1 Introduction

The middle-lower part of the Yangtze Valley is one of the most important areas for Jurassic-Cretaceous poly-Cu-Fe-Au deposits in China (Chang et al., 1991; Zhai et al., 1996; Pan and Dong, 1999). Although porphyry Cu-(Mo-Au) deposits are the world’s primary source of these metals, porphyry Cu deposits in this poly-metallogenic belt are a major source of Cu. The Shaxi porphyry Cu-Au deposit is one of the important discoveries during the 1970s. It is located in the northwestern Luzong volcanic basin, the central part of Anhui Province, east-central China, where the Tan-Lu (Tancheng-Lujiang) fault passes through the ore district. According to Chang et al. (1991) and Zhai et al. (1996), the eastern part of the Yangtze Craton in eastern China is an important Fe-Cu metallogenic province, whose metallogeny was controlled by faults and aulacogens in the continental plate during the Jurassic. The dominant WNW and E-W trending deep fault system controlled the distributions of Cu mineralization. A series of igneous rocks in this region can be grouped into two associations according to their relationship to the metal genesis. The first one is a Fe-related group, whereas the second one is a Cu-related group.

This paper is focused on the second group in order to understand the relationship between its petrogenesis and Cu mineralization, particularly age determination of porphyry in association with the Shaxi Cu-Au deposit. Previous geochronological studies of igneous rocks in the Lower Yangtze Valley, including K-Ar and Rb-Sr ages and thus provide better constraints on the time of porphyry formation and associated Cu-Au mineralization along the middle to lower part of the Yangtze metallogenic belt. The ages of 126 to 135 Ma are interpreted to represent the intrusive time of the Shaxi porphyry, so that the Cu-Au mineralization should have occurred later due to the post-magmatic hydrothermal event.

2 Geological Setting

The Shaxi porphyry intrusive is a small intrusion with an outcrop area of approximately 1 km², but it is heavily copper mineralized and accompanied by Au mineralization (Yang, 1996; Yang et al., 2001b, 2002,
The studied region is located on the northern margin of the Yangtze Craton (Ren, 1980), but still south of the Dabie ultrahigh-pressure (UHP) metamorphic belt (Zhao et al., 2004a). The Dabie orogen was formed by Triassic subduction of the South China Block beneath the North China Block to result in continental collision (e.g., Zheng et al., 2003, 2005). The Dabie UHP metamorphic complex is truncated at its eastern end by the Tanlu fault, which offsets it by approximately 500 km northward to the Shandong Peninsular where it occurs as the Sulu orogen. Many studies have contributed to understanding of the geodynamics of the continental subduction and subsequent exhumation from various aspects of field geology, structural geology, mineralogy, petrology, geochemistry, geophysics, petrophysics and tectonics in the Dabie-Sulu orogenic belt (Zheng et al., 2004b, 2005; Xie et al., 2006). Available results from element and isotope analyses indicate that the Early Cretaceous granitoids in the Dabie orogen have the geochemical characteristics similar to the subducted continent in many aspects. Therefore, they are petrogenetically considered as being generated by partial melting of the South China Block due to extension collapse of the collision-thickened orogen (Zhao et al., 2004b, 2005).

The whole district is affected by two multiple faults: the Tan-Lu fault which passes through the whole district, and the Fanshan-Tongling fault, which is also a regional deep
fault belt controlling the distribution and mechanism of the porphyry intrusive (Dong, 1984; Chang et al., 1991). The Tan-Lu fault belt, as a major wench fault cut to the northwest of the Pacific Ocean, cuts the eastern continental crust of northeastern Asia and crosses more than several thousands kilometers in eastern China (Xu et al., 1987). Its northern part enters the Kurtuvin fault belt in the far east of Russia (Salon, 1977). Xu et al. (1987) presented the fact that this fault system would be traced for more than 3600 km, extending intermittently to South China, with a strike from NE to NNE, assuming an “S-shaped or snake-shaped” curve. This fault is 10–50 km in width and shows a fractural down-warping zone with highly plastic deformed ductile shear zones at levels of the middle to lower crust, and there are a series of ductile shear zones also with NE or NNE trends which were developed in the slide formation of the major fault belt within or near the studied region (Wang et al., 1983; Yang, 1992; Zhang, 1992; Yang et al., 1998a, b; 2001a).

### 3 Petrography and Geochemistry

#### 3.1 Petrography

Igneous rocks are widely distributed in the studied region with the characteristics of multiple magmatic activities. The period of the magmatic activity is clear from the field observation, where volcanic rocks in the deposit are overlying sandstones of the Xiangshan Group (middle-upper Jurassic) and have an intrusive contact with the lower Cretaceous red beds. Therefore, the volcanic activity was limited to the late Jurassic to early Cretaceous. The intrusive rocks in the Shaxi porphyry Cu-Au deposit are stocks, tongues, apophyses, ethmoliths and dikes, and include deep-shallow-ultra-shallow intrusive bodies. According to drilling and geophysical exploration (The No. 327 Geological Party, 1982; Yang et al., 2001b), all of the intrusive bodies have the same basement, and the ore bodies are resident in the upper part of the intrusive at 0–800 m depth. There are two active stages of igneous activity in this region. The early stage is an intrusive one, with different extents of Cu-Au mineralization, hosted mainly by quartz diorite porphyry and biotite quartz diorite porphyry with lesser amounts of amphibole diorite porphyry and breccia diorite porphyry. The late stage of magmatic activity is an injection accompanying with a large amount of basic magma with volcanic explosion and sub-volcano activity without any Cu-Au mineralization.

There are several kinds of intrusive rocks with porphyry copper mineralization in the Shaxi porphyry Cu-Au deposit. These are quartz diorite porphyry, biotite-quartz diorite porphyry and fine- to medium-grained porphyry diorite, which have a subhedral seriate texture.

#### 3.2 Geochemistry

Late Mesozoic igneous rocks associated with Cu-Au mineralization crop out widely in the Lower Yangtze region. They intruded into either the Neoproterozoic low-grade metamorphic rocks or the Paleozoic to Triassic sedimentary strata.

##### 3.2.1 Major elements

Several rock associations were recognized in this region. The Luzong meso-volcanic rocks and some in the Tongling region with skarn Cu-Au mineralization fall into the shoshonite field in the $K_2O$ vs. $SiO_2$ plot (Fig. 3). The K-enriched rock association contains shoshonite series and ultrapotassic rocks classified by high Na$_2$O+K$_2$O of 8.1% to 12.0%, high K$_2$O content of 4.1% to 8.5%, and with K$_2$O/Na$_2$O ratios of about 0.8 to 1.4 (Bureau of Geology and Mineral Resources of Anhui Province, 1987; Wang and Yang, 1996; Yang, 1996; Xing and Xu, 1999; Yang and Lee, 2005). They are basaltic trachyandesite, trachyanidesite and syenite in composition. However, the rocks in the Shaxi porphyry Cu-Au deposit are of calc-alkaline series, and the rocks in the Anqing and Tongling areas are of high-potassic cal-calc-alkaline series. According to Chen et al. (2001), there exists a kind of rock series with Na-rich alkaline mafic association in this region showing low SiO$_2$ of 46–56% and high alkali content with Na$_2$O/K$_2$O ranging from 5.0–7.1% and Na$_2$O/K$_2$O ratios of 1.4 to 4.3 (Xing and Xu, 1999). The associations of high potassic calc-alkaline series or calc-alkaline series occurring in the area north of the Yangtze River consisting of monzonite and granite stocks, diorite, quartz diorite and granodiorite stocks are distributed along the Yangtze River. These rocks are closely associated with the mineralization of copper, iron, sulfur and gold ore deposits.

Figure 2 shows the petrologic characteristics from observations of the intrusives from the Shaxi Cu-Au-bearing igneous intrusive in the lower part of the Yangtze metallogenic belt.

They contain phenocrysts of plagioclase and alkalifeldspar with sizes of 8–3 mm and 5–1.5 mm, respectively. Some feldspars are severely altered to sericite, chlorite and kaolinite in the alteration zones (Fig. 2a, b). The diorites in this region contain amphibole, quartz, microcline, biotite, muscovite, apatite, sphene, pyrite, magnetite and rare rutile. The microcline occurs as subhedral crystals with cross-hatch twinning of microperthitic and contains plagioclase. The biotite is all subhedral (Fig. 2c); however, the amount of biotite is more than that of muscovite in the diorite porphyry samples. All the opaque minerals are distributed among the main rock-forming minerals. The plagioclase in the diorite porphyry usually occurs as subhedral polysynthetically twinned crystals (Fig. 2d).
making the area an important metal production base in China. Intrusions distributed in the region south of the Yangtze River include granites and granodiorites, occurring as batholiths and stocks. They are S-type granites in terms of chemical composition and mineralogy (Chang et al., 1991).

3.2.2 REE

The total (REE+Y) contents range from 256 ppm to 79 ppm (with an average value of 115.93 ppm) in the intrusive rocks in the Shaxi area (Yang, 1996). Almost all of the samples have the characteristics of enrichment in LREE and depletion in HREE without Eu anomaly compared to those of REE data from the other regions adjacent to Shaxi, such as the Anqing, Tongling, Luzong and Chuxian areas (see Fig. 4). The REE patterns in the intrusive rocks from the Shaxi area are more similar to those of the lower crust rocks (Taylor et al., 1985).

3.2.3 Trace elements

The spidergram of trace elements in the Shaxi area is shown in Fig. 5, which has the characteristics of mantle compatible elements such as Sc, Cr, Co and Ni and some transitional compatible elements such as Ti, V, Mn, Fe and Cu, with strong fractionation compared to the average contents of trace elements of crust rocks and adjacent dioritoids along the Yangtze metallogenic belt (Thorpe, 1976; Taylor et al., 1985; Bureau of Geology and Mineral Resources of Anhui Province, 1987; Chang et al., 1991; Ren et al., 1991), especially those of Cu with very largely...
The positive anomaly, which may be interpreted as an important cause for Cu mineralization in this region. The lithophile elements such as K, Rb, Th, Sr, Ba, Li and La are also enriched compared to the average contents of the crustal rocks and adjacent dioritoids (Bureau of Geology and Mineral Resources of Anhui Province, 1987; Chang et al., 1991; Ren et al., 1991), which manifests the regional geochemical anomalies of these elements and may be interpreted as an important cause for Cu mineralization in this region. The hydrothermal alteration to some of the Cu-related intrusive rocks is another cause for the increase of these elements.

4 $^{40}$Ar/$^{39}$Ar Dating

4.1 Sample selection and experimental methods

Biotite and plagioclase are commonly used for the $^{40}$Ar/$^{39}$Ar geochronometer. The fresh rocks selected for analysis in this study are porphyrites from the Shaxi intrusive. The rocks were crushed, separated using heavy liquid, and single biotite and plagioclase crystals were picked by hand under the binocular microscope to get pure monominerals mainly avoiding the intergrowths of minerals, fluid inclusions and alteration. Figure 2 (c, d) are the microscopic images of petrologic observation of the two selected porphyrite samples in the Shaxi porphyry Cu-Au deposit, showing the fresh minerals of both biotite and plagioclase suitable for the $^{40}$Ar/$^{39}$Ar geochronometer in this study.

It is well known that obtaining meaningful ages from such spectra is very difficult because of the possibility of alteration of minerals. Although biotite is a common rock-forming mineral suitable for Ar-Ar dating, it is often affected by alteration related to unique geological localities. The capability to obtain reliable ages depends on delicate choice and preparation of the fresh minerals, which will be the extremely important for obtaining the true geological dating. In this work great efforts were made, e.g., high-resolution binocular microscope was hired to check the pure biotite after heavy liquid separation in order to avoid the affects of alteration. In this way the purification of minerals was ensured for the further measurement, which is essential to the $^{40}$Ar/$^{39}$Ar geochronometer.

The preparation and conditions of the biotite and plagioclase samples and standard samples for analysis...
with the fast neutron irradiation incremental heating for Ar extraction is described as follows: the separated monomineral samples were wrapped up in aluminum foil and placed in the central part of the B8 hole site of the 49-2 type reactor for fast irradiation with an irradiation time of 52 h 47 min, intermittent flux of neutrons $6.63 \times 10^{12}$ n/cm$^2$·s and integrated flux of neutrons $1.26 \times 10^{18}$ n/cm$^2$.

The standard samples used to monitor neutron fluxes included Chinese standard ones of ZBJ (hornblende) and ZBH-25 (biotite) with ages of 132.8±1.4 Ma and 132.7±1.2 Ma, respectively, and French B600 (biotite), Australia 77600 (hornblende) and international standard BSP (hornblende) with ages of 322 Ma, 414.5±3.7 Ma and 2060±8 Ma, respectively. The values of irradiation parameters $J$ are 0.012826 (for sample ZK3303-07, biotite and plagioclase) and 0.012831 (for sample ZK3303-01, biotite and plagioclase), respectively.

The measurements were performed on an English RGA-10 Model gas-source mass spectrometer (VSS Company); the sample weights are from 0.14930 g to 0.1022 g. The decay constant $\lambda$ is $5.54 \times 10^{-10}$/a in the static mode. The blanks of the whole system are $40\text{Ar}=1.6 \times 10^{-14}$ mol and $36\text{Ar}=1.2 \times 10^{-16}$ mol and the errors involved in the Ar measurement are within the range of 0.5%–1%.

### 4.2 Results of the $40\text{Ar}/39\text{Ar}$ dating

The gas released from the samples when heated in a tight container was analyzed on the mass spectrometer for Ar isotopes. Both biotite and plagioclase separates from two samples were analyzed and the results are shown in Table 1. Figures 6–9 show the apparent $40\text{Ar}/39\text{Ar}$ age spectra and the isochron ages for the 4 selected samples. The Ar isotope data acquired at 11 heating stages range from 420°C to 1450°C for each sample, though the heating temperature steps were slightly different. The data points involved in plateau age calculation can satisfy such preconditions that the sample was formed under a chemically closed condition. The two biotite samples and two plagioclase samples represent ideal grains for $40\text{Ar}/39\text{Ar}$ dating, giving relatively reproducible ages with a high level of confidence ranging from 126 to 135 Ma according to the result of isochron age and plateau age analysis.

### 5 Discussion

It is desirable to identify apparent ages that are adversely influenced by alteration and to obtain meaningful ages from all rocks regardless of the conditions because many rocks are geologically unique and/or representative of key localities. However, it is difficult to obtain geologically meaningful ages from highly altered biotite using incremental step-heating. Even those biotites which appear pristine in thin sections can yield variable plateau and unexpected apparent ages (e.g., Lo and Onstott, 1989; Ruffet et al., 1991; Onstott et al., 1995; Roberts et al., 2001; Burgess et al., 2004). Biotite and plagioclase are the minerals most commonly dated by $40\text{Ar}/39\text{Ar}$ geochronology. However, secondary alteration of biotite to phases such as chlorite is a common and widespread occurrence in nature and has long been known to lead to a lowering of biotite ages (Mitchell and Taka, 1984; Kelley et al., 1997; Adams and Kelley, 1998; Haines et al., 2004). Although later thermal disturbance can also yield plateau ages, alteration and weathering of grains are often correlated with $40\text{Ar}/39\text{Ar}$ age spectra that are seriously disturbed.

From the results of biotite and plagioclase, it can be
Table 1 Data for $^{40}$Ar/$^{39}$Ar dating from the Shaxi porphyry intrusive, Anhui Province

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<th>Temperature</th>
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<th>$^{36}$Ar/$^{39}$Ar$_{m}$</th>
<th>$^{37}$Ar/$^{39}$Ar$_{m}$</th>
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<th>$^{39}$Ar$K_{m} \times 10^{-12}$ mol</th>
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<th>$t$ (Ma) ± 1 σ</th>
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Sample ZK3303-07, plagioclase, $J = 0.012826$, weight = 149.3 mg

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Sample ZK3301-01, plagioclase, $J = 0.012831$, weight = 138.3 mg

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<th>$t$ (Ma) ± 1 σ</th>
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</table>
judged that these Ar-Ar ages can well represent the timing of the Shaxi porphyry emplacement, which can also be compared to the other ages by Ar-Ar, Rb/Sr and zircon U-Pb dating for many intrusives along the middle-lower Yangtze valley ranging from 140 to 122 Ma (Chen et al., 1985a, b, 1991, 1993, 1994; Zhou et al., 1987, 1988; McKee, 1988; Xu and Xing, 1994; Zhao et al., 2004a; Yang, 2006). The post-collisional magmatism in the Dabie orogen also occurred at 120 to 130 Ma (Chen et al., 1995; Zhao et al., 2004b, 2005; Xie et al., 2006). It is known that there is widespread occurrence of Early Cretaceous mineralizations in eastern China, but, significantly different settings of geotectonics are responsible for the same period of magmatism. Therefore, it remains to be resolved whether the Early Cretaceous magmatism along the middle-lower Yangtze Valley was triggered by mantle superwelling in response to the Pacific Superplume event (Zhao et al., 2004b, 2005) or it is related to subduction of the Pacific plate (Wu et al., 2005).

Recently, Xu et al. (2005) studied the Tongling skarn copper mineralized region and dated the main orebodies of the Dongguashan copper deposit with the Rb-Sr isotopic method, and they obtained the isochron ages of 136.5±1.4 Ma in the Qingshanjiao intrusive and 134±11 Ma of the later mineralized fluid inclusions in quartz vein. Di et al. (2005) studied the crystallization ages of the Xiaotongguanshan quartz monzodiorite and Shatanjiao quartz monzonite porphyry in the Tongling area using the SHRIMP zircon U-Pb method, and found that the crystallization age of the former is 142.8±1.8 Ma, that of the latter is 151.8±2.6 Ma. All the geochronology of the igneous rocks along the middle-lower Yangtze region indicates that these intrusives related to Cu-Au mineralization belong to the Late Jurassic-Early Cretaceous. It is believable that the ages from 126 to 135 Ma can represent the intrusive time in the Shaxi region, and the Cu-Au mineralization should have occurred later by a strong hydrothermal event of magmatism. These ages are also in accordance to the study of the movement of the Tan-Lu fault belt obtained by Ar-Ar dating such as Zhu et al. (2004), whose results of the Ar/Ar ages of mylonite whole-rock and muscovite from the later Tana ductile shear zone suggest another sinistral strike-slip cooling event at 128 Ma. Thus the strike-slip faulting of the Tan-Lu fault belt would induce a large-scale intrusion and doming uplift within its adjacent Shaxi area. Such a case was studied by Wu et al. (2004) in the Tongling region, and they provided a mechanism of emplacement in the deep and found the fact that the left-lateral shear shown by the ductile shear zone and the rheomorphic fold reveals that the pluton emplacement and the deformation of surrounding rock are controlled by a NNE-striking left-lateral shear stress field.
6 Conclusion

The Cu-Au mineralization in the Shaxi porphyry deposit occurs in a complex intrusive composed of quartz diorite porphyry, biotite-quartz diorite porphyry and fine- to medium-grained porphyry diorite along the lower part of the Yangtze metallogenic belt. The four reproducible Ar-Ar ages ranging from 126 to 135 Ma with a high level of confidence represent the formation ages of the Shaxi porphyry intrusive with Cu-Au mineralization. The ages constraining on the Cu-Au mineralization in the central Anhui Province are consistent with those of the majority of the adjacent acid intrusives with mass Cu-Au mineralization along the Yangtze metallogenic belt in the Yanshanian Period (Mesozoic).

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