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Xiao-Yong Yang & Insung Lee


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Review of the stable isotope geochemistry of Mesozoic igneous rocks and Cu–Au deposits along the middle–lower Yangtze Metallogenic Belt, China

Xiao-Yong Yang^{a,b,*} and Insung Lee^{c,*}

^aCAS Key Laboratory of Crust–Mantle Materials and Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China; ^bState Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China; ^cSchool of Earth and Environmental Sciences, Seoul National University, Seoul 151-742, Korea

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Ore deposition took place in the Yangtze Valley episodically during the Jurassic and Cretaceous periods, generating approximately 200 polymetallic Cu–Fe–Au, Mo, Zn, Pb, and Ag deposits. We analysed the stable isotopes of sulphur, oxygen, and hydrogen from the Cu–Au deposits and correlated our new data with published stable isotope for associated Yanshanian (Mesozoic) igneous rocks. The latter bears a close relationship to Cu–Au mineralization in the area. Cu–Au deposits in the middle–lower Yangtze Valley can be divided into three types: skarn, porphyry, and volcanic. The S–O–H isotopic values allow constraints to be placed on the conditions of origin of these famous Cu–Au ores and their related igneous rocks.

Sulphur from the sulphide ores mostly was derived from a magmatic source; however, a few deposits reflect a sedimentary source of sulphur. Oxygen isotope values in quartz from the Shaxi porphyry Cu–Au deposit and from the Tongling skarn Cu–Au deposits range from 2.6‰ to 12.5‰ and from –1.3‰ to 24.5‰, respectively; these values represent larger variations compared with those from other Cu–Au deposits in this metallogenic belt. Hydrogen versus oxygen isotope plots of the Cu–Au ore-forming fluids demonstrate that the fluids came from different sources: the most important involved the mixing of magmatic and meteoric water; the second most important was strictly magmatic water; and the third most important may have been a mixture of formation water or meteoric water that had reacted with carbonate wall rocks.

Keywords: porphyry Cu–Au deposits; stable isotope geochemistry; sulphur; hydrogen; oxygen isotopes; middle–lower Yangtze metallogenic province

Introduction

The Yangtze Valley is one of China's most important metallogenic provinces. Fe–Cu ore deposition in the eastern Yangtze Craton of central to eastern China was controlled by faults and aulacogens during the early Yanshan Epoch of the Jurassic period (Chang *et al.* 1991; Zhai *et al.* 1996). The associated igneous rocks can be grouped into two series according to their relationship to the metallogenesis: the Fe-related group and the Cu-related group. In this article, we mainly study the relationship between the igneous rocks of the Cu-related

*Corresponding authors. Email: xyyang555@163.com; insung@snu.ac.kr

mineralization. Ore deposition was controlled by the dominant WNW and E–W deep faults that characterize the whole region.

The study area is located along the northern margin of the Yangtze platform and in the southeastern part of the Sino-Korean platform (Ren *et al.* 1980). The Yangtze River, which developed along deep fracture zones, is about 450 km long, extending from SE Hubei eastward to Zhenjiang. The area along the middle and lower reaches of the Yangtze River is commonly referred to as the lower Yangtze region. Mesozoic igneous rocks in this region are closely associated with important copper, iron, gold, and sulphur ore deposits (Chang *et al.* 1991), and this region is one of the richest copper production areas in China. The lower part of the Yangtze Valley, from Wuhan in Hubei Province in the W to Zhenjiang in Jiangsu Province in the E, contains more than 200 polymetallic (Cu, Fe, Au, Mo, Zn, Pb, and Ag) deposits.

In this study, we have focused on several intrusive bodies situated along the lower part of the Yangtze Valley related to Cu–Au mineralization: the Shaxi diorite porphyry, the Anqing diorite, the Tongling granite, and the Chuxian granite. We also studied the Luzong volcanic basin to compare such extrusive rocks with the intrusives because the source magmas seem to have a close relationship with the Cu–Au mineralization.

Geological setting

The dominant W–NW and E–W lithospheric faults control the distributions of Cu (\pm Au or Mo) mineralization. Igneous rocks of the region have been intensely studied throughout the past century. As early as the 1920s, Chinese geologists recognized that granitoids from the lower Yangtze region were different from those of the Nanling region in southeastern China.

Figure 1 is the regional sketch of a geological–tectonical map, showing the distributions of the granitoids related to Cu–Au mineralization. Altogether five localities of granitoid rocks associated with Cu–Au mineralization are recognized: the Shaxi porphyry intrusive and the Huangtun diorite intrusive related to porphyry Cu–Au deposits; the Anqing diorite intrusive related to massive hydrothermal and skarn Cu–Au deposits; and both the Tongling granitic intrusive and the Chuxian diorite intrusive heavily related to the skarn Cu–Au deposit. In addition, we also studied for comparison the igneous rocks in the Luzong volcanic basin located in between these Cu–Au deposits, because this volcanic basin belongs to the Jurassic to Cretaceous periods (Ren *et al.* 1991), in which many relatively small-scale hydrothermal Cu–Au deposits are distributed. The main igneous rocks are Cu-related intrusives that form several types of Cu deposits, but in most of them Au is associated with Cu mineralization.

Comparing with these Cu–Au deposits along the lower parts of the Yangtze Metallogenic Valley, we first summarize the detailed information on geology, tectonical background, some geochemical features, and the mineralization (Table 1).

The five Cu–Au deposits distributed in the lower part of the Yangtze Metallogenic region in East China have some common characteristics: the age of the intrusive or volcanic activities in the middle to late Mesozoic period, ranging from 80 Ma to 170 Ma. Except for the volcanic thermal-type Cu–Au deposits in the Luzong volcanic basin (Ren *et al.* 1991; Yang 1996), the Cu–Au deposits are related to the granitoid intrusives, some of which have high potassic contents (Chang *et al.* 1991; Yang 1996). The geological setting of the study areas includes the tectonical depression of the SE margin of the Dabie orogenic belt along the edge of the Tanlu fault zone.

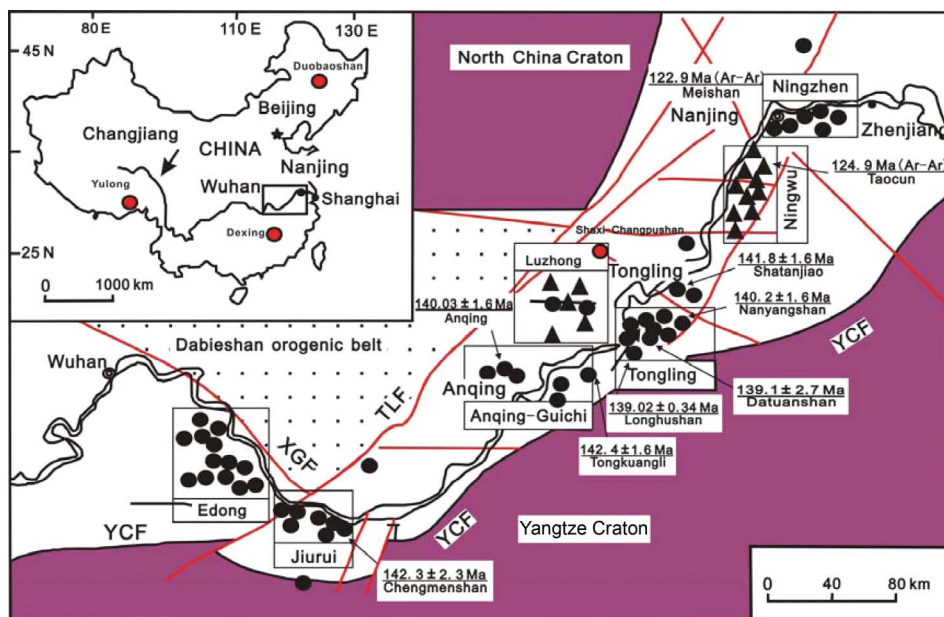


Figure 1. Distributions of famous metallic deposits and their forming ages along the middle-lower Yangtze Metallogenic Belt (MLYMB), based on the collection maps from Chang *et al.* (1991), Zhai *et al.* (1992), and Pan and Dong (1999); isotopic ages are based on Mao *et al.* (2006).

Note: Dexing porphyry Cu–Au deposit is not shown in the main map. It belongs to the MLYMB, shown in the box map; Yulong and Duobaoshan porphyry Cu–Au deposits are not distributed along the MLYMB, but they are two other famous porphyry Cu–Au deposits in China; their localities are also shown in the box map.

Petrography and petrochemistry

Petrography

There are several kinds of intrusive rocks associated with the porphyry and skarn Cu–Au in the Yangtze Metallogenic Valley. These intrusives comprise quartz diorite porphyry, biotite-quartz diorite porphyry, and fine- to medium-grained diorite porphyry, which have a subhedral seriate texture. These rocks contain phenocrysts of plagioclase and alkali-feldspar. The size of the plagioclase and feldspar crystals ranges from matrix dimensions up to 8–3 mm and 5–1.5 mm, respectively. Some feldspars were severely altered to sericite, chlorite, and kaolinite in the alteration zones. The diorite is composed of amphibole, microcline, biotite, quartz, muscovite, pyrite, magnetite, apatite, sphene, and rare rutile. Some quartz has undulatory extinction and is of several generations; most of them contain inclusions of other minerals and needles of some metallic minerals, of which most are magnetite and pyrite. The microcline occurs as subhedral crystals with cross-hatch twinning, showing the characteristics of micropertthitic intergrowth with some plagioclase. The subhedral plagioclase in the diorite porphyry usually occurs as polysynthetically twinned crystals, which have the composition of oligoclase to andesine (mostly An_{25} – An_{45}) and some plagioclase is oligoclase-albite (An_5 – An_{20}) because of its thermal alteration (Chang *et al.* 1991; Yang 1996). The amphibole crystals usually occur as subhedral with sizes usually ranging from 1.3 mm to 0.1 mm, up to 10 mm. In some diorite porphyry, amphiboles can make up

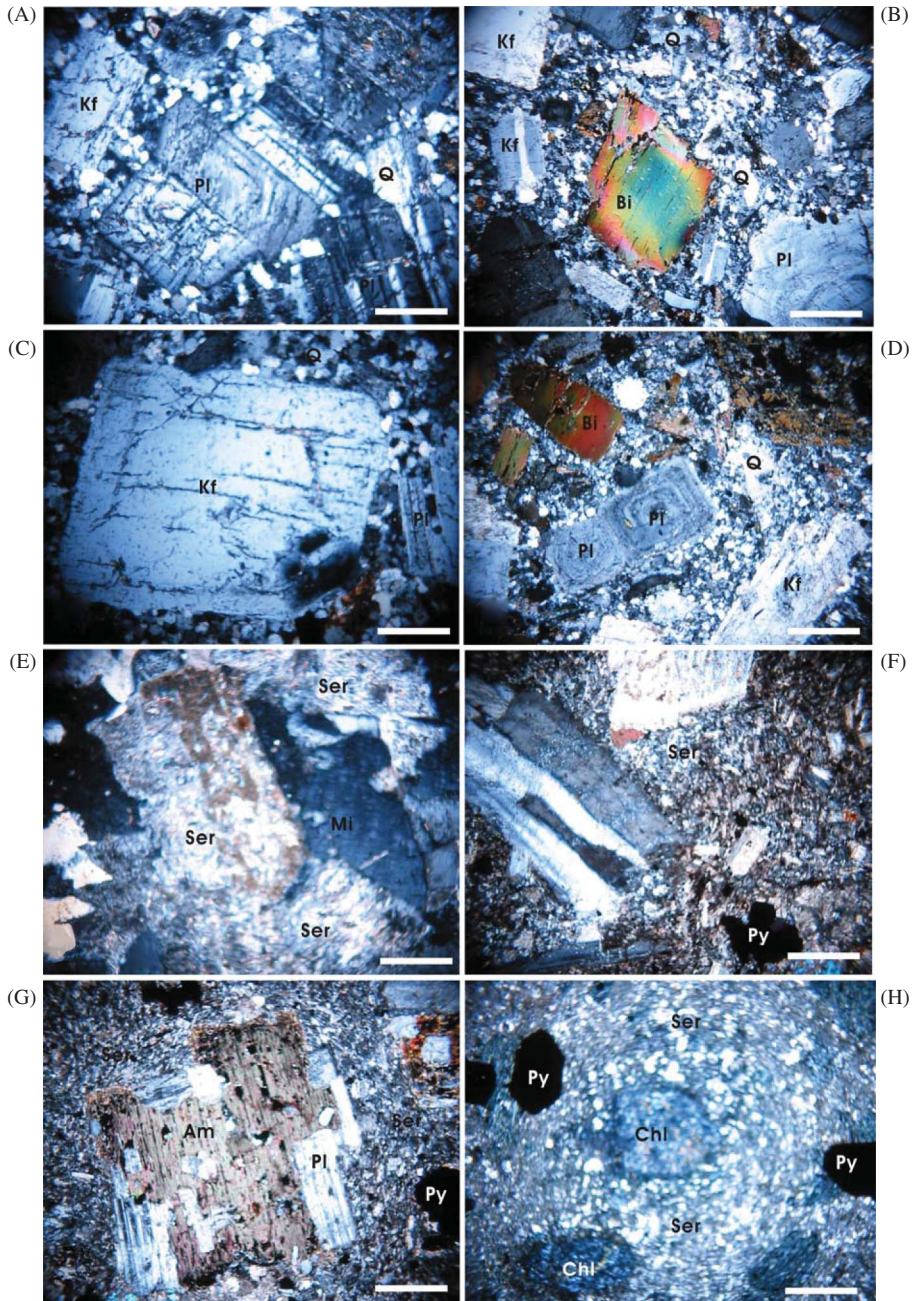
Table 1. Characteristics of copper (-gold) polymetallic deposits in the lower Yangtze region, China.

Cu-Au province	Name of deposit	Commodity	Tectonical setting/orogeny	Host rock/period	Igneous rocks/size and age (Ma)	Resource of Cu (t)	Grade (%)	Major ore minerals	Alteration minerals
Central Anhui Province, East China	Shaxi porphyry deposit	Cu-Au	At the edge of Tanlu fault; southeastern margin of Dabie Mountains	Silty stone, muddy stone, and sandstone/S ₁₋₂ D, J ₁₋₂	Porphyrite, diorite (1–2 km ²)/130 ±	5 × 10 ⁵	0.2–0.5	Cp, Py, Mo, Bor, Ga, Sph, Hem, Mt	Ser, Anh, Gy, Kf, Mus, Bi, Chl, Ep, Kao
Southwest Anhui Province, East China	Anqing skarn deposit	Cu-Fe-Mo-Au	Between depression and uplifting, southern margin of Dabie Mountains	Carbonate, shale, dolomite, and sandstone/C-P-T	High-potassic diorite (10–90 km ²)/105–145	2–3 × 10 ⁵	2–5	Cp, Py, Mo, Bor, Hem, Mt	Ser, Kf, Mus, Anh, Gy, Bi, Chl, Ep, Kao
South Anhui Province, East China	Tongling skarn deposit	Cu-Au	Uplifting, South China granitoids	Carbonate, shale, dolomite, and sandstone/C-P-T	Diorite and granite (<10 km ²)/110–168 Ma	>1 × 10 ⁶	2–5	Cp, Py, Bor, Hem, Mt	Ser, Kf, Mus, Anh, Gy, Bi, Chl, Ep
East Anhui Province, East China	Chuxian skarn deposit	Cu-Au	Uplifting, East China granitoids	Carbonate, shale, dolomite, and sandstone/C-P-T	Diorite (<5 km ²)/ Mesozoic	10 × 10 ⁵	2–5	Cp, Py, Bor, Hem, Mt	Ser, Kf, Mus, Anh, Gy, Bi, Chl, Ep
Central Anhui Province, East China	Luzong volcanic thermal deposit	Cu-Au-S-Ag	Cenozoic volcanic basin; depression, southeastern margin of Dabie Mountains	Mudstone, sandstone, carbonate, and dolomite/I-K	Potassic granitoids and andesite (1–100 km ²)/80–160	Unknown	5–10	Cp, Py, Bor, Hem, Mt	Ser, Kf, Mus, Anh, Gy, Bi, Chl, Ep, Kao

Northern Jiangxi Province, East China	Dexing porphyry deposit	Cu–Mo–Pb–Zn	Uplifting, East China granitoids	Silica and aluminium sedimentary rocks/Pt ₃	Granodiorite porphyry (<km ²)/Mesozoic	80 × 10 ⁵	0.3–0.5	Cp, Py, Mo, Bor, Ga, Sph	Ser, Kf, Si, Mus, Bi, Chl, Ep, Cc, Kao
Eastern Tibet, SW China	Yulong porphyry deposit	Cu–Mo–Fe	Tethyan–Himalaya tectonic belt, SW China	Shale and limestone /T	Granodiorite porphyry (0.64 km ²)/37.9–55.0	> 12 × 10 ⁵	0.3–0.5	Cp, Py, Mo, Bor, Hem, Mt	Kf, Ser, Si, Bi, Chl, Ep, Kao
Heilongjiang, EW China	Duobaoshan porphyry deposit	Cu–Mo	Regional extensional fault zone	Tuff, andesite, and limestone/O	Granodiorite porphyry (0.16 km ²)/292–245	5 × 10 ⁵	0.3–0.5	Cp, Py, Mo, Bor	Ser, Kf, Cc, Bi, Chl, Ep, Kao

Abbreviations: Anh, anhydrite; Bi, biotite; Bor, bornite; Cc, calcite; Chl, chlorite; Cp, chalcopyrite; Hem, hematite; Ga, galena; Gy, gypsum; Ep, epidote; Kao, kaolinite; Kf, potassic feldspar; Mo, molybdenite; Mt, magnetite; Mus, muscovite; Py, pyrite; Ser, sericite; Si, silification; Sph, sphalerite.

as much as 15% of the total mineral volume. Some amphibole is replaced by chlorite alteration at the edges where general muscovite and quartz formed. The muscovite and biotite are all subhedral; however, biotite is more abundant than muscovite in the diorite porphyry. Figure 2 shows the petrological characteristics of the intrusives from the Shaxi, Anqing, Tongling, Chuxian, and Luzong areas, from which some information can be obtained about



the different types of Cu–Au mineralization in the lower part of the Yangtze Metallogenic Belt.

Figure 3 shows the petrological characteristics observed in several Cu–Au ore deposits, where some relationships can be determined regarding the different mineralization periods of ore minerals in different types of Cu–Au mineralization in the area.

Petrochemistry

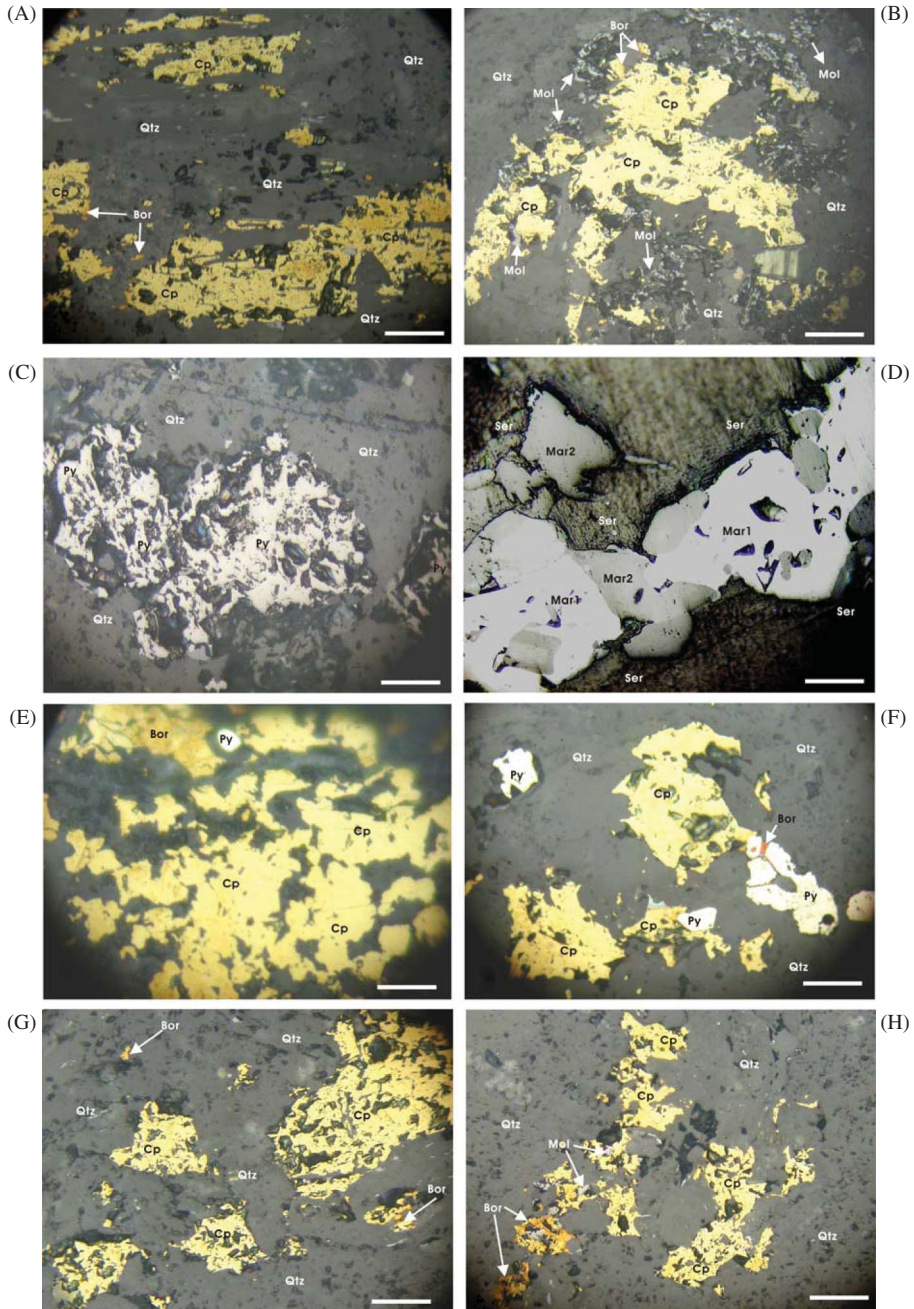
Late Mesozoic igneous rocks with Cu–Au mineralization form regional outcroppings in the lower Yangtze region. They intrude into Neoproterozoic low-grade metamorphic rocks or Palaeozoic to Triassic sedimentary strata. Several rock types are identified: in Figure 4, the K_2O versus SiO_2 identifies shoshonites, which are mostly distributed in the Luzong meso-volcanic rocks, some of which lie in the Tongling region with skarn Cu–Au mineralization. The K-enriched rock association in the other ore deposits contains both shoshonite series and ultra-potassic rocks identified by high values of $Na_2O + K_2O$ (8.1–12.0%), high K_2O values (4.1–8.5%), and with K_2O/Na_2O ratios of 0.8–1.4. They also outcrop to the N of the Yangtze River and along the Yangtze River (Anhui 1987; Wang and Yang 1996; Xing and Xu 1999). They are plotted in basaltic trachyandesite, trachyandesite, and syenite fields in composition. However, the Shaxi porphyry Cu–Au deposit shows characteristics of calc-alkaline series magmatism. The rocks in the Anqing and Tongling areas belong to the high-potassic calc-alkaline series. The rock series with Na-enriched alkaline mafic association in the region show low values of SiO_2 (46–56%), high alkali values of K_2O (5.0–7.1%), and high values of Na_2O/K_2O ratio (1.4–4.3) (Yang 1996; Xing and Xu 1999; Chen *et al.* 2001). These rocks occur along the Yangtze River near the cities of Nanjing, Wuhu, and Tongling with one outcrop close to the Tancheng–Lujiang fault. The associations of high-potassic calc-alkaline series or calc-alkaline series occurring in the area N of the Yangtze River consist of monzonite and granite stocks. Diorite, quartz diorite, and granodiorite stocks are distributed along the Yangtze River. These rocks are closely associated with the important copper, iron, sulphur, and gold ore deposits (Chang *et al.* 1991). Intrusions distributed in the region S of the Yangtze River include granites and granodiorites, occurring as batholith and stocks. They are sulphur-type granites in terms of



Figure 2. Microscopic images of petrologic observations made of granitoids related to Cu–Au mineralization along the lower part of the Yangtze Metallogenic Valley. (A) Zoning texture of plagioclase of granite in the Tongling intrusive related to the skarn Cu–Au deposit. (B) The potassic feldspar, plagioclase, quartz, and biotite are made up of the main mineral components of the granite in the Chuxian intrusive related to the skarn Cu–Au deposit. (C) The idiomorph crystal grain of potassic feldspar in the Tongling intrusive. (D) Zoning texture of plagioclase of granite in the Anqing intrusive related to the skarn–hydrothermal Cu–Au deposit. (E) The heavy alteration of sericitization and argillation in porphyrite from the Shaxi intrusive related to the porphyry Cu–Au deposit. (F) The heavy sericitization alteration of porphyrite in the Luzong volcanic rocks related to hydrothermal Cu–Au deposit. (G) Amphibole replaced with plagioclase around heavy sericitization altered Luzong's volcanic rocks. (H) The heavy alteration of sericitization and chloritization in porphyrite from the Shaxi intrusive.

Note: All the images are taken with a Laca microscope under polarized light conditions. The scale bar for each of the images is 0.20 mm. Abbreviations in the images: Am, amphibole; Bi, biotite; Chl, chlorite and chloritization; Kf, potassic feldspar; Mi, microcline; Pl, plagioclase; Py, pyrite; Q, quartz; Ser, sericite and sericitization.

chemical composition and mineralogy (Chen *et al.* 1993). Some molybdenum ore deposits are associated with this group of intrusions (Chang *et al.* 1991).



Isotopic geochemistry

Sulphur isotope

To determine the isotopic variations of the ores, we systematically collected samples from the different ore bodies. We separated the minerals by handpicking and by standard heavy liquid and magnetic separator techniques. We broke down the samples into less than 120 meshes to obtain purified pyrite and chalcopyrite. Sulphur isotope data measured in this deposit and those of typical Cu deposits in China are summarized in Table S1 (see online supplementary data available at <http://www.informaworld.com/tigr>). Some measurements were performed at the Institute of Coal Science, Xi'an, China, using standard techniques. The reappearance of the data is good and the accuracy is below 0.5‰. All the results are expressed relative to the CDT standard.

The sulphur isotopic ratios in the Shaxi–Changpushan porphyry Cu–Au deposit range from -0.3‰ to 3.0‰ in $\delta^{34}\text{S}$ values; it can be calculated that the total $\delta^{34}\text{S}$ value is nearly 1.1‰ with the paragenesis of sulphides (Pickney 1972). The very narrow variation in $\delta^{34}\text{S}$ values is similar to those of the larger or superlarge porphyry Cu deposits such as those porphyry Cu–Au deposits in Dexing, Yulong, and Duobaoshan in China (Rui *et al.* 1984). The result shows the very homogeneous resources of sulphur and ore solution during mineralization, demonstrating that the mineralization mechanism in the Shaxi–Changpushan porphyry Cu–Au deposit is similar to those large or superlarge porphyry Cu deposits in China. However, the sulphur isotope composition in the adjacent areas such as the Tongling skarn Cu–Au deposit, the Luzong volcanic basin, and the Anqing deposit shows a larger difference, ranging from -29.6‰ to 15.3‰ , -11.2‰ to 18.8‰ , and -11.1‰ to 15.2‰ , respectively.

The regional variations of sulphur isotope compositions from some Cu–Au deposits in China are shown in Figure 5. It can be seen that the sulphur isotope values from sulphides are very homogeneous in the Shaxi porphyry Cu–Au deposit, the Duobaoshan porphyry Cu deposit, the Yulong porphyry Cu deposit, and the Dexing porphyry Cu deposit; whereas in the Tongling skarn Cu–Au deposit, the Luzong volcanic area, and the Wushan skarn Cu–Au deposit, the sulphur isotope values are very heterogeneous. The narrow sulphur isotope values in these Cu–Au deposits may indicate that sulphides have a relatively homogeneous source in contrast to those deposits with an inhomogeneous source of sulphides.

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Figure 3. Microscopic petrological images of ore minerals and rocks in the Shaxi porphyry Cu–Au deposit, the Luzong volcanic Cu–Au deposit, and the Tongling skarn type of Cu–Au deposit. (A) In the massive copper mineralization in the quartz vein, most of the copper-bearing mineral is chalcopyrite, and the lesser amount is bornite (Yueshan massive Cu–Au deposit). (B) Most of the copper-bearing mineral is chalcopyrite surrounded by tiny grained molybdenite (Yueshan massive Cu–Au deposit). (C) Pyrite in the quartz vein of the Luzong volcanic thermal Cu–Au deposit. (D) Marcasite formation accompanied with sericitization in the Luzong volcanic thermal Cu–Au deposit, where two periods of marcasite (Mar1 and Mar2) can be clearly identified. (E) Chalcopyrite and bornite appear in the Tongling skarn Cu–Au deposit, chalcopyrite is the main copper mineral, and bornite is a minor phase. (F) Chalcopyrite and pyrite appear in the Tongling skarn Cu–Au deposit and chalcopyrite is the main copper mineral. (G) Chalcopyrite and bornite appear in the Shaxi porphyry Cu–Au deposit. Chalcopyrite is the main copper mineral, whereas bornite occurs in minor amount. (H) Chalcopyrite, bornite, and molybdenite occur in the Shaxi porphyry Cu–Au deposit. Chalcopyrite is the main copper mineral, whereas bornite occurs in minor amount.

Note: Abbreviations for the images: Cp, chalcopyrite; Py, pyrite; Bor, bornite; Mol, molybdenite; Mar, marcasite; Qtz, quartz; Ser, sericite. The scale bar for each image is 0.20 mm.

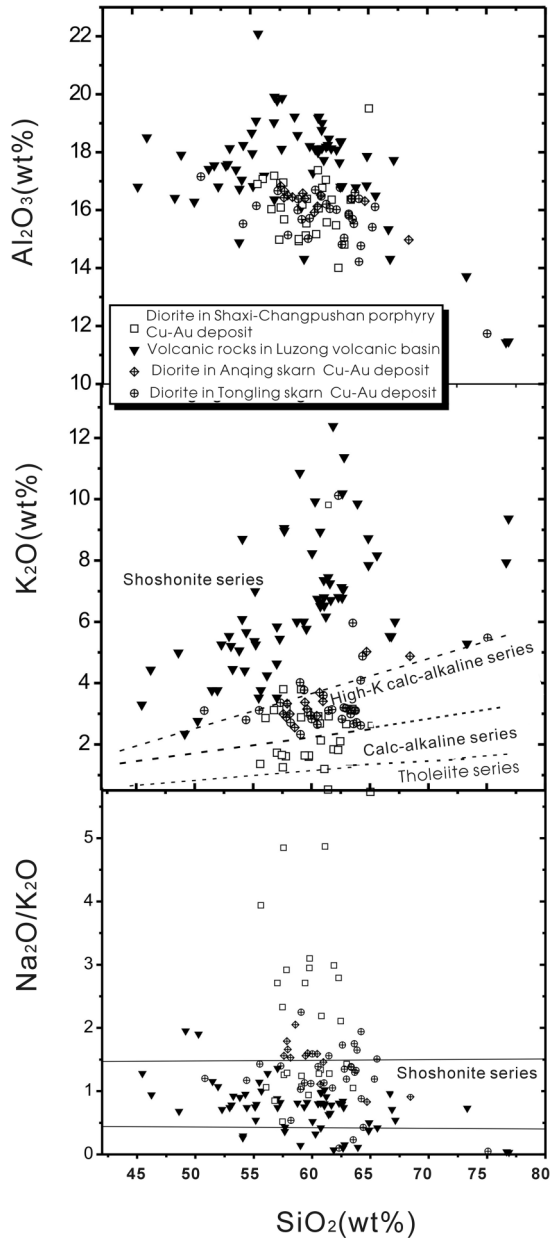


Figure 4. SiO_2 versus Al_2O_3 , K_2O , and $\text{Na}_2\text{O}/\text{K}_2\text{O}$ diagrams (after Rickwood 1989; Rollinson 1993), which show variations of the different igneous rock associations concerning the Cu–Au mineralization in Anhui Province (data after Chang *et al.* 1991; Ren *et al.* 1991; Xing and Xu 1995; Xing and Xu 1996; Xing 1998; Xing and Xu 1999; Yang *et al.* 2006).

The sulphur isotopes in these deposits show a large range distribution according to their different sources of ore-forming processes during the formation of these different types of Cu–Au deposits. This can be explained by the different Cu–Au mineralizations caused by different geological processes and fluid interaction.

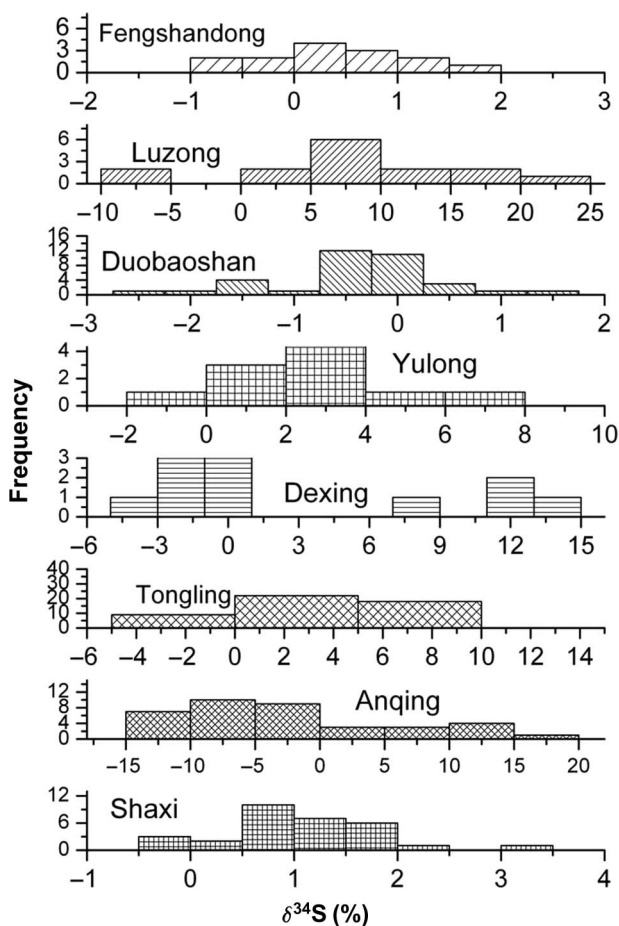


Figure 5. Histogram diagram showing the regional variations of sulphur isotope compositions of sulphides in Cu–Au deposits in China.

Oxygen and hydrogen isotopes

Oxygen and hydrogen isotopic data from some typical Cu deposit in China are summarized in Table S2 (see online supplementary data). Figure 6 plots the range of oxygen isotope values for some Cu–Au deposits. It can be seen that the largest variations in quartz are in the Shaxi porphyry Cu–Au deposit and the Tongling skarn Cu–Au deposits with ranges from -1.3‰ to 24.5‰ . Variations in quartz in the Anqing massive hydrothermal Cu–Au deposit and the Yulong porphyry Cu deposit in Tibet have narrow values ranging from 6.7‰ to 13.8‰ and from 7.3‰ to 10.3‰ , respectively. However, the oxygen isotope values vary in fluids in equilibrium with quartz and other monominerals: around -4.7‰ to 5.5‰ variations in the Shaxi porphyry Cu–Au deposit; 2.1‰ – 8.9‰ variations in the Anqing massive hydrothermal Cu–Au deposit; around -2.6‰ to 8.0‰ variations in the Dexing porphyry Cu deposit; -6.9‰ to 8.3‰ variations in the Yulong porphyry Cu deposit; and 1.3‰ – 10.7‰ variations in the Tongling skarn Cu–Au deposits. These characteristics may reflect the different fluid histories during the formation of each deposit.

According to the hydrogen isotopic data from fluid inclusion and oxygen isotopic data from quartz and other monominerals in this study and other studied results (e.g. Riu

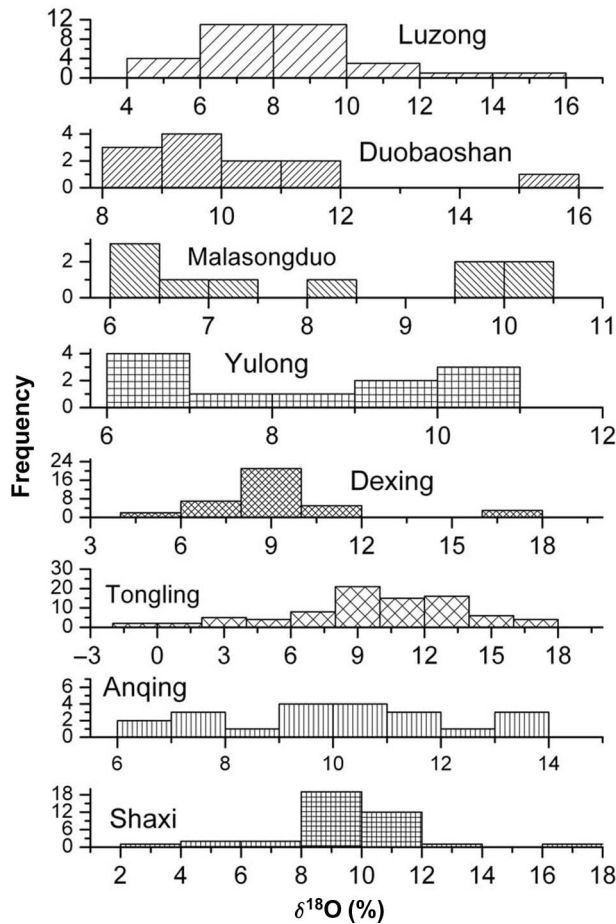


Figure 6. Histogram diagram showing the regional variation of oxygen isotope compositions in the Cu–Au deposits in the lower Yangtze region in China.

et al. 1984; Chang *et al.* 1991; Ren *et al.* 1991), δD and $\delta^{18}O$ values of ore-forming fluids range from -59.9‰ to -82.4‰ and from 3.5‰ to 5.5‰ in the Shaxi–Changpushan porphyry Cu–Au deposits, respectively; from -46.1‰ to -127.3‰ and from -3.4‰ to 10.0‰ in the Dexing porphyry Cu deposit, respectively; and from -6.9‰ to 5.5‰ in the Yulong and Malasongduo porphyry Cu deposits in Tibet, respectively. This indicates that the ore-forming fluids in these different porphyry Cu–Au deposits have different evolutionary histories with large variations in oxygen and hydrogen isotopic compositions. In other kinds of Cu–Au deposits along the middle and lower parts of the Yangtze region, such as the Tongling, Anqing, Luzong, and Wushan regions, the δD and $\delta^{18}O$ values of ore-forming fluids range from -53‰ to -191‰ and from 0.2‰ to 11.8‰ , respectively; from -62‰ to -78‰ and from 2.1‰ to 8.9‰ , respectively; from -66‰ to -111‰ and from -5.6‰ to 11.2‰ , respectively; and from -51.6‰ to -84.4‰ and from -3.5‰ to 9.6‰ , respectively. The ore-forming fluids for these different types of Cu–Au deposits have even larger variations of oxygen and hydrogen isotopic compositions compared with those of the porphyry Cu–Au deposits along the middle–lower parts of the Yangtze region.

Figure 7 shows δD versus $\delta^{18}O$ of the ore fluids from different Cu–Au deposits, from which it can be seen that most of the data from the Wushan Cu–Au deposit show the mixtures of magmatic water and meteoric water: one sample near the box of origin of magmatic water and one sample within the box of origin of magmatic water. In the Shaxi Cu–Au deposit, four data sets show the mixture of magmatic water and meteoric water. Two samples are plotted in the box of origin of magmatic water, and three samples are near the edge of the box of magmatic water; however, there are several samples plotted far outside the box of magmatic water, which cannot be interpreted as simply a mixture of magmatic water and meteoric water. In the Luzong volcanic thermal Cu–Au deposit, two samples belong to a mixture of magmatic water and meteoric water and one sample is outside the box of magmatic water. In the Tongling skarn Cu–Au deposit, most of the plots are located within the box of magmatic water but some samples are outside the box, which could be interpreted as a participation of formation water or meteoric water that reacted with carbonate wall rock during the Cu–Au mineralization.

Summary

- (1) Cu–Au mineralization in the middle–lower Yangtze Valley consists mainly of three types: skarn, porphyry, and volcanic/thermal mineralization. The sulphur isotope study shows that the major source of sulphur in the sulphides was magmatic in origin, whereas some was derived from a sedimentary source.
- (2) Oxygen isotope values for quartz in the Shaxi porphyry Cu–Au deposit and the Tongling skarn Cu–Au deposit – ranging from 2.6‰ to 12.5‰ and from –1.3‰ to 24.5‰, respectively – exhibit wide variations compared with other Chinese Cu–Au deposits.
- (3) Sulphur isotope data indicate a very homogeneous source of sulphur and ore solutions during most porphyry Cu–Au mineralization, although relatively large, heterogeneous variations of sulphur and ore solutions were present during skarn Cu–Au mineralization.

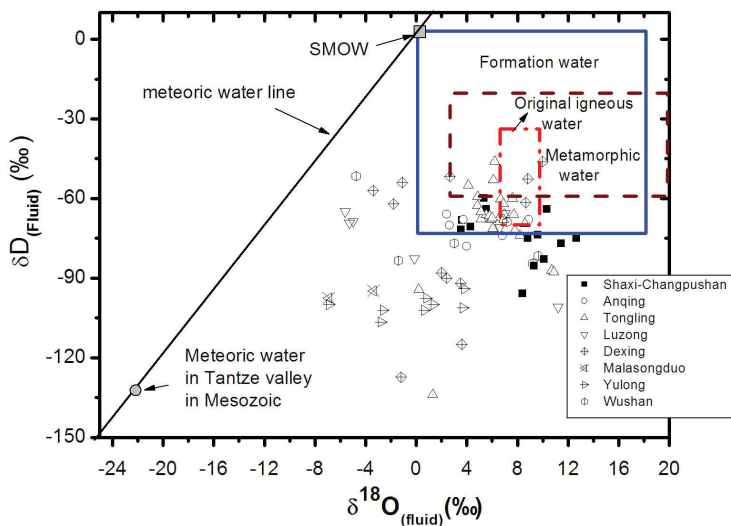


Figure 7. Hydrogen versus oxygen isotope diagram of the ore fluids in Cu–Au deposits in China.

- (4) Based on the hydrogen and oxygen isotopic data, we infer that the ore-forming fluids had different origins. The most important involved mixtures of magmatic water and meteoric water (such as in the Wushan, Shaxi, and Luzong regions); the second most important was a strictly magmatic water source (also as in the Wushan, Shaxi, and Luzong regions); and the third most important probably was from a mixture of formation water and meteoric water that reacted with carbonate wall rocks (such as in the Tongling, Shaxi, and Luzong regions).

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References

- Anhui (Bureau of Geology and Mineral Resources of Anhui Province), 1987, Regional Geology of Anhui Province: Beijing, Geology Publishing House, p. 1–721 (in Chinese with English abstract).
- Chang, Y.F., Liu, X., and Wu, Y.C., 1991, The Copper-Iron Belt of the Middle and Lower Reaches of the Changjiang River: Beijing, Geological Publishing House, p. 1–379 (in Chinese with English abstract).
- Chen, B., Jiang, Z., Zhang, W., Xu, Z., Lu, X., Lu, S., and Huang, S., 2002, Study on altered fluids of diplogenetic stratified copper hydrothermal solution in Dongguanshan, Anhui Province: *Jiangsu Geology*, v. 26, no. 2, p. 65–69 (in Chinese with English abstract).
- Chen, J.F., Yan, J., Xie, Z., Xu, X., and Xing, F., 2001, Nd and Sr isotopic compositions of igneous rocks from the Lower Yangtze Region in Eastern China. Constraints on Sources: *Physics and Chemistry of the Earth (A)*, v. 26, p. 719–731.
- Chen, J.F., Zhou, T.X., Li, X.M., Foland, K.A., Huang, C.Y., and Lu, W., 1993, Sr and Nd isotopic constraints on source regions of the intermediate and acidic intrusions from southern Anhui province: *Geochimica*, v. 22, no. 3, p. 261–268 (in Chinese with English abstract).
- Chen, W.M., 1984, Ore source and evolution indicators of porphyry copper deposits in China. *Bull. Inst. Ore deposits: Bulletin of Chinese Academy of Geological Science*, v. 12, p. 1–78 (in Chinese with English abstract).
- Chu, G., Huang, X., and Zheng, C., 1995, Discussion on the ore-control factors of the Tongling area, Anhui: *Geology of Anhui*, v. 5, no. 1, p. 47–58 (in Chinese with English abstract).
- Clayton, R.N., O'Neil, J.R., and Meyeda, T.K., 1972, Oxygen isotope exchange between quartz and water: *Journal of Geophysical Research*, v. 77, p. 3057–3067.
- Cui, B., 1987, The alteration zoning and origin of the Tongguanshan stratabound skarn type copper deposit: *Mineral Deposit*, v. 6, no. 1, p. 35–44 (in Chinese with English abstract).
- Cui, B., and Li, Z., 1994, Copper and Gold Metallogenic Series in Jiu-Rui Area, Jiangxi Province: Beijing, Geological Publishing House, p. 1–130 (in Chinese).
- Fu, B., 1994, Geology and geochemistry of metallogeny in Shaxi porphyry Cu(Au) deposit [Unpublished MS thesis]: Jiangsu, Nanjing University (in Chinese with English abstract).
- Gu, L., and Xu, K., 1986, On massive sulfide ore deposit of Carboniferous sea floor origin from middle-lower Yangtze River: *Acta Geologica Sinica*, v. 70, no. 3, p. 176–188 (in Chinese with English abstract).
- Gu, L., Chen, P., Ni, P., Xu, Z., Xiao, X., Qiu, J., Zhang, Z., and Zhang, G., 2002, Comparative research on ore-forming fluids for the main types of hydrothermal copper-gold deposits in the middle and lower reaches of the Yangtze River: *Journal of Nanjiang University (Natural Science)*, v. 38, p. 391–407 (in Chinese with English abstract).

- Guo, G., Ren, Q., Fang, C., and Xu, W., 1994, Computer simulation for hydrothermal fluid migration during mineralization of Dexing porphyry copper deposit, Jiangxi province: *Geochimica*, v. 23, p. 401–410 (in Chinese with English abstract).
- Guo, J., Qian, Y., and Huang, Y., 1995, Oxygen isotopics of skarn deposits in Anqing: *Volcanology and Mineral Resources*, v. 21, no. 1, p. 21–29 (in Chinese with English abstract).
- Guo, X., Ji, K., Huang, Y., and Cheng, J., 1999, The origin and evolution for the ore-forming fluids of Tongchang porphyry copper deposit, Dexing: oxygen isotopic constrains of granodiorite: *Geological Journal of China Universities*, v. 5, p. 258–268 (in Chinese with English abstract).
- Hu, W.X., Xu, K.Q., Hu, S.X., and Ren, Q.J., 1991, Exhalative Sedimentation and Hydrothermal transformation superimposition iron and pyrite deposits in Ningwu-Luzong continental volcanic basins: Beijing, Geological Publishing House, p. 1–142 (in Chinese with English Abstract).
- Huang, S., Shi, Q., and Cui, B., 1985, The origin and the geological assemblage feature of the Tongguanshan copper deposit: *Mineral Deposits*, v. 4, no. 2, p. 13–22 (in Chinese with English abstract).
- Huang, S., Xu, Z., and Ni, P., 2003, Inclusion geochemistry of Dongguashan hydrothermal superimposition copper deposit in the Tongling area, Anhui: *Bulletin of Geology and Exploration*, v. 18, p. 34–38 (in Chinese with English abstract).
- Jin, Z., Zhu, J., and Li, F., 2002, Sr and Nd isotopic tracing of ore-forming process in Dexing porphyry copper deposit, Jiaingxi Province: *Mineral Deposits*, v. 21, p. 341–348 (in Chinese with English abstract).
- Jin, Z., Zhu, J., Li, F., Liu X., and Huang, Y., 2000, Oxygen isotope implication for source and evolution of ore-forming fluids in Dexing porphyry copper deposit, Jiaingxi Province: *Journal of Xi'an Engineering University*, v. 22, p. 27–32 (in Chinese with English abstract).
- Li, W., Wang, W., and Fan, H., 1997, The possibility of forming super-large Cu-Au deposit along middle-lower Yangtze region: *Volcanic Geology and Mineral Resources*, v. 20, no. (Suppl.), p. 1–131 (in Chinese with English abstract).
- Li, X., Li, B., Zhang, X., and Zhou, T., 1987, Sulfur isotopic compositions of the Mashan gold deposit in Tongling region: *Journal of China University of Science and Technology*, v. 30, no. 5, p. 467–476 (in Chinese with English abstract).
- Mao, J.W., Wang, Y.T., Lehmann, B., Yu, J.J., Du, A.D., Mei, Y.X., Li, Y.F., Zang, W.S., Stein, H.J., and Zhou, T.F., 2006, Molybdenite Re-Os and albite Ar-40/Ar-39 dating of Cu-Au-Mo and magnetite porphyry systems in the Yangtze River valley and metallogenic implications: *Ore Geology Reviews*, v. 29, p. 307–324.
- Nie, G., Liu, L., Xu, Z., Gao, G., Yang, X., and Li, H., 2007, Gold bearing and sulfur isotopic compositions of ore rocks at Caoshan gold deposit, Anhui: *Jiangsu Geology*, v. 31, no. 3, p. 200–205 (in Chinese with English abstract).
- No. 321 Geology Party, 1990, A comprehensive prospecting on the multiple metallic deposits in Tongling area, south Anhui Province: A Report by No.321 Geology Party, Anhui Bureau of Geology and Mineral Resources, Tongling, p. 1–136 (in Chinese).
- No. 327 Geology Party, 1982, A report of geological survey on Shaxi porphyry copper deposit: A Report No. 327 Geology Party, Anhui Bureau of Geology and Mineral Resources, Hefei, p. 1–163 (in Chinese).
- Northrop, D.A., and Clayton, R.N., 1966, Oxygen isotope fractionation in system containing dolomite: *Journal of Geology*, v. 74, p. 174–196.
- O'Neil, J.R., and Taylor, H., Jr., 1967, The oxygen isotope and cation exchange chemistry of feldspars: *American Mineralogist*, v. 52, p. 1414–1437.
- O'Neil, J.R., Clayton, R.N., and Mayeda, T., 1969, Oxygen isotope fractionation between muscovite and water: *Journal of Geophysical Research*, v. 74, p. 6012–6022.
- Pan, Y.M., and Dong, P., 1999, The Lower Changjiang (Yangzi/Yangtze River) metallogenic belt, east central China: intrusion- and wall rock-hosted Cu-Fe-Au, Mo, Zn, Pb, Ag deposits: *Ore Geology Reviews*, v. 15, p. 177–242.
- Pickney, D.M., 1972, Fraction of sulfur isotopes during ore-deposition in the Upper Mississippi Valley zinc-lead District, *Economic Geology*, v. 67, p. 315–340.
- Puchelt, H., Sables, B.R., and Hoering, T.C., 1971, Preparation of sulfur hexafluoride for isotope geochemical analysis: *Geochimica Cosmochimica Acta*, v. 35, p. 625–628.
- Qiu, J.S., Wang, D.Z., and Ren, Q. J., 1993, Physicochemical conditions and mineral sources for mineralization of the Shaxi porphyry Cu-Au deposit, Anhui Province: *Journal Nanjing University (Earth Science)*, v. 5, p. 386–397 (in Chinese with English abstract).

- Ren, J., Jiang, C., Zhang, Z., and Qin, D., 1980, *Geotectonic Evolution of China*: Beijing, Science Press, p. 1–124 (in Chinese).
- Ren, Q.J., Liu, X.S., and Xu Z.W., 1991, Luzong volcanic basin of Mesozoic era and the mineralization, Anhui, East China: Beijing, Geology Publishing House, 206 p. (in Chinese).
- Rickwood, C., 1989, Boundary lines within petrologic diagrams which use oxides for major and minor elements: *Lithos*, v. 22, p. 247–263.
- Rollinson, H.R., 1993, *Using geochemical data. Evaluation, presentation, interpretation*: New York, Longman Science and Technology, p. 48–51.
- Rui, Z.Y., Huang, Z.K., Qi, G.M., Xu Y., and Zhang, H.T., 1984, Porphyry copper (molybdenum) deposit of China: Beijing, Geology Publishing House, p. 201–241 (in Chinese).
- Su, X., and Liu, T., 1999, Application of isotopes to the geological study on iron and copper deposits in southeastern Hubei: *Geology and Prospecting*, v. 30, p. 27–32 (in Chinese with English abstract).
- Su, Y., Liu, X., and Chu, L., 1991, The stable isotopes study of seynitoid in Lujiang-Zongyang area, Anhui Province: *Acta Petrologica Sinica*, v. 7, p. 95–97 (in Chinese with English abstract).
- Tang, Y., Wu, Y., and Chu, G., 1998, The multiple metal deposits along middle-lower Yangtze region in Anhui: Beijing, Geological Publishing House, p. 1–240 (in Chinese with English abstract).
- Tian, S., Ding, T., Hou, Z., Yang, Z., Xie, Y., Wang, Y., and Wang, X., 2005, REE and stable isotope geochemical of the Xiaotongguanshan copper deposit in Tongling, Anhui: *Geology in China*, v. 32, no. 4, p. 604–613 (in Chinese with English abstract).
- Tian, S., Ding, T., Yang, Z., Meng, Y., Zeng, P., Wang, Y., Wang, X., and Jiang, Z., 2004, REE and stable isotope geochemical characteristics of Chaoshan gold deposit in Tongling, Anhui Province: *Mineral Deposits*, v. 23, no. 1, p. 365–374 (in Chinese with English abstract).
- Tian, S., Hou, Z., Yang, Z., Ding, T., Meng, Y., Zeng, P., Wang, Y., and Wang, X., 2007, REE and stable isotope geochemical characteristics of the Mashan gold deposit in Tongling, Anhui Province: *Acta Geologica Sinica*, v. 81, no. 7, p. 929–938 (in Chinese with English abstract).
- Tianjing (Tianjing Institute of Nonferrous Metals), 1984, *Geochemical study of Shaxi porphyry copper deposit: a special research report by Tianjing Institute of Nonferrous Metals* (in Chinese).
- Wang, K.R., and Yang, X.-Y., 1996, Geochemistry of Shaxi-Changpushan porphyry Cu-Au deposit from Anhui Province, East China, in Pan, Z.H. et al., ed., *Advances in Solid Earth Sciences*: Beijing, Science Press, p. 154–164.
- Wang, X., 1981, Preliminary study on Mashan sulfide-gold deposit in Tongling- Geochemistry and ore accumulation: *Metallurgy Geology of East China*, no. 2, p. 23–32 (in Chinese with English abstract).
- Wang, Y., 1987, Stable isotopic study of some gold deposits in China: *Geological Information of the Northeastern China*, v. 2, p. 5–12 (in Chinese with English abstract).
- Wang, Z.R., 1995, Geochemistry of Mashan gold deposit in Tongling: *Bulletin of East China Geological College*, v. 25, p. 37–42 (in Chinese with English abstract).
- Xing, F.M., 1998, The geochemistry of mafic rocks in the east of Yangtze magmatic belt: *Geochimica* v. 27, p. 258–268 (in Chinese with English abstract).
- Xing, F.M., and Xu, X., 1995, The essential features of magmatic rocks along the Yangtze River in Anhui province: *Acta Petrologica Sinica*, v. 11, p. 409–422 (in Chinese with English abstract).
- Xing, F.M., and Xu, X., 1999, *Yangtze Magmatic Belt and Metallogenesis*: Hefei, Anhui People's Publishing House, p. 1–170 (in Chinese).
- Xu, W., Yang, Z., Meng, Y., Zeng, P., Shi, D., Tian, S., and Li, H., 2004, Genetic model and dynamic migration of ore-forming fluids in Carboniferous exhalation sedimentary massive sulfide deposits of Tonling District, Anhui Province: *Mineral Deposits*, v. 23, p. 353–364 (in Chinese with English abstract).
- Xu, Z, Qui, J., Ren, Q., Xu, W., Niu, C., and Fu, B., 1999, Geological and geochemical characteristics and genesis of the Shaxi porphyry Cu-Au deposits, Anhui Province: *Acta Geologica Sinica*, v. 73, p. 8–18.
- Xu, Z., Huang, S., Ni, P., Lu, X., Lu, J., Fang, C., Hua, M., and Jiang, S., 2005, Characteristics and evolution of ore fluids in Dongguanshan copper deposit, Anhui Province, China: *Geological Review*, v. 51, no. 1, p. 36–41 (in Chinese with English abstract).
- Xu, Z., Lu, X., Cao, G., Fang, C., Wang, Y., Yang, X., Jiang, S., and Chen, B., 2007, Isotope geochemistry and mineralization in the Dongguanshan diplogenetic stratified copper deposit, Tongling area: *Geological Review*, v. 53, no. 1, p. 44–51 (in Chinese with English abstract).

- Xu, Z., Ren, Q., Yang, R., and Wang, S., 1992, Distribution regularities and metallogenic patterns of veinlike Cu(Au)-deposits in the Lujiang-Zhongyang area: *Geology and Prospecting*, v. 28, p. 8–15 (in Chinese with English abstract).
- Yang, X.-Y., 1996, The Cu-Au metallogenic prospecting areas from middle-lower reaches of Changjiang River. A study on metallogenic geochemistry of some typical copper and gold ore deposits [Unpublished Ph.D. thesis]: Hefei, University of Science and Technology of China, p. 1–214 (in Chinese with English abstract).
- Yang, X.Y., Wang, K.R., Sun, L.G., Yang, X.M., Li, Y.X., and Shi, K.F., 2001, A prospecting porphyry Cu-Au deposit in Changpushan area by geochemical and geophysical exploration, central Anhui, east China: *Chime der Erder*, v. 61, p. 254–276.
- Yang, X.Y., Yang, X.M., Jiang, L.L., Wang, K.R., and Sun, L.G., 2006, Geochemical study of Shaxi porphyry copper-gold deposit in southern part of Tan-Lu fault belt, East China: *Journal of the Geological Society of India*, v. 67, p. 475–494.
- Yang, X.Y., Yang, X.M., Zhang, Z.W., Chi, Y.Y., Yu, L.F., and Zhang, Q.M., 2011, A porphyritic copper (gold) ore-forming model for the Shaxi-Changpushan district, Lower Yangtze metallogenic belt, China: Geological and geochemical constraints: *International Geology Review*, v. 53, p. 580–611.
- Yang, Z., Hou, Z., Meng, Y., Zeng, P., Li, H., Xu, W., Tian, S., Wang, X., Yao, X., and Jiang, Z., 2004, Spatial-temporal structures of Hercynian exhalative-sedimentary fluid system in Tongling ore concentration area, Anhui Province: *Mineral Deposits*, v. 23, p. 281–297 (in Chinese with English abstract).
- Yao, C., Lu, J., Sun, X., Dai, Y., and Qian, P., 2005, Geochemical difference between quartz veins of two generations at the Tongchang porphyry copper deposit, Jiangxi Province: *Geochimica*, v. 34, p. 357–365 (in Chinese with English abstract).
- Yu, C.W., 2001, Study on the genesis of Tongshan copper ore deposit in Guichi: *Geology and Prospecting*, v. 37, p. 12–16 (in Chinese with English abstract).
- Zhai, Y., Xiong, Y., Yao, S., and Lin, X., 1996, Metallogeny of copper and iron deposits in the Eastern Yangtze Craton, east-central China: *Ore Geology Review*, v. 11, p. 229–248.
- Zhang, L., Liu, J., Chen, Z., and Yu, G., 1996, Oxygen and hydrogen stable isotopic evolution of water-rock system in Tongchang copper deposit, Dexing, Jiangxi Province: *Scientia Geologica Sinica*, v. 31, p. 250–261 (in Chinese with English abstract).
- Zhao, B., and Zhao, J., 1997, O and Sr isotopic geochemistry for massive and vein calcareous skarns from some iron-copper (gold) deposits along the middle-lower reaches of the Yangtze River area: *Geochimica*, v. 26, no. 5, p. 34–53 (in Chinese with English abstract).
- Zheng, Y., Fu, B., and Gong, B., 1995, The thermal history of the Huangmeijian intrusion in Anhui and its relation to mineralization: isotopic evidence: *Acta Geologica Sinica*, v. 69, p. 337–348 (in Chinese with English abstract).
- Zheng, Y., Wei, C., Wang, Z., Huang, Y., and Zhang, H., 1997, An isotope study on the cooling history of the Dalongshan granitic massif and bearing on mineralization process: *Scientia Geologica Sinica*, v. 32, p. 465–477 (in Chinese with English abstract).
- Zhou, T.F., Yuan, F., and Yue, S.C., 1994, Sulphur isotope of Yueshan copper deposit: *Geology and Volcanology*, v. 15, p. 98–108 (in Chinese with English abstract).
- Zhou, T.F., Yue, S.C., and Yuang, F., 2001, H, O isotope geochemistry and transport-reaction dynamic processes of ore-forming fluid for Cu, Au deposits in the Yueshan orefield, Anhui Province: *Anhui Geology*, v. 11, p. 131–139 (in Chinese with English abstract).
- Zhou, Z., and Wang, Z.Q., 1984, Geological characteristics and origin of the Mashan gold deposit in Tongling region: *Geological Review*, v. 30, no. 5, p. 467–476 (in Chinese with English abstract).
- Zhu, X., Huang, Z.K., and Rui, Z.Y., 1983, The Dexing Porphyry Copper Deposit: Beijing, Geological Publishing House, p. 1–336 (in Chinese).