Short Communication

Rb–Sr Dating of Gold-Bearing Pyrite in the Jinchang Porphyry Cu–Au Deposit, Heilongjiang Province, NE China

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Abstract

The Jinchang Cu–Au deposit in Heilongjiang Province, NE China, is located in the easternmost part of the Central Asian Orogenic Belt. Rb–Sr analyses of auriferous pyrite from the deposit yielded an isochron age of 113.7 ± 2.5 Ma, consistent with previously reported Re–Os ages. Both sets of ages represent the timing of Cu–Au mineralization because (i) the pyrite was separated from quartz–sulfide veins of the mineralization stage in granite porphyry; (ii) fluid inclusions have relatively high Rb, Sr, and Os content, allowing precise measurement; (iii) there are no other mineral inclusions or secondary fluids in pyrite to disturb the Rb–Sr or Re–Os decay systems; and (iv) the closure temperatures of the two decay systems are ≥500°C (compared with the homogenization temperatures of fluid inclusions of 230–510°C). It is proposed that ore-forming components were derived from mantle–crust mixing, with ore-forming fluids being mainly exsolved from magmas with minor amounts of meteoric water. The age of mineralization at Jinchang and in the adjacent regions, combined with the tectonic evolution of the northeast China epicontinental region, indicates that the formation of the Jinchang porphyry Cu–Au deposit was associated with Early Cretaceous subduction of the paleo-Pacific Plate.

Keywords: Heilongjiang Province, Jinchang Cu–Au deposit, NE China, Pyrite, Rb–Sr dating.

1. Introduction

The Jinchang Cu–Au deposit in Heilongjiang Province, NE China, is located in the easternmost part of the Central Asian Orogenic Belt (CAOB) and contains a > 76 t lode, making it one of the largest gold deposits discovered in China since the 1990s (Mu et al., 2000; Chen et al., 2002; Zhou et al., 2002; Goldfarb et al., 2014). Most research to date has focused on the ore geology and its controlling factors (Zhu et al., 2003; Jia et al., 2008); the geochemistry of fluid inclusions (Men et al., 2008; Wang et al., 2007a, 2007b, 2007c; Zhang et al., 2006, 2008a, 2008b, 2008c); the age of granodiorite, granophyric granite, diorite porphyry, and gold mineralization; and the genesis of the deposit. Zhang et al. (2016) reported Re–Os isotopic data for five gold-bearing pyrites from the Jinchang deposit with an isochron age of 114 ± 22 Ma. Zhang et al. (2013) reported that the emplacement of mineralized granophytic granite, biotite monzogranite, granodiorite, and granite porphyry occurred at 201 ± 3, 203 ± 4, 201 ± 5, and 110 ± 3 Ma, respectively, with sericite from the gold-mineralized, phyllic-altered granodiorite and granite porphyry yielding Rb–Sr isochron ages of 110 ± 4 Ma (MSWD = 1.04) and 107 ± 5 Ma (MSWD = 0.91).
respectively. Zhao et al. (2012) reported that the emplacement of diorite porphyry occurred at 118.1 ± 1.6 to 116 ± 2 Ma, while Qing et al. (2012) reported 40Ar–39Ar isochron ages of quartz–sulfide veins of 129 ± 0.8 to 119 ± 5 Ma. The genesis of the Jinchang Cu–Au deposit has been variously described as an epithermal deposit that formed from low-temperature fluid with low concentrations of CO2 in auriferous quartz–sulfide veins (based on fluid inclusion studies, Zhu et al., 2003), a porphyry–epithermal deposit (Wang et al., 2007a, 2007b, 2007c), a deposit of porphyry-related origin involving high-temperature fluids with high salinities (Jia et al., 2008), an orogenic deposit that formed from CO2-rich fluids in breccias (Zhang et al., 2008a, 2008b, 2008c), or an oxidized intrusion-related deposit that formed from high-temperature fluids (Zhang et al., 2014). Debate continues concerning the age of mineralization and the genesis of the deposit.

Accurate determination of the mineralization age is important in elucidating its genesis and the coupling relationships between mineralization and geological events (Lu et al., 1999). In recent decades, Rb–Sr dating has been successfully applied in the dating of various types of ore deposits (Brannon et al., 1992; Nakai et al., 1993; Christensen et al., 1995; Yang & Zhou, 2001; Hu et al., 2012; Wang et al., 2014). The present study focused on detailed field observations and Rb–Sr isotopic data of individual gold-bearing pyrite grains from the Jinchang Cu–Au deposit, with the aim of constraining the timing of gold mineralization and the nature of the metal sources.

2. Regional geology

The Jinchang Cu–Au deposit is located in the easternmost part of the Xingmeng orogenic belt, eastern CAOB (Fig. 1a). The study area is bordered by the Ji–Hei fold system and the Khanka and Jiamusi blocks to the north and the North China Craton (NCC) to the south (Xu et al., 2009; Wu et al., 2011; Zhou & Wilde, 2013). The gold district is located at the junction of the Laoheishan Depression and Taipingling Uplift (Chen et al., 2002; Jia et al., 2008; Zhang et al., 2013). These two units are separated by the NNE-trending transcurrent Suiyang Fault (Fig. 1b), which controls the distribution of subsidiary faults in the Jinchang area. The area has a tectono-magmatic history that includes tectonism and magmatism.

Fig. 1 (a) Regional geological map showing the location of the study area within the CAOB and (b) detailed geological sketch map of the Jinchang mine area (after Zhang et al., 2013).
controlled by the evolution of the Paleo-Asian Ocean in the Paleozoic and the subduction of the paleo-Pacific Plate during the Mesozoic.

The Huangsong Group, which occurs among undeformed Mesozoic granitoids (Fig. 1b), mainly comprises mica schist, gneiss, amphibolite, and marble, with a protolith mainly of clastic rocks with intercalated calc-alkaline volcanic rocks that are widely distributed in the region. Mesozoic intermediate–acidic plutons are dominant, with minor volcano-sedimentary rocks and mafic to felsic dikes (Fig. 2). The intrusions mainly occur as stocks and dikes of diorite, granophyric granite, monzogranite, and granite porphyry. Previous studies grouped these rocks chronologically into four formation stages (Chen et al., 2002; Jia et al., 2008): (i) biotite diorite, inferred to be early Indosinian; (ii) granodiorite, biotite granite, plagiogranite, and moyite formed in the late Indosinian to early Yanshannian, yielding zircon U–Pb ages of 203–201 Ma (Zhang et al., 2013); (iii) 200 Ma granophyric granite and biotite granite inferred to be early to middle Yanshannian; and (iv) mid to late Yanshannian quartz porphyry and diorite–porphyry (118.1 ± 1.6; Zhao et al., 2012) and granite porphyry (111 ± 2 Ma; Lu et al., 2009).

3. Deposit geology

Mesozoic granitoids are dominant in the mine area, surrounded by minor Jurassic volcano-sedimentary rocks and mafic to felsic dikes (Fig. 2). The granitoids include granophyric granite, diorite, granite porphyry, and monzogranite and were emplaced at ca 200 Ma, and mafic to felsic dikes were intruded at ca 120–110 Ma (Lu et al., 2009; Zhao et al., 2012; Zhang et al., 2013). Zircon U–Pb ages of the volcano-sedimentary rocks are 220–200 Ma (Xu et al., 2009). Faults striking NE–SW, NW–SE, N–S, and E–W are dominant in the mine area. The major gold-bearing structures are breccia pipes, which are controlled by two sets of faults striking in different directions. There are four types of orebodies in the Jinchang mine: breccia ore, ring-radial fault-controlled veins, layered micro-vein and disseminated ore, and fractured alteration ore. Many orebodies have been recognized (Fig. 2), including eight of the breccia type, dozens of quartz–sulfide veins (filling fractures), and several of the alteration type, with the different types having similar mineral assemblages. Metallic minerals are mainly pyrite, galena, chalcopyrite, and sphalerite (Fig. 3a), while non-metallic minerals include quartz,
feldspar, sericite, chlorite, and calcite. Types of ore-body structures include veinlet-disseminated, nodular, eutectic, and brecciated, while textures are crystalline, cataclastic, or metasomatic with solid-solution phenomena. In terms of the paragenetic assemblages and crosscutting relationships, gold mineralization in the Jinchang deposit can be subdivided into four hypogene stages, namely, K-feldspar–quartz–pyrite, pyrite–quartz, quartz–polymetallic sulfide, and pyrite–calcite. Alteration in the deposit is pervasive and mainly includes sericitization, silicification, kaolinization, potassic alteration, carbonatization, and chloritization.

4. Sampling and analytical techniques

4.1 Samples for Rb–Sr dating

Four gold-bearing pyrite samples of the quartz–polymetallic sulfide stage with no obvious deformation features were taken from a single hand specimen of ore for Rb–Sr dating (Fig. 3a, b). The hand specimen contains dull-gray, pyrite-bearing quartz with a veinlet-disseminated structure. Pyrite occurs as pentagonal dodecahedrons between quartz fragments and contains inclusions of Au and minor chalcopyrite.

4.2 Analytic procedures

After leaching the four samples from Jinchang with acetic acid, residues were analyzed for their $^{87}$Rb/$^{86}$Sr ratios. Rb–Sr isotopic analyses were performed in the Nanjing Soil Institute, Chinese Academy of Sciences. The selected pyrite crystals were ground into powder and ultrasonically cleaned for 30 min with Milli-Q water. After drying at low temperature, 100–200 mg pyrite powder was mixed with $^{85}$Rb–$^{84}$Sr diluent into 1 mL HNO$_3$ + 1 mL HCl mixed acid at 120°C on an electric hot plate. After drying by distillation, the sample contained hydrochloric acid, and centrifugal separating of Rb, Sr, and other elements was performed through an ion exchange column from the liquid supernatant. The Rb and Sr concentrations of the samples and their isotopic ratios were determined by VG-354 multicollector mass spectrometer at the Advanced Analysis Center, Nanjing University, China. The standard used was the United States NIST SRM 987 Sr, and the total procedure blank for Rb and Sr analyses is $3 \times 10^{-9}$ g. The accuracy of the Rb–Sr ratio and Sr concentration are 1% and better than $10^{-5}$, respectively. The details of sample preparation for Rb and Sr analyses, mass spectrometer analytical method, and results for various standard materials are described in Wang et al. (2007a, 2007b). The Rb–Sr isochron ages were calculated using the Isoplot program (Ludwig, 2008).

4.3 Dating of gold-bearing pyrite

Results of Rb–Sr isotopic analyses are presented in Table 1 and Fig. 4. Rb and Sr contents of the four samples are 0.370–1.864 ppm and 1.426–6.991 ppm,
Rb-Sr dating of Jinchang Cu-Au deposit

Table 1 Measured Rb–Sr isotopic data for gold-bearing pyrite from the Jinchang gold deposit

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Rb (ppm)</th>
<th>Sr (ppm)</th>
<th>$^{87}$Rb/$^{86}$Sr</th>
<th>2σ</th>
<th>$^{87}$Sr/$^{86}$Sr</th>
<th>2σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>0.370</td>
<td>6.991</td>
<td>0.157</td>
<td>0.010</td>
<td>0.710852</td>
<td>0.000005</td>
</tr>
<tr>
<td>Pyrite</td>
<td>0.754</td>
<td>2.358</td>
<td>0.944</td>
<td>0.010</td>
<td>0.712039</td>
<td>0.000005</td>
</tr>
<tr>
<td>Pyrite</td>
<td>1.864</td>
<td>1.426</td>
<td>3.859</td>
<td>0.010</td>
<td>0.716827</td>
<td>0.000005</td>
</tr>
<tr>
<td>Pyrite</td>
<td>0.8464</td>
<td>4.649</td>
<td>0.538</td>
<td>0.010</td>
<td>0.711483</td>
<td>0.000005</td>
</tr>
</tbody>
</table>

respectively, with $^{87}$Rb/$^{86}$Sr ratios of 0.157–3.859. The observed ranges probably indicate the heterogeneity of the initial Sr isotopic composition of the pyrite or its inclusions (Lüders & Ziemann, 1999). The isochron plot (Fig. 4) indicates an age of 113.7 ± 2.5 Ma (2σ, MSWD = 1.09) with a $(^{87}$Sr/$^{86}$Sr)$_i$ ratio of 0.71058 ± 0.00007.

5. Discussion

5.1 Rb–Sr dating of pyrites

Single-grain dating of microsamples of minerals associated with gold formation, under low blank levels and with precise mass spectrometric techniques, has been successfully applied to quartz, pyrite, and sericite in determining the timing of mineralization (Li et al., 2008; Chen et al., 2009). Rb–Sr dating of sulfide minerals, particularly sphalerite and pyrite, is often used to date the formation of hydrothermal deposits (Brannon et al., 1992; Christensen et al., 1995; Yang & Zhou, 2001; Hou et al., 2006), although it has not always been successful. Many factors affect the Rb–Sr dating of sulfide minerals (Pettke & Diamond, 1996), with fluid and mineral (mica or feldspar) inclusions being considered major causes of variations in pyrite Rb–Sr ratios (Yang & Zhou, 2001). Secondary fluids and closure temperatures of the decay systems also contribute to the disturbance of the Rb–Sr system, which may be overprinted or reset by high-temperature hydrothermal alteration or the introduction of secondary fluids.

Measures were taken in the present study to improve the accuracy of Rb–Sr dating. Inclusions of sericite and feldspar were avoided, and different samples representing the same orogenic episode (avoiding postmineralization effects) in the same orebody were selected for analysis. Previous studies washed crushed samples in water and dilute acids to separate secondary inclusions (Brannon et al., 1992; Yang & Zhou, 2001), and the size (200 mesh) of pyrite selected for analysis was kept as small as possible, which can also minimize the secondary fluid inclusions (Wang et al., 2014). Here, samples with mineral assemblages of quartz, pyrite, and chalcopyrite were hand-picked, kept as small as possible, and leached with acetic acid for analysis to avoid secondary inclusions. The isochron pyrite age of 113.7 ± 2.5 Ma (Section 5) can therefore be considered to represent the timing of gold mineralization.

Pyrite from gold-bearing quartz–sulfide veins and auriferous pyrite veins, in the matrix of breccia or in granite porphyry, yield an Re–Os isochron age of 114 ± 22 Ma (Zhang et al., 2016). Re–Os dating has proven to be a powerful geochronological tool for dating sulfide minerals (Shirey & Walker, 1998), but there are problems associated with the very low Os contents of sulfide minerals (<1 ppt) and the closure temperatures of decay systems. However, pyrite has a relatively high Os content of 14–38 ppt, which allows precise measurement.

The closure temperature of the Re–Os isotope system in pyrite is >500°C (Brenan et al., 2000; Nozaki et al., 2010). Homogenization temperatures of fluid inclusions at Jinchang are in the order of 230–510°C (Men et al., 2008), identical to the inclusion-trapping temperatures. These trapping temperatures are lower...
than or similar to the radiogenic closure temperature, indicating that the Re–Os system was not reset and that the pyrite Re–Os age (114 ± 22 Ma) reflects the age of mineralization.

Pyrite samples selected for Rb–Sr and Re–Os dating were separated from quartz–sulfide veins of the mineralization stage in granite porphyry, and the age data agree within error, along with zircon U–Pb ages of granite porphyry and diorite porphyry (Zhang et al., 2013). This agreement among Rb–Sr, Re–Os, and U–Pb ages confirms that the Rb–Sr isotopic system in small pyrite grains can be used to determine meaningful mineralization ages.

5.2 Origin of the Jinchang deposit

Recent decades have examined the geological ore features, wall-rock alteration, ore-controlling structures, geochemistry of fluid inclusions, and geochronology of gold mineralization of the Jinchang gold deposit, yet the genesis of the deposit remains controversial. The deposit has been described variously as (i) a stockwork–breccia deposit (Liu et al., 1999); (ii) a medium- to high-temperature magmatic hydrothermal deposit (Mu et al., 2000); (iii) a low- to medium-temperature magmatic hydrothermal deposit (Zhu et al., 2003); (iv) a porphyry deposit (Wang, 2006); (v) an orogenic deposit (Zhang et al., 2008a, 2008b, 2008c); (vi) an epithermal porphyry deposit (Zhao et al., 2012); and (vii) a superposition of epithermal and porphyry deposits (Yu et al., 2017). The source of ore-forming fluid is one of the key issues in ore genesis (Yu et al., 2017). Hydrogen and oxygen isotopic compositions of quartz from the Jinchang ores indicate that the ore-forming fluids were mainly exsolved from magmas with minor amounts of meteoric water (Zhang et al., 2013). Pyrite sulfur δ34S values range from 1.1 to 8.8‰ (Mu et al., 2000; Li et al., 2003; Jia et al., 2008), indicating a magmatic/volcanic origin. The Pb isotopic compositions of pyrite and galena from quartz–sulfide veins of the deposit indicate that Pb was sourced from the lower crust (Mu et al., 2000). Pyrite from gold-bearing quartz–sulfide veins and auriferous pyrite veins in the matrix of breccias and in granite porphyry yields (187Os/188Os) ratios of 0.01, 0.02, 0.09, and 0.29, respectively, indicating mantle–crust mixing (Zhang et al., 2016). Pyrite samples from the Jinchang deposit have Co/Ni ratios ranging from <0.4 to 40, similar to those from volcanic and hydrothermal deposits, indicating a magmatic–hydrothermal origin (Zhang et al., 2016).

He and Ar isotopic compositions of fluid inclusions in pyrite from breccias and stockwork yield 3He/4He and 40Ar/36Ar ratios of 0.13–2.42 Ra and 308.9–336.7, respectively, indicating that ore-forming fluids were a mixture of crust- and mantle-derived fluids contaminated by circulating meteoric water. Data of the present study constrain the timing of mineralization to 113.7 ± 2.5 Ma, temporally related to the granite porphyry. The measured (87Sr/86Sr) ratios for pyrite from quartz–sulfide veins, 0.71058 ± 0.00007, are higher than those of the upper mantle (<0.704) and lower than those of terrigenous silicate (>0.719) (Faure, 1986), indicating that the ore-forming materials, especially Rb and Sr, were originally derived from mixed mantle and crustal materials. In addition, the (87Sr/86Sr) ratio for pyrite is higher than that of sericite from granite porphyry and granodiorite (0.7053 ± 0.0033 and 0.7063 ± 0.0047, respectively) (Zhang et al., 2013). The Hf isotopic compositions of the porphyry and granodiorite indicate that the source rocks incorporated mantle-derived material, either directly or indirectly (Zhang et al., 2013), indicating that the Sr isotope maybe did not reach uniformity (Chen et al., 2011). The sericite formed as a result of the hydrothermal alteration of the granite porphyry and granodiorite, which was formed ca 110 Ma (Zhang et al., 2013). Thus, the sericite inherited the Sr isotopic composition of porphyry and granodiorite. As the initial Sr ratio of sericite is low, the explanation for such sericite Sr isotopic compositions is that they may be more affected by mantle fluid or the other reasons that not well known.

The chronology of mineralization thus indicates that the main source of ore-forming materials for the Jinchang Cu–Au deposit was closely associated with Cretaceous granite porphyry.

5.3 Implications for regional gold mineralization

Pyrite Rb–Sr ages determined in the present study, and previously published alteration and mineralization ages, indicate that Cu–Au mineralization at Jinchang occurred during the Early Cretaceous. Numerous published high-precision age data indicate that the timing of gold mineralization in Heilongjiang and Jilin provinces is similar to the ore-formation age of the Jinchang deposit. The zircon laser ablation–inductively couple plasma–mass spectrometry (LA–ICP–MS) U–Pb age of porphyritic dacite veins is consistent with the mineralization age of the Naozhi deposit (126.3 ± 1.7 Ma; Ren
et al., 2016), and quartz in the Naozhi deposit yields an \(^{40}\)Ar–\(^{39}\)Ar age of 123.6 ± 2.5 Ma (Meng et al., 2001). The quartz \(^{40}\)Ar–\(^{39}\)Ar age for the Duhuangling deposit is 107.0 ± 6 Ma, and zircon in the deposit yields LA–ICP–MS U–Pb ages of 109.9 ± 2.5 and 118.9 ± 2.2 Ma (Men, 2011). Metallogenic porphyritic quartz diorite in the Jiusangou deposit yields a zircon LA–ICP–MS U–Pb age of 108.1 ± 1.4 Ma (Ren et al., 2016). Sensitive high-resolution ion-microprobe (SHRIMP) U–Pb dating of altered, fine-grained diorite and postmineralization porphyritic andesite in the Xiaoxinancha deposit yielded ages of 123.45 ± 2.2 and 102.1 ± 2.2 Ma, respectively (Zhao, 2007; Sun et al., 2013), and a molybdenite Re–Os isochron age of 111.1 ± 3.1 Ma has been reported (Ren et al., 2016). The quartz \(^{40}\)Ar–\(^{39}\)Ar age of the Wufeng–Wuxingshan deposit is 123.0 ± 7 Ma (Zhao et al., 2010), and the pyrite Rb–Sr isochron age for the Tuanjiegu deposit is 113.8 ± 4.4 Ma (Wang et al., 2014), with a zircon LA–ICP–MS U–Pb age of 112–103 Ma for ore-bearing granodiorite porphyry (Sun et al., 2013). The LA–ICP–MS U–Pb ages of zircons from granitic rock and diabase of the Sandaowanzi deposit are 135.3 ± 3.9 and 115.98 ± 0.89 Ma, respectively (Han, 2013). The sericite \(^{40}\)Ar–\(^{39}\)Ar age of the Dongan deposit is 107.2 ± 0.6 Ma, with a zircon SHRIMP U–Pb age of 108.1 ± 2.2 Ma for rhyolite porphyry. These data indicate that gold mineralization and Early Cretaceous magmatic activity have close temporal and spatial relationships, consistent with a tectonic setting involving large-scale mantle upwelling and underplating triggered by subduction of the Paleo-Pacific slab (Wang et al., 2006; Zhang et al., 2010; Wu et al., 2011).

6. Conclusions

Rb–Sr isotope analyses of auriferous pyrite from the Jinchang Cu–Au deposit yield an age of 113.7 ± 2.5 Ma, representing the timing of mineralization. This age is consistent with previously reported Re–Os ages, with both types of dating having been applied to pyrite separated from quartz–sulfide veins of the same mineralization stage in granitic porphyry. Fluid inclusions in pyrite have relatively high Rb, Sr, and Os contents and can therefore be measured precisely. There are no mineral inclusions or secondary fluids in pyrite to disturb the Rb–Sr and Re–Os systems, which have closure temperatures of ≥500°C, compared with fluid inclusion homogenization temperatures of 230–510°C.

Isotope analyses indicate that ore-forming components were sourced from mantle–crust mixing, with ore-forming fluids being mainly exsolved from magmas with minor amounts of meteoric water. The Jinchang Cu–Au deposit was therefore closely associated with Cretaceous granite porphyry.

The age of mineralization at Jinchang and in adjacent regions, together with the tectonic evolution of the northeastern China epicontinental region, indicates that the formation of the Jinchang porphyry Cu–Au deposit was associated with Early Cretaceous subduction of the Paleo-Pacific Plate.

Acknowledgments

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