

Evaluating the Use of the Molybdenite Re-Os Chronometer in Dating Gold Mineralization: Evidence from the Haigou Deposit, Northeastern China

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Abstract

The Haigou lode gold deposit (>40 tons [t] at 3.4 g/t), which is located near the eastern boundary of the Central Asian orogenic belt and the North China craton, is one of the largest gold deposits in northeastern China. Native gold is intergrown with molybdenite and pyrite in auriferous quartz veins hosted by a monzogranitemonzonite stock and locally by Proterozoic gneiss, thereby offering an excellent opportunity to directly date the mineralizing event. Uranium-Pb age determinations for zircon yielded ages for the monzogranite and monzonite of 327.1 ± 1.1 and 329.5 ± 1.0 Ma, respectively. Numerous mafic to felsic dikes, which are crosscut by ore veins (pre-ore), parallel to these veins (possibly synore), or crosscut by them (post-ore), were carefully examined and dated. Their zircon 206 Pb/ 238 U ages are 318.3 ± 1.0, 310.9 ± 1.1, and 134.9 ± 0.4 Ma, respectively, thereby placing the timing of gold mineralization within the relatively large interval of 318.3 ± 1.0 to 134.9 ± 0.4 Ma. The age of mineralization was determined directly using the Re-Os method applied to molybdenite. A total of 19 molybdenite samples separated from auriferous quartz veins yielded widely differing Re-Os model ages of 467 to 155 Ma, and replicate analyses of individual samples also yielded widely differing ages. Significantly, the wide range is attributable entirely to the results obtained for some coarse-grained molybdenite samples and is interpreted to be due to Re and Os isotope decoupling, the considerable spatial Re heterogeneity, the analytical procedure (e.g., use of small sample aliquots), and the post-ore deformation. Nine of the samples, which are all fine grained, yielded a robust weighted mean model age of 310 ± 3 Ma and an isochron age of 309 ± 8 Ma. Thus, the molybdenite Re-Os ages are identical, within uncertainty, to those of the dikes that are parallel to the ore veins, indicating that these dikes were emplaced contemporaneously with the ore and that they and the Haigou gold mineralization are of late Paleozoic age (ca. 310 Ma). Finally, a sericite sample obtained from an auriferous vein returned a 40 Ar/ 39 Ar plateau age of 165.3 ± 1.2 Ma, which is much younger than the age of the mineralization constrained by Re-Os age determinations of molybdenite. This indicates that the ⁴⁰Ar/³⁹Ar isotope system was reset by post-ore thermal events.

Our new geochronological data provide evidence for late Paleozoic gold mineralization in Haigou, which makes it the oldest known lode gold deposit in the easternmost Central Asian orogenic belt, a finding that has important implications for precious metal mineral exploration in the eastern part of the Solonker-Xar Moron-Changchun-Yanji suture zone between the Central Asian orogenic belt and the North China craton. This study also indicates that accurate and reproducible molybdenite Re-Os ages representing the true timing of ore deposition need an integrated combination of careful petrography, proper sampling procedures, sufficiently large analyzed aliquots, multiple analyses of individual samples, and multiple dating methods.

Introduction

Direct dating of economic mineralization is essential for establishing robust genetic models of ore formation and for understanding the tectonic controls on ore deposition in large metallogenic provinces. Among the currently available radiometric dating methods, the Re-Os method is the only method that can be used to date sulfide minerals directly (Stein et al., 1998, 2001; Selby and Creaser, 2001a; Selby et al., 2002; Morelli et al., 2010; Ootes et al., 2011; Saintilan et al., 2017a, b, 2018). Petrographically constrained, precise, and reproducible Re-Os isotope data of mineral separates of individual sulfide/sulfarsenide species permit the ages of discrete mineralizing events to be determined accurately (Saintilan et al., 2018). In particular, they allow the duration of a magmatic-hydrothermal event to be reliably established when combined with state-of-the-art U-Pb age determinations of individual zircons in magmatic rocks (e.g., von Quadt et al., 2011; Chiaradia et al., 2013, 2014; Zimmerman et al., 2014; Chelle-Michou et al., 2015a; Li, Y., et al., 2017).

Molybdenite has been shown to yield remarkably robust Re-Os ages for the following reasons: (1) it typically incorporates Re in ppm concentrations and excludes Os, thereby allowing common ¹⁸⁷Os to be ignored and all the ¹⁸⁷Os to be attributed to the in situ decay of ¹⁸⁷Re, (2) inheritance of older cores and overgrowths and chemical isotopic exchange are exceedingly rare, (3) the Re-Os system in molybdenite can

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ISSN 0361-0128; doi:10.5382/econgeo.4667; 19 p. Digital appendices are available in the online Supplements section. withstand intense deformation and high-grade thermal metamorphism, (4) the closure temperature of the Re-Os isotope system in molybdenite is relatively high, and (5) neither Re nor Os are accommodated by silicate minerals, thereby ensuring that they remain in molybdenite (e.g., Stein et al., 1998, 2001, 2003; Selby and Creaser, 2001a, b, 2004; Selby et al., 2002, 2007; Lawley and Selby, 2012; Stein, 2014; Stein and Hannah, 2015, and references therein).

During the past decade, the implementation and improvement of the Re-Os and U-Pb methods and their use in combination with other chronometers has helped constrain the timing and duration of ore-forming events with a high level of accuracy and precision (e.g., von Quadt et al., 2002, 2014, 2016; Chiaradia et al., 2009a, b, 2013, 2014; Chelle-Michou et al., 2014, 2015b; Zimmerman et al., 2014; Buret et al., 2017; Chang et al., 2017; Li, Y., et al., 2018; Cao et al., 2019). Porphyry Cu-Mo-(Au) deposits provide, by far, the best examples of the direct dating and bracketing of ore formation using the molybdenite Re-Os dating method because of the common occurrence of significant proportions of molybdenite in these deposits. The timing of intrusion-related Sn mineralization can also be determined directly using the cassiterite U-Pb method (Yuan et al., 2008, 2011). In contrast, the ages of other magmatic-hydrothermal ore deposits are still poorly constrained, and most of the ages that have been determined for these deposits (e.g., Au) are based on indirect isotopic methods, e.g., sericite Ar-Ar and Rb-Sr, calcite Sm-Nd, and monazite U-Pb ages (Hart et al., 2002; Li, J., et al., 2006, 2012; Su et al., 2009; Zhai et al., 2015; Li, X., et al., 2019). However, these gangue minerals may not be coeval with gold deposition from the ore fluids, and/or the isotopic systems have been disturbed by post-ore events. Thus, interpretations based on their ages should be made with caution (Selby et al., 2002).

In this study, we test the reliability of a variety of chronometers in determining the age of the Haigou lode gold deposit, namely the molybdenite Re-Os, pyrite Re-Os, zircon U-Pb, and sericite Ar-Ar chronometers. We also discuss and decipher the important controls on the accuracy and reproducibility of the molybdenite Re-Os ages. Our new geochronological data, in combination with geologic observations and a knowledge of the regional metallogeny, place important constraints on the genesis of the Haigou lode gold deposit in the context of the tectonic evolution of the Central Asian orogenic belt. In so doing, they identify a previously unknown Paleozoic Au mineralization event along the suture between the Central Asian orogenic belt and the North China craton and provide new insights into the evolution of one of China's most important gold mining districts.

Regional Geology

The Haigou lode gold deposit is located in the Jiapigou-Haigou gold belt in northeastern China (Fig. 1A, B), which is one of the most important gold-producing districts in China and was responsible for nearly half of China's gold production during the early 1960s (estimated Au reserves >150 tons [t]; Deng et al., 2009; Zeng et al., 2014). This belt lies on the boundary between the Central Asian orogenic belt and the North China craton (Fig. 1A).

The Central Asian orogenic belt evolved through a complex closure of the Paleo-Asian Ocean from the Neoproterozoic

to the late Phanerozoic (Wilde, 2015), which separated the Siberian craton in the north from the Tarim and North China cratons in the south (Fig. 1A). Microcontinental blocks, which are widely distributed in the Central Asian orogenic belt, have been proposed to have originated as part of Rodinia along the global Grenville orogenic belt between 1100 and 750 Ma (Zhou et al., 2018). This region records the complex processes of tectonic events that marked the transition from the dominantly NE-SW-directed motion of the Paleo-Asian plate to the EW-directed motion of the Paleo-Pacific plate (e.g., Li, 2006; Wilde, 2015; Liu et al., 2017; Zhou et al., 2018, and references therein). There was an overlap in the late Permian-Early Triassic between activity associated with the Paleo-Asian Ocean closure and the onset of tectonism related to Paleo-Pacific Ocean subduction-a switch in geodynamic setting that is interpreted to have occurred between ~260 and 250 Ma (Zhou and Wilde, 2013; Wilde, 2015).

The evolution of the Central Asian orogenic belt involved the accretion of numerous island arcs at the margins of the North China craton and the Siberian craton during the Paleozoic (Fig. 1B; Sengör and Natal'in, 1996). It also has been shown that tectonic features within the North China craton were reactivated by multiple Paleozoic to Mesozoic orogenic events along its margin, e.g., the closure of the Paleo-Asian Ocean during the late Permian and continued convergence from the north that resulted in thrusting and significant crustal thickening on its northern margin (Xiao et al., 2003); these events continued into the Triassic in the eastern part of the suture (Wilde, 2015). The accreted marginal orogenic belts collided along the Solonker-Xar Moron-Changchun-Yanji suture and represent the terminal closure event within the southeast Paleo-Asian Ocean (Sengör and Natal'in, 1996; Xiao et al., 2003; Wilde, 2015).

There are five major terranes in the Chinese portion of the eastern Central Asian orogenic belt (Fig. 1B). These are, from west to east, the Erguna block, the Xing'an block, the Songliao block, a Paleozoic accretionary complex along the northern margin of the North China craton known as the Liaoyuan terrane, and the combined Jiamusi/Khanka block (which is linked to the Bureya block in Russia). The different units are separated by distinct sutures (Fig. 1B). The Erguna, Xing'an, and Songliao blocks are commonly referred to as the Xing'an-Mongolian orogenic belt in the Chinese literature (Wu et al., 2004; Xu et al., 2015). However, it is still unclear whether the combined Bureya-Jiamusi-Khanka block (Fig. 1B) is part of the Central Asian orogenic belt or a separate crustal fragment that owes its location to Paleo-Pacific subduction (Wu et al., 2007; Zhou et al., 2010).

Paleozoic igneous rocks along the Solonker-Xar Moron-Changchun-Yanji suture are mainly Carboniferous to Permian in age, with the youngest arc-related rocks having formed during the Early Triassic, thereby providing compelling evidence for a Permian/Triassic closure of the Paleo-Asian Ocean (Xiao et al., 2003; Li, 2006; Liu et al., 2016; Eizenhöfer and Zhao, 2018, and references therein). The region was subsequently affected by tectonism associated with the westward subduction of the Paleo-Pacific plate in the late Permian-Early Triassic (ca. 260–250 Ma). In the Early Cretaceous (ca. 140 Ma), the Paleo-Pacific plate retreated eastward, producing an extensional setting associated with regional thinning and



Fig. 1. (A) Tectonic elements of the Central Asian orogenic belt (CAOB, based on Zhai et al., 2018c). (B) Major tectonic units and sutures in the eastern Central Asian orogenic belt (based on Wilde, 2015). (C) A geologic map of the Jiapigou-Haigou gold belt in northeastern China showing the distribution of major gold deposits (modified from Zeng et al., 2014).

delamination of the lithosphere in northeastern China (e.g., Li, 2006; Zhang et al., 2010; Wu et al., 2011; Wilde, 2015; Liu et al., 2017; Zhou et al., 2018). Paleozoic and Mesozoic granites are common in the Jiapigou-Haigou gold belt (Fig. 1C) as a result of multiple tectonic events. Consequently, most of the ore deposits in the region (e.g., porphyry Cu-Mo-Au deposits, Ag-Pb-Zn veins, and epithermal and orogenic Au deposits) are interpreted to be of Mesozoic age (Yang et al., 2003; Zeng et al., 2012; Mao et al., 2014; Zhai et al., 2014a, b, 2018a, b, c, 2019; Ouyang et al., 2015; Shu et al., 2016; Chen et al., 2017; Gao et al., 2018, and references therein). Deposits of confirmed Paleozoic age are extremely rare (Yang et al., 2015; Gao et al., 2018; Yang and Cooke, 2019).

The regional faults (Mesoproterozoic to Mesozoic) include two groups, i.e., the NE- and NW-oriented fault or shear zones (Fig. 1C). The NE-oriented faults include the Dunhua fault, which is part of the regional Tanlu fault in eastern China, and the Liangjiang fault. Between these faults, there are several parallel NW-oriented faults and shear zones (~100 km long and 1–3 km wide; Fig. 1C). These faults commonly crosscut the Paleozoic and Mesozoic granitic intrusions (Fig. 1C). The Jiapigou shear zones controlled the location of the Jiapigou gold belt, whereas the Haigou gold deposit occurs north of the Jinyinbie fault (Fig. 1C).

Ore Deposit Geology

The Haigou quartz veins are located in an area underlain by the Proterozoic Seluohe Complex (Fig. 2), which is composed mainly of gneiss, quartz-plagioclase-hornblende schist, amphibolite, and metarhyolite. On the basis of whole-rock K-Ār and muscovite K-Ār age determinations, the Seluohe Complex is interpreted to have formed between 1654 and 1646 Ma (Bureau of Geology and Mineral Resources of Jilin Province, 1988). However, most of the auriferous Haigou quartz veins are hosted by a granitic stock (Haigou stock), comprising a central monzogranite and a border monzonite (Fig. 2). The contact between them is gradational (Zhang et al., 2012). The stock has an outcrop area of $\sim 5 \text{ km}^2$ and was initially interpreted to have been emplaced at 186 to 167 Ma based on a whole-rock K-Ar age determination (Jiao et al., 2008). A recent zircon U-Pb geochronological study has constrained the age of the granitic stock in the Carboniferous between 322.9 ± 3.4 and 320.3 ± 3.5 Ma (Zhang et al., 2012). There are two other intrusions in the area. A Mesozoic biotite granite pluton (Huangnihe pluton), which has been dated at 120 Ma using the zircon U-Pb chronometer, is located immediately to the west of the ore deposit (Fig. 2) (Zhang et al., 2012), and a diorite intrusion in the eastern part of the ore district was emplaced in the Cretaceous (124 Ma, zircon U-Pb; this study; Fig. 2). None of the above Mesozoic plutons host any gold. Numerous mafic to felsic dikes cut the Haigou stock (Fig. 2). Compositionally, they comprise diabase, andesite, granodiorite, and diorite porphyry (Fig. 3A). Most of the dikes crosscut auriferous quartz veins, and some were truncated by auriferous veins (e.g., diorite porphyry; Fig. 3A, B). Several studies have concluded that these dikes formed in the Cretaceous on the basis of zircon U-Pb ages between 132.4 \pm 1.5 and 124.6 \pm 2.2 Ma (e.g., Li, X., et al., 2012; Chang et al., 2013; Zeng et al., 2017). The distribution of the dikes and the Au-bearing quartz veins was controlled mainly by numerous NE-NNE-oriented faults and less so by NS- and EWoriented faults (Fig. 2). The southern part of the ore district was controlled by an EW-oriented fault zone (Jinyinbie fault, Fig. 2), which is part of a regional fault system (Fig. 1B).

The Haigou deposit was discovered in 1965 and has been mined since 1984. Fifteen auriferous quartz veins have been identified in the monzogranitic stock and gneiss. These veins extend vertically up to 800 m, and their lengths and widths vary from ~100 to ~1,000 m and ~1 to ~20 m (Figs. 2, 3), respectively. Reserves of more than 40 t Au with an average grade of 3.4 g/t have been identified (Zeng et al., 2017). The auriferous quartz veins occur in three clusters, namely, the V38, V28, and V43 clusters in the eastern, central, and western parts of the ore district, respectively. The V28 cluster is the most important, and hosts ~30 t gold with grades from 3 to 10 g/t (avg 8 g/t) (Zeng et al., 2017). This ore cluster consists of several continuous and parallel veins, which generally strike northeast (45°) and dip northwest $(312^{\circ}-318^{\circ})$ at angles of 45° to 85° . The veins are $\sim 1,000$ m long and have widths of 0.2 to 17.7 m (avg 3.9 m). They commonly extend vertically over intervals of up to 500 m. The V38 ore cluster contains ~6 t of gold reserves grading from 3 to 5 g/t Au, and the veins in this cluster strike northeast and dip northwest (312°) at angles of 30° to 45°. They are generally about 500 m in length, have widths of 0.3 to 20 m,



Fig. 2. A geologic map of the Haigou gold deposit (modified from Zhang et al., 2012).



Fig. 3. (A) A geologic map of the 407-m mining level (modified from Zeng et al., 2017). (B) A representative cross section of the Haigou gold deposit. (C) Auriferous quartz veins hosted by monzonite with accompanying K-feldspar and quartz alteration. (D) An auriferous quartz vein hosted by gneiss with pyrite-sericite alteration halo.

and extend >200 m vertically. Minor disseminated Au mineralization occurs along the margins of the major veins.

Hydrothermal alteration is widespread, with the most intense alteration usually occurring in and around the mineralized quartz veins (Fig. 3C, D). The main alteration minerals are quartz, K-feldspar, sericite, chlorite, epidote, kaolinite, and calcite. Alteration halos are distributed asymmetrically and discontinuously on either side of the mineralized veins (they are typically wider on the hanging-wall side, e.g., 3–5 m) and are widest around the thickest veins. Silicic and potassic alteration were early and widespread. These alteration facies were overprinted by an assemblage of quartz, pyrite, sericite, and epidote. An assemblage of quartz, sericite, chlorite, and kaolinite overprinted the preceding alteration and was closely associated with abundant gold and sulfide mineral deposition. Finally, several calcite-quartz veins and veinlets crosscut the altered rocks. There is no apparent spatial zonation of alteration types regionally, as, in most cases, alteration assemblages were superimposed on one another. However, the alteration varies with the nature of the host rocks, e.g., early K-feldsparquartz alteration in monzonite (Fig. 3C) is accompanied by early pyrite-sericite-quartz alteration in gneiss (Fig. 3D).

Sampling and Analytical Methods

Mineral identification and molybdenite characterization

Representative samples were collected from drill holes and from different mining levels accessible via ongoing underground mine development. The gold-bearing samples were collected from variable depths. Well-polished thin sections were examined in reflected and transmitted light. Mineral compositions were determined using a JEOL 8230 Superprobe equipped with wavelength- and energy-dispersive X-ray detectors and a backscattered electron detector at the Chinese Academy of Geological Sciences (CAGS). The rhenium concentrations in fine-grained molybdenite (5–20 μ m) were determined using a Cameca SX FIVE FE microprobe equipped with energy- and wavelength-dispersive spectrometers at the Department of Earth and Planetary Sciences, McGill University, Canada. The operating conditions were an acceleration voltage of 20 kV, a beam current of 20 nA, and a counting time of 200 s for Re. The beam diameter was $5 \,\mu$ m. The standard used was Re metal, and the detection limit for Re was ~50 ppm. A field emission scanning electron microscope (FESÊM), a Zeiss Supra 55 Sapphire, at the China University of Geosciences Beijing (CUGB) was used to image ore textures and determine mineral compositions semiquantitatively for the purpose of identification. The accelerating voltage was 20 kV and the working distance 15 mm.

In situ laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) trace element analysis of molybdenite

In situ trace element analyses of relatively coarse grained molybdenite (50–>300 μ m) were conducted using LA-ICP-MS at the Wuhan SampleSolution Analytical Technology Co., Ltd., China. The analytical method for these analyses is based on that described in Ciobanu et al. (2013). A GeolasPro laser ablation system consisting of a COMPexPro 102 ArF excimer laser (wavelength of 193 nm and maximum energy of 200 mJ) was employed in conjunction with a MicroLas optical system. An Agilent 7700e ICP-MS instrument was used to acquire the ion signals. Helium was used as a carrier gas and argon as the makeup gas. The spot diameter and frequency of the laser were set to 32 μ m and 10 Hz, respectively. Trace element compositions were calibrated using the reference standards NIST-610 and MASS-1. An internal molybdenum standard was also used for calibration. Each analysis involved a background acquisition of approximately 20 to 30 s followed by 50 s of data acquisition from the sample. An Excel-based program, ICPMSDataCal, was used to perform off-line selection and integration of background and analyzed signals, time-drift correction, and quantitative calibration (Liu et al., 2008).

U-Pb dating of zircon

Nine samples of unaltered igneous rocks (comprising samples from six dikes and three larger intrusions, including the Haigou granitic stock and the diorite intrusion) were collected from different mining levels and drill core, based on their crosscutting relationships with auriferous quartz veins. Two samples (monzogranite and monzonite) from the stock hosting the deposit and a sample from a diorite intrusion that does not host auriferous veins but intruded the stock in the eastern part of the ore district were analyzed to represent the larger intrusions. The numerous mafic to felsic dikes were carefully described with respect to their chronological relationships with the ore veins. They include a diorite porphyry dike (pre-ore) that is crosscut by ore veins, an unaltered and unmineralized andesite dike, which is parallel to an ore vein and may therefore have formed synchronously with mineralization, and a diabase dike that truncates veins and therefore postdated the ores.

Zircon crystals in the intrusions/dikes were separated by standard heavy-liquid and magnetic techniques and further purified by handpicking under a binocular microscope. Prior to LA-ICP-MS analysis, the zircon crystals were imaged by cathodoluminescence (CL) using an FESEM. The U-Pb dating of the zircon was carried out using an LA-ICP-MS in the State Key Laboratory of Geological Processes and Mineral Resources at CUGB. The crystals were ablated using an excimer laser ablation system (UP193SS), and an Agilent 7500a ICP-MS instrument was used to acquire the ion signals. A laser spot diameter of 36 μ m, a laser energy density of 8.5 J/cm², and a repetition rate of 10 Hz were used during the analyses. Helium and argon were used as the carrier and makeup gases, respectively, and were mixed via a T connector before entering the ICP. Uranium, Th, and Pb concentrations were calibrated by using ²⁹Si as an internal standard and the NIST 610 glass as the reference standard. The ²⁰⁷Pb/²⁰⁶Pb, ²⁰⁶Pb/²³⁸U, ²⁰⁷Pb/²³⁵U, and ²⁰⁸Pb/²³²Th ratios were corrected for both instrumental mass bias and depth-dependent elemental and isotopic fractionation using Harvard zircon 91500 as the external standard (Wiedenbeck et al., 1995). The zircon standard TEMORA was used as a secondary standard to monitor the deviation of the age measurement (Black et al., 2003). Isoplot 3.0 was used to calculate the ages and make concordia plots (Ludwig, 2003). The data obtained for the Harvard zircon 91500 and TEMORA zircon standards yielded weighted mean ages of 1062.5 \pm 0.5 and 418.0 \pm 6.9 Ma, respectively, which are very similar to the reported ages (1065 and 417 Ma, respectively; Wiedenbeck et al., 1995; Black et al., 2003).

Re-Os dating of molybdenite and pyrite

A total of six molybdenite- and 11 pyrite-bearing auriferous quartz vein samples were collected. The molybdenite-bearing samples are from the lower part of the deposit (>500 m depth), whereas the pyrite-bearing samples were taken from a variety of depth intervals. Molybdenite occurs either as small veins or veinlets in the auriferous veins (commonly 0.3-5 mm in thickness) (Fig. 4A) or as very fine coatings (<0.1–0.2 mm thick) on the walls of quartz veins immediately adjacent to the host granitic stock in association with potassic and sericitic alteration assemblages (Fig. 4B). In several locations, the occurrences of molybdenite on vein margins have been partially sheared due to post-ore deformation. The molybdenite is associated locally with pyrite in potassically altered quartz veins (Fig. 4C). Pyrite commonly occurs as mineral aggregates in auriferous quartz veins. To deal with the possible mobilization of minor radiogenic ¹⁸⁷Os from molybdenite into the adjacent pyrite (Stein et al., 2003), the pyrite samples were collected from sites that were far removed from the molybdenite. The grain size of the molybdenite in the samples either is very fine (i.e., $<10-200 \mu$ m), or relatively coarse (i.e., 0.3–5 mm). The diameter of pyrite grains generally varies from 1 to 5 mm.

The sample preparation and mineral separation were performed using the methodology recommended by Du et al. (1995), Stein et al. (2003), and Selby and Creaser (2004). In brief, clean mineral separates of molybdenite and pyrite were



Fig. 4. (A) Molybdenite veins and veinlets associated with K-feldspar near the margins of an auriferous quartz vein hosted by gneiss. (B) A sample containing fine-grained molybdenite as coatings on the surface of auriferous quartz veins and showing the results of Re-Os dating. (C) A sample containing relatively coarse grained molybdenite as veins and veinlets in a quartz vein with a potassically altered wall-rock halo. The results of the Re-Os dating are shown. Abbreviations: Kfs = K-feldspar, Mol = molybdenite, Py = pyrite, Qtz = quartz.

obtained using traditional isolation methods (e.g., crushing, magnetic, and/or heavy-liquid separation) and were further handpicked under a binocular microscope. Individual samples of 200 to 300 mg were checked for homogeneity by multiple analyses of the mineral separates obtained using the material prepared with the different sampling procedures, i.e., bulk sampling, and multiple mineral separates were split from one sample (e.g., Stein et al., 1998, 2001; Selby and Creaser, 2001a, 2004; Li, Y., et al., 2017). In addition, a total of six model ages were determined for fine-grained molybdenite at four locations along a traverse across a single sample (HG-32); the distance between adjacent locations was less than 1 cm (Fig. 4B).

The analyses were carried out in three laboratories: the Laboratory for Sulfide and Source Rock Geochronology and Geochemistry at Durham University (DU), United Kingdom, the Re-Os Laboratory at the National Research Center of Geoanalysis (CAGS), China, and the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences (IGCAS). All mineral separations, with the exception of those performed at Durham, were carried out at CUGB. The analytical procedures for determining the rhenium and osmium contents and their isotopic compositions in the molybdenite and pyrite mineral separates were those recommended by Du et al. (2004), Qi et al. (2010), and Lawley and Selby (2012), and references therein. The Carius tube method was used for the dissolution of the molybdenite and equilibration of the samples with a Re and Os tracer solution (Selby and Creaser, 2001a). Molybdenite was dissolved

and equilibrated with ¹⁸⁵Re and ¹⁹⁰Os spike solutions at CAGS and IGCAS and with a mixed ¹⁸⁵Re and isotopically normal Os spike composition at DU. Pyrite was dissolved with 10 mL of concentrated HNO3 and 2 mL of HCl and known amounts of ¹⁸⁵Re and ¹⁹⁰Os spikes. The Re-Os isotope data for molybdenite were obtained using isotope dilution-negative thermal ionization mass spectrometry (ID-NTIMS; Creaser et al., 1991; Völkening et al., 1991) at DU in the Arthur Holmes Laboratory and isotope dilution ICP-MS at CAGS (TJA PQ ExCell) and IGCAS (PE ELAN DRC-e). The Re-Os isotope analysis for pyrite was carried out at CAGS and IGCAS using isotope dilution ICP-MS. The uncertainties in the Re and Os isotope composition measurements, tracer calibration, sample and tracer weighing, reproducibility of Re and Os isotope standards, blank abundances, and isotopic compositions were all propagated. The blanks were <3 pg for Re and <0.5 pg for ¹⁸⁷Os for measurements at DU and <10 pg for Re and <2 pg for ¹⁸⁷Os at CAGS and IGCAS. In order to evaluate the accuracy and reproducibility of the analyses, the reference materials Henderson molybdenite (RM8599, 27.66 ± 0.10 Ma; Markey et al., 2007; Zimmerman et al., 2014), JDC (139.6 ± 3.8 Ma; Du et al., 2004), and HLP (221.4 ± 5.6 Ma; Du et al., 2004) were run during the course of this study; the model ages obtained were 27.695 ± 0.038 Ma (n = 9, DU; Li, Y., et al., 2017), 140.1 \pm 2.8 Ma (n = 6, CAGS; Zhai et al., 2017), and 223.0 \pm 2.4 Ma (n = 5, IGCAS; Huang et al., 2013), respectively. The molybdenite Re-Os age was calculated using a ¹⁸⁷Re decay constant of 1.666 10⁻¹¹ yr⁻¹ with an uncertainty of 0.31% (Smoliar et al., 1996; Selby et al., 2007).

Isoplot 3.0 was used to calculate the isochron ages (Ludwig, 2003).

Ar-Ar dating of sericite

A sericite sample was collected from a pyrite-sericite-altered auriferous quartz vein (~8 m in width) hosted by monzonite from the underground mine. The sericite-altered auriferous vein was cut, crushed, washed, and then handpicked to obtain sericite grains, which were irradiated together with the ZBH-25 biotite standard (132.7 \pm 1.2 Ma at 1 σ ; Wang, 1983) for 55 h in the swimming pool reactor, Chinese Institute of Atomic Energy (Beijing). After three months of cooling, the sample was analyzed using the ⁴⁰Ar/³⁹Ar stepwise incremental heating method and a MM-1200B mass spectrometer at the Institute of Geology, CAGS. Details of the method were reported by Chen et al. (2006). Measured isotopic ratios were corrected for mass discrimination, atmospheric argon, blanks, and irradiation-induced mass interference. Correction factors for the interfering isotopes during irradiation were determined by an analysis of pure irradiated K₂SO₄ and CaF₂ having values of $({}^{36}\text{Ar}/{}^{37}\text{Ar})_{Ca} = 0.0002389$, $({}^{40}\text{Ar}/{}^{39}\text{Ar})_k = 0.004782$, and $({\rm ^{39}Ar}/{\rm ^{37}Ar_0})_{Ca}$ = 0.000806. The ${\rm ^{40}K}$ decay constant used was the value of 5.543×10^{-10} yr⁻¹ recommended by Steiger and Jäger (1977). The age uncertainties with decay uncertainty are reported at the 95% confidence level (2σ) , and the Ar-Ar age was calculated using Isoplot 3.0 (Ludwig, 2003).

Results

Ore paragenesis and gold occurrence

Four primary paragenetic stages (I to IV) were identified in the Haigou Au deposit, based on the nature of the mineralization

and the mineral assemblages (Fig. 5). Stage III is the most important stage for Au deposition. The gold typically occurs as the native metal with <10 wt % Ag and commonly coexists with galena embedded in early formed pyrite (Fig. 6A). Native gold also occurs as isolated grains in quartz (Fig. 6B), which were observed to coexist with minor tellurides (i.e., altaite, coloradoite, and hessite; Figs. 6B, 7). Locally, the gold is present as small grains within or adjacent to molybdenite platelets (Fig. 6C-F), suggesting that the two phases formed coevally. The codeposition of native gold and molybdenite enables the gold mineralization to be dated directly using the molybdenite Re-Os chronometer.

The Re distribution in molybdenite

The Re concentrations in fine- and coarse-grained molybdenite determined using the electron microprobe (EMP) and in situ LA-ICP-MS are reported in Appendix Tables A1 and A2, and some of the results are illustrated in Figure 8. The EMP data show that the Re concentrations of different fine-grained molybdenite crystals in a single sample vary widely, i.e., from 79 to 468 ppm (all the values are above the detection limit for Re) (App. Table A1; Fig. 8A). The in situ LA-ICP-MS spot analyses of the coarse-grained molybdenite crystals and their veins also demonstrate a heterogeneous distribution of Re concentration with a range of 49 to 210 ppm (App. Table A2; Fig. 8B-D).

Zircon U-Pb geochronology

Numerous zircon U-Pb age determinations have been carried out for the different intrusive rocks in the ore district. These are reported in Appendix Table A3 and are summarized here. The monzogranite and monzonite that host the



Fig. 5. A chart summarizing the mineral paragenesis of the Haigou Au deposit. Abbreviations: Cal = calcite, Kfs = K-feldspar, Py = pyrite, Qtz = quartz.



Fig. 6. Photomicrographs showing the mode of gold occurrence in the Haigou deposit. (A) Coexisting native gold and galena filling fractures in pyrite (reflected light). (B) Native gold and electrum associated with galena, altaite, and coloradoite (reflected light). (C, D) Native gold intergrown with molybdenite and quartz (backscattered image). The inset graph in C shows the spot analysis result of native gold. (E, F) Maps showing the distribution of Mo and Au in C and D. Abbreviations: Alt = altaite, Au = native gold, Col = coloradoite, Elt = electrum, Gn = galena, Mol = molybdenite, Py = pyrite, Qtz = quartz.

ore have mean ${}^{206}\text{Pb}/{}^{238}\text{U}$ ages of 327.1 ± 1.1 Ma (n = 20, mean square of weighted deviates [MSWD] = 0.75) and 329.5 ± 1.0 Ma (n = 19, MSWD = 0.18) (Fig. 9H, I), respectively, showing that the stock crystalized in the late Paleozoic. In contrast, the diorite intrusion in the eastern part of the ore district yielded a mean ${}^{206}Pb/{}^{238}U$ age of 128.4 ± 0.3 Ma (n = 15, MSWD = 0.78) (Fig. 9G). A diorite porphyry dike, which was cut by auriferous quartz veins (Fig. 9A), yielded a mean ${}^{206}\text{Pb}/{}^{238}\text{U}$ age of 318.3 ± 1.0 Ma (n = 25, MSWD = 0.19). In contrast, an andesite dike, which is oriented parallel to gold-bearing quartz veins and was free of evidence of alteration and mineralization (Fig. 9B), was dated at $310.9 \pm$ 1.1 Ma (n = 15, MSWD = 0.29). However, a similar andesite dike, which was collected from a site at lower elevation and is also oriented parallel to the ore veins, yielded a mean 206 Pb/ 238 U age of 2446.5 ± 9.0 Ma (n = 23, MSWD = 0.19)

(Fig. 9D), providing clear evidence that the analyzed zircon crystals were all inherited from the Proterozoic protolith. A diabase dike, which cut the orebodies (Fig. 9C), has a mean 206 Pb/ 238 U age of 134.9 ± 0.4 Ma (n = 19, MSWD = 0.27), whereas a diorite porphyry dike, which also crosscut the orebodies, yielded a mean 206 Pb/ 238 U age of 340.3 ± 1.9 Ma (n = 16, MSWD = 0.79) (Fig. 9F). As this age is greater than that of the intrusions hosting the deposit, we conclude that all of the analyzed zircon crystals were inherited from older rocks. Finally, a granodiorite dike from the ore district has a mean zircon ${}^{206}Pb/{}^{238}U$ age of 259.8 ± 0.4 Ma (n = 46, MSWD = 2.0) (Fig. 9E). The data presented above therefore bracket the age of gold mineralization between 318.3 and 134.9 Ma, although the results for the andesite dike that was emplaced parallel to the quartz veins may indicate an age of gold mineralization closer to the former.



Fig. 7. Element maps of molybdenite from the Haigou gold deposit. Abbreviations: Elt = electrum, Hes = hessite, Mol = molybdenite, Qtz = quartz.



Fig. 8. Rhenium concentrations (ppm) in molybdenite of the Haigou gold deposit determined from in situ LA-ICP-MS and EMP analyses. (A) Locations of EMP analyses and corresponding Re concentrations in fine-grained molybdenite (backscattered electron) and (B-D) Locations of LA-ICP-MS spot analyses and Re distributions in coarse-grained molybdenite and its veins (reflected light).



Fig. 9. Crosscutting relationships involving representative dikes and auriferous quartz veins and their zircon U-Pb ages. (A) A pre-ore porphyry dike with a zircon U-Pb age of 318.3 ± 1.0 Ma cut by a gold-mineralized vein. (B) A vein-parallel andesite dike (possibly synore) having a zircon U-Pb age of 310.9 ± 1.1 Ma. (C) A post-ore diabase dike, which yielded a zircon U-Pb age of 134.9 ± 0.4 Ma. (D) A vein-parallel andesite dike, which returned a zircon U-Pb age of 2446.5 ± 9.0 Ma. (E) A granodiorite dike with a zircon U-Pb age of 259.8 ± 0.4 Ma displaying an unclear relationship with ore veins. (F) A post-ore diorite porphyry dike with a zircon age of 340.3 ± 1.9 Ma. (G-I) Zircon U-Pb ages of 128.4 ± 0.3 , 327.1 ± 1.1 , and 329.5 ± 1.0 Ma for diorite, monzogranite, and monzonite intrusions.

Molybdenite/pyrite Re-Os geochronology

The total Re concentration of the molybdenite samples ranges from 0.02 to 142.8 ppm (19 analyses of six samples; Table 1). Only two analyses of multiple mineral separates from one sample yielded very low Re contents (0.02 and 0.21 ppm, sample HG-34); the other 17 analyses returned Re concentrations ranging from 8.0 to 142.8 ppm (avg 78.8 ppm). As is the case for the Re contents, the model ages for the molybdenite vary considerably, i.e., from 467.1 ± 41.0 to 155.3 ± 1.8 Ma (Table 1). The ages determined at DU using NTIMS range from $345.6 \pm$ 19.9 to 306.7 ± 1.2 Ma, and those determined at CAGS and IGCAS using ICP-MS range from 467.1 \pm 41.0 to 155.3 \pm 1.8 Ma and $\overline{3}14.6 \pm 6.2$ to $\overline{2}98.7 \pm 2.4$ Ma, respectively. After excluding one extremely old (467.1 \pm 41.0 Ma) and two very young $(193.5 \pm 2.2 \text{ and } 155.3 \pm 1.8 \text{ Ma})$ model ages, the data for the remaining 16 molybdenite samples yield a weighted mean age of 314.6 ± 5.0 Ma (Fig. 10A) and an isochron age of $304.8 \pm$ 7.6 Ma (Fig. 10B). Nine of these 16 samples returned similar model ages of 318.2 ± 3.9 to 305.8 ± 5.7 Ma and a weighted mean age of 310.0 ± 2.6 Ma (MSWD = 12) (Fig. 10C), which, within uncertainty, is the same as the ¹⁸⁷Re/¹⁸⁷Os isochron age of 308.6 ± 8.1 Ma (MSWD = 9) (Fig. 10D).

The total Re and Os concentrations in the pyrite vary from 0.25 to 2,372.43 ppb and 1.64 to 7,825.12 ppt, respectively (n = 13). The ¹⁸⁷Re/¹⁸⁸Os ratios range from ~600,000 to ~1,000, with the majority of the samples returning values

greater than 5,000 (n = 9; App. Table A4). The extremely high ¹⁸⁷Re/¹⁸⁸Os ratios classify the bulk of the sulfide samples as low level highly radiogenic (Stein et al., 2000; Selby et al., 2009), and this is reflected in the low common Os values (App. Table A4). The $^{187}\text{Os}/^{188}\text{Os}$ ratios vary from ~10 to ~3,000 with the majority of the samples yielding values greater than 30 (n = 8;App. Table A4). Given the relatively high Re concentrations in some of the samples (~2.4 ppm in HG-47-b; App. Table A4) and their high Re/Os, it is very likely that much of the Re is not crystallographically contained within the pyrite structure. Instead, this Re and Os may have originated from micro- to nanoscale molybdenite inclusions hosted in the bulk analyzed pyrite, despite careful sampling and microscale observations designed to exclude them from Re-Os analysis. The 13 pyrite analyses collectively yield an isochron age of 319.7 ± 6.2 Ma, which overlaps with the age of molybdenite. However, the initial ¹⁸⁷Os/¹⁸⁸Os ratio from the best fit is strongly negative, and the associated error is very large $(-6 \pm 17; \text{App. Fig. A1})$. Moreover, the best fit is largely controlled by one sample (HG-27), and the scatter about the best fit is considerable (MSWD = \sim 2,000), indicating that the data do not meet the requirements necessary to return a meaningful isochron age.

Sericite Ar-Ar geochronology

The ⁴⁰Ar/³⁹Ar data for sericite from a pyrite-sericite–altered auriferous quartz vein are reported in Appendix Table A5,

Table 1.	Molvbdenite	Re-Os Data	of the Haigou	Gold Deposit
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Sample	Weight (mg)	Re (ppm)	$\pm 2\sigma$	$^{187}\mathrm{Re}\ \mathrm{(ppm)}$	$\pm 2\sigma$	¹⁸⁷ Os (ppb)	$\pm 2\sigma$	Age	$\pm 2\sigma^1$	$\pm 2\sigma^2$	Laboratory
HAIG-23 (0.3–5 m	nm)										
HAIG-23-a1	21	43.34	0.65	27.13	0.41	149.06	1.04	327.53	4.99	6.31	CAGS
HAIG-23-a2	5	41.85	0.31	26.30	0.20	152.75	0.99	347.55	3.83	4.85	CAGS
HAIG-23-a3	6	47.69	0.40	29.97	0.25	96.76	0.63	193.47	2.22	2.81	CAGS
HAIG-23-b	20	48.25	0.36	30.32	0.22	171.27	1.20	338.05	3.78	4.79	CAGS
HAIG-23-c	19	23.84	0.09	14.98	0.06	80.89	0.27	323.16	1.34	1.67	DU
HAIG-23-d	31	25.12	0.09	15.79	0.06	85.21	0.24	323.12	1.33	1.67	DU
HG-30 (10–100 µr	n)										
HG-30	20	8.01	0.15	5.01	0.10	26.35	0.66	314.59	6.17	7.82	IGCAS
HG-31 (2–30 µm)											
HG-31-a	20	86.98	1.58	54.45	0.99	271.64	2.82	298.70	2.44	3.09	IGCAS
HG-31-b	5	96.26	0.91	60.50	0.57	321.55	2.32	318.17	3.88	4.91	CAGS
HG-32 (3–50 µm)											
HG-32-a	30	111.89	3.76	70.04	2.35	357.73	8.42	305.77	5.67	7.18	IGCAS
HG-32-b	20	115.25	1.28	72.44	0.81	372.56	2.44	307.93	3.95	5.00	CAGS
HG-32-c1	2	99.32	0.92	62.42	0.58	161.74	1.00	155.32	1.82	2.31	CAGS
HG-32-c2	6	132.63	1.35	83.36	0.85	433.44	2.99	311.29	3.88	4.91	CAGS
HG-32-d1	20	105.12	0.39	66.07	0.25	338.47	1.08	306.72	1.24	1.56	DU
HG-32-d2	20	117.02	0.44	73.55	0.28	381.01	1.21	310.15	1.25	1.58	DU
HG-33 (5–50 μm)											
HG-33-a	17	93.44	0.37	58.73	0.23	308.01	1.07	313.97	1.27	1.60	DU
HG-33-b	30	142.80	2.08	89.39	1.30	459.18	3.39	307.53	1.79	2.26	IGCAS
HG-34 (0.5–2 mm)										
HG-34-a	29	0.02	0.001	0.02	0.001	0.09	0.003	345.60	19.86	19.95	DU
HG-34-b	5	0.21	0.02	0.13	0.01	1.04	0.07	467.12	40.96	51.85	CAGS

Note: Numbers in brackets after samples represent the grain size of the analyzed molybdenite; samples with letters are different mineral separates from individual sample; samples with letter-numbers are replicate analyses of the same aliquot from individual sample; laboratory abbreviations are in the text ¹Full analytical uncertainty

²Full analytical and decay constant uncertainty of Smoliar et al. (1996)



Fig. 10. Re-Os model and isochron ages for molybdenite from the Haigou Au deposit. (A, B) Re-Os data for 16 molybdenite separates. (C, D) Re-Os data for nine of the separates shown in A.

and the apparent age spectra and isochron diagram are illustrated in Figure 11. The plateau age is 165.3 ± 1.2 Ma (MSWD = 0.19; Fig. 11A), and the inverse isochron age is 166.0 ± 1.6 Ma (MSWD = 3.9; Fig. 11B), which are the same within the analytical uncertainty. The plateau age is defined by seven continuous heating steps corresponding to 75.4% of the total ³⁹Ar released. The initial ⁴⁰Ar/³⁶Ar ratio of 284 ± 14 is indistinguishable from the atmospheric value.

Discussion

The Re-Os geochronology

Although we were able to reliably determine the age of the Haigou gold mineralization using the molybdenite Re-Os geochronometer, several of the samples yielded anomalously old or young ages. Significantly, the fine-grained molybdenite separates returned geologically meaningful ages, whereas the coarse-grained samples commonly yielded anomalously old or young model ages.

The ages for the fine-grained molybdenite samples (i.e., HG-30, 31, 32, and 33; Table 1), involving both replicate

analyses of the same aliquot and multiple measurements of different mineral separates, are commonly close to the calculated weighted mean model age of 314.6 ± 5.0 Ma (n = 16; including analyses from DU, CAGS, and IGCAS). Several model ages for a single sample also suggest that, except in one case, the model ages of fine-grained molybdenite are very similar (305.8 \pm 5.7–311.3 \pm 3.9 Ma); the remaining model age is 155.3 ± 1.8 Ma (Fig. 4B). It should be noted, however, that the mass of molybdenite analyzed from this location was very small—the smallest for all the samples analyzed (2 mg). Another sample from this location returned a model age of 311.3 ± 3.9 Ma (the sample weight was 6 mg). Consequently, the anomalously young model age for the fine-grained samples is attributed to the small aliquot of material used for analysis (cf. Stein et al., 2001, 2003; Selby et al., 2003, 2004; Selby and Creaser, 2004). In contrast, the coarse-grained molybdenite samples (i.e., HAIG-23 and HG-34) all yielded ages (mostly older) that are inconsistent with the geology of the deposit (Table 1). It should be noted that the three samples of coarsegrained molybdenite that returned highly anomalous ages were small (HG-34-b, 467.1 Ma with 5 mg; HAIG-23, 347.6



Fig. 11. A sericite plateau Ar-Ar age (A) and isochron age (B) for the Haigou gold deposit.

and 193.5 Ma with 5 and 6 mg, respectively). In summary, all molybdenite samples weighing more than 15 mg yielded reliable Re-Os ages (Fig. 12; Table 1).

Although the isochron and weighted mean model ages of molybdenite samples in the deposit were well constrained (Fig. 10C, D), replicate determinations of the age of the same aliquot (e.g., HG-32-d1 and d2, weighing 20 mg, 306.7 ± 1.2 and 310.2 ± 1.3 Ma, respectively; Table 1; Fig. 4B) and multiple analyses of different aliquots from the same sample (e.g., HG-33-a and b, 314.0 ± 1.3 and 307.5 ± 1.8 Ma, weighing >15 mg; Table 1) were not strictly reproducible within the analytical uncertainty. A likely explanation for this and some of the anomalous ages is spatial decoupling of daughter ¹⁸⁷Os from parent ¹⁸⁷Re within single crystals, a phenomenon that increases in importance with increasing grain size (Stein et al., 2001, 2003; Selby and Creaser, 2004; Porter and Selby, 2010). Alternatively, some of the molybdenite may have been deformed after crystallization, creating dislocations or defects into which ¹⁸⁷Os could preferentially accumulate (Stein et



Fig. 12. Analyzed aliquot size versus model age for the molybdenite separates.

al., 2003; Selby and Creaser, 2004). Therefore, the Re-Os data obtained for molybdenite in a shear plane/vein (Fig. 4B), which was active over a period of several million years (e.g., 311–306 Ma), could be meaningful. The hypothesis of decoupling between ¹⁸⁷Os and ¹⁸⁷Re, however, is supported by the observation that within single molybdenite crystals, the Re content varies considerably, e.g., from 49 to 101 ppm in a single crystal from sample HG-32 (Fig. 8B; App. Table A2). The reason for the heterogeneous distribution of Re in the molybdenite of these samples is still unclear but may be related to the overall abundance of Re in the hydrothermal fluid (Rathkopf et al., 2017), compositional changes in the hydrothermal fluid with time (Stein et al., 2001), or partitioning of Re between vapor and liquid (Stein, 2014); analogous behavior has been reported for Mo (Hurtig and Williams-Jones, 2014; Williams-Jones and Migdisov, 2014) and/or the post-ore deformation of the molybdenite.

As reported above, a total of 13 pyrite separates free of molybdenite that could be detected using a scanning electron microscope were analyzed for the purpose of Re-Os geochronology. Because some of these samples had high Re contents and high Re/Os ratios, we conclude that they likely contained nanoparticles of molybdenite that could not be observed. Moreover, although the 13 samples yielded an isochron date of 319.7 ± 6.2 Ma, which overlaps with the age of molybdenite, the initial ¹⁸⁷Os/¹⁸⁸Os ratio predicted by this isochron is strongly negative. We therefore conclude that the pyrite Re-Os chronometer could not be used to determine the age of the gold mineralization and do not consider this chronometer further.

A previously unrecognized Paleozoic gold mineralization

The vast majority of the magmatic-hydrothermal ore deposits in the eastern Central Asian orogenic belt formed between the Jurassic and Cretaceous (i.e., 160–120 Ma; Mao et al., 2014; Ouyang et al., 2015; Gao et al., 2018). However, very few ages have been reported for the lode gold deposits in this region, and the only ages that are available are consistent with a Mesozoic age for this mineralization; these ages were determined mainly from sericite associated with the gold mineralization using the Ar-Ar method (e.g., Hart et al., 2002; Yang et al., 2003; Yu et al., 2010; Chai et al., 2016). Thus, most researchers consider the lode gold deposits in this region to be genetically related to Mesozoic granites emplaced during Paleo-Pacific oceanic plate subduction (e.g., Yang et al., 2003; Yu et al., 2010). This includes the Haigou gold deposit, which is the focus of the current study (e.g., Yu et al., 2010; Li, L., et al., 2017; Zeng et al., 2017). Li, L., et al. (2017) proposed an age of 161.9 ± 1.3 Ma for the Haigou deposit based on Ar-Ar dating of associated sericite, and Yu et al. (2010) and Feng (1998) obtained ages of 171 ± 16 and 144 Ma, respectively, for fluid inclusions in auriferous quartz veins using Ar-Ar and K-Ar methods. Finally, several studies have concluded that the gold mineralization at Haigou took place between 132 and 125 Ma, based on zircon U-Pb age determinations for dikes that crosscut the orebodies (e.g., Li, X., et al., 2012; Chang et al., 2013; Zeng et al., 2017). However, the zircon U-Pb ages for the dikes cutting orebodies can only establish the lower age limit for gold deposition at Haigou and not the actual timing of gold mineralization.

Our new Re-Os and U-Pb geochronological results indicate that the gold mineralization at Haigou is much older than previously thought and took place in the late Paleozoic. The granitic stock, which hosts the auriferous quartz veins, yielded mean zircon 206 Pb/ 238 U ages between 329.5 ± 1.0 and 327.1 ± 1.1 Ma (Fig. 9H, I), consistent with its emplacement during the late Paleozoic. The molybdenite, which is closely associated with gold in the deposit (Fig. 6C-F), yielded a weighted mean Re-Os age of 310.0 ± 2.6 Ma (n = 9, MSWD = 12; Fig. 10C) and a well-constrained 187 Re/ 187 Os isochron age of 308.6 ± 8.1 Ma (MSWD = 9; Fig. 10D). Significantly, this age is the same as that of a dike (mean ²⁰⁶Pb/²³⁸U zircon model age of 310.9 ± 1.1 Ma; Fig. 9B), which, based on its orientation parallel to the auriferous veins, we speculate may have been emplaced contemporaneously with the ore. In summary, we conclude from the Re-Os ages of molybdenite closely associated with native gold in quartz veins and a similar U-Pb zircon age for a possible synore dike that the Haigou gold deposit formed at 310 Ma (Fig. 13).

The discovery that the Haigou gold deposit, one of the largest in the region, is of late Paleozoic age and not late Mesozoic age, as previously proposed, raises considerable doubt over the conclusion that the gold deposits in the region all formed in the late Mesozoic (ca. 160–120 Ma; e.g., Hart et al., 2002; Yang et al., 2003; Zeng et al., 2012; Mao et al., 2014; Ouyang et al., 2015; Zhai et al., 2015; Chen et al., 2017; Gao et al., 2018, and references therein). It also raises doubts about the appropriateness of using the Ar-Ar method to date these deposits (most of the gold deposits in the region have been dated using this method), because of the ease with which these dates can be reset by later thermal events. Indeed, our own analysis of sericite from an auriferous vein in the Haigou deposit exemplifies the problem nicely. Although the analysis yielded a very convincing plateau age of 165.3 ± 1.2 Ma (Fig. 11A), the Re-Os and U-Pb data demonstrate very clearly that this represents an age that was reset during the emplacement of late Mesozoic intrusions (mostly in the western part of the ore district; Fig. 2) and dikes (Figs. 2, 3). Two previous studies (e.g., Yu et al., 2010; Li, L., et al., 2017) for the Haigou deposit also demonstrated that the Ar-Ar ages have been largely reset by the post-ore magmatic events. Thus, sericite Ar-Ar ages should be interpreted with caution if there was post-ore magmatism in the region. Our new geochronological data, by showing that the gold mineralization is of late Paleozoic age, emphasize the need for careful geochronological studies to evaluate the true timing of gold mineralization in relatively complex geologic settings.

The tectonic setting of the Haigou Paleozoic gold mineralization

Northeastern China and adjacent regions belong to the Paleozoic accretionary margins of the Siberia craton and the North China craton (Wang et al., 2016; Yang et al., 2016). The final closure of the Paleo-Asian Ocean in northeastern China was along the Solonker-Xar Moron-Changchun-Yanji suture, and this was largely completed in the late Permian, although



Fig. 13. A summary of the timing of mineralization, hydrothermal alteration, and magmatism in the Haigou gold deposit. Some of the U-Pb and Ar-Ar ages are from Feng (1998), Shen et al. (1999), Yu et al. (2010), Zhang et al. (2012), Chang et al. (2013), Zeng et al. (2017), and Li, L., et al. (2017).

activity continued into the Triassic (Wilde, 2015). Thereafter (late Permian to Early Triassic), the tectonic setting of northeastern China changed from one dominated by NS-directed movement to one dominated by east-west movement when the Paleo-Pacific plate motion became the dominant tectonic control (Li, 2006; Wilde, 2015; Wang et al., 2016; Liu et al., 2017, and references therein). Thus, the Haigou gold deposit (~310 Ma) was emplaced before the onset of tectonism associated with the Paleo-Pacific Ocean subduction but was temporally associated with the Paleo-Asian subduction. The location of this deposit in the southern part of the Solonker-Xar Moron-Changchun-Yanji suture is consistent with the hypothesis that gold mineralization in northeastern China was closely related to mid-late Paleozoic magmatism (330-310 Ma), localized in an island-arc setting along the craton margin. This hypothesis is supported by the occurrence of several late Paleozoic-Early Triassic subduction-accretion metamorphic complexes along the suture, e.g., the Shitoukoumen-Yantongshan piemontiteschist, the Hulan Complex, the Seluohe Complex, the Qinglongcun Complex, and the Kaishantun Complex (Zhou et al., 2013), as well as the Permian granite belt along the Dunhua-Yanji (Sun et al., 2013), all of which indicate an island-arc setting for northeastern China in the late Paleozoic.

Although Paleozoic lode gold deposits temporally and genetically associated with Paleozoic magmatism are common between the southern segment of the Central Asian orogenic belt and the northern margin of the North China craton and the Tarim craton, almost all of them occur in the western segment of the Central Asian orogenic belt (e.g., Shen et al., 2014; Dong et al., 2018; Wang et al., 2018). The reason the eastern part of this important metallogenic belt seems to be largely devoid of Paleozoic lode gold deposits is unclear. It is possible that, as was the case for the Haigou deposit, they have not been correctly dated. Thus, as most of the gold deposits in the eastern Central Asian orogenic belt have been dated using the Ar-Ar method, they may be Paleozoic deposits that were affected by later magmatic events. Alternatively, granitoid magmatism may have been much less voluminous in the Paleozoic than in the Mesozoic, when subduction of the Paleo-Pacific plate was associated with slab retreat and rollback that resulted in regional thinning and delamination of the lithosphere and promoted this type of magmatism (e.g., Wu et al., 2011; Wilde, 2015; Zhou et al., 2018). Nevertheless, there is a significant number of granitoids in the eastern Central Asian orogenic belt of similar age to the Haigou granitoid stock, e.g., the Silengshan, Xincuntun, and Jinxing stocks (Liu et al., 2009; Wu et al., 2011). Irrespective of the reason for the apparent lack of Paleozoic lode gold deposits in the eastern Central Asian orogenic belt, the new Re-Os and zircon U-Pb data reported in this study, providing evidence of Paleozoic gold mineralization at Haigou, suggest that gold exploration strategies in the region may need to be reevaluated.

Conclusions

Systematic Re-Os dating of molybdenite that is spatially and temporally associated with gold mineralization in the Haigou lode Au deposit, one of the largest gold deposits in the eastern Central Asian orogenic belt, has shown that, contrary to the results of earlier studies, the deposit was emplaced during the Paleozoic (312–310 Ma) and not the late Mesozoic. This age is consistent with U-Pb zircon ages determined for the host monzogranite and monzonite of 327 and 329 Ma, respectively, and a zircon U-Pb age of 310 Ma for a dike parallel to the auriferous veins and therefore potentially synore. The new geochronological data reported here provide clear evidence for a late Paleozoic gold mineralization event in the easternmost Central Asian orogenic belt. The new Re-Os and U-Pb data suggest that gold exploration strategies in the region may need to be reevaluated.

This study also demonstrates that accurate and reproducible molybdenite Re-Os ages require a combination of careful petrographic documentation, proper sampling procedures, relatively large aliquots for analysis, particularly if the Re contents are low, and multiple analyses of individual samples. In geologic environments affected by multiple thermal events, Re-Os geochronology may provide the only means of reliably determining the true age of mineralization, and in all cases Ar-Ar ages should be treated with caution because of the ease with which thermal disturbances can overprint the ore-forming event.

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combines field investigation, mineralogy, multiple isotopes, geochronology, and numerous thermodynamic modeling techniques to understand the genesis of hydrothermal ore deposits in the eastern segment of the Central Asian orogenic belt, northeastern China, typically focusing on the epithermal gold and silver deposits.

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