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Re-Os isotope dating of pyrite from the footwall mineralization zone of the Xinqiao deposit, Tongling, Anhui Province: Geochronological evidence for submarine exhalative sedimentation

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The Xinqiao deposit is located in the Tongling area, Anhui Province. This deposit is dominantly composed of stratiform sulfide orebodies, which are restricted to the transitional zone from clastic rocks to carbonates at the base of the Late Carboniferous Huanglong Formation. There are discordant veinlets or networks of mineralization in the footwall rocks below the stratiform sulfide orebodies. The underlying discordant mineralization zones coexist with conformable stratiform sulfide orebodies, which are considered to be the most representative features of massive sulfide deposits formed by submarine exhalative sedimentation. This study reports a pyrite ^{187}Re-^{187}Os isotopic age of 319±13 Ma (MSWD=16) for the footwall mineralization zone. This isochron age is consistent with the interval of strata hosting the conformable stratiform sulfide orebody, and provides direct geochronological evidence for Carboniferous exhalative sedimentary mineralization.

footwall mineralization, Re-Os isotope dating, exhalative sedimentation, Xinqiao deposit

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There are a number of large and economically important stratiform sulfide deposits hosted by Carboniferous strata in the Middle and Lower Yangtze River Belt (MLYRB). In the past several decades, great attention has been given to the economic significance and distinctive geological features of these deposits. There are two distinctive models for the ore genesis of these deposits: (1) they are strata-bound skarn deposits associated with Yanshanian granitoids [1–4]; or (2) they are massive sulfide deposits formed by submarine exhalative sedimentation during the Late Carboniferous, and then altered by Yanshanian granitoid magmatism and related hydrothermal fluids [5–10]. Disagreements regarding these two models are focused on whether exhalative sedimentary mineralization existed. Previous studies concerning exhalative sedimentation mostly concentrated on the geology, geochemistry and fluids of the ore deposit [5–10]. However, the lack of reliable ages for the mineralization has resulted in a scarcity of research on the metallogenic geochronology needed to resolve the genetic debate.

Massive sulfide deposits formed by submarine exhalative sedimentation generally are characterized by veinlet, stockwork, disseminated and brecciaed mineralization developed in footwall rocks of stratiform sulfide orebodies [11–15]. In the MLYRB, a similar discordant veinlet and stockwork mineralization below the stratiform sulfide orebody generally is observed, and is thus considered as one of the most important pieces of evidence for the exhalative sedimentary origin of ore deposits [7,10,16–20]. Previously, the timing of massive sulfide deposits was estimated by dating the minerals in the stratabound sulfide orebody [21–25]. However, geochron ages of the footwall mineralization are scarce. Nesbitt et al. [26] obtained a U-Pb age of hydrothermal zircons in the footwall mineralization zone of the Los Frailes VMSD deposit from the Iberian Pyrite Belt.

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This finding provided the timing of submarine exhalative sedimentation for that region.

In recent years, the Re-Os isotope system has been used increasingly to date ages of ore deposits. Besides molybdenite [27–31], sulfides (e.g. pyrite) with low Re and Os concentrations also has been used successfully to date ages of ore deposits using the rhenium-osmium (Re-Os) method [32–36]. The Xinqiao deposit is one of the most representative stratiform sulfide deposits in the MLYRB. In this study, we present a date for the pyrite from the footwall mineralization zone based on the Re-Os method to constrain the time of the footwall mineralization of the Xinqiao deposit. In addition, we discuss the metallogenic significance of this deposit.

1 Regional geological setting

The MLYRB is located on the northern margin of the Yangtze Craton, and is bordered by the North China Craton and Dabieshan orogenic belt to the north. It is one of the most important metallogenic belts in China. This belt has been a fault-bounded depression zone since the Sinian Period. Its formation and development have been controlled by several deep faults [5,6]. During the Late Paleozoic, the belt generally received several thousand meters of sediment consisting predominantly of carbonates and alternating marine and terrigenous coal-bearing formations. In addition, intensive vertical movement has resulted in the absence of Lower Carboniferous strata and the formation of several parallel unconformity surfaces and deepwater siliceous rocks of the Permian Gufeng and Dalong formations. After the collision between the Yangtze Plate and the North China Plate in the Late Triassic, extensive intermediate to felsic magmatism took place during the Yanshanian Period. This activity formed a great number of Yanshanian intrusive bodies, and Upper Jurassic to Lower Cretaceous terrestrial volcanic and volcaniclastic rocks [1–4,37–41].

The Cu-Au deposits in the MLYRB can be divided into two groups according to their geological characteristics. The first group is stratiform sulfide deposits hosted by Late Carboniferous strata [5–10] (e.g. Xinqiao, Dongguashan, Tongguashan, Chengmenshan and Chengshan deposits). The orebodies are stratiform or stratoid, often extending over 1000 m along the strike, and having an attitude similar to that of their host rocks. The ore-hosted rocks consist of clastic rocks, dolomite and limestone. Sedimentary anhydrite and volcaniclastic rocks or lava sometimes are found in the host rocks of these deposits [6,8,10]. The ores show generally lamellar, banded or massive structures. The second group of Cu-Au deposits has a close relationship with Yanshanian granitoid intrusions. This group includes two dominant genetic types: skarn and porphyry deposits [1–4]. The ores have typical fabrics and mineral assemblages, indicating a magmatic hydrothermal origin. Wall-rock alterations are well-developed. Orebodies of these deposits are generally complicated, and occur at the contact zones between the Yanshanian intrusions and the Late Paleozoic-Early Mesozoic sedimentary rocks, or are within the Yanshanian granitoid intrusions. Typical examples of these deposits are the Datuanshan, Jinkouling, Fenghuangshan and Tongshankou deposits. Molybdenite Re-Os or Os-Os and albite or phlogopite Ar-Ar age data define a range from 145 to 135 Ma for these skarn and porphyry mineralizations [28–31]. These dates are identical with the emplacement ages of the associated granitoid intrusions [37–39].

2 Deposit geology

The Xinqiao deposit is to the south of the E-S trending Tongling-Shunan base fault, and is located in the intersection of both the plunging part of the Shujiadian anticline and the Dachengshan anticline in the Tongling area of the MLYRB. The sedimentary rocks outcropping in the Xinqiao orefield consist mainly of upper-middle Silurian sandstone and siltstone, Upper Devonian Wutong Formation sandy shale and sandstone, Upper Carboniferous Huanglong Formation dolomite and limestone, Chuanshan Formation limestone, Lower Permian Qixia Formation limestone and Gufeng Formation sillcalite (Figure 1). Some Upper Permian and Lower Triassic strata crop out in the northwest side of the orefield. Magmatic rocks exposed in the Xinqiao district are dominated by the Jitou intrusion with an ellipsoidal surface area of 0.5 km^2. The Jitou intrusion consists primarily

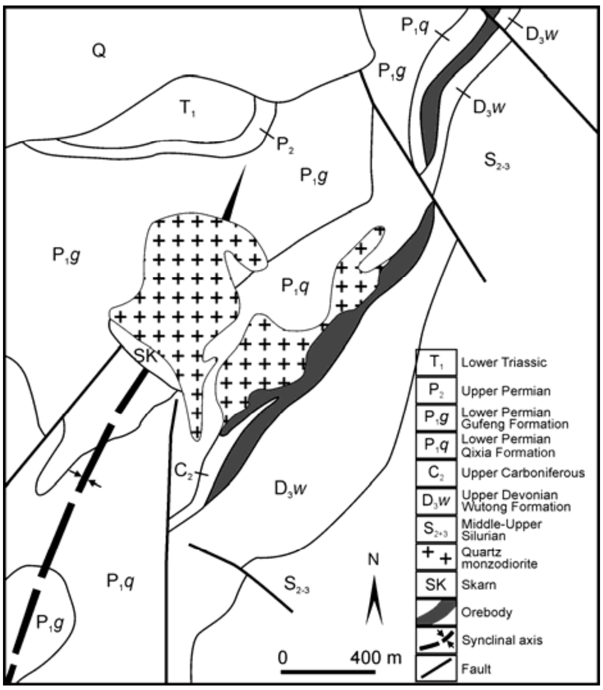

Figure 1 Geological map of the Xinqiao deposit (modified after Tang et al. [2]).

of quartz monzodiorite. Wang et al. [42] reported a zircon SHRIMP U-Pb age of 140.4±2.2 Ma for the Jitou intrusion. Marble, hornfel and skarn alterations are developed in the contact zone between the sedimentary rocks and the intrusion.

There are two different types of mineralization in the Xinqiao deposit: the stratiform sulfide orebody and skarn orebody. The stratiform sulfide orebody is the most economically important, and accounts for 90% of the reserve of the ore deposit. It has clear stratabound features and similar occurrence to their host rocks. It occurs in the transitional zone from clastic rocks (sandy conglomerate, sandstone and muddy sandstone) to carbonates (dolomite and dolomitic limestone) at the base of the Late Carboniferous Huanglong Formation (Figure 2). The stratiform orebody is about 2650 m long, 1810 m wide and 21 m thick, on average. The ore minerals are dominantly pyrite, colloform pyrite, chalcopyrite and magnetite. Gangue minerals mainly include dolomite, calcite, siderite and quartz, associated with minor anhydrite, gypsum and barite. The sulfide ores generally show micro-layer, banded, brecciaed and massive structures, and colloidal, spherical and concentric ring textures [2,43]. The skarn-type orebody is less important in the Xinqiao deposit, and only accounts for about 10% of the reserve of the ore deposit. It often occurs as lenticular or irregular shapes, and is mainly distributed at the contact zone between the Jitou intrusion and the Late Paleozoic-Early Mesozoic carbonates. The skarn minerals primarily are garnet with some diopside and actinolite. Ore minerals include mainly pyrite, with magnetite, chalcopyrite and pyrrhotite occurring as disseminated deposits and veinlets in skarn ores.

Both the discordant alteration and mineralization are developed in the footwall of the stratiform sulfide orebody in the Xinqiao deposit [7,16,20]. The alteration types are dominantly silicification and sericitization, and occasionally accompanied by chloritization, baritization and sideritization. Silicification and sericitization are mainly distributed in sandstone beds, whereas the siltstone and mudstone beds are characterized by sericitization. Silicification is strongest in the footwall rocks under the stratiform orebody, and tends to weaken gradually downwards. Chloritization also is locally developed to various extents. Sulfide stockwork and veinlets are commonly present in the footwall rocks. This type of mineralization consists mostly of pyrite with accessory quartz and calcite (Figure 3), and accounts for a minor portion of the reserves in the Xinqiao deposit [16].

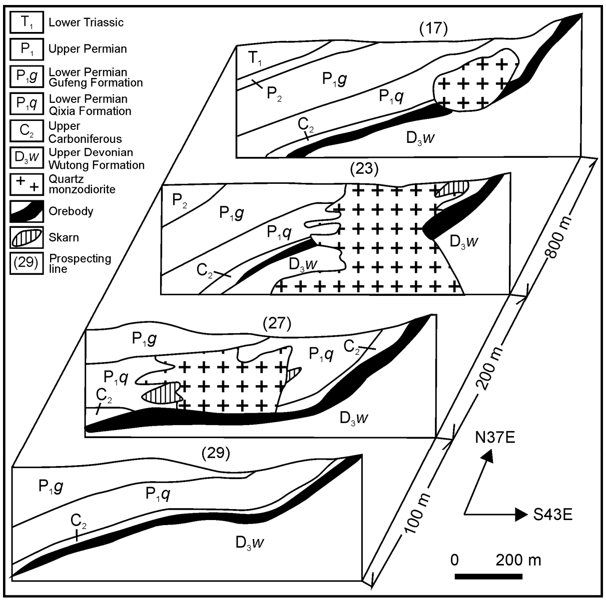

Figure 2 Composite section of the orebodies in the Xinqiao deposit (modified after Tang et al. [2]).

3 Analytical methods

Nine pyrite samples were collected for Re-Os isotope dating from the pyrite stockwork and veinlets in the late Devonian Wutong Formation sandstone beneath the stratiform sulfide orebody in the Xinqiao deposit (Figure 3). Re-Os isotope analysis was carried out on an ELAN DRC-e ICP-MS, at the State Key Lab of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang. The instrument sensitivity was greater than 40000 cps/1 ng/g ^{115}In, and the relative standard deviation (RSD%) was less than 3%. Detailed analytical procedures, including chemical separation of Rhenium and Osmium and mass spectrometric determination, are described by Qi et al. [44].

4 Results

Re-Os data of the nine pyrite samples are listed in Table 1. The Re contents (18.82 to 2919.08 ppb) of these samples varied greatly. Pyrite had low common Os (0.0036 to 0.0796 ppb), high radiogenic Os concentrations and high

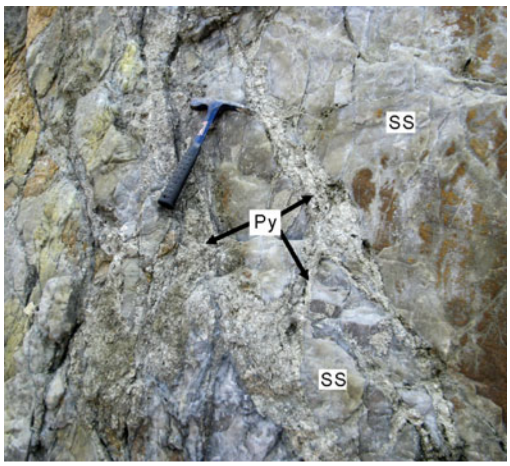

Figure 3 Pyrite veins in the footwall rocks below the stratiform sulfide orebody of the Xinqiao deposit. Py, Pyrite; SS, Late Devonian sandstone.

Table 1 Re-Os isotopic data of pyrite from the footwall mineralization zone in the Xinqiao deposit

Sample No.	Re (ppb)	^{187}Re (ppb)	^{187}Os (ppb)	Common Os (ppb)	^{187}Re/^{188}Os	^{187}Os/^{188}Os
XQ09-2-01	30.96 ± 0.26	19.38 ± 0.17	0.056 ± 0.002	0.0103 ± 0.0011	14101 ± 1523	40.5 ± 4.4
XQ09-2-02	20.84 ± 0.47	13.05 ± 0.29	0.043 ± 0.001	0.0037 ± 0.0002	26231 ± 1219	85.7 ± 3.6
XQ09-2-03	1847.47 ± 16.95	1156.51 ± 10.61	6.316 ± 0.136	0.0324 ± 0.0244	267977 ± 201636	1464 ± 1101
XQ09-2-04	153.04 ± 2.00	95.80 ± 1.25	0.526 ± 0.038	0.0077 ± 0.0009	93333 ± 10378	512 ± 57
XQ09-2-05	41.46 ± 1.30	25.95 ± 0.82	0.080 ± 0.001	0.0036 ± 0.0024	53959 ± 35375	166 ± 109
XQ09-2-06	115.07 ± 5.32	72.03 ± 3.33	0.290 ± 0.013	0.0096 ± 0.0034	56447 ± 20068	227 ± 80
XQ09-2-07	488.89 ± 7.50	306.05 ± 4.69	1.396 ± 0.020	0.0459 ± 0.0039	50084 ± 4335	229 ± 20
XQ09-2-08	2919.08 ± 50.20	1827.35 ± 31.43	9.630 ± 0.089	0.0796 ± 0.0208	172709 ± 45321	910 ± 239
XQ09-2-09	18.82 ± 0.16	11.78 ± 0.10	0.030 ± 0.001	0.00427 ± 0.0012	20762 ± 6030	52.6 ± 15.3

^{187}Re/^{188}Os ratios (>14000), which are similar to the Low Level Highly Radiogenic (LLHR) sulfides proposed by Stein et al. [36]. Due to the low common Os concentrations of pyrite, it was difficult to accurately measure Os. To avoid measurement errors from common Os for pyrite, which could lead to larger analytical uncertainties and correction errors, we introduce here an ^{187}Re-^{187}Os plot for LLHR sulfides, instead of the previously published ^{187}Re/^{188}Os-^{187}Os/^{188}Os plot [36]. This procedure allowed us to obtain the ^{187}Re-^{187}Os isochron age of 319±13 Ma (MSWD=16) (Figure 4(a), (b)).

5 Discussion

Discordant alteration and mineralization zones are generally developed in the footwall rocks of the conformable stratiform sulfide orebody in many VMSD and SEDEX deposits, such as the Gacun (Sichuan Province, China), Baiyinchang (Gansu Province, China), Sullivan, Tom and Jason (Canada), Kuroko type (Japan), and Rammelsberg (Germany) deposits

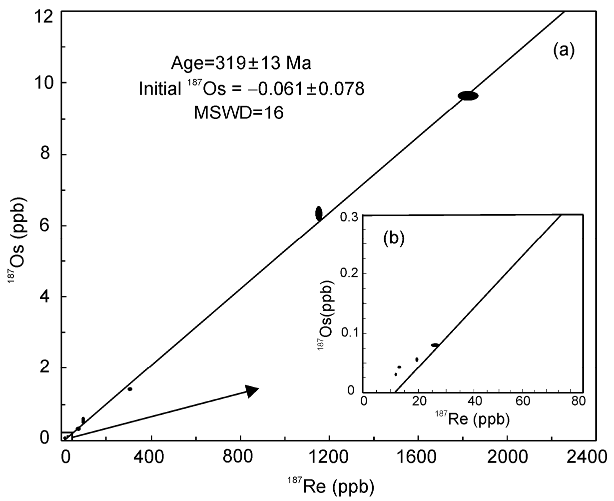

Figure 4 (a) ^{187}Re-^{187}Os isochron diagram for pyrite in the footwall mineralization zone of the Xinqiao deposit; (b) enlargement of the square in (a) showing low concentration samples with the same regression line.

[11–15,45–47]. Typically, discordant zones consist of altered or brecciated sedimentary rocks overprinted by veinlets and stockwork composed principally of quartz, carbonates and sulfides. As one of the most representative characteristics of massive sulfide deposits, the underlying discordant zones, considered to be feeder zones of upward discharged hydrothermal fluids, may coexist with the conformable stratiform sulfide orebody [11–15]. In the stratiform sulfide deposits of the MLYRB, such as Xinqiao, Dongguashan, Mashan, Tongguanshan, Shuizhuling and Shimengkou, both the veinlet and stockwork mineralization were observed commonly in the footwall rocks below the conformable stratiform sulfide orebody [7,10,16–20]. Locally, a breccia pipe can also be found in places, such as in the Taoyuan deposit. Alteration in the footwall rocks of the stratiform sulfide deposit also is common, and mainly includes silicification and sericitization with weak chloritization [16,20].

With respect to the exhalative sedimentary origin of the Xinqiao deposit and the same deposit types in the MLYRB, many studies have considered different aspects, including the geology, geochemistry and fluid characteristics of the deposit [5–10,16–20]. Besides the coexistence of a concordant stratiform sulfide orebody and discordant footwall mineralization and alteration, other lines of evidence also have been put forth to support a submarine exhalative sedimentary origin of the Xinqiao stratiform sulfide orebody. These include the stratiform nature with sharp host-rock contacts, a simple metallic mineral assemblage, banded, colloidal and massive structures of the sulfide ores, and widespread hydrothermal sedimentary rocks in ore-bearing strata [7,10,16,48]. These features are quite similar to those of the SEDEX-type deposits [13–15]. Through alteration-fluid mapping and fluid inclusion studies, hydrothermal systems associated with Carboniferous exhalative sedimentation have been identified in stratiform sulfide deposits in the Tongling area [48–50]. In addition, in the contact zone of the Yanshanian Jitou quartz monzodiorite with the wall rocks or the stratiform orebody, both skarnization and skarn-type mineralization are developed. This indicates the apparent superimposition of Yanshanian magmatic hydrothermal fluids on the stratiform orebody. Similar phenomena can also be observed in other stratiform sulfide deposits in the MLYRB, such as the Dongguashan, Tongguanshan, Chengmenshan and Wushan examples [6,8,10,17,19,51].

The pyrite ^{187}Re-^{187}Os isochron age of 319±13 Ma (MSWD=16) is consistent with the host strata at the base of the Upper Carboniferous Huanglong Formation, and reveals that the footwall mineralization of the Xinqiao deposit occurred during the early part of the Late Carboniferous. This new isochron age confirms the existence of submarine exhalative sedimentary mineralization in the Xinqiao deposit. Xie et al. [43] derived Rb-Sr isochron ages of 313.2±32.7 Ma and 328±21 Ma for pyrite from both the Xinqiao and Wushan deposits, respectively. Meng et al. [52] provided an age of 303.2±33 Ma for the Shimenkou deposit using pyrite Re-Os dating. These three age data together with the Re-Os pyrite isochron age obtained in this study clearly indicate the occurrence of exhalative sedimentary mineralization during the Carboniferous in the MLYRB. Wang et al. [53] obtained an Rb-Sr pyrite isochron age of 112.6±7.8 Ma, and Xie et al. [54] reported a Re-Os pyrite isochron age of 126±11 Ma from the Xinqiao deposit. These two ages are completely different from the age of the ore-bearing strata, and also clearly differ from the emplacement age of the Jitou intrusion (140.3±2.2 Ma) [42]. Furthermore, the timing of regional magmatism in the Tongling area concentrates mainly between 145 Ma and 135 Ma, while after 130 Ma magmatism is very weak [2,37,38,42]. Thus, these two ages may reflect the superimposition of Yanshanian magmatic hydrothermal fluids on the stratiform sulfide orebody, and may also indicate that Yanshanian magmatism lead to isotopic resetting in pyrite within the stratiform sulfide orebody.

6 Conclusions

The Xinqiao deposit is composed mostly of a stratiform sulfide orebody, which occurs in places where the sedimentary facies changed from clastic rocks to carbonates at the base of the Late Carboniferous Huanglong Formation. The discordant veinlet and stockwork mineralization were developed in footwall rocks below the stratiform sulfide orebody. The ^{187}Re-^{187}Os isochron age of 319±13 Ma (MSWD =16) for pyrite from the footwall mineralization zone is consistent with the age of the host strata, which supports the exhalative sedimentary origin of the stratiform sulfide orebody. The ^{187}Re-^{187}Os isochron age of the pyrite from the footwall mineralization represents the timing of the exhalative sedimentary mineralization.

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