International Geology Review
Vol. 53, Nos. 5–6, April–May 2011, 580–611

A porphyritic copper (gold) ore-forming model for the Shaxi-Changpushan district, Lower Yangtze metallogenic belt, China: geological and geochemical constraints

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(*Accepted 13 Juiy 2009*)

Ore-forming P-T-X conditions and the nature of gold occurrence in the Shaxi-Changpushan porphyry copper deposit, central Anhui Province, eastern China, were investigated employing a wide range of geological and geochemical methods. Our results document liquid-vapour conditions and show that abundant fluid inclusions occur in quartz veins accompanied by pyrite-chalcopyrite-gold mineralization. Most economic deposits involved coexisting liquid and gas phases, whereas a few formed in equilibrium with a homogeneous aqueous liquid. The ore-forming temperature lies between 230 and 350°C. Isotope studies show that the $\delta^{34}S$ values are between –0.20 and 3.00‰ for most of the sulphides; $\delta^{34}S$ values of chalcopyrite are somewhat more homogenous than those of pyrite. Ore-forming fluids and materials were mainly derived from magmatic sources. Meteoric water played a small role in the ore-forming process, judging by the oxygen and hydrogen isotope data for fluid inclusions measured by the explosion method ($\delta^{18}O$ values ranging from 3.51 to 5.52‰, and δD ranging from −59.8‰ to −82.4‰). In the ore deposit, the gold occurs as micro-inclusions heterogeneously distributed in chalcopyrite and pyrite. Gold mineralization is positively correlated with As in chalcopyrite, pyrite, and some Cu-bearing ores.

Igneous rocks and sedimentary rock distributions in the Shaxi-Changpushan ore district were strictly controlled by the regional fault system since the Jurassic period, especially the Tan-Lu fault system in east China. Intrusive bodies comprising porphyritic quartz dioritoid, biotite-quartz dioritoid, and fine-grained dioritoid are ore-bearing, cutting sedimentary rocks of the Upper Jurassic and Middle–Lower Silurian series. Sediments exposed in the ore district consist of Upper Devonian–Middle Silurian clastic rocks, Middle and Lower Jurassic and Upper Cretaceous terrestrial clastic rock series. Petrologic data show that formation of Cu-Au ore bodies was related to adakitic intrusives in the Shaxi-Changpushan area. Based on geochemical exploration and the tectonic background of the southern part of Tan-Lu fault zone, we propose a porphyric copper (gold) ore-forming model for the Lower Yangtze metallogenic belt: ore bodies were controlled by structural shielding in the core of the regional anticline. Combined geological and geochemical evidence suggests that a super-large porphyry (gold) deposit may be present in the region.

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ISSN 0020-6814 print/ISSN 1938-2839 online

DOI: 10.1080/00206810903211906
http://www.informaworld.com

Keywords: porphyry copper (gold) deposit; Geochemical survey; Cu-Au genetic model; adakite; Shaxi-Changpushan porphyry Cu-Au mineralization district

Introduction

The Shaxi porphyry copper (gold) deposit represents one of the important discoveries during the 1970s mineral exploration in the middle-lower reaches of the Yangtze River. The geological survey and exploration work on the Shaxi deposit has been undertaken by several governmental geological institutes as well as mining companies, including No. 327 Geological Team of the Anhui Bureau of Geology and Mineral Resources, which has conducted exploration work in the area for more than 20 years. It has demonstrated that there are 258,500 tons of contained copper (grading >0.4% Cu) and 231,000 tons of copper with lower grade (0.2–0.4% Cu) in this region, belonging to the middle–lower parts of the Yangtze metallogenic belt, where more than 200 poly-metal deposits have been discovered, mainly consisting of Cu, Fe, Cu, Pb, and Zn. Scholars have intensively studied the Yangtze metallogenic belt in terms of its geology and geochemistry, and obtained several important conclusions (e.g. Chang *et al.* 1991; Ren *et al.* 1991; Pan and Dong 1999; Xu *et al.* 1999; Wu *et al.* 2003, 2004; Zang *et al.* 2004; Mao *et al.* 2004; Yang and Lee 2005; Yang *et al.* 2006, 2007a,b; Deng *et al.* 2006, 2007; Zhang *et al.* 2006; Lan *et al.* 2009; Xie *et al.* 2009; Zhou *et al.* 2008; Yu *et al.* 2009). However, the genesis of some Cu-Au deposits is still debated, including the Shaxi-Changpushan porphyry Cu-Au deposit, one of the most important porphyry Cu-Au deposits in the Yangtze metallogenic belt.

This paper focuses on the geochemistry and gold occurrences of the Au-bearing porphyry copper deposit to better understand metallogenic processes and associated intrusive bodies. We discuss genetic models for this Cu-Au deposit and conclude that a large or super-large porphyry Cu-Au deposit is present in the Shaxi-Changpushan region.

Geological settings

The Shaxi-Changpushan porphyry copper (gold) deposit is located in the northwestern Luzong volcanic basin, in the southern part of the Tan-Lu fault belt, one of the largest deep faults in the east Asian continent (Xu *et al.* 1987). It also belongs to the north of the middle and low part of the Yangtze iron and copper metallogenic zone, the location of multiple faults, where Fanshan–Tongling deep fault and the Tan–Lu fault belt come through the whole mineralization region and resulted in serious rock deformation in the Jurassic (Chang *et al.* 1991; Yang 1996; Yang *et al.* 1996, 1998a, 2001). In the southeast is the Luzong volcanic basin, where Jurassic–Cretaceous volcanic activities occurred, with more than 10 deposits or occurrences of Cu, Au, Ag, Pb, and Zn commodities.

Figure 1 shows the regional geologic-tectonic map and the distribution of the granitoid intrusions related to Cu-Au mineralization, such as the Shaxi porphyry, Huangtun diorite intrusion, Anqing diorite intrusion related to massive hydrothermal and skarn Cu-Au deposits, and Tongling granodiorite intrusion and Chuxian diorite intrusion, both associated with skarn Cu-Au deposits. As a comparison, the volcanic rocks in the Jurassic–Cretaceous Luzong volcanic basin are also studied in this contribution, because previous study (Ren *et al.* 1991) suggests that volcanic rocks may be linked to the formation of the Shaxi intrusion.

The tectonic background in Shaxi has been controlled by the Tan–Lu slip fault system since the formation of Jurassic sedimentary rocks (Chang *et al.* 1991). The igneous

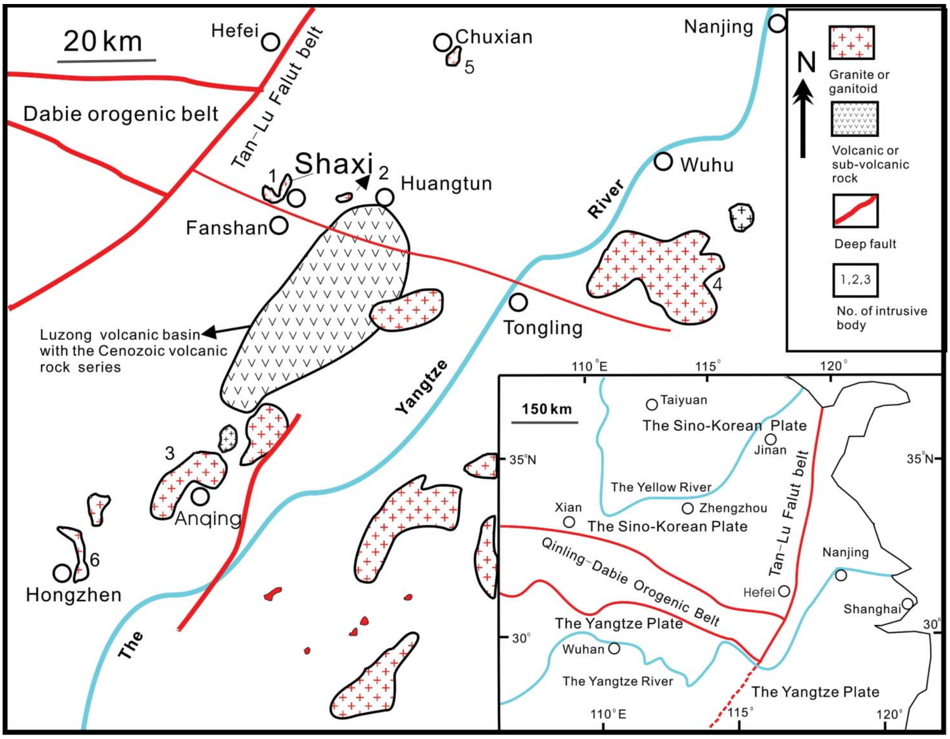

Figure 1. Regional sketch geologic-tectonic map and the distributions of the granitoids related to Cu-Au mineralization along the lower part of the Yangtze metallogenic valley in east China (after Chang *et al.* 1991). (1) Shaxi porphyritic intrusion; (2) Huangtun diorite intrusion; (3) Anqing diorite intrusion; (4) Tongling granitic intrusion; (5) Chuxian granitic intrusion; (6) Huangzhen granitic intrusion.

rocks and the distributions of sedimentary rocks have been strictly controlled by the fault system since the Jurassic period. The sediments exposed in the Shaxi deposit consist of Upper Devonian–Middle Silurian clastic rocks of continental-sea facies, Middle and Lower Jurassic inland clastic rocks of climatic facies, and Cretaceous red sandstone and conglomerate. There is also wide distribution of intrusive rocks of Upper Jurassic to Early Cretaceous series and continental volcanic rocks. Some of the intrusive bodies comprising porphyritic quartz dioritoid, biotite-quartz dioritoid, and fine-grained dioritoid are ore-bearing, cutting the sedimentary rocks of the Upper Jurassic series and the Middle–Lower Silurian series.

From north to south, the Shaxi porphyry copper (gold) deposit is divided into four ore zones based on the morphological units, that is, Qipanshan, Tongquanshan, Shizishan, and Duanlongjing (No. 327 Geological Team 1982). Drilling proved these ore zones to be united, however, controlled by a composite fold trending NNE in this region. The Changpushan prospecting area is located in the southern part of the Shaxi porphyry copper (gold) deposit, which is separated by the Duanlongjing fault; the structural line is slightly declined to the east compared with the Shaxi deposit, suggesting that it may be an independent ore deposit, although it has a close relationship with the structure of the Shaxi deposit in terms of regional geological setting (Figure 2; Yang *et al.* 2001).

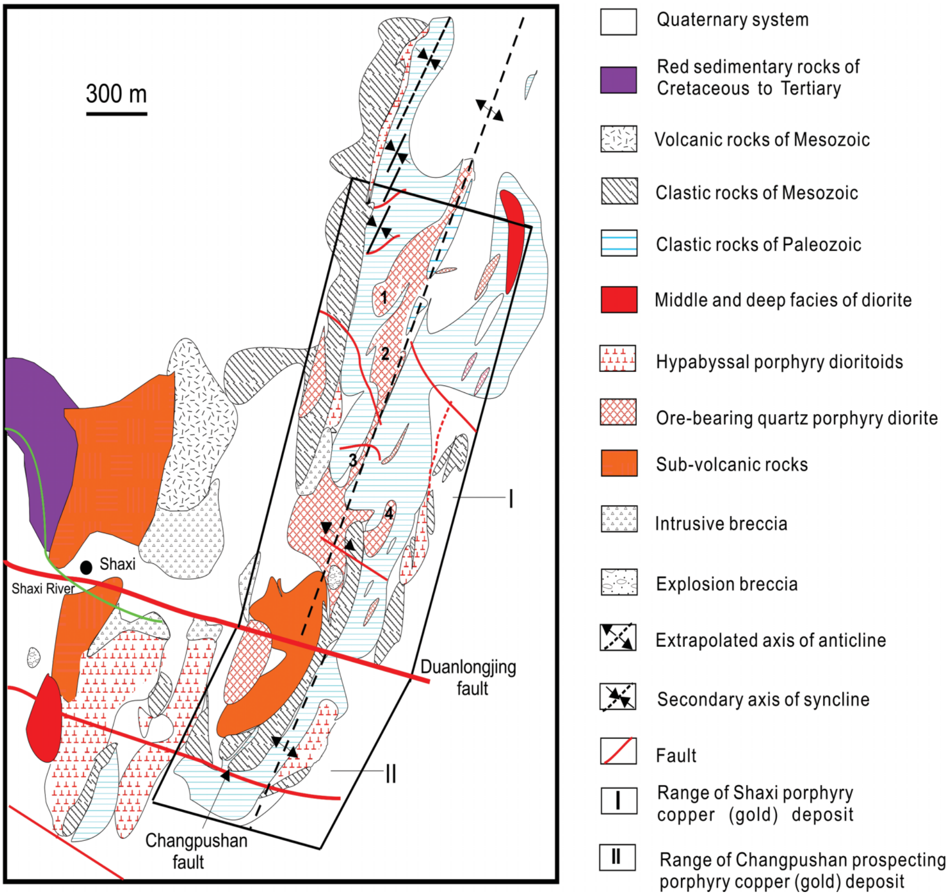

Figure 2. Geological map of the Shaxi–Changpushan porphyry copper (gold) deposit, central Anhui, China. 1, 2, 3, and 4 in the map denote the Qipanshan, Tongquanshan, Shizishan, and Duanlongjing sub-ore districts, respectively.

Mineralogy and metallogeny

Ore types

Five types of copper (gold) ore are present, based on field observations: chalcopyrite ore, Cu-bearing pyrite ore, magnetite-chalcopyrite ore, pyrite-bornite-chalcopyrite ore, and chalcopyrite-molybdenite ore. These types of ore are not distributed homogeneously, and vary horizontally and vertically in this ore district. For example, the chalcopyrite-molybdenite ore is only found in the very northern part of the deposit in a small amount. The ore assemblages are characterized by relatively simple ore minerals, such as chalcopyrite, pyrite, pseudomorph haematite, bornite, magnetite, chalcocite, covellite, and arsenopyrite; the ore grade ranges from 0.2 to 0.4% copper; the gangue minerals are quartz, K-feldspar, calcite, gypsum, and anhydrite.

Alteration and mineralized stages

The alteration varies from the interior to outside of the deposit: potassic zone, sericitic zone, and propylitic zone. Generally, the contact between each alteration zone is not clear.

Alteration zoning is evident in mineralized quartz porphyry and biotite-quartz porphyry dioritoids, where Cu ore is hosted mainly in the potassic alteration zone. The ore contains gold averaging 3.16 ppm.

Detailed observations on the assemblages of alteration minerals and their relationship in the field indicate that three mineralized stages may have been present in the deposit (No. 327 Geological Team 1982): (1) the early biotite-K-feldspar-magnetite stage formed above 400°C, suggested by studies of fluid inclusions in quartz (this is not the main Cu (Au) mineralization stage); (2) the sericite-quartz-sulphide stage, the major Cu mineralization stage, formed at temperatures ranging from 250 to 300°C; and (3) the late quartz-carbonate-sulphide stage comprising carbonate, chlorite, sericite, kaolinite, and albite, which was formed at temperatures of 200–150°C. At this late stage, Cu mineralization is less important compared with the second stage. These three mineralized stages are coherent to one another, which accords with the diagenetic period of the main intrusion – the quartz diorite porphyry in this region. The alteration of the intrusive rocks in the deposit is similar to that of most porphyry copper deposits associated with diorite to granodiorite porphyry elsewhere, such as the Kounrad and Erdentuin porphyry copper deposits in central Asia (Vadim *et al.* 1993), Peschanka and Bingham porphyry copper deposits in the USA (Lowell and Guilbert 1970). The main mineralized stage, however, is not in the same period as wall-rock alteration. For example, in the Kounrad porphyry copper deposit, the main copper mineralization is related to the medium to late stages of alteration formed at 230–360°C (Vadim *et al.* 1993).

Table 1 (see supplementary material in the online version of this article at http://www.informaworld.com/tigr) gives the mineral assemblages of the ore deposit, indicating that the ore assemblage is relatively simple, consisting of chalcopyrite, pyrite, pseudomorph magmatite, bornite, magnetite, chalcocite, covellite, and arsenopyrite; the ore grade is 0.2–0.4% Cu.

Petrography

The intrusive rocks in the Shaxi–Changpushan porphyry copper (gold) deposit occur as stock, tongue, ethmolith, and dike. The ore deposit is associated with quartz diorite porphyry, biotite-quartz diorite porphyry, and fine- to medium-grained porphyry diorite that exhibit subhedral seriate texture. The porphyritic rocks contain plagioclase and alkali-feldspar phenocrysts, ranging from 8–3 to 5–1.5 mm in size. Some of the feldspars are altered to sericite, chlorite, and kaolinite in alteration zones. The dioritic rock consists of plagioclase, amphibole, quartz, microcline, and biotite, and minor muscovite, apatite, sphene, pyrite, magnetite, and rutile. Some quartz crystals show undulatory extinction and have several generations; most of them contain inclusions of other minerals and needles of some metal minerals. Microcline occurs as subhedral crystals with cross-hatch twinning. Microperthite is also evident. Plagioclase is subhedral with albite twinning; it is mainly andesine (An values ranging from 25 to 45 by EPMA analysis), although oligoclase-albite (An5-An20) is present because of hydrothermal alteration. Amphibole is subhedral, 1.3–0.4 to 0.2–0.1 mm (locally up to 10 mm) in size. It is noted that some diorite porphyries contain up to 15% amphibole. Some amphibole grains are replaced by chlorite at their margins, where muscovite and quartz are present. Biotite grains are commonly subhedral. Ore minerals are scattered among the main rock-forming minerals.

Figure 3 shows the relationship between ore minerals and rock-forming minerals and also the characteristics of fluid inclusions in the Shaxi porphyry Cu (Au) deposit, and Figure 4 shows photomicrographs of ore minerals and mineralized rocks in the Shaxi porphyry Cu (Au) deposit.

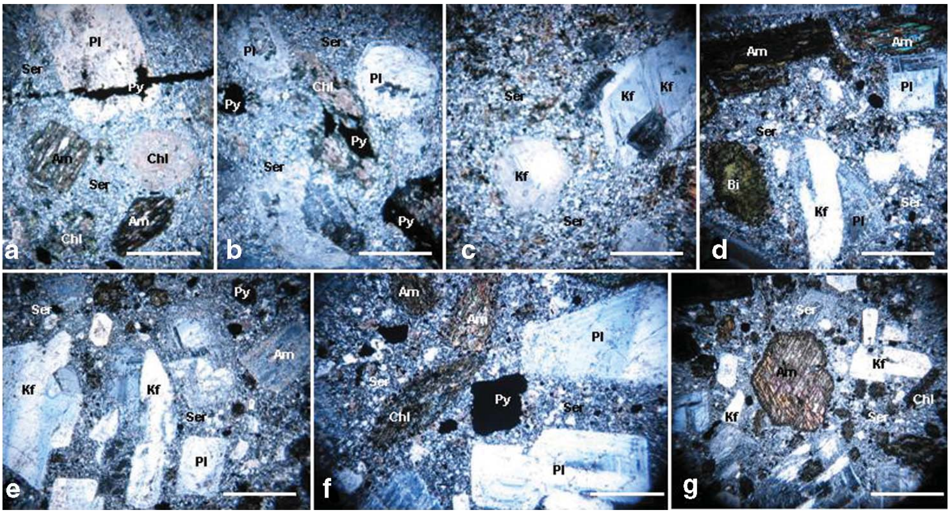

Figure 3. Photomicrographs of granitoids associated with Cu-Au mineralization in the Shaxi–Changpushan porphyry Cu-Au deposit, central Anhui. (All the images were taken with a Leica microscope under polarized light conditions, the scale bar for each of the images is 0.30 mm. Am, Amphibole; Bi, biotite; Chl, chlorite and chloritization; Kf, potassic feldspar; Pl, plagiocalse; Py, pyrite; Ser, sericite and sericitization). (a) Amphibole and plagioclase crystals with strong chloritization and sericitization in porphyrite, the vein-type pyrite cutting across plagioclase; (b) plagioclase with strong chloritization and sericitization in the porphyrite, amphibole is totally chloritized resulting in the formation of pyrite; (c) idiomorphic crystal grains of potassic feldspar with sericitization; (d) crystals of plagioclase, amphibole, and biotite with strong sericitization; (e) crystals of potassic feldspar, plagioclase, and amphibole with sericitization in the porphyrite associated with the porphyry Cu-Au deposit; (f) plagioclase and amphibole in the porphyrite with strong sericitization associated with the porphyry Cu-Au deposit; (g) idiomorphic crystal grains of amphibole and plagioclase replaced by sericite and chlorite.

Mineralogy of gold-carrier minerals

The porphyry copper ore is commonly associated with fine-grained gold mainly occurring in the surface of pyrite and chalcopyrite crystals (No. 327 Geological Team 1982; Ji *et al.* 1987; Yang 1996; Yang *et al*. 1998b, 2002).

Various studies show that gold is mainly hosted in pyrite and chalcopyrite (Ji *et al.* 1987; Yang 1996; Yang *et al*. 1998a, 2002). In this study, 16 new samples of pyrite and chalcopyrite were selected for compositional analyses using a JEOL JXA-50A electron microprobe equipped with 5WDS spectrometers and a CAMECA SX50 probe linked with an EDS system under conditions of 15 kV, 15 nA, and 100 cps. The results are listed in Tables 2 and 3 (see online supplementary material), respectively. It is noted that silver is enriched in these gold-carrier minerals, and arsenic is relatively elevated, too. Figure 5 shows the S-Cu-Fe ternary diagram to illustrate the composition of both pyrite and chalcopyrite, which fall into a small area in the compositional space reflecting the unique source of ore fluids during mineralization.

The relationship between gold and As contents in pyrite and chalcopyrite is shown in Figure 6, revealing a positive correlation between these two trace elements.

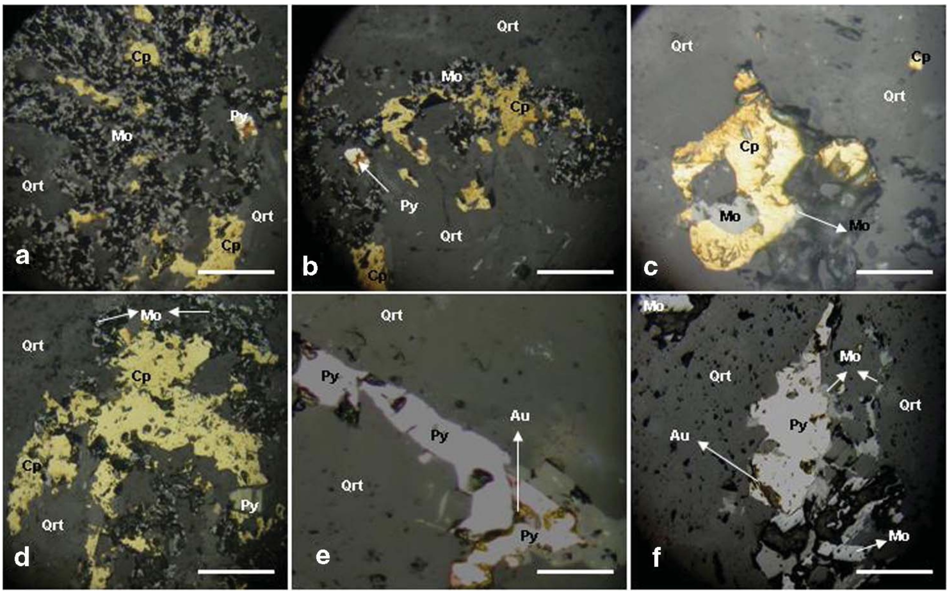

Figure 4. Photomicrographs of ore minerals and rocks in the Shaxi–Changpushan porphyry Cu-Au deposit, central Anhui. All the images were taken with a Leica microscope under reflection light conditions, the scale bar for each of the images is 0.30 mm. Cp, chalcopyrite; Py, pyrite; Mo, molybdenite; Au, gold; Qrt, quartz. (a) Scattered grains of mineralization of chalcopyrite, molybdenite and pyrite in quartz-porphyry diorite, which shows the correlations with fine quartz veins. (b) Relatively large grains of chalcopyrite combined with small grains of molybdenite and pyrite mineralization. (c) Big grains of chalcopyrite are surrounded by molybdenite, which shows the later mineralization of molybdenite than chalcopyrite. (d) Big grains of chalcopyrite are surrounded by small grains of molybdenite. (e) Big grains of pyrite and vein-type pyrite with gold mineralization. (f) Big grains of pyrite are surrounded by molybdenite, a very fine grain of gold is seen at the edge of a pyrite grain.

Petrochemistry of intrusive rocks

Major elements

The chemical compositions of the intrusions associated with Cu (Au) mineralization are presented in Table 4 (see online supplementary material). This indicates that the Shaxi-Chagpushan intrusive rocks mainly belong to calc-alkaline to high-K calc-alkaline series, and only a few samples are shoshonitic or tholeiitic series (Figure 7). In contrast, samples from both Tongling and the Luzong volcanic basin mainly belong to shoshonitic to high-K calc-alkaline series; samples in Anqing are high-K calc-alkaline series. These data imply different characteristics of sources for these Cu-Au metallogenic districts, reflected also by REE and trace elements data as shown below.

The chemical classification of the TAS diagram shows that most samples from Shaxi–Changpushan fall into the diorite region, similar to those of Tongling and Anqing diorite, whereas the volcanic rocks in Luzong volcanic basin are much different (Figure 8).

Rare earth elements

The data of REE and trace elements are listed in Table 5 (see online supplementary material). The intrusive rocks associated with mineralization in the Shaxi–Changpushan district have total REE contents between 66 and 263 ppm, with enriched LREE relative to

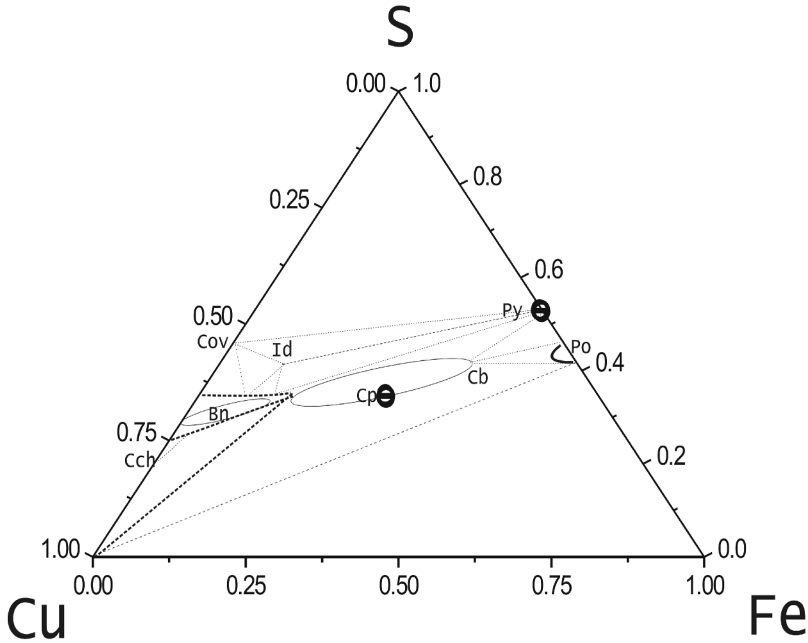

Figure 5. Isothermal section of a S-Fe-Cu diagram at 300°C from the Shaxi–Changpushan porphyry Cu-Au deposit, central Anhui (after Yund and Kullerud 1966). Py, pyrite; Cp, chalcopyrite; Cov, coversite; Bn, bornite; Id, idaite; Cb, cubanite; Cch, chalcocite; Po, pyrrhotite.

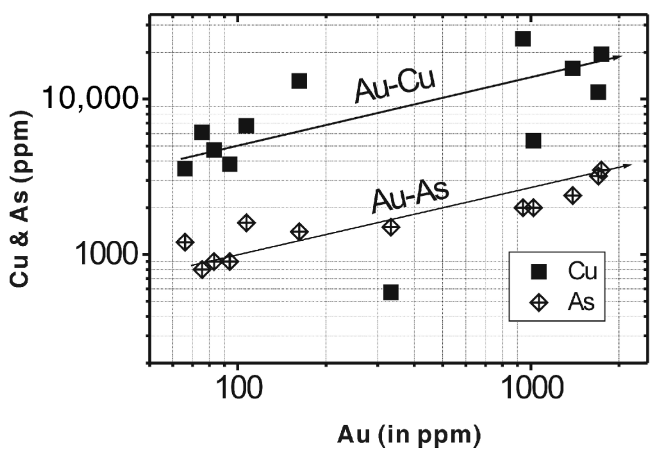

Figure 6. The relations between element contents of Au and As in pyrite and chalcopyrite.

heavy REE (HREE) without Eu anomaly (Figure 9). It is not evident for a significant change in REE patterns of the altered intrusive rocks with increasing depth (Figure 9). Compared with the average contents of the continental crust, the REE patterns of the intrusive rocks area are more similar to the lower crust (Taylor and McLennan 1985), although their total REE contents are higher; and fractionation of LREE and HREE is larger. This may be an important indication for Cu mineralization in this region. Furthermore, the light REE patterns of Shaxi, Luzong, Anqing, and Tongling Cu-Au-mineralized intrusive rocks

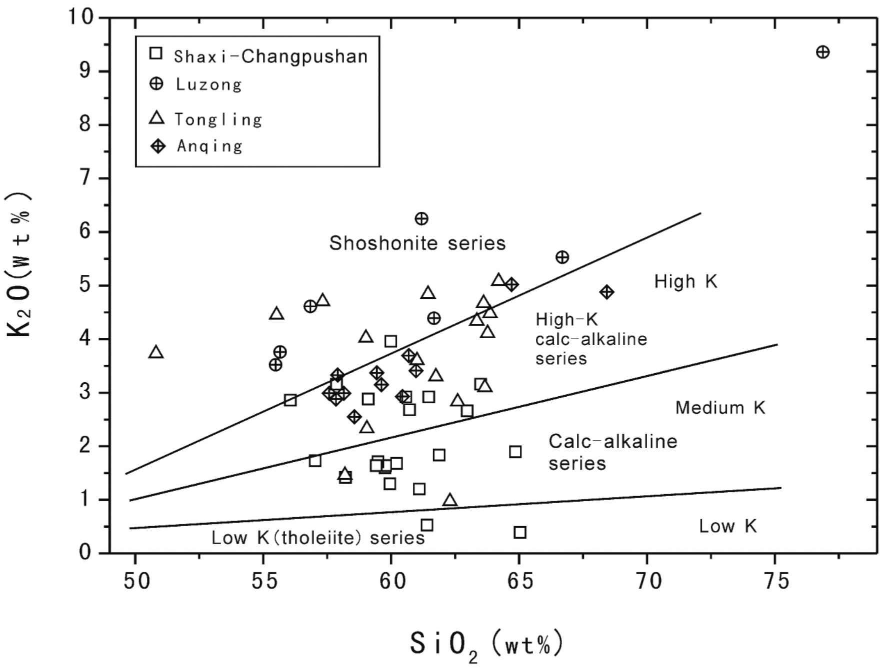

Figure 7. SiO_2-K_2O diagram for the granitoid rocks in Table 2 (see online supplementary material) (after Le Maitre *et al.* 1989; Rickwood 1989).

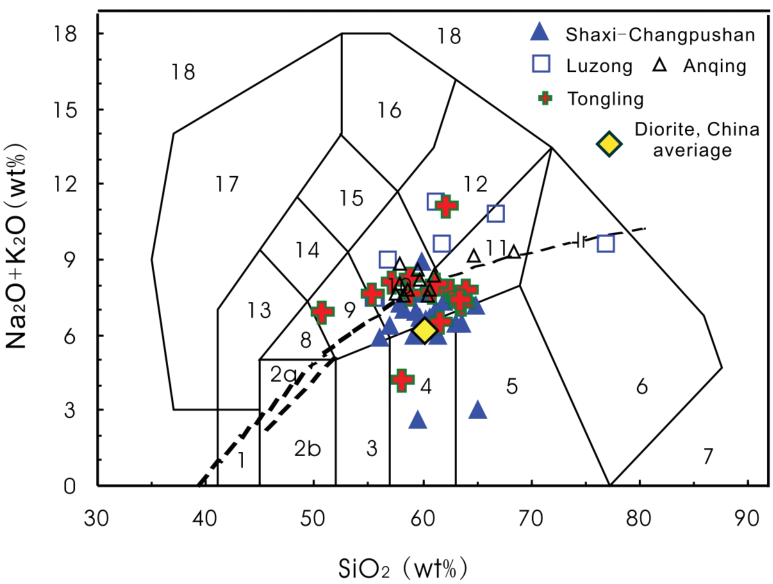

Figure 8. Chemical classification of the TAS diagram (Wilson 1989).

are very similar, although their heavy REE distributions are different. It is worth noting that the intrusive rocks associated with Cu (Au) mineralization have similar ages (Cretaceous) and display comparable Sr and Nd isotopic compositions (Chang *et al*. 1991; Yang 1996; Chen and Jahn 1998). Intriguingly, different styles of Cu (Au) mineralization are

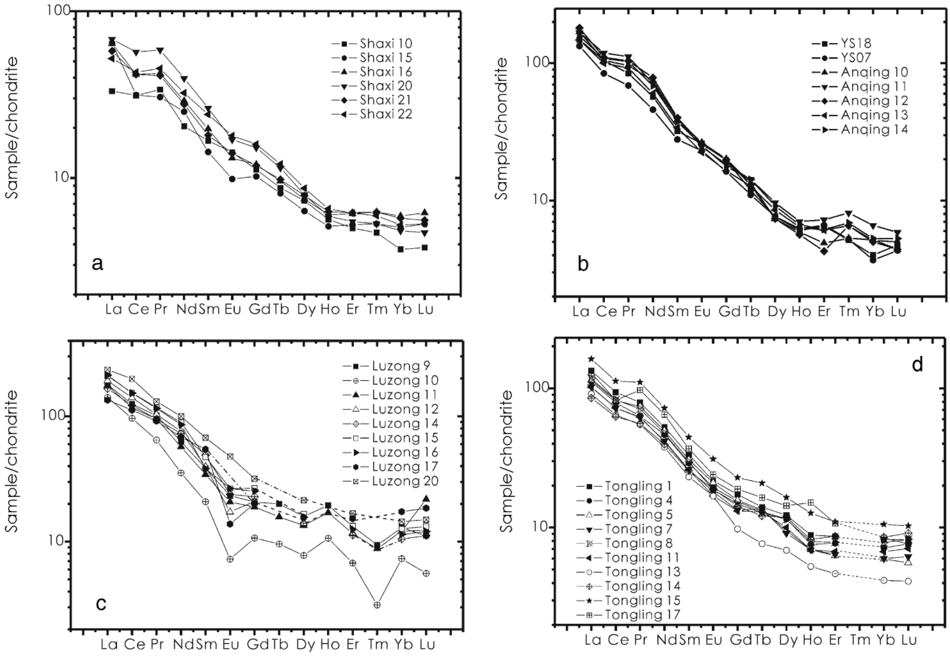

Figure 9. The chondrite-normalized REE distribution patterns of the altered intrusive rocks from the Shaxi–Changpushan porphyry copper (gold) deposit and its surrounded copper ore deposits. (a) Shaxi–Changpushan porphyry Cu-Au deposit; (b) Anqing skarn Cu-Au deposit; (c) Luzong volcanic basin; (d) Tongling skarn Cu-Au deposits.

evident in different areas of the region. For example, in Luzong volcanic basin and Anqing high-potassic diorites that are near the Shxi–Changpushan deposit, Cu (Au) mineralization occurs mainly as massive sulphidation, whereas in the Tongling area to the south of the Shaxi–Changpushan deposit, the Cu-Au mineralization is mainly hosted in skarn.

Trace elements

The spider diagrams of the intrusive rocks from the Shaxi–Changpushan area compared with those related to Cu-Au mineralization from the Luzong, Anqing, and Tongling areas in Anhui Province of the lower Yangtze metallogenic belt are shown in Figures 10–13, suggesting that the mantle compatible elements (e.g. Sc, Cr, Co, Ni) and some transitional elements (e.g. Ti, V, Mn, Fe, Cu) in these rocks are strongly fractionated relative to the crust rocks (Taylor and McLennan 1985; Thorpe 1976, 1982), with pronounced Cu positive anomalies. This could be an important indication for Cu mineralization in this region. Large ion lithophile elements such as K, Rb, Th, Sr, Ba, and Li are also enriched compared to the average contents of crust rocks, which manifest the regional geochemical anomalies of these elements, which may be a favourable feature for mineralization.

Age of the Shaxi–Changpushan intrusive complex and its tectonic environment

Age of the Shaxi–Changpushan intrusive complex

The age of the Shaxi–Changpushan intrusive complex has been debated for long time. There is a wide distribution of igneous rocks in this region with characteristics of multiple

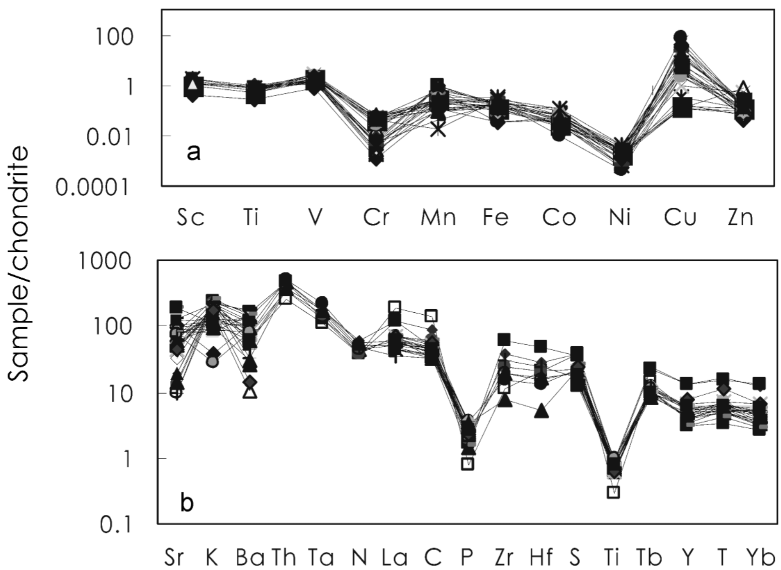

Figure 10. Spider diagrams of trace elements in the Shaxi–Changpushan district. (a) Diagram of transitional elements. (b) Diagram of large lithophile elements.

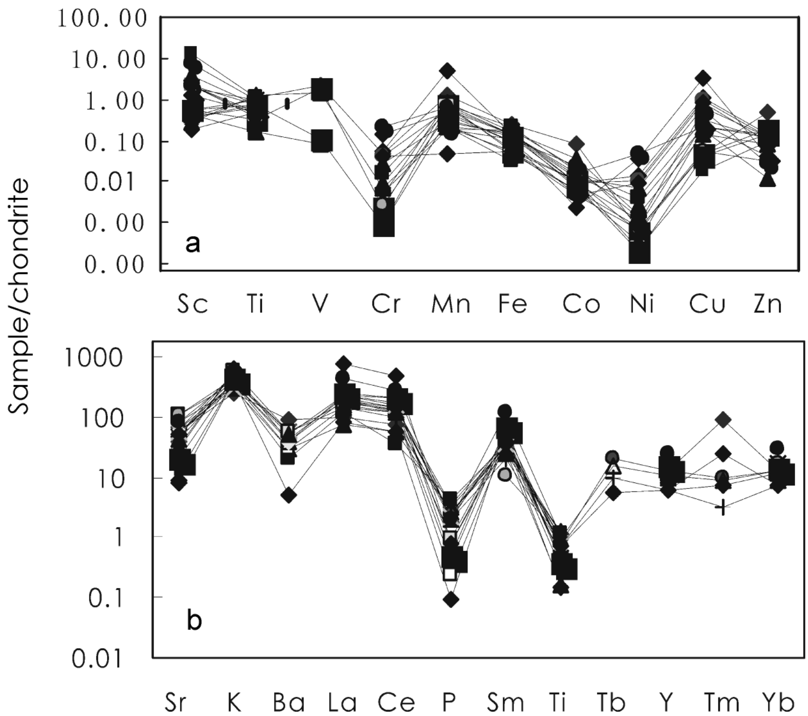

Figure 11. Spider diagrams of trace elements in the Luzong volcanic basin, central Anhui. (a) Diagram of transitional elements. (b) Diagram of large lithophile elements.

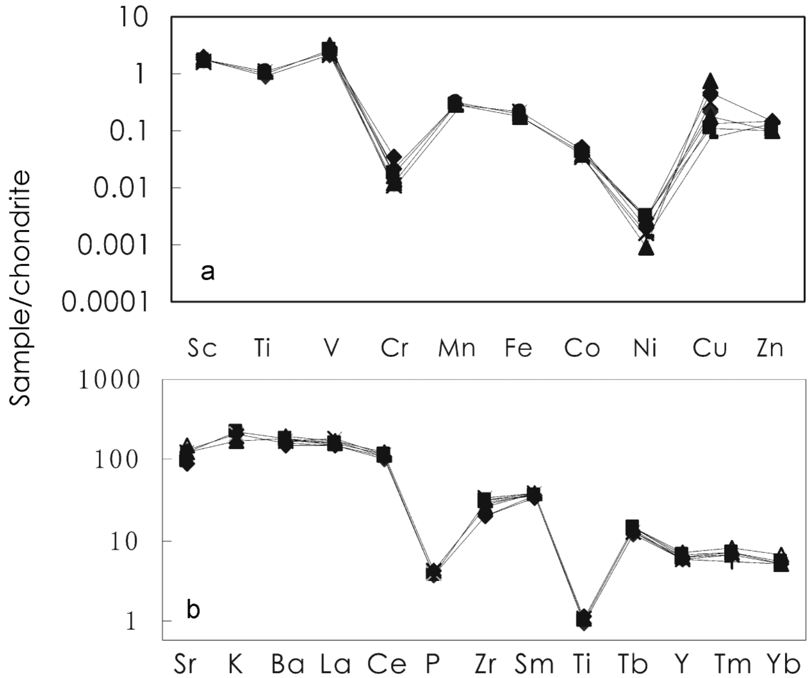

Figure 12. Spider diagrams of trace elements in the Anqing Cu-Au-bearing region, southwest Anhui. (a) Diagram of transitional elements. (b) Diagram of large lithophile elements.

magmatic activities that are manifested by field observations; the volcanic rocks overlie the Middle–Upper Jurassic sandstones of the Xiangshan group and have intrusive contact with the Lower Cretaceous red beds. Therefore, the volcanic activities were confined between the Late Jurassic to Early Cretaceous. Earlier dating with the K-Ar method on whole rock samples presented 173–123 Ma (No. 327 Geological Party 1982).

Recently, relatively high-precision dating methods, such as Ar-Ar and SHRIMP, have been used to date the Shaxi–Changpushan intrusive complex and surrounding intrusions. The results of $^{40}Ar/^{39}Ar$ dating on four monominerals (two biotite and two plagioclase) separated from the Shaxi–Changpushan complex yield ages ranging from 126 to 135 Ma, which are interpreted to represent the age of formation of the intrusion host to the Shaxi Cu-Au deposit (Fu *et al* 1997; Yang *et al.* 2007b). The concordia age of ~131 Ma determined by SHRIMP zircon U-Pb dating on the Huangtun intrusion (see location in Figure 1; Yu *et al*. 2009) indicates that two intrusions of Shaxi–Changpushan and Huantun in the Shaxi–Luzong area may have occurred in the same magmatic event when the regional porphyry Cu-Au formed.

The two intrusive bodies of Shaxi–Changpushan and Huangtun may have been derived from the same magmas sourced from the deep crust (No. 327 Geological Team 1982; Wang *et al.* 1994), displaying two stages of magmatism in the Shaxi–Changpushan–Huangtun regions. The early stage is an intrusive magmatism associated with variable copper (gold) mineralization, represented by quartz diorite porphyry, biotite quartz diorite porphyry, and the less important amphibole diorite porphyry and brecciated diorite porphyry.

In the Luzong vocanic basin nearby (Figure 1), the volcanic rocks are shoshonitic and have similar ages of 136–124 Ma (Yuan *et al.* 2008) to the Shaxi–Changpushan complex.

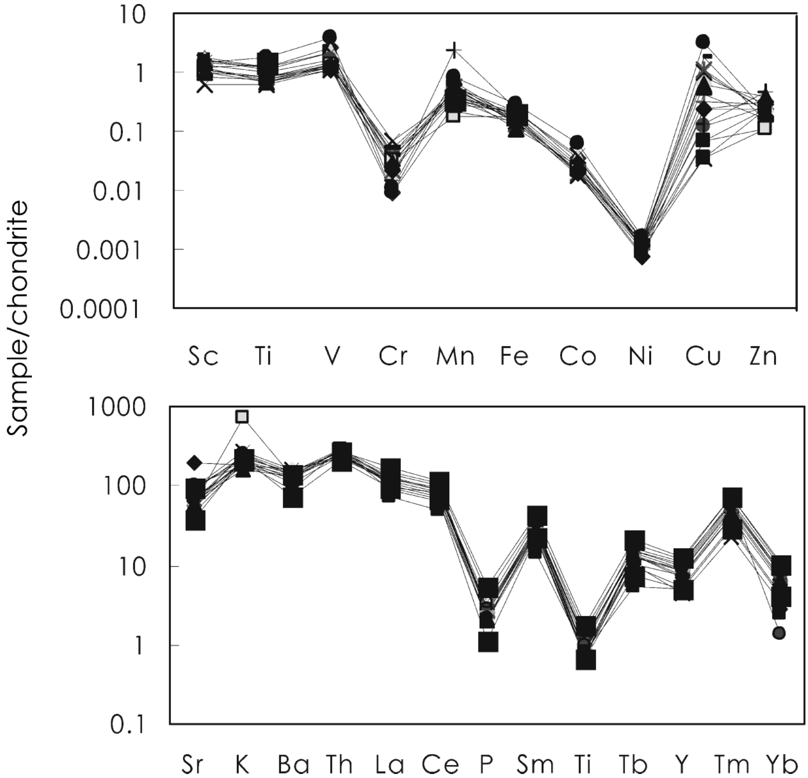

Figure 13. Spider diagrams of trace elements in the Tongling Cu-Au-bearing region, south Anhui. (a) diagram of transitional elements; (b) diagram of large lithophile elements.

Chemical composition and isotopic data suggest that the intrusive rocks from both Shaxi–Changpushan area and Luzong volcanic basin require a source like enriched mantle (Yang 1996; Yuan *et al*. 2008).

The late stage of magmatic activity is represented by magma injection accompanied by volcanic explosion and sub-volcano activities of a large amount of basic, intermediate, and intermediate-acid magmas without copper (gold) mineralization.

The tectonic environment of Shaxi–Changpushan complex

On the tectonic discrimination diagram of Batchelor and Bowden (1985), the intrusive rocks in the Shaxi–Changpushan area fall in the fields of syn-collision and post-collision uplift environments (Figure 14). In the Nb-Y and Yb-Ta trace element discrimination diagram (Figure 15a,b), the Shaxi–Changpushan intrusive rocks are located in syn-collision or volcanic arc fields. Considering the early Cretaceous age of the Shaxi–Changpushan complex and the tectonic background of east China in the Yanshanian period (Zhou and Li, 2000; Deng and Wu 2001; Sun *et al.* 2007), the Shaxi–Changpushan intrusive complex is likely to be related to the West Pacific plate subduction under the East China continent.

Where did the collision environment come from? To answer this question, we must first consult the background of east China since the Jurassic. After the completion of subduction of the Yangtze and North China plates, the east part of China jointed together as a single craton. However, this part was soon affected by the subduction of the West Pacific plate

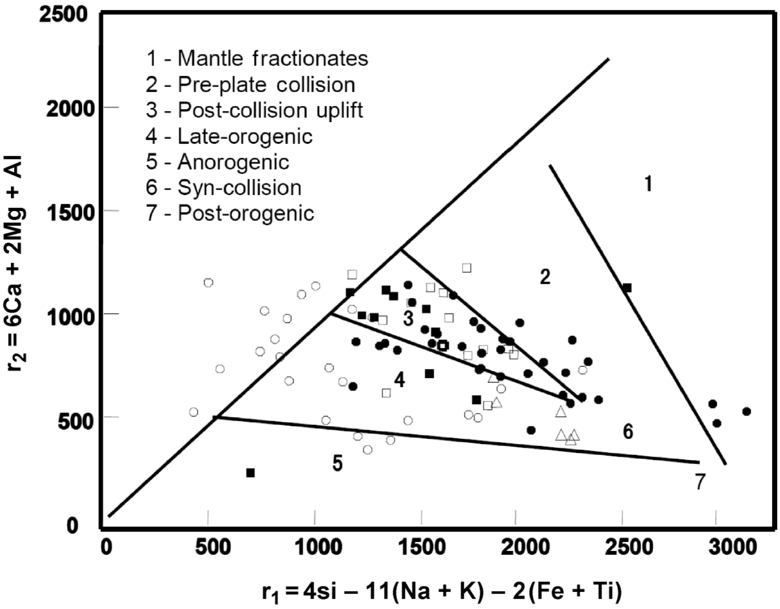

Figure 14. The R_1-R_2 diagram of granitoid samples in the Shaxi-Changpushan porphyry Cu-Au deposit and other Cu deposits in China (after Batchelor and Bowden 1985). Circle filled denotes rocks in Shaxi-Changpushan porphyry copper-gold deposit; circle open denotes intrusive rocks related to the hydrothermal copper mineralization in Luzong volcanic basin; square open denotes intrusive rocks related to skarn copper mineralization in Tongling area; square filled denotes intrusive rocks related to skarn copper mineralization in Anqing area; triangle denotes the other porphyry copper deposits in China (Yulong; Dexing and Duobaoshan porphyry copper deposits).

since the Jurassic (Sun *et al.* 2007), which almost controlled the igneous activities and their metallogenesis in east China, traditionally called the Yanshanian movement by Chinese geologists. By using the discrimination diagrams, we obtained Figure 16a,b, which can be fully used to interpret the forming environment of these Cretaceous intrusives related to Cu-Au deposits along the Yangtze metallogenic belt. Among them, Shaxi intrusive activity with an age range of 126–135 Ma (Yang *et al.* 2007b) is a typical Cretaceous magmatism, with distinguished characteristics of adakitic origin (Drummond and Defant 1990a,b). According to the La/Yb vs. Sm/Yb diagram (Figure 17), the Shaxi–Changpushan intrusive engaged a high-middle extent of melting.

From the above discriminations, we inferred that the Shaxi porphyry copper (gold) deposit has some relation to the collision of the plate tectonics.

Fluid inclusions

Fluid inclusions in gold-bearing quartz veins from the Shaxi deposit are liquid-gas coexisting inclusions. The composition of representative fluid inclusions together with homogenization temperatures are given in Table 6 (see online supplementary material). The relationship between Na^+ and Cl^-/F^-, Na^+/K^+, and $Na^+/(Ca^{2+} + Mg^{2+})$ ratios is shown in Figure 18, from which two trends can be obtained. One is for Na^+ to $Na^+/(Ca^{2+} + Mg^{2+})$ and the other is for Na^+ to Cl^-/F^- and Na^+/K^+. The homogenization temperatures range from 230 to 350°C, similar to most porphyry Cu deposits and some hydrothermal

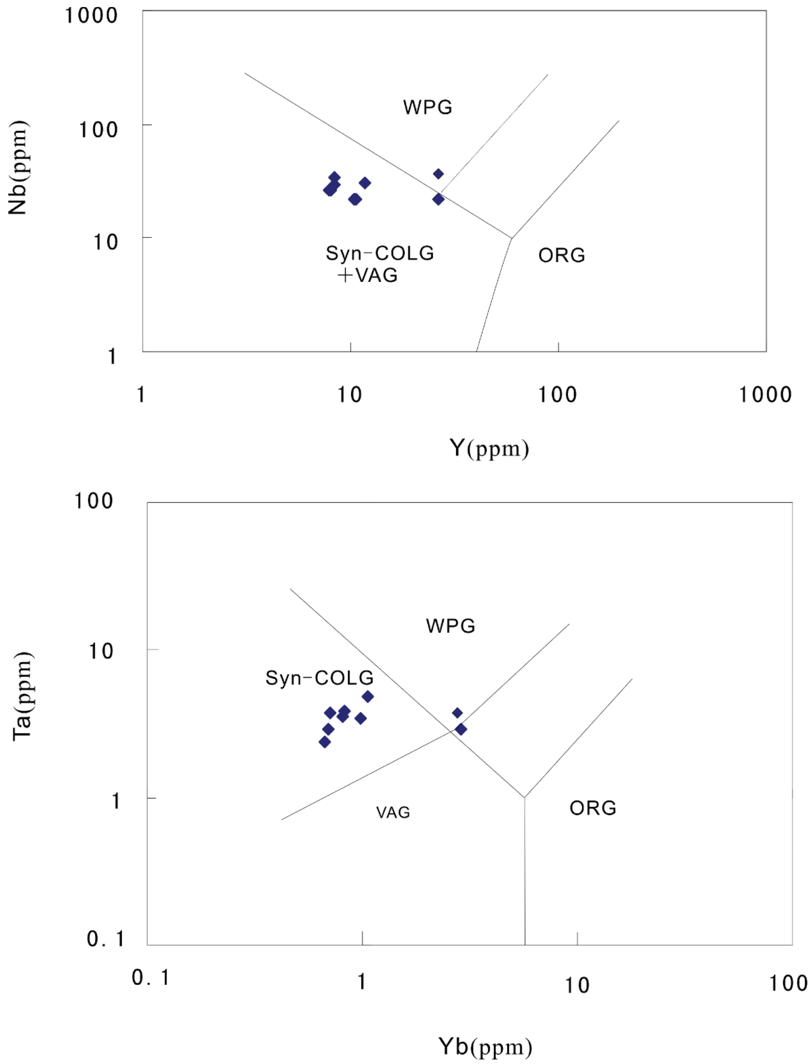

Figure 15. Tectonic environmental discriminations by trace elements of Y vs. Nb and Yb vs. Ta of granitoid samples in the Shaxi–Changpushan porphyry Cu-Au deposit (after Pearce *et al.* 1984). VAG, volcanic arc granite; Syn-COLG, syncollision granite; ORG, middle ridge granite; WPG, within plate granite.

Cu-Au deposits elsewhere (e.g. Lowell and Guilbert 1970; Kamili and Ohmoto 1977; Barton *et al.* 1977; Shelton 1983; Shelton and Lofstro 1988; Choi *et al.* 1997; So *et al.* 1997).

Stable isotopes

Sulphur isotope

Bulk samples were systematically collected from the different ore bodies in the deposit to examine sulphur isotopes. The samples were crushed to <120 meshes in size, which were used for mineral separation. Pure pyrite and chalcopyrite concentrates were obtained by Rantz magnetic separator, standard heavy liquid, and handpicking, which were analysed

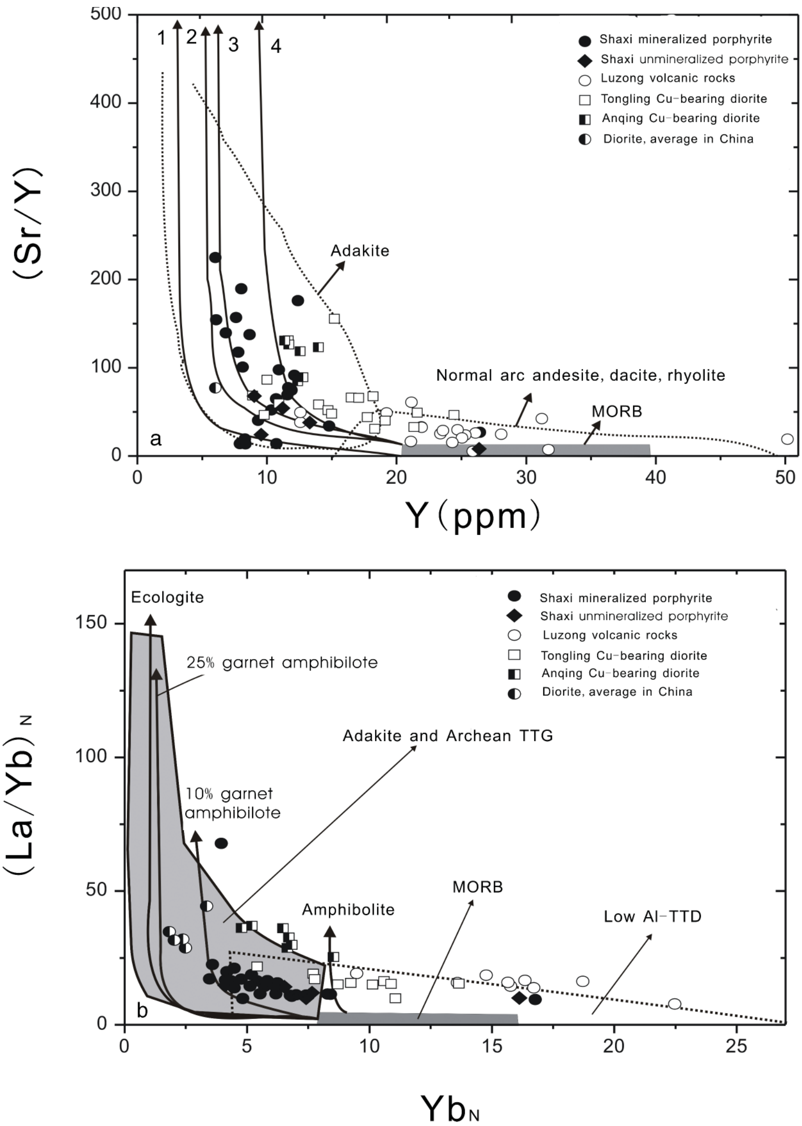

Figure 16. Discrimination diagram for the origin of intrsive rocks in Shaxi–Changpushan and its adjacent region. (a) Y (ppm) versus Sr/Y diagram (Drummond and Defant, 1990b). The curves represent various models of the partial melting of depleted and altered MORB with an amphibolite or eclogite resitite: 1, eclogite (gt/cpx = 50/50); 2, garnet amphibolite (gt/am = 10/90); 3, amphibolite eclogite (am/gt/cpx = 10/40/50); 4, garnet amphibolite (gt/am = 10/90). Starting compositions for curves 1 and 2: Sr = 141 ppm and $Y = 21$ ppm; curves 3 and 4: Sr = 264 ppm. and $Y = 38$ ppm. gt, garnet; cpx, clinopyroxene; am, amphibolite. (b) Chondrite-normalized Yb_N versus $(La/Yb)_N$ diagram modified after Jahn *et al.* (1981), Martin (1986) and Drummond and Defant (1990b). Four partial melting curves are displayed, two of which (amphibolite and 10% garnet amphibolite resitite curves) assume a MORB source and the other two partial melting curves (eclogite and 20% hornblende eclogite curves) assume a MORB source with YbN = 12 and (La/Yb) $N = 1$. Percent partial melt values are listed on each of the model curves.

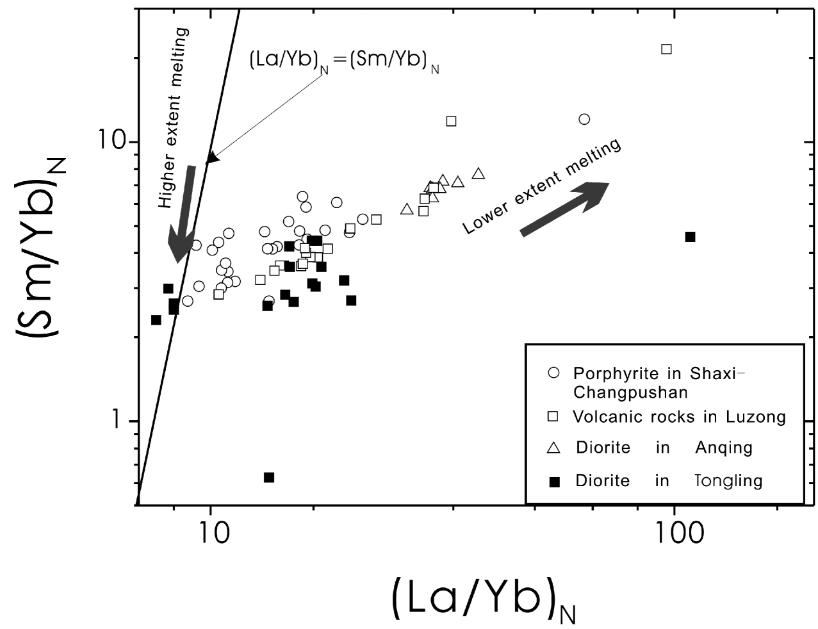

Figure 17. La/Yb v.s. Sm/Yb diagram for intrsive rocks in Shaxi–Changpushan and its adjacent region (Martin 1986).

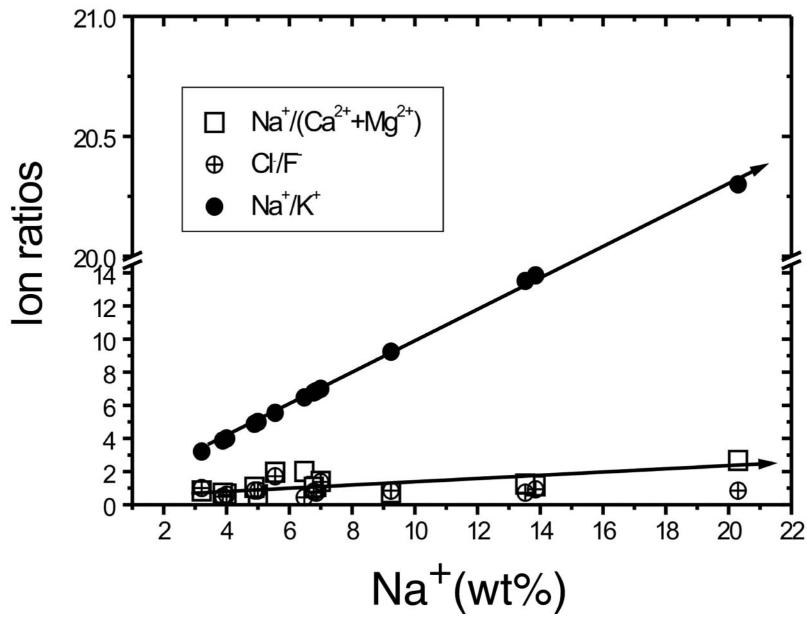

Figure 18. The relation between the Na^+ and ratios of Cl^-/F^-, Na^+/K^+ and $Na^+/(Ca^{2+} + Mg^{2+})$ in fluid inclusions from the Shaxi–Changpushan porphyry Cu-Au deposit.

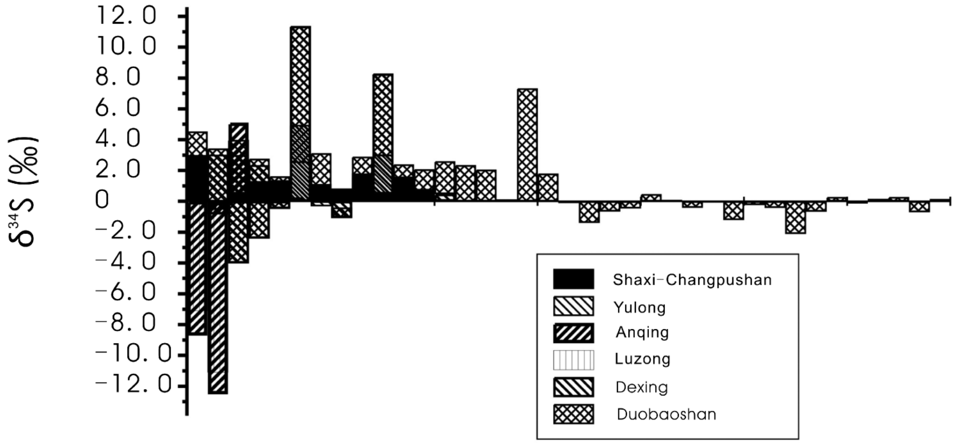

Figure 19. Diagram showing the regional variation of sulphur isotope compositions of sulphides in the Shaxi–Changpushan porphyry Cu-Au deposit and other Cu deposits in China. Shaxi–Changpushan denotes Shaxi–Changpushan porphyry copper (gold) deposit; Luzong denotes hydrothermal copper deposits in Luzong volcanic basin; Anqing denotes skarn copper deposits in Anqing; Dexing denotes Dexing porphyry copper deposit in north Jiangxi Province; Yulong denotes Yulong porphyry copper deposits in east Tibet; Duobaoshan denotes Duobaoshan porphyry copper deposit in northeast China.

for sulphur isotopes in the Institute of Coal Science, Xi'an, China. The analytical accuracy is about 0.5‰. All the results are expressed as δ^{34}S values relative to the Cañon Diablo Troilite sulphur (CDT). Sulphur isotope data in this deposit and those from some typical Cu-deposits in China are summarized in Table 7 (see online supplementary material).

The $\delta^{34}S$ values in the Shaxi–Changpushan porphyry Cu-Au deposit range from –0.01 to 0.30‰, which can be calculated for the total $\delta^{34}S$ values of 0.11‰ based on sulphide assemblages using the method of Pickney (1972). The narrow variation in $\delta^{34}S$ values is similar to those of large to super-large porphyry copper deposits, such as Dexing, Yulong, and Duobaoshan in China (Rui *et al.* 1984), suggesting similar sulphur sources for these deposits. However, the sulphur isotope compositions in the copper deposits in the Luzong volcanic basin, Anqing, and Tongling areas adjacent to the Shaxi–Changpushan district are remarkably different, which is also reflected by their different styles of mineralization mentioned above. Figure 19 presents the diagram of sulphur isotopic results for regional variations of both pyrite and chalcopyrite in the Shaxi–Changpushan porphyry copper (gold) deposit and other copper deposits in China. It is noted that the sulphur isotopic values of chalcopyrite are relatively narrow compared to pyrite.

Oxygen and hydrogen isotopes

Oxygen and hydrogen isotopic data in this deposit and those from some typical Cu-deposits in China are summarized in Table 8 (see online supplementary material), showing that δD and $\delta^{18}O$ values of ore fluids range from –71.7 to –82.4‰ and from 4.0 to 4.6‰, respectively, whereas the $\delta^{18}O$ value of post-mineralization fluid is –4.38‰. The $\delta^{18}O$ values of whole rocks range from 8.3 to 11.6‰, appearing to decrease with increasing depth of alteration and mineralization. Figure 20 is the histogram showing the variation of $\delta^{18}O$ values in different minerals of the Shaxi–Changpushan, Dexing, and Yulong porphyry

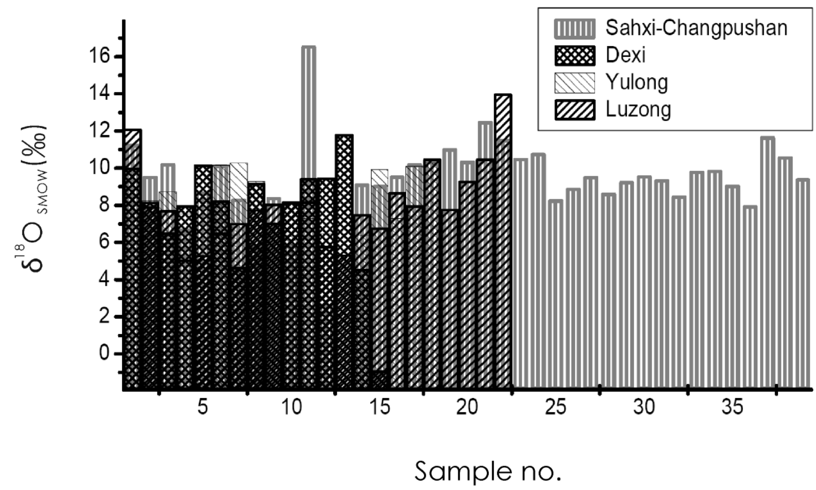

Figure 20. Histogram showing the regional variation of oxygen isotope compositions in the Shaxi–Changpushan porphyry Cu-Au deposit and other copper deposits in China.

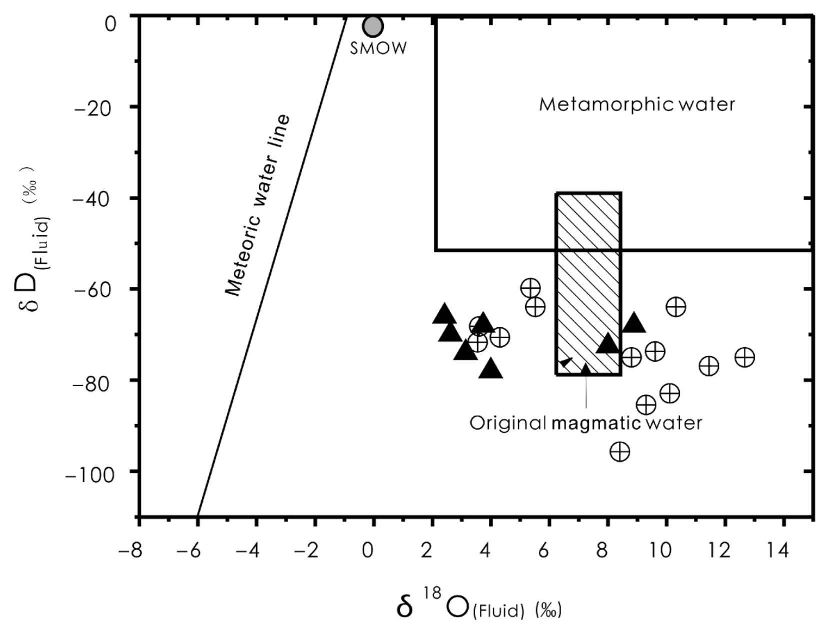

Figure 21. Hydrogen versus oxygen isotope diagram for ore fluids of the Shaxi–Changpushan porphyry Cu-Au deposit, central Anhui.

copper deposits, and the other three copper-mineralized areas adjacent to the Shaxi–Changpushan district.

Hydrogen and oxygen isotopic data show that ore-forming fluids are composed mainly of magmatic water with minor meteoric water (Figure 21), while post-mineralization fluids are dominated by meteoric water. Thus the ore-forming fluids and materials were mainly derived from magmatic sources, and meteoric water may have played little role in the formation of ore. This is consistent with the result of sulphur isotopes.

Geochemical exploration and ore-forming model

Geochemical exploration

The characteristics of mineralization for different elements in the ore deposit are summarized in Table 9 (see online supplementary material). It can be seen that Mo, Pb, Zn and Co, Au, and Ag anomalies are evidently associated with Cu mineralization; F and Cl are also enriched. Potassium, Rb, Si, Na, and Sr are enriched in the magmatic stage, whereas Ti and Mn are enriched in both magmatic and hydrothermal stages.

Figure 22 shows these chemical variations of the alteration zones, illustrating that the ore bodies are surrounded by anomalous Cu and Co halos. However, Mo and Ag anomalies do not show any relationship to the ore bodies. Zinc and Pb anomalies are evident on the surface of the ore bodies, which may be related to the oxidation of ore bodies.

The element contents in the Cu-Au bearing ores in the Shaxi–Changpushan porphyry Cu-Au deposit are listed in Table 10 (see online supplementary material), the correlation between Au and As, Cu, and S is shown in Figure 23, and two linear trends are evident between Au, Cu, and As, suggesting that they are closely related in ore fluids, consistent with the relationship shown in pyrite and chalcopyrite (see Figure 6).

Table 11 (see online supplementary material) lists results of some major and trace elements from exploration drilling samples from different alteration and mineralization zones. The results are plotted in Figures 24 and 25, showing chemical variations in different alteration zones.

From Figure 24, it can be seen that SiO_2 and Al_2O_3 are enriched in the quartz-sericitization zone and depleted in both potassic alteration and propylitization zones; Fe_2O_3, MgO, and CaO are enriched in both potassic alteration and propylitization zones and depleted in the quartz-sericitization zone. K_2O is elevated in the potassic alteration zone and depleted in the other alteration zones; H_2O is enriched in the propylitization zone. The other major elements do not show significant variation in the different alteration zones.

From Figure 25, it can be seen that Cu, Mo, Ag, Zn, Ba, and Rb are highly enriched in the potassic alteration zone, but relatively depleted in the other alteration zones. Co, Sr, and Ni are depleted in the potassic alteration zone and relatively enriched in the other alteration zones. Cl, S, F, and I show relatively constant contents in the different alteration zones except in Silurian and Jurassic sedimentary rocks.

Ore-forming model for the Shaxi-Changpushan prospecting region

The drilling data reveal that most of the ore bodies have an overturned U-shape, and the porphyry dioritoids are also emplaced in the core of a composite anticline in this region (Figure 26), suggesting that the fold may have controlled the emplacement of the intrusions and associated ore formation. The Upper to Lower Silurian clastic rocks, in particular mudstone and siltstone, may serve as the shielding of the ore bodies and the intrusive rocks, and the distribution of the ore bodies and porphyry doiritoids near the core of the anticline now exposed on surface may result from the denudation of the sediments. This structural analysis suggests that the Changpushan district adjacent to the south of Shaxi porphyry Cu (Au) deposit may have high potential for mineralization, where the Silurian sediments are also exposed and Cu-bearing gossans were discovered during our field work (Figure 27). Three grab samples contain 560 to 1450 ppm Cu (Table 12, see online supplementary material); they also contain relatively high Pb, Zn, Co, S, F, and Cl (Figure 28). Moreover, mineralization occurs in the core of the Shaxi–Changpushan anticline, which provides a favourable setting for the formation of ore deposit.

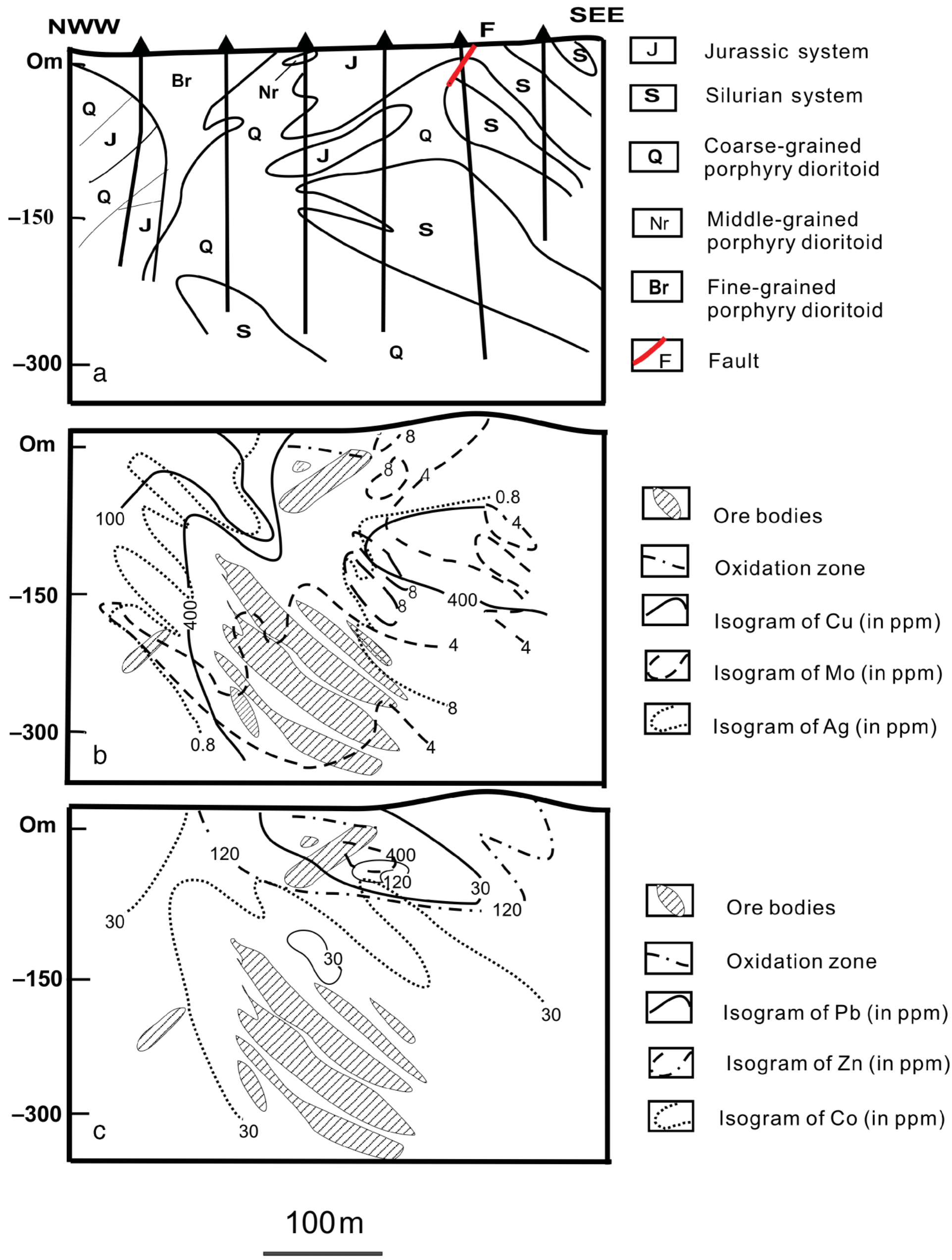

Figure 22. Distributions of rock facies and element zoning in No. 9 explored line in the Shaxi–Changpushan Cu-Au deposit, central Anhui (after No. 327 Geological Team 1982). (a) The distributions of the rock facies by drilling exploration in No. 9 explored line in Shaxi porphyry Cu-Au deposit; (1) Jurassic system; (2) Silurian system; (3) coarse grained porphyry dioritoid; (4) middle grained porphyry dioritoid; (5) hypabyssal porphyry dioritoid; (6) fault; (7) the top boundary line of intrusive facies distinguished by grain size. (b) Element zoning in No. 9 explored line; (1) ore bodies; (2) the oxidation zone; (3) isogram of Cu (in ppm); (4) isogram of Mo (in ppm); (5) isogram of Ag (in ppm). (c) Element zoning in No. 9 explored line; (1) ore bodies; (2) the oxidation zone; (3) isogram of Pb (in ppm); (4) isogram of Zn (in ppm); (5) isogram of Co (in ppm).

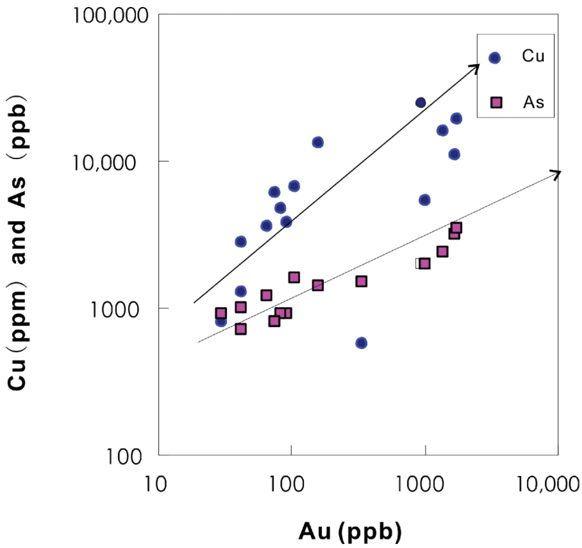

Figure 23. Relationship between Au, Cu, and As in the mineralized samples in the Shaxi–Changpushan porphyry Cu-Au deposit, central Anhui.

The movement of Tan–Lu fault in the Triassic resulted in relatively strong deformation of the Cu-Au-mineralized quartz porphyries and their wall rocks consisting of Silurian and Jurassic clastic sediments (Yang 1996). Barren intrusive rocks exposed in the two limbs of the anticline may be transitional facies of the central intrusion, which are mainly volcanic and subvolcanic rocks (Figure 2).

From the above facts, a model for controlling ore bodies in the core of the anticline, where the hydrothermal fluids and mineralization are concentrated, is illustrated as Figure 29. In the limbs of the anticline, little fluid could be concentrated so that no ore bodies were formed (Yang 1996). The Tan–Lu fault belt had been a larger scale of left translation in the Indo-Sinian period, which caused a series of secondary faults and plumose fractures with NNE direction in the sedimentary rocks. This tectonic process formed the anticline structure in the Shaxi–Changpushan region (Xu *et al*. 1987; Yang 1996; Yang *et al*. 1998a,b). The secondary faults and fractures in the sedimentary rocks provide channels for ore fluids that generate mineralization in the core of the anticline and form economic ore bodies.

Discussion

Structural analysis suggests that the Tan–Lu fault belt had played a key role in transporting ore fluids. This deep fault, reaching the mantle, and derivative fault and fracture systems cut sedimentary rocks in the ore district, providing an ideal channel for ore fluids derived from the intrusions. This setting is also present in other large to super-large porphyry copper deposits in China. For example, the Dexing super-large porphyry copper deposit in the middle part of the Yangtze valley is situated in the tip of the waved arc structure, and the Tongchang porphyry copper deposit (also in the middle part of the Yangtze valley) is located in the core of the local anticline (Zhou 1983; Rui *et al.* 1984). Chang *et al*. (1991) and Zhai *et al.* (1996) pointed out that the Eastern Yangtze Craton in central to eastern China is an important Fe-Cu metallogenic province, and metallogenic belts were controlled by faults and aulacogens in the continental plate in the early Yanshan epoch

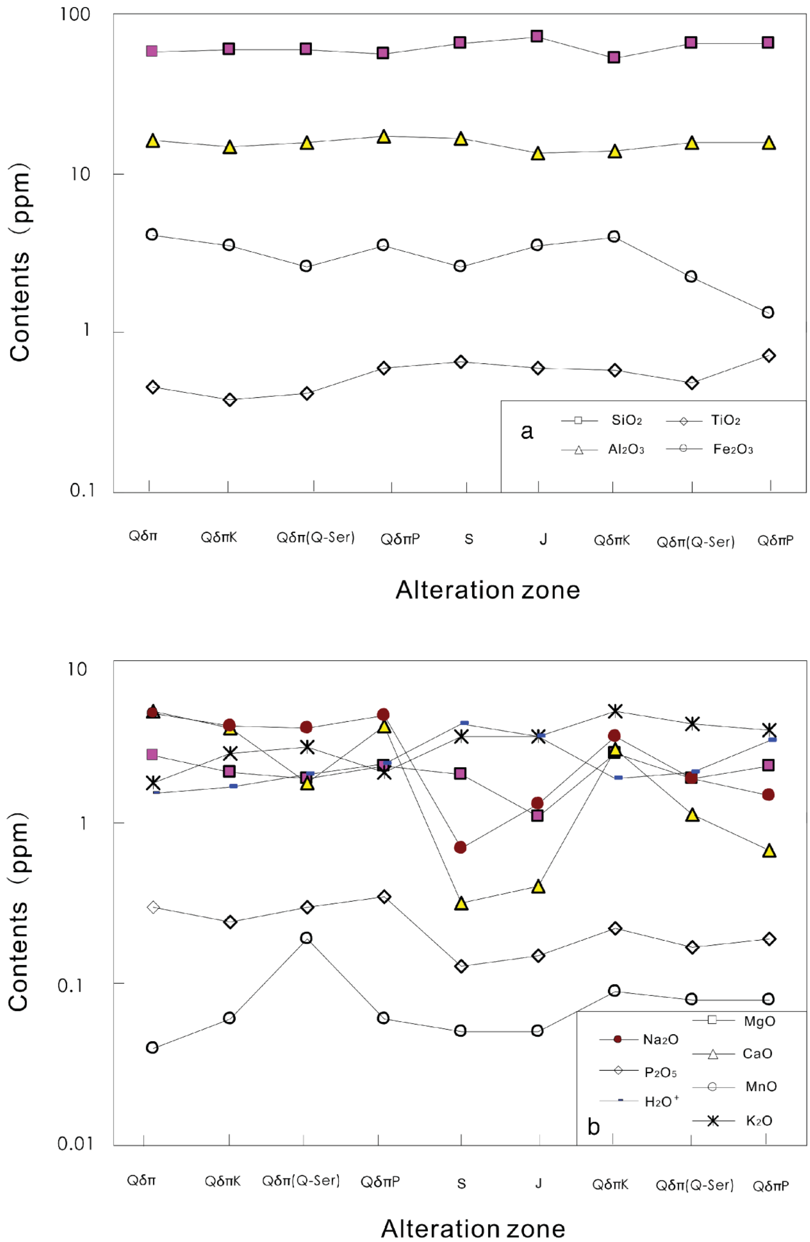

Figure 24. Major element migrations during alteration processing in the Shaxi–Changpushan porphyry Cu-Au deposit, central Anhui (from left to right of the X axial of the diagram, representing the decreasing depth of samples from ore bodies and wall rocks). Q$\delta\pi$, quartz porphyrite; Q$\delta\pi$K, quartz porphyrite in potassic alteration zone; Q$\delta\pi$(Q-Ser), quartz porphyrite in quartz-sericitization zone; Q$\delta\pi$P, quartz porphyrite in propylitization zone; S, Silurian sedimentary rocks with copper mineralization; J, Jurassic sedimentary rocks with copper mineralization.

(Jurassic); the dominant west-northwest and east-west lithospheric faults control the distributions of Cu (Mo and Au) mineralization.

Geochemical mapping in the China continent (Xie *et al*. 1997) shows that Cu and Au in the Shaxi and Tongling areas are high, favourable for the formation of Cu and Au deposits. Metals

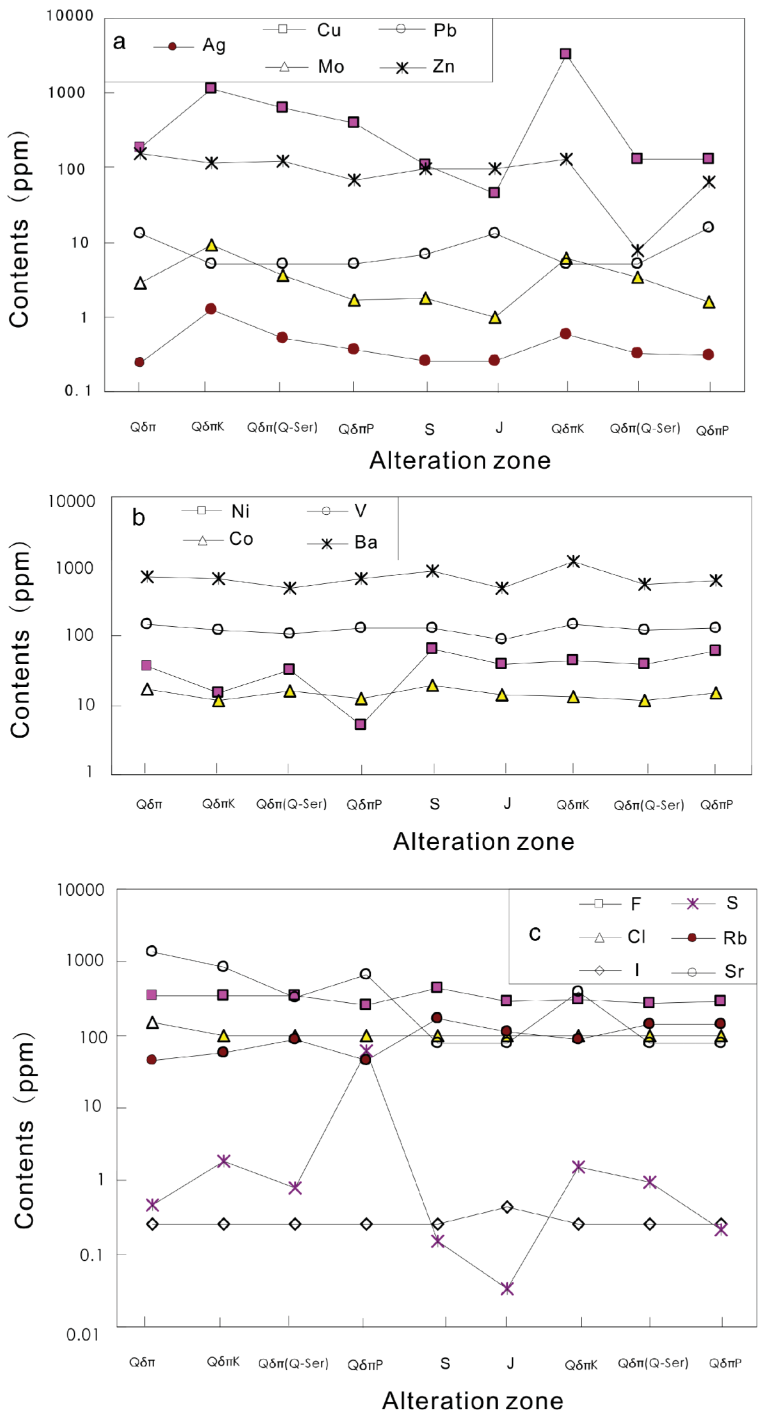

Figure 25. Trace element migrations during alteration processing in the Shaxi–Changpushan porphyry Cu-Au deposit, central Anhui (From left to right of the X axial of the diagram, representing the decreasing depth of samples from ore bodies and wall rocks; all the legends are the same as those in Figure 24).

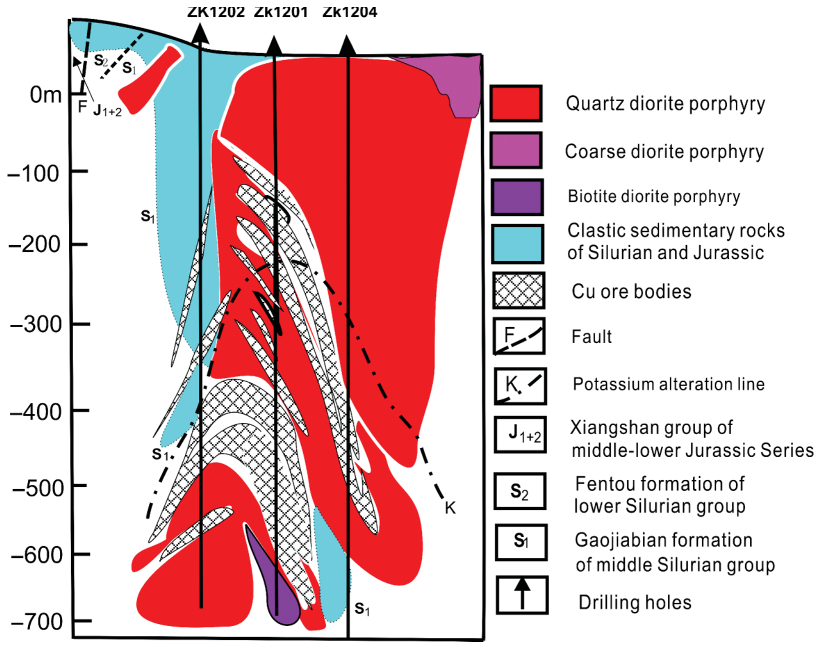

Figure 26. Geological profile of the No. 12 exploration line in the Shaxi–Changpushan porphyry Cu-Au deposit, central Anhui (after No. 327 Geological Team 1982).

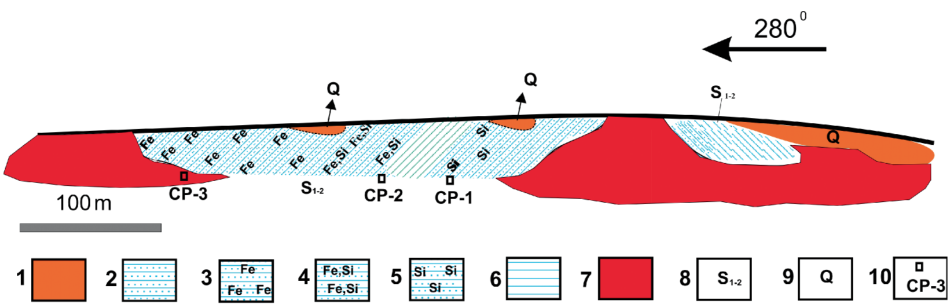

Figure 27. Geological profile and sample localities in the Changpushan area, central Anhui.

may be derived from the low crust and/or upper mantle, which had undergone extensive fractionation in trace and rare earth elements in particular, which may be important for porphyry copper mineralization. It is likely to form the mineralization of large and super-large porphyry copper deposits in China (Zhou 1983; Wang and Qin 1991). The S, H, and O isotopic data suggest that ore-forming fluids and materials were mainly derived from magmatic sources. Chen and Tang (1993) proposed that tectonic setting and palaeo-sedimentary environment are two main factors for forming large and super-large copper deposits in China. The Yanshanian-Himalayan episodes are the dominant times for development of porphyry copper deposits in China, such that Yulong, Dexing, Jinduigcheng, Deheishan, and Nanihu deposits all occur in this period, where all the large and super-large deposits occur in the earlier stage of geosynclinal regions. The ore-bearing intrusions generally occur as stocks striking obliquely to the strike of the surrounding strata, which display many similarities to those in the Shaxi–Changpushan district (Chang *et al.* 1991).

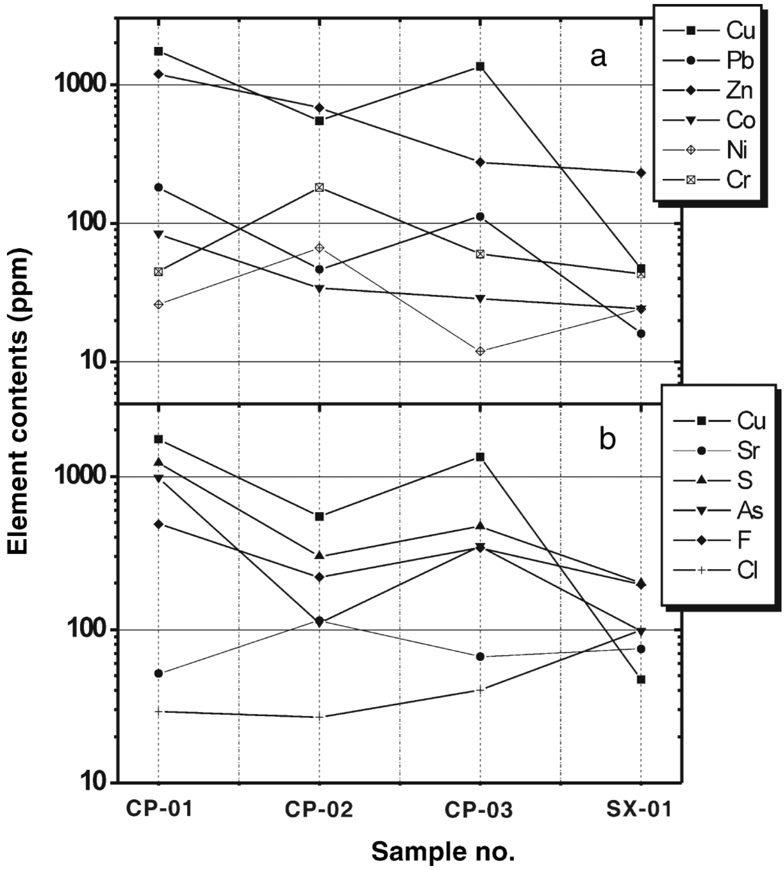

Figure 28. Diagrams showing the relationships between Cu and other elements from samples in Figure 27. (a) The relation between Cu and Pb, Zn Co, Ni, and Cr. (b) The relation between Cu and S, As, F, Cl, and Sr.

After the Indo–Sinian period (Mesozoic–Cenozoic), the great majority of crust in China was in the stage of platform activation-depression (Chen 1982). The thickness of the continental crust increased notably; the activities of fractures were strong. A large number of intermediate-acid rock intrusive bodies and down-faulted basins were formed, and the mainly humid, hot palaeoclimate (Palaeozoic) changed to the mainly dry hot one, that is, indicative of large-scaled red beds in this period. This geological setting was well developed in the Shaxi–Changpushan district with Cu-Au mineralization, which is fertile in the formation of large to super-large porphyry copper deposits (Guo *et al.* 1978; Rui *et al.* 1984; Chen 1984; Chen and Tang 1993).

According to the mapping standard of Cu and Au anomalies in the Yangtze metallogenic belt (Xie *et al.* 1997), several grades of anomalies have been proposed, such as for Cu anomalies, there are six grades with 12.0, 18.0, 25.0, 40.0 and 50.0 ppm, respectively; and for Au anomalies, there are two grades with 3–60 ppb and more than 6 ppb, respectively. Compared to our study, the Cu content is largely variable in the Shaxi porphyry copper deposit, varying from 14.2 up to 9569.0 ppm. In Luzong region nearby, Cu content is variable from 5.1 to 353.6 ppm; in Anqing area, Cu content ranges from 55.1 to 148.0 ppm; in the Tongling area, Cu content is varied from 0 to 182.5 ppm. Au content in

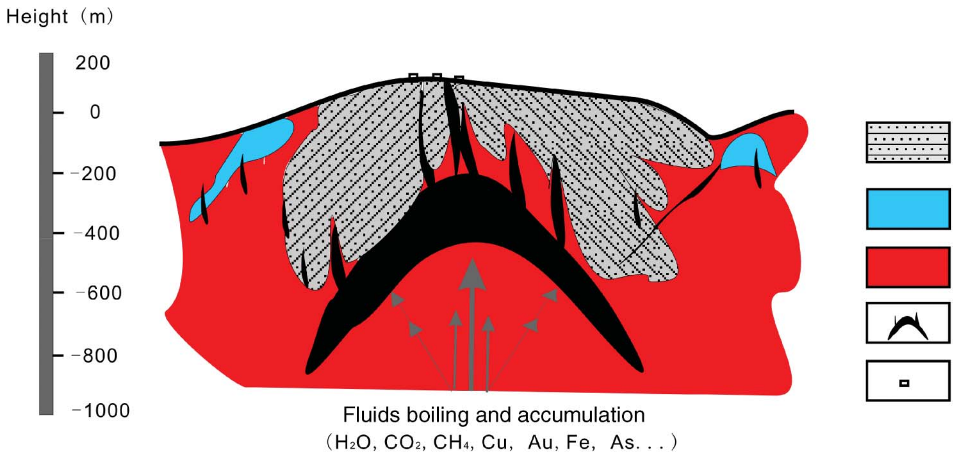

Figure 29. Tectonic and geochemical model for controlling the porphyry copper ore bodies in Shaxi–Changpushan region, central Anhui.

the Shaxi and Tongling area range from 3.2 to 93.8 ppb, and 0.7 to 36.1 ppb, respectively (Table 3, see online supplementary material).

In summary, the formation of Shaxi–Changpushan porphyry copper (gold) deposit is mainly controlled by the abundances of ore-forming elements coming from the lower crust or the upper mantle by a large extent of fractionation, the other important factor is the special evolution of the crust in this region, where there is great potential to form a large porphyry copper deposit.

Tectonic envrionmental discriminations

In recent years, petrologists favoured adakite to trace the Cu-Au mineralization in east China and presented a number of petrochemical proofs (e.g. Zhang *et al.* 2001; Xu *et al.* 2002; Chung *et al.* 2003; Wang *et al.* 2006).

What is adakite or adakitic rock? According to the definition proposed by scholars (e.g. Drummond and Defant 1990a; Martin 1999), adakites are intermediate to felsic igneous rocks, andesitic to rhyolitic in composition (basaltic members are lacking), which should have trondhjemitic affinities (high-Na_2O contents and K_2O/Na_2O of 0.5) and their Mg no. (0.51), high contents of Ni (20–40 ppm) and Cr (30–50 ppm) contents are higher than in typical calc-alkaline magmas (Martin 1987; Drummond and Defant 1990b). Sr contents in adakite are usually high (>300 ppm, until 2000 ppm) and REE show strongly fractionated patterns with very low HREE contents (Yb $\leq$ 1.8 ppm, Y $\leq$ 18 ppm). These adakatic rocks are depleted in Nb and Ta compared with other igneous rock. The origin of adakites was due to the remelting of young subducted oceanic crust.

However, in a large sense, the tectonic formation of adakites are still disputed at present, the points of views are (1) the melting of young oceanic crust during the subduction; (2) delamination or foundering of dense mafic lower crust rocks (e.g. eclogite and garnet pyroxenite) in mafic lower crust to the mantle during continental orogenesis. Consequently, the Fe-Cu-Mo mineralization is closed related to the formation of adakites.

Figure 4 presents a clue that intrusive rocks in Shaxi porphyry copper (gold) deposit have some relation to the collision of the plate tectonics. But where did the collision environment come from? To answer this question, we must first consult the background of east

China since the Jurassic. After the completion of subduction of the Yangtze and North China plates, the east part of China jointed together as a single craton. Thereafter, this jointed craton was soon affected by subduction of the West Pacific Plate since the Jurassic. By using discrimination diagrams of adakite, we obtained Figures 6 and 7, which can be reasonably used to interpret the forming environment of these Cretaceous intrusives related to Cu-Au deposits along Yangtze metallogenic belt, among them, Shaxi intrusive activities with ages ranging from 126 to 135 Ma are typical Cretaceous magmatism (Yang *et al.* 2007b), with distinguished characteristics of adakitic rocks (Lan *et al.* 2009). Recently, Chinese scholars have identified typical high-Mg adakites (131 ± 3 Ma) with lower radiogenic lead in the Dabie UHP orogenic belt north adjacent to the Shaxi–Changpushan region (Huang *et al.* 2008), which is of significance to understand the adakitic formation and regional crust evolution.

From the above discussion, the adakitic origin is reasonable for an explanation of the formation of Cu-Au related intrusives in Shaxi–Changpushan area, where there is a great possibility to form a large–super-large Cu-Au deposit.

Conclusions

Fluid inclusions in Shaxi–Changpushan quartz veins associated with Cu (Au) mineralization consist dominantly of liquid and gas phases, although some inclusions are composed only of a liquid phase. Ore-forming temperatures were between 230 and 350°C. Sulphur isotope studies show that $\delta^{34}S$ values of chalcopyrite are somewhat more homogenous than those of pyrite; the ore-forming fluids and materials were mainly derived from magmatic sources, but meteoric water played a minor role consistent with the results of oxygen and hydrogen isotope study. Gold occurs as micro-inclusions heterogeneously distributed in chalcopyrite and pyrite. Formation of the Shaxi–Changpushan porphyry copper (gold) deposit was mainly controlled by the abundance of ore-forming elements derived from the lower crust or the upper mantle by a high degree of crystal-melt fractionation. The other important factor is the special evolution of the crust in this region (the medium–fine-grained altered diorite complex, good sedimentary bedding, and deep-cutting fault system), provided great potential to form a large porphyry copper deposit. The existence of widespread porphyry Cu-Au mineralization in the Changpushan district adjacent to the Shaxi deposit is significant for this orogenic belt. The metallogenic and tectonic background was controlled by slip along the Tan-Lu fault system, with the Jurassic sedimentary rocks as well as the igneous rocks associated with the Cu (Au) mineralization.

Whatever the ultimate origin, the presence of a giant porphyry Cu-Au deposit in the Shaxi–Changpushan district appears to be highly likely.

Acknowledgements

This study is supported by the Knowledge Innovation Project of the Chinese Academy of Sciences (grant no. KZCX1-YW-15-3), the National Natural Science Foundation of China (no. 90814008), and the Opening Foundation of State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, CAS (no. 2008011). We wish to thank Prof. Chang Yinfo for his kind guidance and Prof. D. Ritz for constructive comments on an early version of the manuscript.

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