



# Zircon geochronology and Hf isotopic composition of Mesozoic magmatic rocks from Chizhou, the Lower Yangtze Region: Constraints on their relationship with Cu–Au mineralization

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## ABSTRACT

Zircon U–Pb ages and Hf isotopic compositions of Mesozoic magmatic rocks from the Chizhou Area are systematically investigated to reveal the tectonic setting of magmatism and their relationship with Cu–Au mineralization in the Lower Yangtze River Belt, southeastern China. The samples cover nearly all types of magmatic rocks in a 30×50 km<sup>2</sup> region, including 6 granite porphyries, 6 dacites and 4 granites. The zircon U–Pb geochronology yields a range of 151–124 Ma, with granite porphyries ranging from 151 to 146 Ma, dacites from 132 to 127 Ma and granites from 127 to 124 Ma, indicating two magmatic episodes of the late Jurassic and the early Cretaceous. The earlier episode mainly formed small granite porphyries (generally <5 km) and is always associated with porphyry Cu–Au deposits. The later episode began with dacites and was then dominated by large granite intrusions (generally >10 km), which are barren in mineralization. The ore-barren dacites and the granites (131–124 Ma) are poor in inherited zircons. Zircons in these rocks yield a very large  $\varepsilon_{\text{Hf}}(t)$  variation of  $-20.8$ – $0.4$ , suggesting a mixing between mantle-derived and crustal-derived magmas. By contrast, the ore-bearing porphyries (151–146 Ma) are rich in inherited zircons. The magmatic zircons have  $\varepsilon_{\text{Hf}}(t)$  values of  $-8.8$ – $0.9$ , and the inherited ones yield U–Pb ages of 1156–811 Ma with  $\varepsilon_{\text{Hf}}(t)$  values of 2.5–11.5. The existence of quantitative inherited zircons indicates that the crustal rocks of 1156–811 Ma significantly contribute to the formation of the ore-bearing porphyries, either being source or contamination. Since these inherited zircons are igneous as indicated by their oscillatory zonings, they may derive from components of the Grenvillian oceanic crust (ca. 1100–1000 Ma), i.e. the Neoproterozoic magmatic rocks related to arc (970–890 Ma) and Nanhua rift (ca. 825 Ma). Recent studies reveal that the ore-bearing porphyries of the Lower Yangtze River Belt have slab melt features and conclude that they could derive from partial melting of the Pacific oceanic crust. Our results provide another possibility for the origin of the ore-bearing porphyries: partial melting of Neoproterozoic crustal rocks that contain the Grenvillian oceanic crust fragment beneath the Yangtze Block. Such a new model can well explain the observations that are difficult to be explained by other models: e.g., the slab melt features with enriched Sr–Nd isotopic composition of the ore-bearing porphyries, the west–east distribution of the Lower Yangtze River Belt.

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## 1. Introduction

The Lower Yangtze River Belt (LYRB) is one of the most important metallogenic belts in eastern China, containing more than 200 polymetallic (Cu–Fe–Au, Mo, Zn, Pb, and Ag) deposits (Chang et al., 1991; Mao et al., 2006; Pan and Dong, 1999; Sun et al., 2003). Most of these deposits are spatially associated with, and are considered to be genetically related to the Late Jurassic to the early Cretaceous igneous rocks (e.g., Chen et al., 1993; Li et al., 2011-this issue; Mao et al., 2006; Sun et al., 2003, 2012; Q. Wang et al., 2006; Wang et al., 2012-this issue; Wu et al., 2012-this issue; Xie et al., 2012-this issue). Many of the ore-bearing igneous rocks in the LYRB are porphyries with adakitic

characteristics (H. Li et al., 2010; Li et al., 2011-this issue; Ling et al., 2009; Liu et al., 2010; Sun et al., 2010, 2012; Q. Wang et al., 2006). Thus, the petrogenesis of these rocks may provide important information on the ore mineralization of LYRB.

However, the origin of these ore-bearing intrusions is still controversial. Several models have been proposed, including partial melting of the delaminated lower continental crust (Q. Wang et al., 2006), or the subducted Pacific oceanic crust (Li et al., 2011-this issue; Ling et al., 2009; Liu et al., 2010; Sun et al., 2010, 2012), and fractional crystallization of basaltic magmas (J.W. Li et al., 2009; Xie et al., 2008).

In addition, the available chronological data suggest that the Mesozoic magmatic activity in the LYRB lasted for ~30 Ma from 152 to 122 Ma (Chen et al., 1985; Di et al., 2005; Hou and Yuan, 2010; J.W. Li et al., 2009; Liu et al., 2002; Lou and Du, 2006; Wang and McDougall, 1980; Wang et al., 2004b, 2006a; C.L. Wu et al., 2008; G.G. Wu et al.,

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2008; Wu et al., 2012-this issue; Xie et al., 2006b; Yan et al., 2009; Zhou et al., 2008), while ore mineralization took place in an interval from 144 to 133 Ma (Mao et al., 2006; Sun et al., 2003; Wu et al., 2012-this issue; Xie et al., 2006a). Many of the magmatic rocks in the LYRB are ore-barren. However, the spatial, temporal and petrogenetic relationships between the ore-bearing and ore-barren magmatic rocks are still unclear. A comparison of the ore-bearing with ore-barren magmatic rocks will shed new light on the mechanism of the ore mineralization and provide a useful guide for ore exploration in the LYRB.

In order to reveal the tectonic setting of magmatic generation and ore mineralization, we analyzed zircon U–Pb ages and Hf isotopic compositions of the late Mesozoic magmatic rocks in Chizhou area, LYRB. Our results indicate that there were two Mesozoic magmatic episodes occurred in the Chizhou area. The earlier episode (151–146 Ma) is related to porphyry Cu deposits, while the later episode (131–124 Ma) is barren in mineralization. The inherited zircons and Hf isotopic data of both episodes are discussed to better constrain their petrogeneses and the mechanism of the ore mineralization in the LYRB.

## 2. Geological background and sample localities

Eastern China is composed of three major tectonic blocks: the North China craton, the Yangtze Block and the Cathaysia Block (Fig. 1). The Yangtze Block is separated from the North China craton to the north by the Triassic Dabie-Sulu orogenic belt (Li et al., 1993), and from the Cathaysia Block to the south by the Jiangshan-Shaoxing Fault (Zhang et al., 2005).

The Yangtze Block consists of the Archean to Paleoproterozoic high-grade metamorphic TTG (tonalite, trondhjemite and granodiorite) gneisses, metasedimentary rocks and amphibolites (e.g., the Kongling complex near the Yangtze Gorge Dam; Gao et al., 1999; Qiu et al., 2000) and variably deformed, low- to middle-grade metamorphosed rocks with late Paleoproterozoic to early Neoproterozoic ages around the southern margin of the Yangtze Block. The Neoproterozoic magmatic rocks developed along the southern margin of the Yangtze Block are composed of the ca. 1134–968 Ma Grenvillian oceanic crust as indicated by ophiolites in southern Anhui and north-eastern Jiangxi Province (Chen et al., 1991; Li et al., 1997), the ca. 970–890 Ma Shuangxiwu magmatic

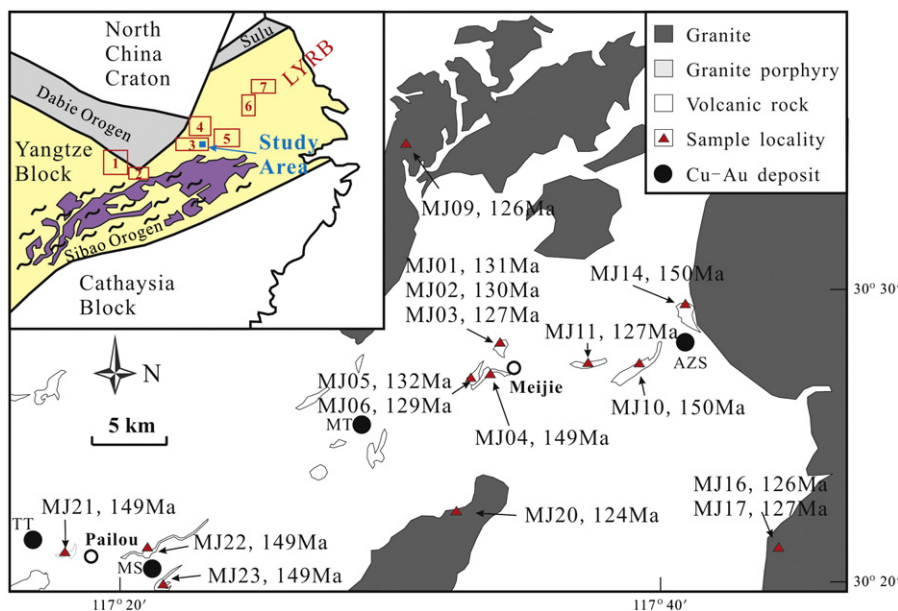
arc (X.-H. Li et al., 2009; Ye et al., 2007), the ca. 850 Ma Shenwu dolerites (Li et al., 2008) and the mid-Neoproterozoic (ca. 820–790 Ma) Nanhua rift volcano-sedimentary sequences and syn-rifting igneous intrusions (Z.X. Li et al., 2003; Li et al., 2008).

The LYRB refers to the middle and lower reaches of the Yangtze River extending ~400 km from the Hubei Province in the southwest to the Jiangsu Province in the northeast. This belt makes up one of the most important metallogenic belts in China and is composed of 7 major deposit districts form southwest to northeast along the Yangtze River: 1. Edong; 2. Jiujiang–Ruicang; 3. Anqing–Guichi; 4. Luzong; 5. Tongling; 6. Ningwu; 7. Ningzhen (Fig. 1). The ore deposits throughout the LYRB mainly consist of contemporaneous skarn, porphyry and strata-bound polymetallic (Cu, Au, Fe, Mo, Zn, Pb, and Ag) deposits. Dating of the ore-forming minerals indicates that they formed in the early Cretaceous (146–133 Ma) (X.-H. Li et al., 2010; Sun et al., 2003; Xie et al., 2007). The host intrusions are mainly dioritic adakite-like rocks and have emplacement ages identical to the formation ages of associated deposits, indicative of spatial and temporal association with ore deposits.

Chizhou area is situated in the Anqing–Guichi deposit district (Fig. 1). Three major types of Mesozoic magmatic rocks distributed in the area, i.e. granite porphyries, granites and dacites. The granite porphyry intrusions are generally small (<5 km) and spatially associated with the ore deposits, while the granite intrusions are large (>10 km) and ore-barren. The dacites are sporadically distributed in the area (Fig. 1). Samples studied here include all three types of the Mesozoic magmatic rocks in a 30×50 km<sup>2</sup> region, including 6 granite porphyries (MJ04, MJ10, MJ14, MJ21, MJ22, MJ23), 6 dacites (MJ01, MJ02, MJ03, MJ05, MJ06, MJ11) and 4 granites (MJ09, MJ16, MJ17, MJ20).

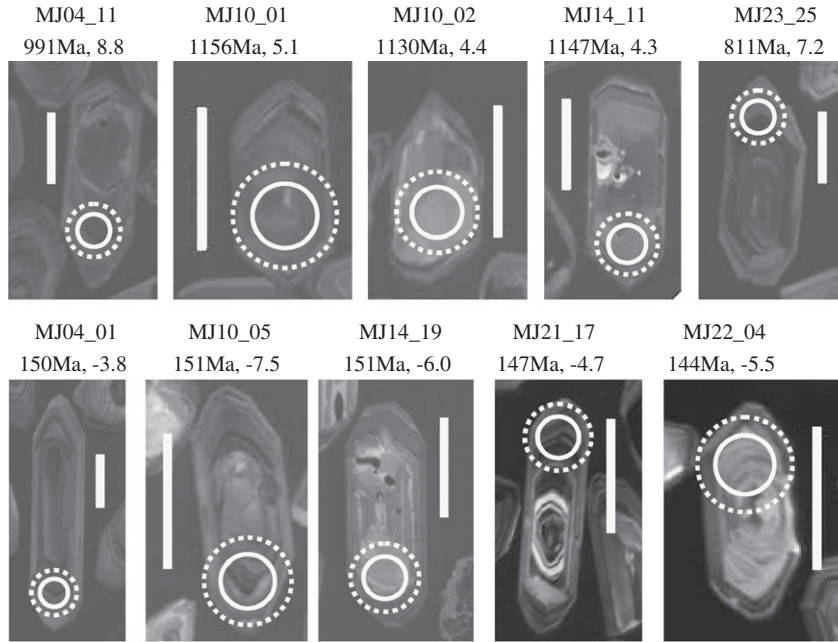
The ore-bearing porphyries comprise 2 granodiorite porphyries (MJ04, MJ22) and 4 granite porphyries (MJ10, MJ14, MJ21, MJ23). Both kind of rocks contain 15–20% volume of phenocrysts. The phenocrysts of granodiorite porphyries are mainly hornblende, plagioclase and quartz, and those of granite porphyries include K-feldspar, plagioclase, and quartz. These rocks are significantly altered with fuzzy mineral boundaries. The main alteration minerals are quartz, sericite and chlorite.

The dacites are brown or gray in color, consisting of (6–12%) plagioclase phenocrysts (<2 mm long) and (3–5%) quartz phenocrysts

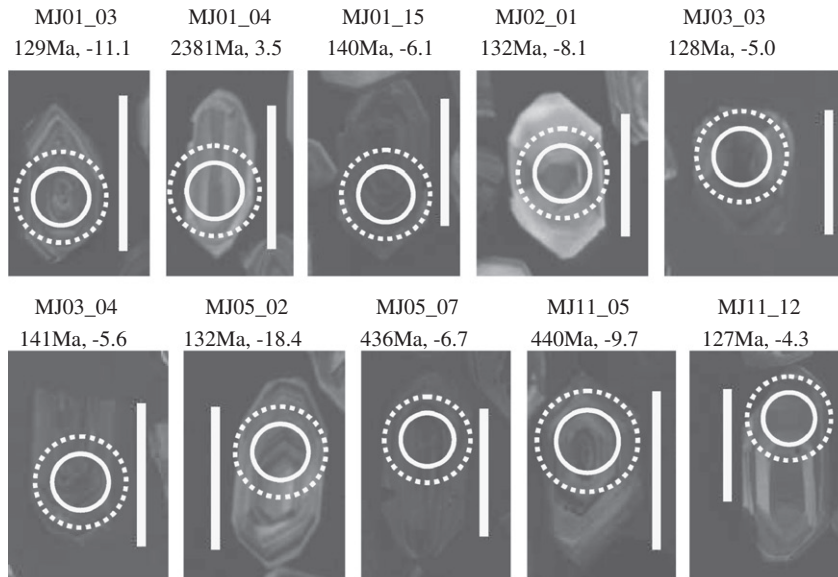


**Fig. 1.** Simplified geological map of the Chizhou area showing the distribution of the Mesozoic magmatic rocks and sample localities. The ages are zircon U–Pb dating results of this study. *Inset* shows location of the Yangtze Block relative to other blocks and fold belts (modified from (Li et al., 2002; Mao et al., 2006)). LYRB represents the Lower Yangtze River Belt, which includes seven ore districts: 1. Edong; 2. Jiujiang–Ruicang; 3. Anqing–Guichi; 4. Luzong; 5. Tongling; 6. Ningwu; 7. Ningzhen. TT: Tangtian Au deposit; MS: Mashi Cu deposit; MT: Matou Au deposit; AZS: Anzishan Cu deposit.

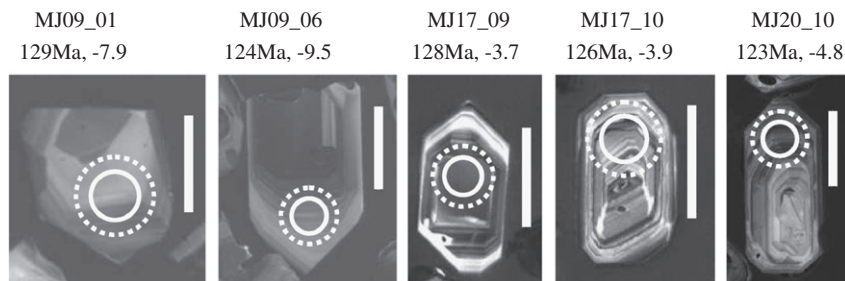
**Zircons in the granite porphyries**



**Zircons in the dacites**



**Zircons in the granites**



**Fig. 2.** Cathodoluminescence (CL) images of representative zircons of the Mesozoic magmatic rocks from the Chizhou area. Solid circles denote U–Pb analysis spots and dashed circles denote Lu–Hf analysis spots. All scale bars are 100  $\mu\text{m}$ . The U–Pb ages and  $\epsilon_{\text{Hf}}(t)$  values are given for each spot. Data are from Table S1 and Table S2.

(<1 mm), and minor biotite. The groundmass is aphanitic microcrystalline that composed of plagioclase and quartz.

The granites consist of 3 monozonitic granites (MJ16, MJ17, MJ20) and one syenogranite (MJ09). They are all coarse-grained and composed of K-feldspar (30–50%), plagioclase (20–35%), quartz (20–30%) and minor biotite, magnetite and zircon.

### 3. Analytical methods

#### 3.1. Zircon U–Pb dating

Zircons were separated using conventional magnetic and density techniques, and then handpicked under a binocular microscope. Zircons, together with standard zircon Temora were mounted in epoxy mounts and then polished to section the crystals in half for analysis. All zircons were documented with transmitted and reflected light micrographs as well as cathodoluminescence (CL) images to reveal their internal structures (Fig. 2), and the mount was vacuum-coated with high-purity gold.

Measurements of U, Th and Pb were conducted using the Cameca IMS-1280 SIMS at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGG), following the procedure outlined by X.H. Li et al. (2009); Q.L. Li et al. (2010). U–Th–Pb ratios and absolute abundances were corrected using the standards Temora (Black et al., 2004) and 91500 (Wiedenbeck et al., 1995), respectively. One spot on the standard zircon Temora was analyzed after every three analyses of unknown zircons. The mass resolution used to measure Pb/Pb and Pb/U isotopic ratios was 5400 during the analyses. Measured compositions were corrected for common Pb using non-radiogenic  $^{204}\text{Pb}$ . Corrections are sufficiently small to be insensitive to the choice of common Pb composition. An average of present-day crustal composition (Stacey and Kramers, 1975) is used for the common Pb assuming that the common Pb is largely surface contamination introduced during sample preparation. Errors on individual spots are based on counting statistics and are reported on the  $1\sigma$  level. Isoplot program of Ludwig (2003) was used for data processing and age calculation.

#### 3.2. Zircon Hf isotopes

Lutetium–Hafnium isotopic analyses were carried out using a Thermo-Finnigan Neptune MC-ICP-MS coupled with a 193 nm ArF Excimer laser ablation system at IGG, described in detail by F.Y. Wu et al. (2006). Data were collected in static mode for  $^{172}\text{Yb}$ ,  $^{173}\text{Yb}$ ,  $^{175}\text{Lu}$ ,  $^{176}\text{Yb} + \text{Lu} + \text{Hf}$ ,  $^{177}\text{Hf}$ ,  $^{178}\text{Hf}$ ,  $^{179}\text{Hf}$ ,  $^{180}\text{Hf}$  and  $^{182}\text{W}$  during 30s of ablation with a spot size of 60–80  $\mu\text{m}$  at laser repetition rate of 6–8 Hz. Both He and Ar carrier gases were used to transport the ablated sample from the laser-ablation cell via a mixing chamber to the ICP-MS torch. In order to correct the interferences of  $^{176}\text{Lu}$  and  $^{176}\text{Yb}$  on  $^{176}\text{Hf}$ , the isotopes  $^{172}\text{Yb}$ ,  $^{173}\text{Yb}$  and  $^{175}\text{Lu}$  were simultaneously monitored during each analysis step to allow the isobaric correction. For instrumental mass bias correction Yb isotope ratios were normalized to  $^{172}\text{Yb}/^{173}\text{Yb} = 1.35272$  (Vervoort et al., 2004) and Hf isotope ratios to  $^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$  using an exponential law. The mass bias behavior of Lu was assumed to follow that of Yb because of their close chemical similarities. The  $^{176}\text{Yb}/^{172}\text{Yb} = 0.5887$  (Vervoort et al., 2004),  $^{176}\text{Lu}/^{175}\text{Lu} = 0.02655$  (Chu et al., 2002) and mean  $\beta\text{Yb}$  value obtained during Hf analysis on the same spot were applied for the interference correction of  $^{176}\text{Yb}$ ,  $^{176}\text{Lu}$  on  $^{176}\text{Hf}$  (Gerdes and Zeh, 2006; Iizuka et al., 2005; Woodhead et al., 2004), respectively. Multiple LA-MC-ICP-MS analyses of the international reference zircon GJ-1 during our analytical session gave a  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio of  $0.282019 \pm 32$  (2SD,  $n = 35$ ), which is identical, within error, to the reference value of  $0.282000 \pm 5$  (Morel et al., 2008).

A decay constant for  $^{176}\text{Lu}$  of  $1.865 \times 10^{-11} \text{y}^{-1}$  (Scherer et al., 2001) and the chondritic ratios of  $^{176}\text{Hf}/^{177}\text{Hf}$  of 0.282772 and  $^{176}\text{Lu}/^{177}\text{Hf}$  of 0.0332 as derived by Blichert-Toft and Albarede (1997) are used to calculate initial  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios. Single stage model ages ( $T_{\text{DM1}}$ ) are

**Table 1**  
Summary of zircon U–Pb results of the magmatic rocks from the Chizhou area.

Sample name	Rock type	Age (Ma)	N	Percentage of inherited zircons
MJ04	Granite porphyry	149.3 ± 1.0	15	6.3%
MJ10	Granite porphyry	149.5 ± 2.1	5	76.2%
MJ14	Granite porphyry	150.8 ± 2.4	12	42.9%
MJ21	Granite porphyry	149.4 ± 1.2	14	30.0%
MJ22	Granite porphyry	146.5 ± 1.5	15	11.8%
MJ23	Granite porphyry	146.2 ± 1.1	27	10.0%
MJ01	Dacite	131.7 ± 1.4	12	25.0%
MJ02	Dacite	130.6 ± 0.9	16	0
MJ03	Dacite	127.4 ± 1.0	17	5.6%
MJ05	Dacite	131.6 ± 0.9	13	7.1%
MJ06	Dacite	128.8 ± 1.0	15	0
MJ11	Dacite	127.2 ± 0.9	14	6.3%
MJ09	Granite	125.5 ± 1.3	15	0
MJ16	Granite	126.4 ± 1.5	13	0
MJ17	Granite	126.9 ± 1.1	16	0
MJ20	Granite	123.7 ± 1.0	15	0

calculated relative to a model depleted mantle with a present-day  $^{176}\text{Hf}/^{177}\text{Hf} = 0.28325$  and  $^{176}\text{Lu}/^{177}\text{Hf} = 0.0384$  (Vervoort and Blichert-Toft, 1999). Two stage model ages ( $T_{\text{DM2}}$ ) are calculated by projecting the initial  $^{176}\text{Hf}/^{177}\text{Hf}$  of the zircon back to the depleted mantle model growth curve, assuming a mean  $^{176}\text{Lu}/^{177}\text{Hf}$  value of 0.015 for the average continental crust (Griffin et al., 2000).

### 4. Results

In situ U–Pb and Hf data on zircons from the magmatic rocks are listed in Table S1 and Table S2, respectively, summarized in Tables 1 and 2.

#### 4.1. Zircon U–Pb age determination

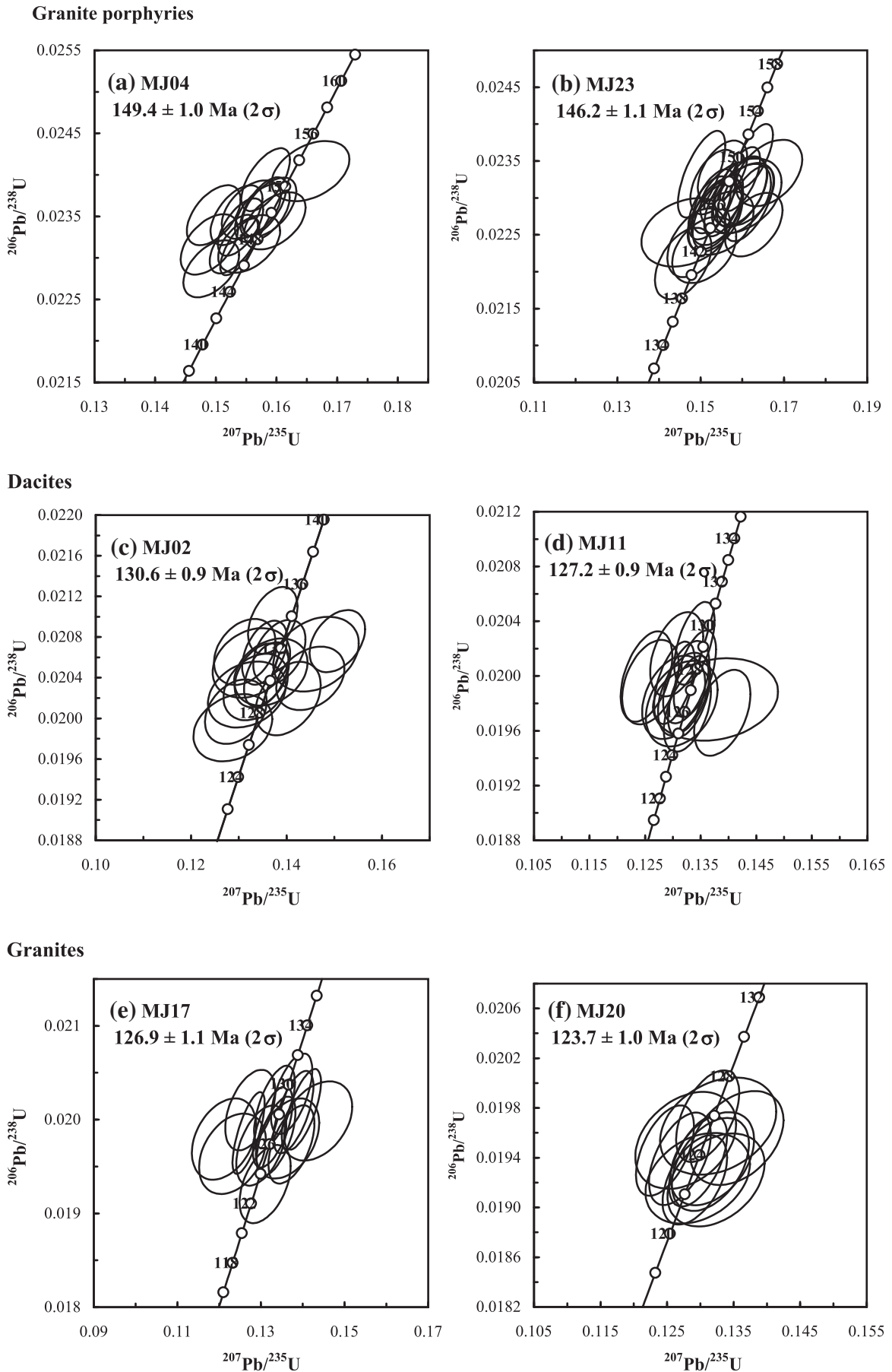
U–Pb concordia diagrams of 6 selected samples are shown in Fig. 3, including 2 granite porphyries (MJ04, MJ23), 2 dacites (MJ02, MJ11) and 2 granites (MJ17, MJ20). In summary, the zircon U–Pb ages of the Chizhou magmatic rocks yield a range of 150.8–123.7 Ma, with granite porphyries ranging from 150.8 to 146.2 Ma, dacites from 131.7 to 127.2 Ma and granites from 126.9 to 123.7 Ma (Table 1).

Zircons in granite porphyries are either euhedral prismatic grains or broken prisms with most of them being about 150 to 200  $\mu\text{m}$  in length (Fig. 2). They all show oscillatory zones (Fig. 2). Sixteen to 30 zircons of each sample were analyzed (Table S1), in which 5 to 27 grains gave concordant U–Pb ages and are selected for weighted

**Table 2**  
Summary of zircon U–Pb ages and Hf isotopic data of the magmatic rocks from the Chizhou area.

Zircon origin	Age (Ma)	Grains	$\epsilon_{\text{Hf}}$ (t)	$T_{\text{DM1}}$ (Ma)	$T_{\text{DM2}}$ (Ma)
<i>Zircons in the granite porphyries</i>					
Magmatic	141–158	85	–8.8–0.9	770–1150	1144–2097
Inherited	811–1156	17	2.5–11.5	1096–1489	1235–1706
		19	Inconcordant		
<i>Zircons in the dacites</i>					
Magmatic	118–136	109	–20.8–1.1	834–1642	1254–2494
Inherited	140–2381	9	–9.7–3.5	1016–2575	1523–2708
<i>Zircons in the granites</i>					
Magmatic	116–134	60	–9.5–0.4	886–1260	1160–1784





**Fig. 3.** U–Pb zircon concordia diagrams for the Chizhou granite porphyries (a, b), dacites (c, d) and granites (e, f). Data are from Table S1.

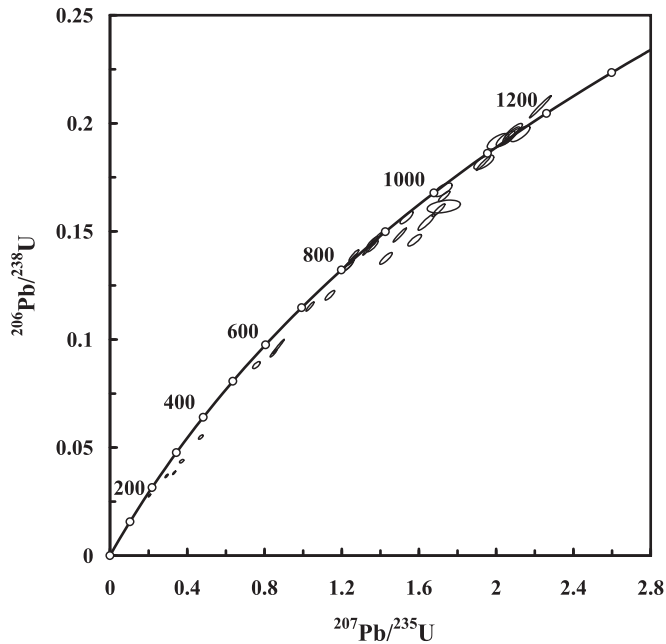


Fig. 4. U–Pb concordia diagrams for the inherited zircons from the Chizhou granite porphyries. Data are from Table S1.

average calculation (Fig. S1). All these granite porphyries (MJ04, MJ10, MJ14, MJ21, MJ22, MJ23) produced similar late Jurassic weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  ages of  $149.3 \pm 1.0$  Ma (2SD,  $n=15$ ),  $149.5 \pm 2.1$  Ma (2SD,  $n=5$ ),  $150.8 \pm 2.4$  Ma (2SD,  $n=12$ ),  $149.4 \pm 1.2$  Ma (2SD,  $n=14$ ),  $146.5 \pm 1.5$  Ma (2SD,  $n=15$ ),  $146.2 \pm 1.1$  Ma (2SD,  $n=27$ ), respectively (Table 1). All the 6 samples contain inherited zircons with percentages ranging from 6.3% to 76.2% (Table 1). Among the inherited zircons, 17 grains gave concordant ages, ranging from 1156 to 811 Ma (Table 2, Fig. 4).

Zircons in dacites are all prismatic with length of from  $\sim 100$   $\mu\text{m}$  to  $\sim 150$   $\mu\text{m}$ , showing oscillatory zoning in CL images (Fig. 2). Fifteen to 42 zircons from each sample were determined (Table S1), in which 12 to 17 grains gave concordant U–Pb ages and are selected for weighted mean calculation (Fig. S1). The 6 dacite samples (MJ01, MJ02, MJ03, MJ05, MJ06, MJ11) all yielded the early Cretaceous ages, which are  $131.7 \pm 1.4$  Ma (2SD,  $n=12$ ),  $130.6 \pm 0.9$  Ma (2SD,  $n=5$ ),  $127.4 \pm 1.0$  Ma (2SD,  $n=12$ ),  $131.6 \pm 0.9$  Ma (2SD,  $n=14$ ),  $128.8 \pm 1.0$  Ma (2SD,  $n=15$ ), and  $127.2 \pm 0.9$  Ma (2SD,  $n=27$ ), respectively (Table 1). Few inherited zircons have been found in these samples (Table 1).

Zircons from granite samples MJ09, MJ16, MJ17 and MJ20 are prismatic grains and 100  $\mu\text{m}$  to 200  $\mu\text{m}$  in size with typical oscillatory zoning (Fig. 2). These samples yielded weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  ages of  $125.5 \pm 1.3$  Ma (2SD,  $n=15$ ),  $126.4 \pm 1.5$  Ma (2SD,  $n=13$ ),  $126.9 \pm 1.1$  Ma (2SD,  $n=16$ ), and  $123.7 \pm 1.0$  Ma (2SD,  $n=15$ ), respectively. No inherited zircon has been found in all of these samples.

#### 4.2. Zircon Hf isotopes

Hf isotopic data are listed in Table S2, summarized in Table 2 and plotted in Fig. 5.

Zircons in granite porphyries can be divided into two major groups according to the age population, magmatic and inherited origin. Among the total 116 zircons analyzed, 85 were crystallized from the magma with U–Pb ages of 141 to 158 Ma and have  $\epsilon_{\text{Hf}}(t)$  values of from  $-8.8$  to  $0.9$ . The other 31 zircons are inherited, among which 17 zircons yield concordant U–Pb ages of 1156–811 Ma with  $\epsilon_{\text{Hf}}(t)$  values of 2.5–11.5 (Table 2 and Fig. 5a).

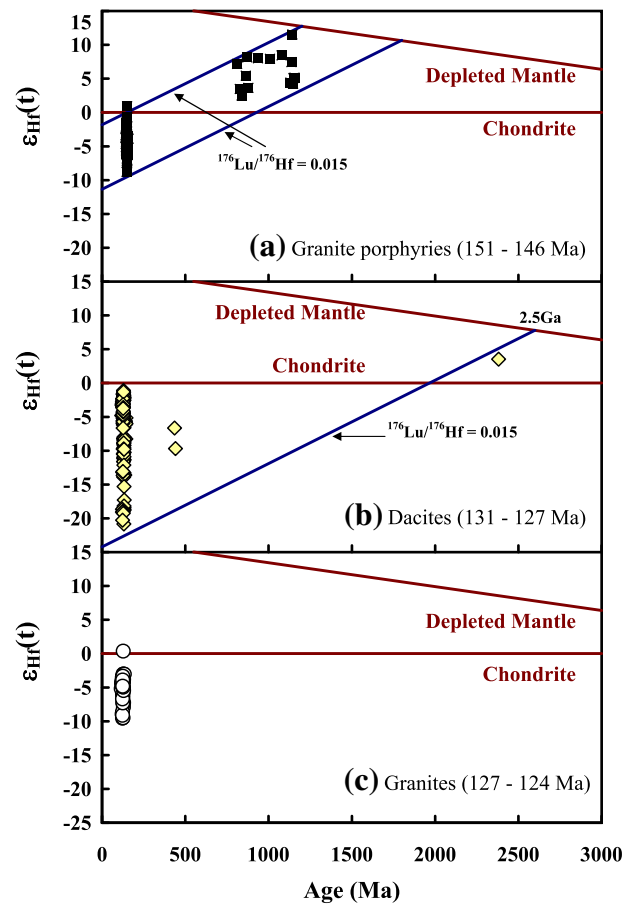


Fig. 5. Relationship between  $\epsilon_{\text{Hf}}(t)$  values and U–Pb ages for zircons from the Chizhou granite porphyries (a), dacites (b) and granites (c). Data are from Table S1 and Table S2. Hf isotopic compositions of chondrite and depleted mantle are from Blichert-Toft and Albaredo (1997); Vervoort and Blichert-Toft (1999).

In dacites, only nine zircons among the total 118 grains analyzed are inherited. They yield U–Pb ages of from 140 to 2381 Ma and  $\epsilon_{\text{Hf}}(t)$  values of from  $-9.7$  to  $3.5$  (Table S2, Table 2 and Fig. 4). The other 109 zircons are magmatic. Although they yield a small variation in U–Pb ages ranging from 118 to 136 Ma, a large variation in  $\epsilon_{\text{Hf}}(t)$  values from  $-20.1$  to  $-1.1$  has been observed (Table 2 and Fig. 5b).

The zircons in granites gave U–Pb ages of from 116 to 134 Ma, which are similar to those of the magmatic zircons in dacites. These zircons have  $\epsilon_{\text{Hf}}(t)$  values of from  $-9.5$  to  $0.4$  (Table 2 and Fig. 5c).

## 5. Discussion

Since ore-bearing intrusions have generally undergone significant hydrothermal alteration, they are not always fresh enough for whole rock analyses. Zircon is a refractory mineral and a highly robust phase in many geological environments and thus is widely used in geochronological studies. In addition, zircon Hf isotopic composition can nearly represent that of the magma from which the zircon crystallized because of negligible radiogenic growth due to its low Lu/Hf ratio (Kinny and Maas, 2003), and is widely used as a geochemical tracer to decipher magma source and petrogenetic processes (Kemp et al., 2006).

Our samples cover nearly all types of magmatic rocks in a  $30 \times 50$   $\text{km}^2$  region (Fig. 1). The zircon U–Pb and Hf isotopic data of these rocks could provide constraints on the timing and origin of these magmatic rocks and their relationship with the Cu–Au mineralization.

### 5.1. Coexistence of two episodes of Mesozoic magmatism in Chizhou area

Although geochronological studies would be very helpful for understanding the relationship between the Mesozoic magmatic event and the Cu–Au deposit in the Chizhou area, no age result of Mesozoic magmatic rock and ore deposit had been previously reported in this area. Our data demonstrate that two episodes of Mesozoic magmatism existed (Fig. 6). The first episode mainly is composed of granite porphyries, which show close relationship with the Cu deposits. This episode occurred at the late Jurassic (151–146 Ma) as identified by the 6 granite porphyries studied here. The second episode took place at the early Cretaceous with the dacites erupted at first (131–127 Ma) and subsequent granites (127–124 Ma).

In contrast to the Chizhou area, considerable geochronological data have been reported for the magmatic rocks from other regions in the LYRB. These data indicate the presence of a long-term magmatic event lasting from 152 to 120 Ma (Fig. 6; Chen et al., 1985; Di et al., 2005; Hou and Yuan, 2010; J.W. Li et al., 2009; X.-H. Li et al., 2010; Liu et al., 2002; Lou and Du, 2006; Wang and McDougall, 1980; Wang et al., 2004b, 2006a; C.L. Wu et al., 2008; G.G. Wu et al., 2008; Wu et al., 2012–this issue; Xie et al., 2006b; Yan et al., 2009; Zhou et al., 2008). The magmatism was marked by an early plutonic intrusion of from 152 to 132 Ma (Di et al., 2005; J.W. Li et al., 2009; X.-H. Li et al., 2010; Lou and Du, 2006; Y. B. Wang et al., 2004; Q. Wang et al., 2006; C.L. Wu et al., 2008; G.G. Wu et al., 2008) and subsequent volcanic eruption and granite emplacement during 140 to 120 Ma (Chen et al., 1985; Hou and Yuan, 2010; Liu et al., 2002; Lou and Du, 2006;

Wang and McDougall, 1980; Xie et al., 2006b; Yan et al., 2009; Zhou et al., 2008).

Our data, like the previous ones, also suggest two-period magmatism, beginning with porphyries associated with ore deposits and then dominated by ore-barren volcanic rocks and granites. However, previous data indicate that the two periods are overlapped, while our data suggest a hiatus of ~15 Ma between the two magmatic events. This is very important because it would be helpful to identify whether there is any origin relationship between the two periods of magmatism. This inconsistency between previous data and ours may come from two aspects. First, there are several inconsistent ages in the previous data. For example, the Zhuangqiao and Shuangmiao volcanic rocks in Luzong have been investigated by several studies. Liu et al. (2002) reported the Ar–Ar ages of  $140.1 \pm 0.8$  Ma and  $125.5 \pm 0.8$  Ma, while Zhou et al. (2008) reported zircon U–Pb ages of  $134.1 \pm 1.6$  Ma and  $130.5 \pm 0.8$  Ma obtained by LA-ICP-MS. Lou and Du (2006) reported a zircon U–Pb SHRIMP age of  $135.5 \pm 4.4$  Ma for the Jiguanshan granodiorites from Tongling, while C.L. Wu et al. (2008) reported an age of  $139.9 \pm 1.1$  Ma by using the same method. Second, the magmatism throughout the LYRB might not be exactly coeval. For example, the first stage occurred at 152–146 Ma in the Chizhou area, while it took place at 148–138 Ma in Tongling (G.G. Wu et al., 2008). However, the database for each ore district in the LYRB is presently too limited to clarify this issue. More detailed studies are still required. Nevertheless, our data have recognized two Mesozoic magmatic episodes at least in the Chizhou area, which may represent two independent magmatic activities.

### 5.2. Origin of these two episode rocks

Besides the difference in emplacement ages, the two periods of magmatism have many other distinctive characteristics. For example, the early episode mainly is composed of granite porphyries, which are generally associated with Cu–Au deposits. These porphyry intrusions are small in sizes, generally less than 5 km in diameter. All the porphyries contain inherited zircons. By contrast, the late episode mainly is composed of dacites and granites, which are ore barren. The granite intrusions are generally large.

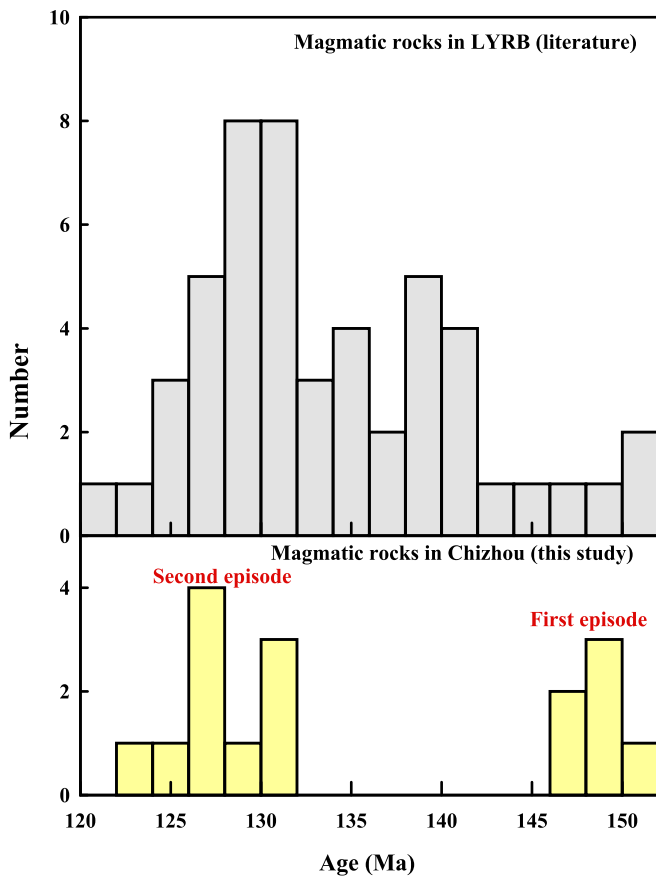
Miller et al. (2003) studied 54 intrusions worldwide and found that inheritance-poor magma is generally hotter than inheritance-rich magma. Both the dacites and granites are inheritance-poor, indicating that they might be “hot” magmas. In general, “hot” magmas with minimal inheritance probably require advective heat input into the crust and readily erupt, whereas “cold”, inheritance-rich magmas require fluid influx and are unlikely to erupt (Miller et al., 2003). Therefore, the magmas formed in the early episode are relatively cold, whereas those in the late episode are hot. Below, we will discuss the possible sources for these rocks based on the zircon Hf isotopic data.

#### 5.2.1. Contribution of Neoproterozoic crustal materials to Cu–Au-bearing granite porphyries

The magmatic zircons in Chizhou granite porphyries exhibit a relatively small Hf isotopic variation with  $\epsilon_{\text{Hf}}(t)$  values ranging from –8.8 to 0.9, which could represent the Hf isotopic composition of the magma from which zircons crystallized. The 17 inherited zircons in granite porphyries yielded concordant U–Pb ages of from 811 to 1156 Ma with  $\epsilon_{\text{Hf}}(t)$  values varying from 2.5 to 11.5.

In general, inherited zircons could be derived from a contributing source material or be entrained from wall rock through late-stage contamination. Since all these inherited zircons have ages from 811 to 1156 Ma with clear oscillatory zoning, the existence of them in the granite porphyries indicated that some 811–1156 Ma igneous rocks contribute to the origin of the granite porphyries, either being source or contamination.

Two episodes of Neoproterozoic magmatism occurred in the southern margin of the SCC. The first one is magmatic arc related to



**Fig. 6.** Histogram for ages of the magmatic rocks from the Lower Yangtze River Belt. Data are from Table S1, Wang and McDougall (1980), Chen et al. (1985), Liu et al. (2002), Y.B. Wang et al. (2004), Di et al. (2005), Lou and Du (2006), Q. Wang et al. (2006), Xie et al. (2006b), G.G. Wu et al. (2008), C.L. Wu et al. (2008), Zhou et al. (2008), J.W. Li et al. (2009), Yan et al. (2009), Hou and Yuan (2010).

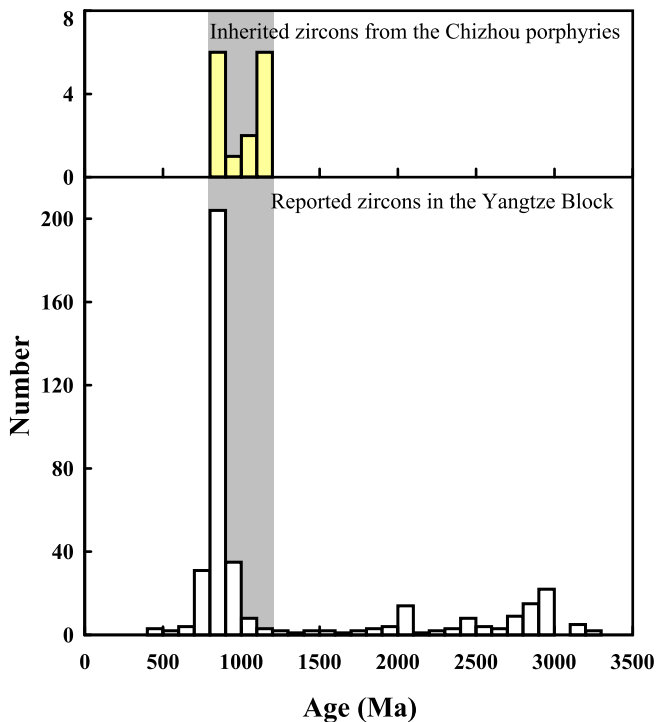


Fig. 7. Histogram for ages of the inherited zircons in the granite porphyries from the Chizhou area with reported zircons in the Yangtze craton. Data are from Table S1, Z.X. Li et al. (2003), X.L. Wang et al. (2006), R.-X. Wu et al. (2006), Zhang et al. (2006), Zheng et al. (2006), Ye et al. (2007), Li et al. (2007), X.-H. Li et al. (2009).

the subduction of the Grenvillian ocean beneath the Yangtze Block, whereas the second is associated with Nanhua rifting, respectively. Typical arc magmatism along the active southeastern continental margin of the Yangtze Block formed during 970–890 Ma (Chen et al., 2009; Li and Li, 2003; X.-H. Li et al., 2009; Ye et al., 2007). The second one is the Nanhua bimodal magmatism which formed at ca. 825 Ma (Z.X. Li et al., 2003). Therefore, the 970–811 Ma zircons may come from the igneous rocks which are related to Grenvillian ocean subduction and/or Nanhua rifting. In addition, the Hf isotopic compositions of the 970–800 Ma inherited zircons are also similar to those of zircons from Neoproterozoic granites (Fig. 8), indicating that they may share a common source.

Notably, half of the inherited zircons (e.g. MJ10\_01, MJ14\_11) are older than 1000 Ma and they are also igneous zircons as indicated by their oscillatory zoning (Fig. 2). However, none of ca. 1100 Ma

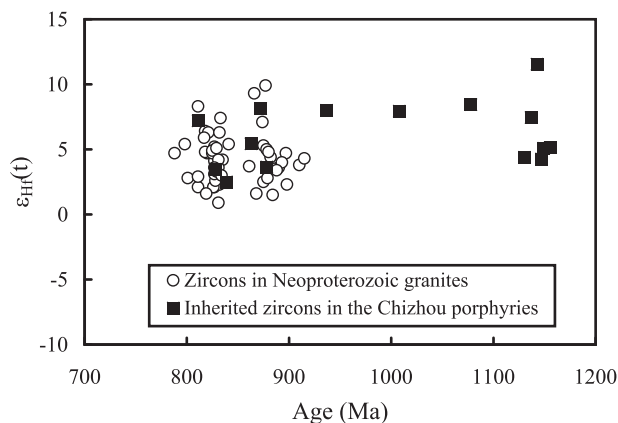


Fig. 8.  $\epsilon_{\text{Hf}}(t)$  value vs U–Pb age diagram for inherited zircons in the Chizhou granite porphyries and zircons in the Neoproterozoic granites from the south margin of the Yangtze Block. Data are from Table S2, R.-X. Wu et al. (2006).

magmatism has been found in the Yangtze Block. Although zircon U–Pb geochronological data on detrital zircons from Cambrian to Silurian sandstones from the Yangtze Block yield major clusters at ~2550, ~1860, ~1100 and ~860–780 Ma (Wang et al., 2010), the Grenville age zircons with a peak at ~1100 Ma are metamorphic and considered to come from metamorphic rocks, e.g. amphibolite and garnet pyroxenite (Wang et al., 2010). The only igneous rocks of ~1100 Ma that can be found in the Yangtze Block could be the Grenvillian oceanic crust remnant. The ophiolites in southern Anhui and north-eastern Jiangxi Province gave Sm–Nd ages of 1134–968 Ma (Chen et al., 1991; Li et al., 1997), which is consistent with the Mesoproterozoic microflora fossils found in the ophiolites belt (Yan et al., 2007).

In summary, the U–Pb age and Hf isotopic compositions of the inherited zircons indicate that the Neoproterozoic crustal rocks, including fragments of Grenvillian oceanic crust (ca. 1100–1000 Ma), the Neoproterozoic magmatic arc (970–890 Ma) and Nanhua rift (ca. 825 Ma) on the southern margin of the Yangtze Block, could contribute to the formation of the granite porphyries, either being source or contamination.

#### 5.2.2. Constraints on the origin of magmatism of the early episode

Several models have been proposed for the origin of ore-bearing porphyries in the LYRB previously, e.g. partial melting of the delaminated lower continental crust (Q. Wang et al., 2006), or the subducted Pacific oceanic crust (Ling et al., 2009; Liu et al., 2010; Sun et al., 2010), and fractional crystallization of basaltic magmas (J.W. Li et al., 2009; Y. Wang et al., 2004; Xie et al., 2008).

The fractional crystallization of basaltic magma model could be excluded here based on our geochronological data. The ore-bearing granite porphyries were formed at 150–146 Ma. None of the basaltic rocks with this age have been found in the Chizhou area or other ore districts in LYRB. The high-precision U–Pb zircon dating indicates that basaltic igneous rocks consisting of gabbros and alkali volcanic rocks from other areas of the LYRB were formed at 131–125 Ma with a peak of ~130 Ma (Zhou et al., 2008), which are clearly younger than the ore-bearing granite porphyries. Therefore, there is no temporal association between these granite porphyries and basaltic rocks. Similarly, lack of basaltic rocks of 150–146 Ma also excludes mantle-crust magma mixing for the origin of these ore-bearing porphyries.

Partial melting of both the delaminated lower continental crust and the subducted Pacific oceanic crust have some difficulties in explaining the current geochemical data of the ore-bearing porphyries in the LYRB. For example, although melting of delaminated lower continental crust offers a possible explanation of enriched Nb–Sr isotope features of ore-bearing porphyries in the LYRB (Q. Wang et al., 2006), it is not supported by the development of extensional basins in the LYRB during the Jurassic to Cretaceous (Ling et al., 2009), which do not facilitate to produce a dense eclogitic lower crust. Similarly, several studies proposed that the ore-bearing porphyries in the LYRB could be derived from partial melting of the Pacific oceanic crust, because (1) they have some slab-derived melt geochemical features, e.g. low  $\text{K}_2\text{O}/\text{Na}_2\text{O}$ , high Ce/Pb and Sr/La ratios (Liu et al., 2010); (2) It has been widely accepted that slab-derived melts/fluids favor Cu–Au mineralization (Ling et al., 2009); (3) The only active subduction beneath the Yangtze Block at the Jurassic–Cretaceous is Pacific plate subduction. However, partial melting of the Pacific oceanic crust is difficult to explain the enriched Nb–Sr isotope features of ore-bearing porphyries in the LYRB (Q. Wang et al., 2006).

Since there are large amount inherited Neoproterozoic zircons in the Chizhou porphyries, another possibility should also be taken into account for the origin of the granite porphyries: partial melting of Neoproterozoic crustal rocks that contain fragments of Grenvillian oceanic crust. Although current data could not totally rule out the possibility that the inherited zircons may come from the wall rock, the following observations suggest that they are more likely to derive



from the source than entrained from the wall rock. First, all these zircons have similar characteristics. For example, they all have clear oscillatory zoning, indicative of igneous origins. If they come from the wall rock, they are expected to have diverse origins. Second, they have a small variation in age from 811 to 1156 Ma compared to the age variation of zircons in the Yangtze Block (430–3253 Ma; Fig. 7), which is expected to be a wide range if the inherited zircon comes from the wall rock. Moreover, when a  $^{176}\text{Lu}/^{176}\text{Hf}$  ratio of the average continental crust (0.015) is assumed (Griffin et al., 2000), the Hf isotopic composition of these inherited zircons could evolve into the same Hf isotopic composition as that of the magmatic zircons (Fig. 5a).

Importantly, such a new model can explain the observations difficult to be explained by other models. For example, partial melting of the delaminated lower crust cannot explain the slab-derived melt geochemical features of ore-bearing porphyries in the LYRB, e.g. low  $\text{K}_2\text{O}/\text{Na}_2\text{O}$ , high Ce/Pb and Sr/La ratios (Liu et al., 2010), whereas partial melting of the Pacific oceanic crust is difficult to explain the enriched Nb–Sr isotope features of ore-bearing porphyries in the LYRB (Q. Wang et al., 2006). However, both the slab-derived melt geochemical features and the enriched Nb–Sr isotope features of ore-bearing porphyries can be explained by partial melting of Neoproterozoic crustal rocks that contain fragments of Grenvillian oceanic crust. The Neoproterozoic crustal rocks could have evolved into such an enriched Nd isotopic composition at the Jurassic (Fig. 9). In addition, the ore-bearing magmatism in the LYRB was developed in a nearly west–east trend. This is not consistent with a south–north distribution as expected by partial melting of the Pacific oceanic crust. However, the west–east distribution of the LYRB can be easily explained by the new model, since the fragments of Grenvillian oceanic crust mainly developed along the south margin of the Yangtze Block.

### 5.2.3. Origin of late episode magmatism and its relationship with lithospheric thinning

The 109 magmatic zircons from the dacites yield a small variation of U–Pb ages from 118 to 136 Ma, however large variations of  $\epsilon_{\text{Hf}}(t)$  values from  $-20.8$  to  $-1.1$  have been observed. Even zircons from one sample, e.g. MJ05, display a large Hf isotopic variation with  $\epsilon_{\text{Hf}}(t)$  values from  $-20.8$  to  $-1.8$  (Fig. 10). This wide range in zircon Hf isotopic compositions precludes a simple, common evolution by

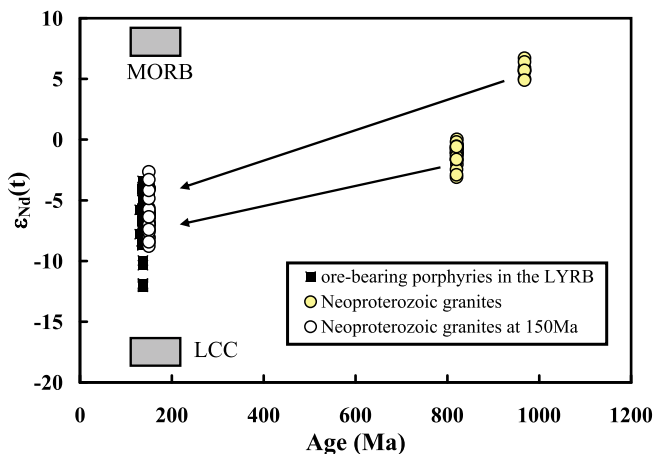


Fig. 9.  $\epsilon_{\text{Nd}}(t)$  value vs age diagram for the ore-bearing porphyries in the LYRB and the Neoproterozoic granites from the south margin of the Yangtze Block. Data of the ore-bearing porphyries in the LYRB are from Wang et al. (2003); Q. Wang et al. (2006); J.W. Li et al. (2009); Liu et al. (2010). Data of the Neoproterozoic granites are from Li and Li (2003); X.-H. Li et al. (2003); R.-X. Wu et al. (2006).  $\epsilon_{\text{Nd}}(t)$  values of the Neoproterozoic granites were calculated back to  $t=150$  by using measured  $^{147}\text{Sm}/^{144}\text{Nd}$  ratios.

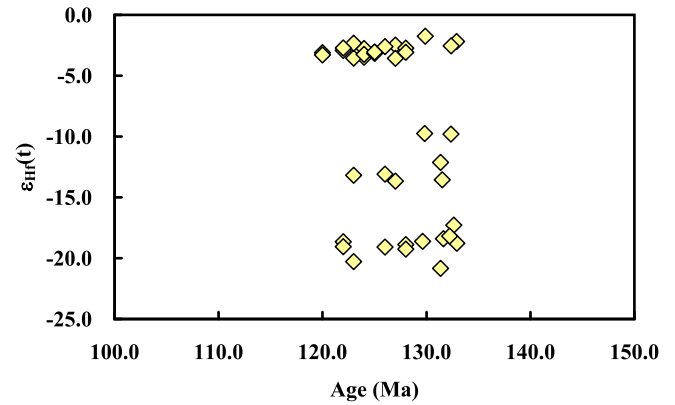


Fig. 10.  $\epsilon_{\text{Hf}}(t)$  value vs U–Pb age diagram for the Chizhou dacite, MJ05. Data are from Table S2.

closed-system fractionation processes, since such a mechanism could not produce the variable isotopic compositions.

Zircons crystallizing in a melt retain a record of changes in ambient conditions during their growth. Zircons in the dacites have a large range of  $\epsilon_{\text{Hf}}(t)$  values, indicative of a magma mixing of two distinct components. One component has  $\epsilon_{\text{Hf}}(t)$  value down to  $-20$ , whereas the other has  $\epsilon_{\text{Hf}}(t)$  value up to 0. Given that the magmatism occurred in the LYRB at this time period (131–124 Ma) is bimodal, the two components could be the lower continental crust and the mantle, respectively. Notably, one inherited zircon has U–Pb age of 2381 Ma with  $\epsilon_{\text{Hf}}(t)$  value of 3.5. When a  $^{176}\text{Lu}/^{176}\text{Hf}$  ratio of the average continental crust (0.015) is assumed (Griffin et al., 2000), this Hf isotopic composition could evolve into the same Hf isotopic composition as the lowest  $\epsilon_{\text{Hf}}(t)$  magmatic zircons (Fig. 5b).

The zircons in the granites gave U–Pb ages of from 116 to 134 Ma, which are similar to those of the magmatic zircons in the dacites. In contrast to zircons in dacites, these zircons yield a relatively small  $\epsilon_{\text{Hf}}(t)$  variation of from  $-9.5$  to 0.4 and no inherited zircon has been found. Although these granites have similar zircon Hf isotopic compositions to the 151–146 Ma granite porphyries, they may have different origins. Previous studies indicate that the two types of rocks are different in many geochemical features, e.g.  $\text{K}_2\text{O}/\text{Na}_2\text{O}$ , Ce/Pb, Sr/La ratios (Liu et al., 2010). Since these granites (127–124 Ma) formed shortly after the dacites (131–127 Ma), we propose that both of them should be originated from magma mixing. The reason why the zircons in these granites have a relatively small Hf isotopic variation might be that the mixing between the mantle derived magmas and the continental crust are totally completed in the magma chamber before zircon crystallization.

### 5.3. Tectonic evolution of the LYRB and Cu–Au mineralization

Chalcophile elements (e.g., Cu and Au) are highly compatible in magmatic sulfide phases, and incompatible in silicate and oxide minerals (Ballard et al., 2002; Fleet et al., 1996). Thus, removal of them from the mantle can only occur under oxidized conditions where the sulfate phases are dominant (Ballard et al., 2002; Mungall, 2002). Slab-derived melts/fluids, which have high oxygen fugacities, are generally considered to favor Cu–Au mineralization (Ballard et al., 2002; Kelley and Cottrell, 2009; Mungall, 2002; Oyarzun et al., 2001). This could explain that the porphyry Cu–Au ore deposits are always associated with adakitic intrusions in subduction zones worldwide (Chiaradia et al., 2004; González-Partida et al., 2003; Gutscher et al., 2000; Imai, 2002; Oyarzun et al., 2001; Rae et al., 2004; Sajona and Maury, 1998).

Mungall (2002) suggested that if an arc magma has  $\log f\text{O}_2 > \text{SSO}$  (sulfide–sulfur oxide buffer), it must contain a component of melted oceanic crust. Then Cu–Au deposits may by their very existence provide

evidence for slab melting (Mungall, 2002). The ore-bearing porphyries in the LYRB have some slab-derived melt geochemical features, e.g. low  $K_2O/Na_2O$ , high Ce/Pb and Sr/La ratios (Liu et al., 2010).

The U–Pb age and Hf isotopic data of the inherited zircons in the Chizhou ore-bearing porphyries indicate that the 1156–811 Ma igneous rocks could significantly contribute to the formation of these porphyries, probably including components of the Grenvillian oceanic crust (ca. 1100–1000 Ma), the Neoproterozoic magmatic rocks related to arc (970–890 Ma) and Nanhua rift (ca. 825 Ma). Among them, the Grenvillian oceanic crust is most likely to have genetic relationship with the Cu–Au mineralization in LYRB. First, it should contain a component of melted oceanic crust to generate a magma with high oxygen fugacities (Mungall, 2002). Second, the Neoproterozoic magmatic rocks related to arc (970–890 Ma) and Nanhua rift (ca. 825 Ma) distribute widely in the Yangtze Block. If they have much genetic relationship with Cu–Au mineralization, the Cu–Au ore should also distribute widely. On the contrary, the fragments of Grenvillian oceanic crust mainly developed along the south margin of the Yangtze Block, which is consistent with the west–east distribution of the LYRB.

Therefore, our zircon U–Pb and Hf isotopic data provide a new possibility that the slab-derived melt geochemical features of the ore-bearing porphyries in the LYRB may derive from the Grenvillian oceanic crust and that the old oceanic crust in or beneath the lithosphere could also be favorable for Cu–Au mineralization.

## 6. Conclusions

Systematically zircon U–Pb age and Hf isotope studies on the Chizhou Mesozoic magmatic rocks allow us to draw the following conclusions:

- (1) Two episodes of magmatism: the late Jurassic and the early Cretaceous have been identified in the Chizhou area. The earlier episode (151–146 Ma) yielded relatively small granite porphyries (generally <5 km) and was generally associated with porphyry Cu deposits. The later episode began with dacites of 131–127 Ma and was then dominated by granites of 127–124 Ma occurring as relatively large intrusions (generally >10 km). Rocks formed in this period are barren in Cu–Au mineralization.
- (2) The ore-bearing porphyries are inheritance-rich. The U–Pb age and Hf isotopic data of these inherited zircons indicate that the 1156–811 Ma igneous rocks could significantly contribute to the formation of these porphyries, probably including components of the Grenvillian oceanic crust (ca. 1100–1000 Ma), the Neoproterozoic magmatic rocks related to arc (970–890 Ma) and Nanhua rift (ca. 825 Ma).
- (3) The barren dacites and the granites are inheritance-poor. The zircons in these rocks yield a very large  $\epsilon_{\text{Hf}}(t)$  variation of –20.8–0.4, suggesting a mixing between mantle-derived and crustal-derived magmas.
- (4) Our results provide another possibility for the origin of the ore-bearing porphyries: partial melting of Neoproterozoic crustal rocks that contain the Grenvillian oceanic crust fragment beneath the Yangtze Block. Such a new model can well explain the observations that are difficult to be explained by other models: e.g., the slab melt features with enriched Sr–Nd isotopic composition of the ore-bearing porphyries, the nearly west–east distribution of the Lower Yangtze River Belt.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.lithos.2012.06.026>.

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