H.L., (Ed.),
733 *Geochemistry of Hydrothermal Ore Deposits*. John Wiley, New York, pp. 22–70.

734 Du, A.D., He, H.L., Yin, N.W., Zou, X.Q., Sun, Y.L., Sun, D.Z., Chen, S.Z., Qu, W.J., 1994. A
735 study on the Rhenium–Osmium geochronometry of molybdenites. *Acta Geologica Sinica*
736 68, 339–347 (in Chinese with English abstract).

737 Fan, H.R., Xie, Y.H., Zheng, X.Z., Wang, Y.L., 2000. Ore-forming fluids in
738 hydrothermal breccia-related gold mineralization in Qiyugou, Henan Province. *Acta*
739 *Petrologica Sinica* 16, 559–563 (in Chinese with English abstract).

740 Fan, H.R., Hu, F.F., Wilde, S.A., Yang, K.F., Jin, C.W., 2011. The Qiyugou gold-bearing
 741 brecciapipes, Xiong'ershan region, central China: fluid inclusion and stable-isotope
 742 evidence for an origin from magmatic fluids. *International Geology Review* 53, 25–45.
 743 Faure, G., 1986. *Principles of Isotope Geology*. John Wiley and Sons, Inc., New York.
 744 Foster, J.G., Lambert, D.D., Frick, L.R., Maas, R., 1996. Re–Os isotopic evidence for genesis
 745 of Archaean nickel ores from uncontaminated komatiites. *Nature* 382, 703–706.
 746 Hall, D.L., Sterner, S.M., Bodnar, R.J., 1988. Freezing point depression of NaCl–KCl–H₂O
 747 solutions. *Economic Geology* 83, 197–202.
 748 Hedenquist, J.W., Lowenstern, J.B., 1994. The role of magma in the formation of
 749 hydrothermal ore deposits. *Nature* 370, 519–527.
 750 Heinrich, C.A., 2007. Fluid–fluid interactions in magmatic–hydrothermal ore formation.
 751 *Reviews in Mineralogy and Geochemistry* 65, 363–387.
 752 Hoefs, J., 1987. *Stable Isotope Geochemistry*, 3rd Edition. Springer-Verlag, Berlin, p. 241.
 753 Hollister, L.S., Burruss, R.C., 1976. Phase equilibria in fluid inclusions from the Khtada Kake
 754 metamorphic complex. *Geochimica et Cosmochimica Acta* 40, 163–175.
 755 Huang, F., Chen, Y.C., Wang, D.H., Yuan, Z.X., Chen, Z.H., 2011. A discussion on the major
 756 molybdenum ore concentration areas in China and their resource potential. *Geology in*
 757 *China* 38, 1111–1134 (in Chinese with English abstract).
 758 Inner Mongolia Autonomous Region Bureau of Geology and Mineral Resource, 1991.
 759 *Regional Geology of Inner Mongolia Autonomous Region*. Geological Publishing House,
 760 Beijing, pp. 32–71 (in Chinese with English abstract).
 761 Jiang, S.H., Liang, Q.L., Bagas, L., 2014. Re–Os ages for molybdenum mineralization in the

762 Fengning region of northern Hebei Province, China: new constraints on the timing of
763 mineralization and geodynamic setting. *Journal of Asian Earth Sciences* 79, 873–883.

764 Klein, E.L., Ribeiro, J.W.A., Harris, C., Moura, C.A.V., Giret, A., 2008. Geology and fluid
765 characteristics of the Mina Velha and Mandiocal orebodies and implications for the
766 genesis of the orogenic Chega Tudo gold deposit, Gurupi Belt, Brazil. *Economic*
767 *Geology* 103, 957–980.

768 Klemm, L.M., Pettke, T., Heinrich, C.A., Heinrich, C.A., 2007. Hydrothermal evolution of the
769 El Teniente deposit, Chile: porphyry Cu–Mo ore deposition from low-salinity magmatic
770 fluids. *Economic Geology* 102, 1021–1045.

771 Klemm, L.M., Pettke, T., Heinrich, C.A., 2008. Fluid and source magma evolution of the
772 Questa porphyry Mo deposit, New Mexico, USA. *Mineralium Deposita* 43, 533–552.

773 Lambert, D.D., Walker, R.J., Morgan, J.W., Shirey, S.B., Carlson, R.W., Zientek, M.L., Lipin,
774 B.R., Koski, M.S., 1994. Re–Os and Sm–Nd Isotope Geochemistry of the Stillwater
775 Complex, Montana: Implications for the Petrogenesis of the JM Reef. *Journal of*
776 *Petrology* 35, 1717–1753.

777 Landtwing, M.R., Furrer, C., Redmond, P.B., Pettke, T., Guillong, M., Heinrich, C.A., 2010.
778 The Bingham Canyon Porphyry Cu–Mo–Au deposit. III. Zoned copper–gold ore
779 deposition by magmatic vapor expansion. *Economic Geology* 105, 91–118.

780 Leng, C.B., Zhang, X.C., Qin, C.J., Wang, S.X., Ren, T., Wang, W.Q., 2008. Study of fluid
781 inclusions in quartz veinlets in the Xuejiping porphyry copper deposit, Northwest Yunan,
782 China. *Acta Petrologica Sinica* 24, 2017–2028 (in Chinese with English abstract).

783 Li, X.Z., Ban, Y.H., Quan, Z., X., Weng, J.C., Wang, W.D., 2012. Discuss on geochemical

784 characteristics and metallogenic model of the Caosiyao molybdenum deposit in Xinghe
785 County, Inner Mongolia. Geological Survey and Research 35, 39–46 (in Chinese with
786 English abstract).

787 Liu, B., 2001. Density and isochoric formulae for NaCl–H₂O inclusions with medium and
788 high salinity and their applications. Geological Review 47, 617–622 (in Chinese with
789 English abstract).

790 Liu, B., Duan, G.X., 1987. NaCl–H₂O Density and isochoric formulae for NaCl–H₂O
791 inclusions and their applications. Acta Mineralogica Sinica 7, 345–352 (in Chinese with
792 English abstract).

793 Lu, H.Z., Fan, H.R., Ni, P., Ou, G.X., Shen, K., Zhang, W.H., 2004. Fluid Inclusions. Science
794 Press, Beijing, pp. 1–444 (in Chinese).

795 Lu, Z.C., Duan, G.Z., Liu, C.Q., Hao, L.B., Li, D.C., Wei, C.D., 2000. Daxing'anling Ag
796 deposit types, metallogenic series and metallogenic geochemical characteristics.
797 Bulletin of Mineralogy, Petrology and Geochemistry 19, 305–309 (in Chinese with
798 English abstract).

799 Ludwig, K.R., 2003. User's Manual for Isoplot 3.0: A Geochronological Toolkit for
800 Microsoft Excel, vol. 4. Berkeley Geochronology Center, pp. 1–71 (special publication).

801 Mao, J.W., Zhang, Z.C., Zhang, Z.H., Du, A.D., 1999. Re–Os isotopic dating of molybdenites
802 in the Xiaoliugou W (Mo) deposit in the northern Qilian mountains and its geological
803 significance. Geochimica et Cosmochimica Acta 63, 1815–1818.

804 Mullis, J., 1987. Fluid inclusion studies during very low-grade metamorphism. Low
805 Temperature Metamorphism, 162–199.

806 Nie, F.J., Liu, Y.F., Zhao, Y.A., Cao, Y., 2012. Discovery of Dasuji and Caosiyao large size
 807 Mo deposits in central Inner Mongolia and its geological significances. *Mineral Deposits*
 808 31, 930–940 (in Chinese with English abstract).

809 Nie, F.J., Li, X.Z., Li, C., Zhao, Y.A., Liu, Y.F., 2013. Re–Os isotopic age dating of the
 810 Molybdenite separated from the Caosiyao giant molybdenum deposit, Xinghe County,
 811 Inner Mongolia, and its geological significances. *Geological Review* 59, 175–181 (in
 812 Chinese with English abstract).

813 No. 2 Geoexploration party of Henan Bureau of Geoexploration and Mineral Development.
 814 2014. The Caosiyao deposit exploration report.

815 Ohmoto, H., 1972. Systematics of sulfur and carbon isotopes in hydrothermal ore deposits.
 816 *Economic Geology* 67, 551–578.

817 Ohmoto, H., 1986. Stable isotope geochemistry of ore deposits. In: Valley, J.W., Taylor, H.P.,
 818 O’Neil, J.R., (Eds.), *Stable Isotopes in High Temperature Geological Processes*. Review
 819 in *Mineralogy* 16, 460–491.

820 Ohmoto, H., Rye, R.O., 1979. Isotopes of sulfur and carbon. In: Barnes, H.L., (Ed.),
 821 *Geochemistry of Hydrothermal Ore Deposit*. Wiley, New York, pp. 509–567.

822 Pirajno, F., 2009. *Hydrothermal Processes and Mineral Systems*. Springer, Berlin, p. 1250.

823 Pirajno, F., 2012. *The Geology and Tectonic Settings of China’s Mineral Deposits*.
 824 Springer, Berlin, p. 679.

825 Redmond, P.B., Einaudi, M.T., Inan, E.E., Landtwing, M.R., Heinrich, C.A., 2004. Copper
 826 deposition by fluid cooling in intrusion-centered systems: new insights from the
 827 Bingham porphyry ore deposit, Utah. *Geology* 32, 217–220.

828 Rusk, B., Dilles, J., Reed, M., 2008. Fluid inclusion evidence for magmatic–hydrothermal
829 fluid evolution in the porphyry copper–molybdenum deposit at Butte, Montana.
830 *Economic Geology* 103, 307–334.

831 Santosh, M., Wilde, S.A., Li, J.H., 2007. Timing of Paleoproterozoic ultrahigh-temperature
832 metamorphism in the North China Craton: evidence from SHRIMP U–Pb zircon
833 geochronology. *Precambrian Research* 159, 178–196.

834 Shepherd, T.J., Rankin, A.H., Alderton, D.H.M., 1985. A Practical Guide to Fluid Inclusion
835 Studies. Chapman & Hall, Blackie, pp. 1–239.

836 Shinohara, H., Hedenquist, J.W., 1997. Constraints on magma degassing beneath the Far
837 Southeast porphyry Cu–Au deposit, Philippines. *Journal of Petrology* 38, 1741–1752.

838 Shirey, S.B., Walker, R.J., 1995. Carius tube digestion for low-blank rhenium–osmium
839 analysis. *Analytical Chemistry* 67, 2136–2141.

840 Simon, A.C., Ripley, E.M., 2011. The role of magmatic sulfur in the formation of ore deposits.
841 *Reviews in Mineralogy and Geochemistry* 73, 513–578.

842 Smoliar, M.L., Walker, R.J., Morgan, J.W., 1996. Re–Os ages of group IA, IIA, IVA and IVB
843 iron meteorites. *Science* 271, 1099–1102.

844 Stein, H.J., Markey, R.J., Morgan, J.W., Hannah, J.L., Schersten, A., 2001. The remarkable
845 Re–Os chronometer in molybdenite: how and why it works. *Terra Nova* 13, 479–486.

846 Tang, H.S., Chen, Y.J., Wu, G., Lai, Y., 2011. Paleoproterozoic positive $\delta^{13}\text{C}_{\text{carb}}$ excursion in
847 the northeastern Sino–Korean craton: evidence of the Lomagundi event. *Gondwana*
848 *Research* 19, 471–481.

849 Taylor, H.P., 1974. The application of oxygen and hydrogen isotope studies to problems of

hydrothermal alteration and ore deposition. *Economic Geology* 69, 843–883.

Taylor, H.P., Frechen, J., Degens, E.T., 1967. Oxygen and carbon isotope studies of carbonatites from the Laacher See District, West Germany and the Alno District Sweden. *Geochimica et Cosmochimica Acta* 31, 407–430.

Todt, W., Cliff R.A., Hanser A., Hofmann A.W., 1993. Re-calibration of NBS lead standards using a ^{202}Pb – ^{205}Pb double spike. *Terra Abstract* 5 (supplement), 396.

Tomilenko, A., Gibsher, N., Dublyansky, Y., Dallai, L., 2010. Geochemical and isotopic properties of fluids from gold-bearing and barren quartz veins of the Sovetskoye gold deposit (Siberia, Russia). *Economic Geology* 105, 375–394.

Wang, S.Q., 1989. The geological features of host rocks and metallogenesis of the Xinghe graphite deposit, Inner Mongolia. *Mineral Deposits* 8, 85–96 (in Chinese with English abstract).

Wang, S.Q., 1994. Carbon isotopic composition and genetic analysis of Wulashan graphite deposits in Inner Mongolia. In: Qian, X.L., Wang, R.M., (eds.), *Geological Evolution of the Granulite Terrain in the North Part of the North China Craton*. Seismological Press, Beijing, pp. 210–227 (in Chinese with English abstract).

Wang, G.R., Wu, G., Wu, H., Liu, J. Li, X.Z., Xu, L.Q., Zhang, T., Quan, Z.X., 2014. Fluid inclusion and hydrogen–oxygen isotope study of Caosiyao superlarge porphyry molybdenum deposit in Xinghe County, central Inner Mongolia. *Mineral Deposits* 33, 1213–1232 (in Chinese with English abstract).

Wilkinson, J.J., 2001. Fluid inclusions in hydrothermal ore deposits. *Lithos* 55, 229–272.

Wood, S.A., Crerar, D.A., Borcsik, M.P., 1987. Solubility of the assemblage

pyrite–pyrrhotite–magnetite–sphalerite–galena–gold–stibnite–bismuthinite–argen–tite–molybdenite in H₂O–NaCl–CO₂ solutions from 200 degrees to 350 degrees. *Economic Geology* 82, 1864–1887.

Wu, G., Chen, Y.C., Li, Z.Y., Liu, J., Yang, X.S., Qiao, C.J., 2014. Geochronology and fluid inclusion study of the Yinjiagou porphyry–skarn Mo–Cu–pyrite deposit in the East Qinling orogenic belt, China. *Journal of Asian Earth Sciences* 79, 585–607.

Wu, H., Wu, G., Tao, H., Wang, G.R., Li, T.G., Chen, J.Q., Yang, N.N., 2014. Molybdenite Re–Os dating and fluid inclusion study of Dasuji porphyry molybdenum deposit in Zhuozhi County, central Inner Mongolia. *Mineral Deposits* 33, 1251–1267 (in Chinese with English abstract).

Wu, G., Li, X.Z., Xu, L.Q., Wang, G.R., Liu, J., Zhang, T., Quan, Z.X., Wu, H., Li, T.G., Zeng, Q.T., Chen, Y.C., 2016. Age, geochemistry, and Sr–Nd–Hf–Pb isotopes of the Caosiyao porphyry Mo deposit in Inner Mongolia, China. *Ore Geology Reviews* xx, xxx–xxx, this issue.

Xu, Z.G., Chen, Y.C., Wang, D.H., Chen, Z.H., Li, H.M., 2008. The Scheme of the Classification of the Minerogenetic Units in China. Geological Publishing House, Beijing, pp. 1–138 (in Chinese).

Yu, X.Q., Chen, W., Li, W., 2008. Discovery and prospecting significance of Dasuji porphyry molybdenum deposit, Inner Mongolia. *Geology and Prospecting* 44(2), 29–37 (in Chinese with English abstract).

Zartman, R.E., Doe, B.R., 1981. Plumbotectonics: the model. *Tectonophysics* 75, 135–162.

Zeng, Q.D., Chu, S.X., Liu, J.M., Sun, S.K., Chen, W.J., 2012a. Mineralization, alteration,

894 structure, and Re–Os age of the Lanjiagou porphyry Mo deposit, North China Craton.
895 International Geology Review 54, 1145–1160.

896 Zeng, Q.D., Liu, J.M., Xiao, W.J., Chu, S.X., Wang, Y.B., Duan, X.X., Sun, Y., Zhou, L.L.,
897 2012b. Mineralizing types, geological characteristics and geodynamic background of
898 Triassic molybdenum deposits in the northern and southern margins of North China
899 Craton. *Acta Petrologica Sinica* 28, 357–371 (in Chinese with English abstract).

900 Zeng, Q.D., Liu, J.M., Qin, K.Z., Fan, H.R., Chu, S.X., Wang, Y.B., Zhou, L.L., 2013. Types,
901 Characteristics, and time–space distribution of molybdenum deposits in China.
902 International Geology Review 55, 1311–1358.

903 Zhai, M.G., Liu, W.J., 2003. Palaeoproterozoic tectonic history of the North China craton: a
904 review. *Precambrian Research* 122, 183–199.

905 Zhang, T., Chen, Z.Y., Xu, L.Q., Chen, Z.H., 2009. The Re–Os isotopic dating of
906 molybdenite from the Dasuji molybdenum deposit in Zhuozi County of Inner
907 Mongolia and its geological significance. *Rock and Mineral analysis* 28, 279–282 (in
908 Chinese with English abstract).

909 Zhao, G.C., Sun, M., Wilde, S.A., Li, S.Z., 2005. Late Archean to Paleoproterozoic evolution
910 of the North China Craton: key issues revisited. *Precambrian Research* 136, 177–202.

911 Zoheir, B.A., El-Shazly, A.K., Helba, H., Khalil, K.I., Bondar, R.J., 2008. Origin and
912 evolution of the Um Egat and Dungash orogenic gold deposits, Egyptian Eastern Desert:
913 evidence from fluid inclusions in quartz. *Economic Geology* 103, 405–424.

914 Zotov, A.V., Kudrin, A.V., Levin, K.A., Shilina, N.D., 1995. Experimental studies of the
915 solubility and complexing of selected ore elements (Au, Ag, Cu, Mo, As, Sb, Hg) in

aqueous solutions. In: Shmulovich, K.I., Yardley, B.W.D., Gonchar, G.G., (Eds.), *Fluids in the Crust*. Chapman & Hall, London, pp. 95–137.

Figure Captions

Fig. 1. (a) Tectonic subdivision of the Archean to Paleoproterozoic basement of the NCC (after Zhao et al., 2005); (b) distribution of major molybdenum deposits in the northern margin of the NCC (modified after Dai et al., 2006; Jiang et al., 2014); and (c) sketch geological map of the Jining area, Inner Mongolia (modified after Xu et al., 2008).

Names of numbered faults: F₁, Guyang–Wuchuan–Shangyi fault; F₂, Linhe–Baotou–Jining fault; F₃, Daihai–Huangqihai fault; and F₄, Shangdu–Xinghe–Weixian 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, Dacaping quartz-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; and 21, Laohudong skarn Mo (Zn) deposit. ECB, Eastern Continental Block; TNCO, Trans-North China Orogen; WCB, Western Continental Block.

Fig. 2. Geological map (a) and geological cross section along No. 8 exploration line (b) of the Caosiyao deposit (modified after No. 2 Geoexploration Party, HBGMD, 2014).

Fig. 3. Representative photographs of ores from the Caosiyao Mo deposit: (a) leaf-like molybdenite of the early stage, plainlight under reflected light; (b) anhedral granular magnetite and molybdenite of the early stage, plainlight under reflected light; (c) anhedral granular pyrite and magnetite and leaf-like molybdenite of the early stage, pyrite replacing magnetite and magnetite replacing molybdenite, developing a metasomatic texture, plainlight under reflected light; (d) leaf-like molybdenite of the middle stage, plainlight under reflected light; (e) anhedral granular pyrite involving anhedral granular molybdenite of the middle stage, developing a poikilitic texture, plainlight under reflected light; (f) anhedral granular molybdenite, pyrite, pyrrhotine, and chalcopyrite of the middle stage, pyrrhotine replacing molybdenite, pyrite, and chalcopyrite, developing a metasomatic dissolution texture, plainlight under reflected light; (g) euhedral–subhedral granular pyrite and anhedral granular pyrrhotine of the late stage, sometimes pyrrhotine replacing pyrite, developing a metasomatic texture, plainlight under reflected light; (h) euhedral–subhedral granular pyrite and anhedral granular pyrrhotine of the late stage, plainlight under reflected light; (i) veinlet disseminated Mo ore of the early stage; (j) densely disseminated Mo ore of the early stage; (k) disseminated molybdenite and pyrite of the middle stage; and (l) pyrite vein of the late stage. Cp, Chalcopyrite; Mo, molybdenite; Mt, magnetite; Po, pyrrhotine; Py, Pyrite.

Fig. 4. Representative photographs and photomicrographs of altered rocks from the Caosiyao

porphyry Mo deposit: (a) silicification and sericitization of Mo ore; (b) silicification and sericitization occurring in Mo ore and potassic alteration in syenogranite porphyry; (c) sericitization developing in K-feldspar phenocrysts and quartz vein occurring in syenogranite porphyry; (d) sericitic alteration of plagioclase phenocrysts and argillic alteration of K-feldspar phenocrysts and groundmass of syenogranite porphyry; (e) sericitization–muscovitization–argillization of syenogranite porphyry; and (f) scapolitization–carbonation of monzogranite porphyry. Arg, argillic alteration; Cbn, carbonate; Kf, K-feldspar; Mu, muscovite; Pa, potassic alteration; Q, quartz; Scp, scapolite; Ser, sericite.

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

Fig. 6. Photomicrographs of representative fluid inclusions in quartz crystals from the Caosiyao Mo deposit: (a) liquid-rich inclusions in quartz phenocryst of syenogranite porphyry; (b) gas-rich inclusions in quartz phenocryst of syenogranite porphyry; (c) H₂O–CO₂ inclusions in quartz of the early stage; (d) coexisting liquid-rich, gas-rich and daughter mineral-bearing inclusions in quartz of the early stage; (e) daughter mineral-bearing inclusions in quartz of the middle stage; and (f) liquid-rich inclusions in quartz of the late stage. L_{H₂O}, Liquid phase H₂O; V_{H₂O}, vapor phase H₂O; L_{CO₂}, liquid phase carbon dioxide; V_{CO₂}, vapor phase carbon dioxide; Ih, halite.

Fig. 7. Histograms of homogenization temperatures and salinities of fluid inclusions in the

Caosiyao Mo deposit, showing average temperatures of various mineralization stages.

Fig. 8. Laser Raman spectra of fluid inclusions of the Caosiyao Mo deposit: (a) vapor phase composition of WL-typeFIs in quartz phenocryst of syenogranite porphyry; (b) vapor phase composition of WG-typeFIs in quartz phenocryst of syenogranite porphyry; (c) vapor phase composition of WL-typeFIs in quartz of the early stage; (d) vapor phase composition of C-typeFIs in quartz of the early stage; (e) vapor phase composition of S-typeFIs in quartz of the middle stage; and (f) vapor phase composition of WL-typeFIs in quartz of the late stage.

Fig. 9. δD versus $\delta^{18}O_{H_2O}$ diagram of the Caosiyao Mo deposit(Base map after Taylor, 1974).

Fig. 10. Carbon isotope histogram: (a) the Caosiyao deposit, showing major carbon isotope reservoirs of the earth (carbon isotope values of organic matter, carbonatite, and marine carbonate after Faure (1986), Taylor et al. (1967) and Hoefs (1987), and Ohmoto (1986),respectively); and (b) graphite deposits in central Inner Mongolia (data after Wang (1989; 1994) and Chen et al. (2000b)).

Fig. 11. Sulfur isotope histogram of the Caosiyao deposit.

Fig. 12. Diagram of lead isotopic compositions of the Caosiyao deposit (Base map from Zartman and Doe, 1981).

1003 Fig. 13.Homogenization temperature versus salinity of fluid inclusions in the Caosiyao Mo
1004 deposit(NaCl saturation curve after Bodnar, 1983).

1005 **Tables**

1006 Table 1 Re–Os analytical results of molybdenite from the Caosiyao Mo deposit.

1007

1008 Table 2 Microthermaometry data and relative parameters of fluid inclusions in the Caosiyao
1009 deposit.

1010

1011 Table 3Hydrogen, oxygen,and carbon isotopic compositions (‰) of the CaosiyaoMo deposit.

1012

1013 Table 4 Sulfur and lead isotopic compositions of sulfides from the Caosiyao deposit.

Figure 1 Tectonic units and regional geological map

Figure 1 consists of two panels: (a) a geological map and (b) a cross-section.

Panel (a) is a geological map of the Huangtuyao area. It shows various geological units: Quaternary sediments (white), Neogene-Paleogene sediments (yellow dotted), Metamorphic rocks of the Mesoarchean Huangtuyao Fm. (brown), Late Jurassic granite porphyry (red dotted), Early Cretaceous granite porphyry (pink dotted), and Neoproterozoic diabase dike (green). It also shows faults (red lines), a Yanshanian granite porphyry vein (red line with dots), and a Neoproterozoic diabase dike (green line). Drill sites are marked with black dots and labeled with numbers (e.g., ZK 823, ZK 815, ZK 807, ZK 800, ZK 808, ZK 816, ZK 824, ZK 1600). A scale bar indicates 0, 200, and 400m.

Panel (b) is a cross-section along Line 9. The vertical axis represents depth in meters (0 to 1200m). The horizontal axis shows drill sites ZK 823, ZK 815, ZK 807, ZK 800, ZK 808, ZK 816, and ZK 824. The cross-section shows the subsurface structure, including the Mesoarchean Huangtuyao Fm. (brown), Late Jurassic granite porphyry (red dotted), Early Cretaceous granite porphyry (pink dotted), and Neoproterozoic diabase dike (green). It also shows faults (red lines), a Yanshanian granite porphyry vein (red line with dots), and a Neoproterozoic diabase dike (green line). Drill sites are marked with black dots and labeled with numbers. A scale bar indicates 0, 200, and 400m.

Legend for (a):

- Quaternary sediments
- Neogene-Paleogene sediments
- Metamorphic rocks of the Mesoarchean Huangtuyao Fm.
- Late Jurassic granite porphyry
- Early Cretaceous granite porphyry
- Neoproterozoic diabase dike
- Geological boundary
- Fault
- Yanshanian granite porphyry vein
- Drill and number
- Exploration line and number

Legend for (b):

- Quaternary sediments
- Neogene-Paleogene sediments
- Metamorphic rocks of the Mesoarchean Huangtuyao Fm.
- Late Jurassic granite porphyry
- Early Cretaceous granite porphyry
- Neoproterozoic diabase dike
- Fracture zone
- Mo orebody/mineralized body
- Drill and number

Figure 3 Representative photos of ores

Figure 4 Representative photographs of altered rocks

Figure 5 Molybdenite Re-Os age

Figure 6 Photomicrographs of representative fluid inclusions

Figure 7 Histograms of homogenization temperatures and salinities

Figure 8 Laser Raman spectra of fluid inclusions

Figure 9 dD versus d18OH2O diagram

Figure 10 Carbon isotope histogram

Figure 11 Sulfur isotope histogram

Figure 12 Diagram of lead isotopic compositions

Figure 13 Diagram of temperature versus salinity

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
SDG135	0.01031	9.353	0.085	0.0153	0.0342	5.878	0.054	14.57	0.13	148.6	2.2
SDG137	0.05004	9.065	0.081	0.0026	0.0059	5.697	0.051	14.19	0.12	149.3	2.2
SDG138	0.05022	9.655	0.076	0.0026	0.0087	6.068	0.048	15.19	0.13	150.1	2.1
SDG139	0.05007	11.090	0.100	0.2390	0.0062	6.969	0.060	17.54	0.14	150.9	2.2
SDG140	0.05004	13.720	0.120	0.0026	0.0059	8.624	0.077	21.57	0.17	149.9	2.2

Table 2 Microthermometry data and relative parameters of fluid inclusions in the Caosiyao deposit.

Type	Size (μm)	V (%)	No.	Aqueous two-phase inclusion		H ₂ O–CO ₂ inclusion		Daughter mineral-bearing inclusion		Salinity (% NaCl eqv.)	Density (g/cm ³)
				<i>T</i> _{m(ice)} (°C)	<i>T</i> _h (°C)	<i>T</i> _{m(cal)} (°C)	<i>T</i> _h (°C)	<i>T</i> _{d(dm)} (°C)	<i>T</i> _{d(bub)} (°C)		
Quartz phenocryst of syenogranite porphyry: samples CM25, CM34, and CM37											
WL	5–22	15–40	7	–8.8 to –7.1	385–436					10.6–12.6	0.60–0.72
WG	5–18	60–85	14	–11.8 to –7.6	388–482					11.2–15.8	0.56–0.68
C	3–15	10–60	6			3.8–6.6	471			6.5–10.9	0.51–0.97
S	4–12	5–30	6					304 to >550	233 to >550	38.5–65.0	1.08–1.21
Quartz of quartz–molybdenite±magnetite±pyrite stage: samples CM54, CM55, CM56, CM61, CM76, and CM87											
WL	3–25	5–45	44	–10.8 to –4.8	243–395					7.6–14.8	0.70–0.90
WG	4–12	50–85	8		328–401						
C	8–14	15–80	9			4.1–6.8	302–365			6.0–10.3	0.42–0.94
S	3–13	5–20	8					236–321	202–354	33.8–39.8	1.02–1.09
Quartz of quartz–molybdenite–pyrite±pyrrhotite±chalcopyrite stage: samples CM67, CM73, and CM93											
WL	3–16	5–40	34	–8.9 to –0.7	208–336					1.2–12.7	0.76–0.95
C	11–16	20–40	4			6.7–7.7	310			4.5–6.3	0.70–0.81
S	3–9	10–15	5					132–247	168–292	29.0–34.1	1.06–1.14
Quartz of quartz–carbonate–pyrite±fluorite±pyrrhotite stage: samples CM68, CM80, and CM84											
WL	4–29	5–20	31	–9.3 to –2.3	124–196					3.9–13.2	0.93–1.03

*T*_{d(bub)}, bubble disappear temperature; *T*_{d(dm)}, daughter mineral disappear temperature; *T*_{m(cia)}, clathrate melting temperature; *T*_{m(ice)}, final melting temperature of ice; *T*_h, total homogenization temperature; *V*, percentage of bubble volume.

Table 3 Hydrogen, oxygen, and carbon isotopic compositions (‰) of the Caosiyao Mo deposit.

Sample No.	Stage	Mineral	$\delta^{18}\text{O}_{\text{Q(V-SMOW)}}$	$T (^{\circ}\text{C})$	$\delta^{18}\text{O}_{\text{H}_2\text{O(V-SMOW)}}$	$\delta\text{D}_{\text{V-SMOW}}$	$\delta^{13}\text{C}_{\text{PDB}}$
CM62	Early stage	Quartz	9.3	333	3.5	—	—
CM63	Early stage	Quartz	9.9	333	4.1	−79	−16.5
CM64	Early stage	Quartz	12.8	333	6.9	—	—
CM74	Early stage	Quartz	13.3	333	7.4	−96	—
CM82	Early stage	Quartz	12.8	333	6.9	−86	−14.0
CM83	Early stage	Quartz	12.8	333	6.9	−78	−11.1
CM85	Early stage	Quartz	12.2	333	6.3	−84	−14.7
CM87	Early stage	Quartz	12.3	333	6.4	−77	−8.8
CM88	Early stage	Quartz	12.3	333	6.4	−79	−11.9
CM73	Middle stage	Quartz	14.2	274	6.2	—	—
CM75	Middle stage	Quartz	13.1	274	5.1	—	—
CM77	Middle stage	Quartz	13.2	274	5.2	—	—
CM93	Middle stage	Quartz	12.3	274	4.3	−85	−9.3
CM68	Late stage	Quartz	13.2	162	−1.4	−88	−6.8
CM69	Late stage	Quartz	12.2	162	−2.3	−88	−11.4
CM70	Late stage	Quartz	14.0	162	−0.6	−112	−7.8
CM78	Late stage	Quartz	11.8	162	−2.7	−85	—
CM80	Late stage	Quartz	12.4	162	−2.1	−85	−7.1
CM84	Late stage	Quartz	11.6	162	−2.9	−77	−5.3

Notes: PDB, Peedee Belemnite; V-SMOW, Vienna standard mean ocean water; —, not obtained analytical data.

Table 4 Sulfur and lead isotopic compositions of sulfides from the Caosiyao deposit.

Sample No.	Stage	Mineral	$\delta^{34}\text{S}_{\text{V-CDT}}$ (‰)	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
CM54	Early stage	Molybdenite	5.2	150	16.317 $\pm$ 0.002	15.215 $\pm$ 0.002	36.049 $\pm$ 0.004	9.0	34.5
CM55	Early stage	Molybdenite	5.3	150	15.962 $\pm$ 0.002	15.200 $\pm$ 0.002	35.918 $\pm$ 0.005	9.1	36.3
CM57	Early stage	Molybdenite	4.5	150	16.383 $\pm$ 0.002	15.243 $\pm$ 0.002	36.613 $\pm$ 0.006	9.1	37.3
CM61	Early stage	Molybdenite	5.7	150	17.243 $\pm$ 0.001	15.344 $\pm$ 0.001	36.712 $\pm$ 0.003	9.1	33.2
CM65	Early stage	Molybdenite	4.9	150	16.490 $\pm$ 0.002	15.299 $\pm$ 0.001	36.777 $\pm$ 0.003	9.2	38.0
CM76	Early stage	Molybdenite	6.1	150	17.695 $\pm$ 0.002	15.475 $\pm$ 0.001	37.757 $\pm$ 0.003	9.3	36.5
CM87	Early stage	Molybdenite	4.6	150	16.985 $\pm$ 0.001	15.369 $\pm$ 0.002	37.043 $\pm$ 0.005	9.2	36.6
CM76	Early stage	Pyrite	4.6	150	17.832 $\pm$ 0.002	15.511 $\pm$ 0.002	37.891 $\pm$ 0.004	9.4	36.6
CM67	Middle stage	Molybdenite	5.3	150	16.676 $\pm$ 0.002	15.311 $\pm$ 0.002	36.571 $\pm$ 0.005	9.2	35.7
CM93	Middle stage	Molybdenite	4.9	150	16.765 $\pm$ 0.001	15.328 $\pm$ 0.001	36.904 $\pm$ 0.003	9.2	37.0
CM49	Middle stage	Pyrite	5.4	150	16.354 $\pm$ 0.001	15.314 $\pm$ 0.001	36.464 $\pm$ 0.003	9.3	37.5
CM51	Middle stage	Pyrite	5.1	150	16.345 $\pm$ 0.002	15.310 $\pm$ 0.002	36.484 $\pm$ 0.004	9.2	37.6
CM73	Middle stage	Pyrite	4.2	150	17.062 $\pm$ 0.003	15.394 $\pm$ 0.002	37.260 $\pm$ 0.005	9.2	37.4
CM75	Middle stage	Pyrite	4.8	150	17.414 $\pm$ 0.002	15.486 $\pm$ 0.002	37.776 $\pm$ 0.005	9.4	38.4
CM68	Late stage	Pyrite	5.2	150	16.415 $\pm$ 0.002	15.308 $\pm$ 0.001	36.652 $\pm$ 0.003	9.2	38.0
CM71	Late stage	Pyrite	4.0	150	17.739 $\pm$ 0.003	15.511 $\pm$ 0.003	37.927 $\pm$ 0.007	9.4	37.3
CM72	Late stage	Pyrite	4.3	150	17.669 $\pm$ 0.002	15.474 $\pm$ 0.002	37.697 $\pm$ 0.004	9.3	36.4
CM79	Late stage	Pyrite	4.2	150	17.399 $\pm$ 0.002	15.471 $\pm$ 0.002	37.653 $\pm$ 0.005	9.3	37.8
CM89	Late stage	Pyrite	4.3	150	17.529 $\pm$ 0.002	15.477 $\pm$ 0.002	37.692 $\pm$ 0.004	9.3	37.2
CM90	Late stage	Pyrite	4.3	150	17.324 $\pm$ 0.002	15.448 $\pm$ 0.002	37.531 $\pm$ 0.004	9.3	37.5

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