

# Late Mesozoic Ore-forming Events in the Ningwu Ore District, Middle-Lower Yangtze River Polymetallic Ore Belt, East China: Evidence from Zircon U-Pb Geochronology and Hf Isotopic Compositions of the Granodioritic Stocks

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**Abstract:** Late Mesozoic volcanic-subvolcanic rocks and related iron deposits, known as porphyry iron deposits in China, are widespread in the Ningwu ore district (Cretaceous basin) of the middle-lower Yangtze River polymetallic ore belt, East China. Two types of Late Mesozoic magmatic rocks are exposed: one is dioritic rocks closely related to iron mineralization as the hosted rock, and the other one is granodioritic (-granitic) rocks that cut the ore bodies. To understand the age of the iron mineralization and the ore-forming event, detailed zircon U-Pb dating and Hf isotope measurement were performed on granodioritic stocks in the Washan, Gaocun-Nanshan, Dongshan and Heshangqiao iron deposits in the basin. Four emplacement and crystallization (typically for zircons) ages of granodioritic rocks were measured as  $126.1 \pm 0.5$  Ma,  $126.8 \pm 0.5$  Ma,  $127.3 \pm 0.5$  Ma and  $126.3 \pm 0.4$  Ma, respectively in these four deposits, with the LA-MC-ICP-MS zircon U-Pb method. Based on the above results combined with previous dating, it is inferred that the iron deposits in the Ningwu Cretaceous basin occurred in a very short period of 131–127 Ma. In situ zircon Hf compositions of  $\varepsilon_{\text{Hf}}(t)$  of the granodiorite are mainly from  $-3$  to  $-8$  and their corresponding  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio are from 0.28245 to 0.28265, indicating similar characteristics of dioritic rocks in the basin. We infer that granodioritic rocks occurring in the Ningwu ore district have an original relationship with dioritic rocks. These new results provide significant evidence for further study of this ore district so as to understand the ore-forming event in the study area.

**Key words:** Zircon U-Pb age, Hf isotope, porphyry iron deposit, Ningwu ore district, Middle-Lower Yangtze River polymetallic ore belt

## 1 Introduction

The Middle-Lower Yangtze River polymetallic ore belt (MLYRB) covers an area of  $\sim 30000 \text{ km}^2$  and is one of the most important metallogenic belts in East China, comprising seven ore districts, including (from west to east) the Edong, Jiurui, Anqing-Guichi, Tongling, Luzong, Ningwu and Ningzhen (Fig. 1) districts (Chang et al., 1991; Zhai et al., 1992a; Mao et al., 2011). There are more than 200 polymetallic (Cu-Fe-Au, Mo, Zn, Pb, Ag) deposits and widespread magmatic rocks (intrusions, volcanic-subvolcanic rocks) in the Late Mesozoic. The

Ningwu ore district is one of the most important ore districts composed of more than 30 magnetite-apatite deposits, which are known as porphyry iron deposits in China (Fig. 2). There are extensive magmatic rocks comprising volcanic-subvolcanic rocks and granodioritic rocks in the Ningwu ore district. The ages of these igneous rocks and associated metallogenic system have been the major concern among geologists. In the past 10 years, the precise SHRIMP zircon U-Pb, LA-ICP-MS zircon U-Pb and mica Ar-Ar methods were applied to the determination of timing of magmatism and mineralization. Formation ages of four volcanic eruption cycles in the Ningwu ore district were dated at 134.8–126.6 Ma (Zhang

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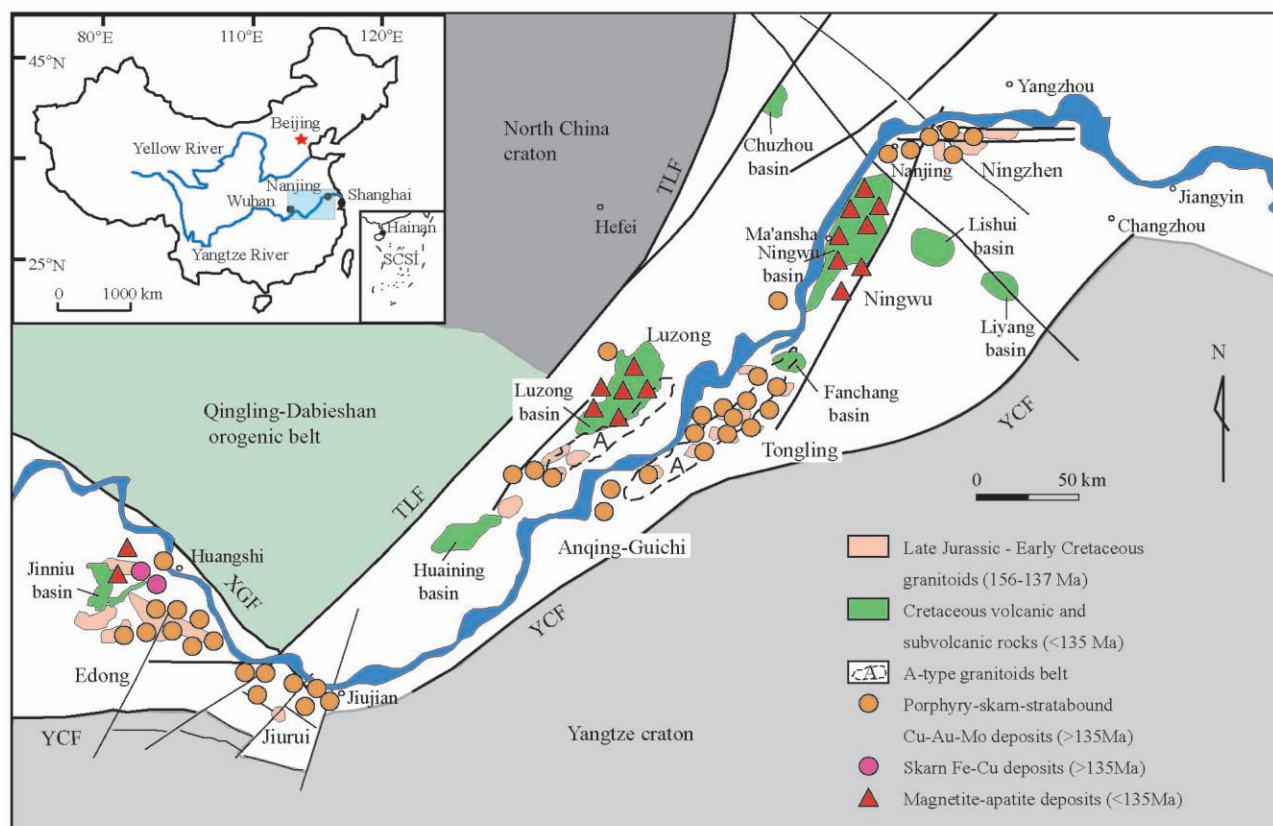


Fig. 1. Geological map of the Middle-Lower Yangtze River polymetallic ore belt, showing the locations of porphyry-skarn-stratabound Cu-Au-Mo-Fe (>135 Ma) and magnetite-apatite deposits (<135 Ma), related granitoids and Cretaceous basins (after Mao et al., 2011). TLF, Tancheng-Lujiang fault; XGF, Xiangfan-Guangji fault; YCF, Yangxing-Changzhou fault.

et al., 2003; Hou and Yuan, 2010; Zhou et al., 2011), and ages of subvolcanic rocks (diorite porphyrite), which are the main wall rock and considered to be related to porphyry iron deposits, were measured at 131.1–128.2 Ma (Fan et al., 2010; Hou and Yuan, 2010; Xue et al., 2010), whereas the range of iron mineralization ages is very broad, 122.9–134.9 Ma (Yu and Mao, 2004; Ma et al., 2006, 2010; Yuan et al., 2010). The ages of iron mineralization throughout the whole period of volcanic activity have been obtained in previous studies, but whether the mineralization continued throughout the whole volcanic period, i.e. all the four volcanic formations, has not been revealed yet.

There are two types of magmatic rocks occurring in iron deposit areas. One is dioritic rocks, which are ore hosted rocks and closely related to iron mineralization, and the other is granodioritic rocks, which occur as stocks and cut ore bodies. To constrain the timing of iron mineralization and better understand the magmatism and iron mineralization, we performed in situ zircon U-Pb and Hf isotopic analyses based on detailed field investigation for granodioritic stocks in the Washan, Nanshan, Dongshan and Heshangqiao iron mines in the middle of the Ningwu ore district.

## 2 Regional Geological Setting and Geology of Mineral Deposits

The MLYRB, featuring widespread porphyry iron deposits, lies on the northern margin of the Yangtze craton and south of the southeastern margin of the North China craton and the Qinling-Dabie Shan orogenic belt. The Ningwu ore district in the Ningwu volcanic basin is situated in the eastern part of the MLYRB (Fig. 1). It extends from Nanjing (Jiangsu Province) in the northeast to Wuhu (Anhui Province) in the southwest, about 60 km long and 20 km wide with a total area of 1200 km<sup>2</sup> (Fig. 2). The ore district is bounded by the (NNE-striking) Yangtze fault, (NNE-striking) Fangshan-Xiaodanyang fault, (NW-striking) Nanjing-Hushu fault and (E-W-striking) Wuhu fault, and is regarded as an NNE-trending inherited fault-controlled basin (Zhai et al., 1992b).

The Ningwu ore district is characterized by extensive well-developed volcanic-subvolcanic rocks and associated magnetite-apatite deposits, which are considered to be porphyry iron deposits (NRG, 1978). The stratigraphic sequence outcropped in the Ningwu ore district is composed of carbonate, silty and clastic rocks of the Middle-Upper Triassic Qinglong, Zhouchongcun and Huangmaqing



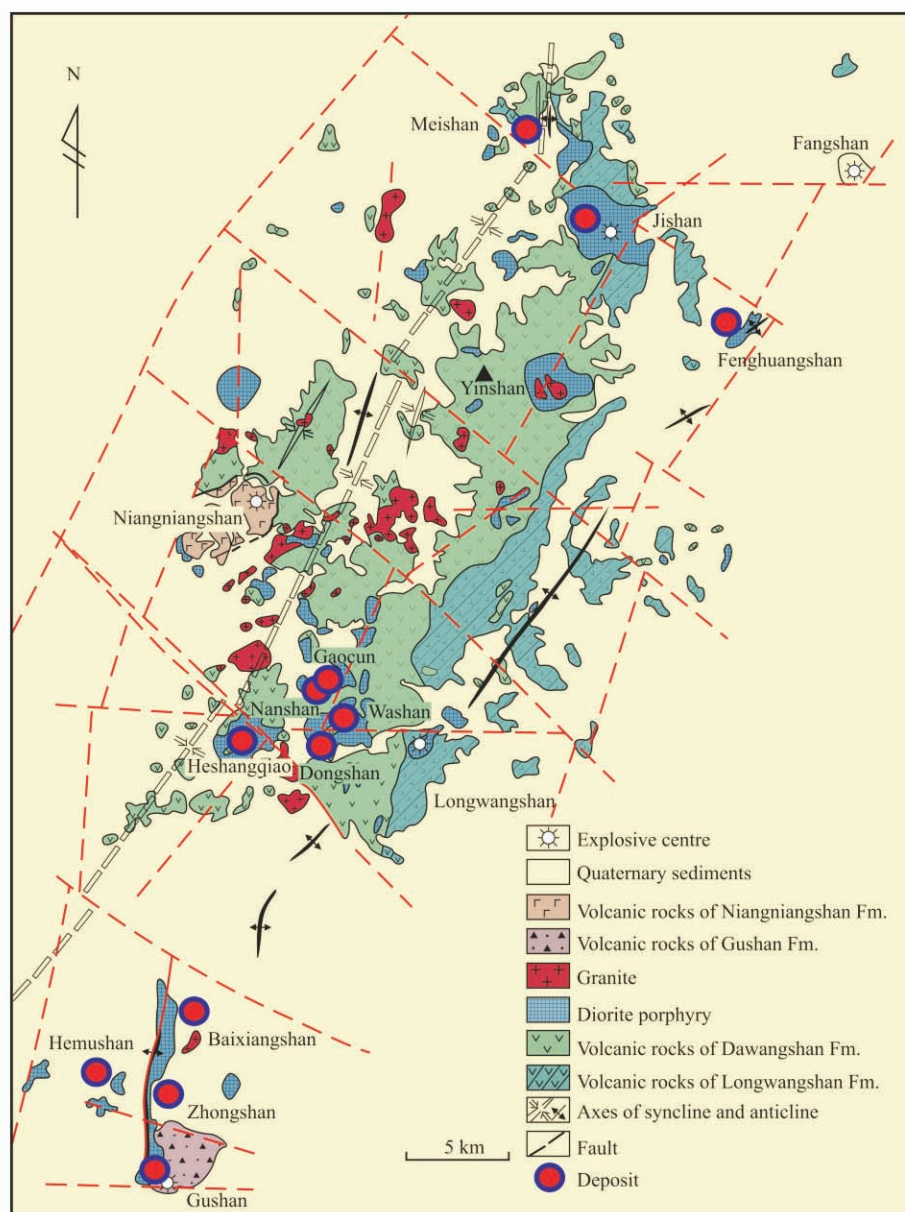


Fig. 2. Geological map showing the distribution of iron deposits of Ningwu ore district (after NRG, 1978).

Formations, and volcanic rock series of the Middle Jurassic Xiangshan and Xihengshan Formations and the Early Cretaceous. At the Late Cretaceous, volcanic rocks were covered by the Pukou and Chishan Formations and Tertiary sedimentary rocks (NRG, 1978; IGCAS, 1987).

Cretaceous volcanic-subvolcanic rocks in the ore district can be divided into four volcanic eruptive-accumulative cycles, i.e. the Longwangshan Formation, the Dawangshan Formation, the Gushan Formation and the Niangniangshan Formation from the bottom up (NRG, 1978) (Fig. 3). Each Formation started with explosive volcanic activity followed by more effusive eruptions, and ended with volcanic sedimentation. The Longwangshan Formation is mainly distributed in the eastern and northern

parts of the basin, covering about 20% of the total area. It consists of sedimentary tuff, silty mudstone and volcanic agglomerate in the lower part, while gibelite, shoshonite and basaltic latite in the upper part. The Dawangshan Formation is the main part of the volcanic rocks, occupying about 75% of the total area. It consists mainly of augite, basaltic latite in the lower part, purple andesite in the middle part, and trachyte and trachytic flood tuff in the upper part. The Gushan and Niangniangshan Formations cover about 5% of the total area, with the former occurring in the south and north parts of the ore district, and composed mainly of andesite, dacite and volcanic breccia, where the latter just occurring near Niangniangshan Mountain in the west, and composed

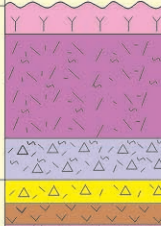
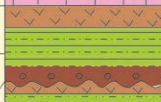
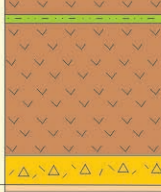
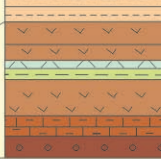
| Formation      |       | Thickness (m) | Lithologic column                                                                  | Age (Ma)          |                  |                    |
|----------------|-------|---------------|------------------------------------------------------------------------------------|-------------------|------------------|--------------------|
| Niangniangshan | Upper | 652           |   | 126.6±1.1         |                  |                    |
|                | Lower | 230           |                                                                                    |                   |                  |                    |
| Gushan         | Upper | 185           |   | 129.5±0.8         | 128.2±1.3        |                    |
|                | Lower | 102           |                                                                                    |                   | 128.5±1.8        |                    |
| Dawangshan     | Upper | 883           |   | 132.2±1.6         | 130.3±0.9        | 127±3              |
|                | Lower | 144           |                                                                                    |                   |                  |                    |
| Long-wangshan  |       | 513           |  | 134.8±1.3         |                  | 131±4              |
| Reference      |       |               |                                                                                    | Zhou et al., 2011 | Hou et al., 2010 | Zhang et al., 2003 |

Fig. 3. Stratigraphic column of the Ningwu volcanic basin with the age of volcanic rocks (Modified after Zhou et al., 2011).

mainly of leucophonolite and hauynite phonolite. These four formations contact one another unconformably (Wang et al., 2001a). Subvolcanic rocks were formed in the late stage of each volcanic cycle and have similar components. The rocks are generally attributed to diorite porphyrite series, i.e. diorite porphyrite, gabbro diorite, gabbro diorite porphyrite, trachyandesitic porphyrite, and andesite porphyrite. Subvolcanic rocks occurring in the Dawangshan cycle is considered to have a close relationship with iron mineralization (NRG, 1978). At the late stage of volcanic activity, a number of granodioritic intrusions occurred in the central part of the area, mostly as small rock bodies (NRG, 1978).

The Ningwu ore district comprises three major orefields: the Meishan, Washan and Zhonggu orefields from north to south (Fig. 2). The Washan, Dongshan, Gaocun (Taocun)-Nanshan, Heshangqiao, Meishan, and Gushan iron deposits are the representatives in these orefields. Mineralization is mostly developed at the apical part of subvolcanic plutons or the surrounding volcanic rocks to form disseminated, massive, breccia, stockwork and hydrothermal vein ore. The ore minerals include chiefly magnetite, hematite, rare pyrite and chalcopyrite, while the major gangue minerals are apatite, albite,

diopside, actinolite, epidote, chlorite and sericite. Hydrothermal alteration is commonly extensive and is characterized by three distinguished alteration zones in space from bottom upwards: 1) alkaline alteration zone, a light colour zone, comprising albite and diopside; 2) dark alteration zone consisting of diopside, actinolite, epidote and chlorite; 3) leucocratic alteration zone made up of quartz, pyrite, hematite, kaolinite, anhydrite and carbonate. Ore bodies mostly occur in secondary alteration zones.

### 3 Sampling and Analytical Methods

#### 3.1 Sampling and petrology

The samples for dating were collected from four intrusions occurred cutting across the ore bodies in the Washan, the Nanshan, the Dongshan, and the Heshangqiao deposits, respectively. The detailed location and description of samples are listed as follows.

The Washan deposit, characterized by the breccia ore and the hydrothermal vein-type ore, is a large-sized typical porphyry iron deposit. Sample WS-92 was collected from the granodiorite porphyry stock at north of 2# line, -90m in the mine. The stock is very thin with width of about



15m which cut across the western end of the ore body (Fig. 4a). The granodiorite porphyry is characterized by a porphyritic texture with phenocrysts of plagioclase (~30%), quartz (~5%), hornblende and biotite. Pyrite is rare.

The Nanshan deposit, characterized by the disseminated ore and the hydrothermal vein-type ore, is a large-sized iron deposit, 2 km to the north of the Washan deposit. Sample NS-6 was collected from the granodiorite porphyry stock. The stock is thin with width of about 10m, and occurred crossing the north end of the ore body in the Nanshan deposit (Fig. 4b). The rock sample is light meat red with porphyritic structure. Phenocryst is content of plagioclase (~60%), K-Na feldspar (>10%), quartz (15–20%) and hornblende (~5%). Microcrystalline matrixes are mainly plagioclase and quartz. Pyritization frequently occurred.

The Dongshan deposit is a medium-sized iron deposit with high ore grade, and is characterized by the stockwork ore and the hydrothermal vein ore. Sample DSC-11 was collected from the granodiorite porphyry stock at middle

of 3# line, -107m in the mine (Fig. 4c). The stock cut across the eastern end of the ore body. It is composed of plagioclase (~25%), albite (~20%), quartz (~5%), hornblende and biotite as phenocrysts, and microcrystalline feldspar and quartz as interstitial matrix.

The Heshangqiao deposit is a large-sized iron deposit started mining recently. The granodiorite porphyry was destructive to the diorite porphyrite which was development of disseminated magnetite (Fig. 4d). Sample HSQ-6 was collected from the drill core of ZKT3908 at -265 m. The granodiorite porphyry is composed of plagioclase (~50%), K-Na feldspar (20–35%), quartz (~15%), and minor hornblende (<3%) and biotite (<5%), with a little chloritization but magnetite mineralization.

### 3.2 Analytical methods

The samples were first crushed. Then, individual zircons were separated using conventional heavy liquid and magnetic techniques. Representative grains were handpicked under a binocular microscope, mounted in epoxy resin discs, and then polished. Zircons were

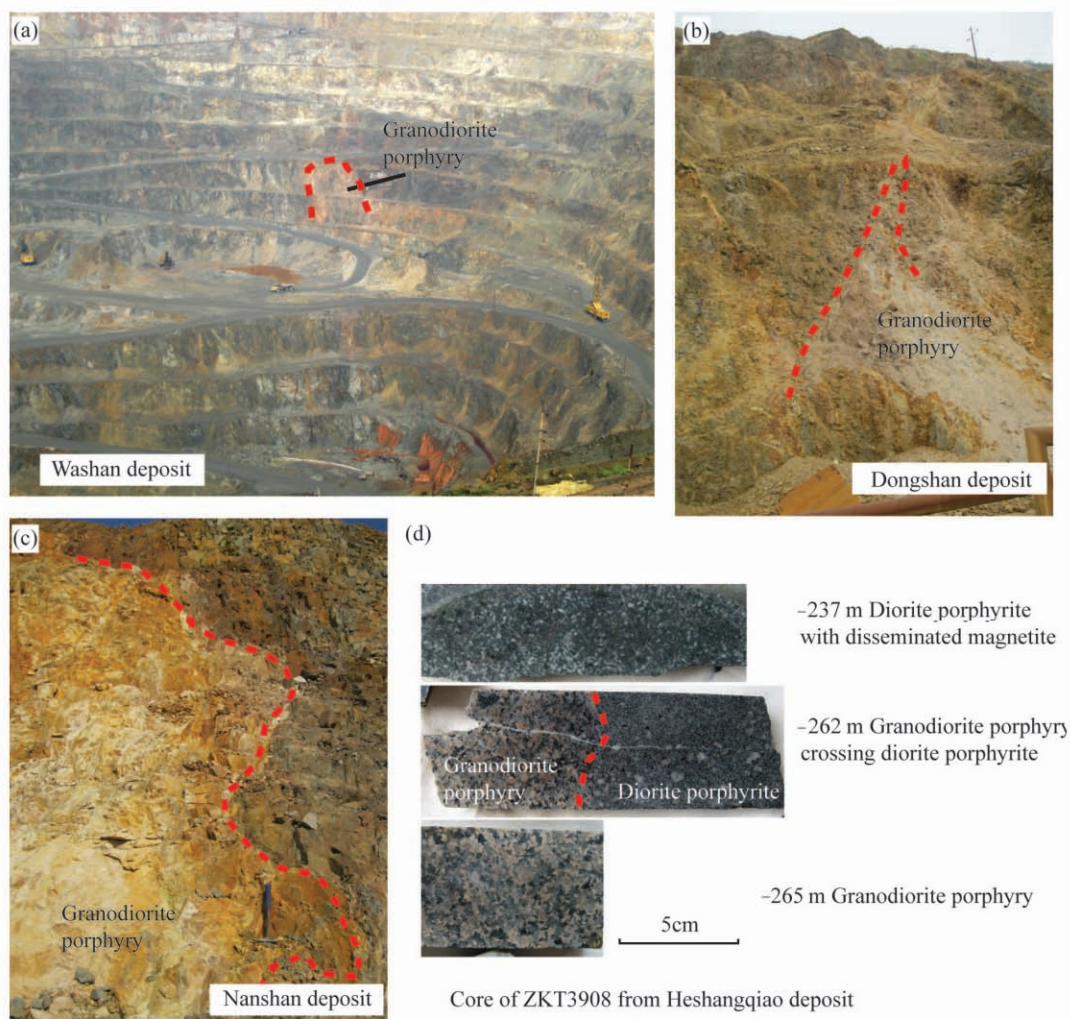


Fig. 4. Positions of sampling.

examined under transmitted and reflected lights, and then imaged by cathode-luminescence (CL) which was obtained using a HITACHI S3000-N microprobe in Institute of Geology, Chinese Academy of Geological Sciences (IGCAS). The zircons, which were euhedral or subhedral, with striped absorption and clear oscillatory zoning rims, were selected for U-Pb and Hf isotope dating.

### Zircon U-Pb dating

U-Pb dating analyses were conducted by LA-MC-ICP-MS at the Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing. Detailed operating conditions for the laser ablation system and the MC-ICP-MS instrument and data reduction are the same as description by Hou et al. (2009). Laser sampling was performed using a Newwave UP 213 laser ablation system. A Thermo Finnigan Neptune MC-ICP-MS instrument was used to acquire ion-signal intensities. The array of four multi-ion-counters and three faraday cups allow for simultaneous detection of  $^{202}\text{Hg}$ (on IC5),  $^{204}\text{Hg}$ ,  $^{204}\text{Pb}$ (on IC4),  $^{206}\text{Pb}$ (on IC3),  $^{207}\text{Pb}$ (on IC2),  $^{208}\text{Pb}$ (on L4),  $^{232}\text{Th}$ (on H2),  $^{238}\text{U}$ (on H4) ion signals. Helium was applied as a carrier gas. Argon was used as the make-up gas and mixed with the carrier gas via a T-connector before entering the ICP. Each analysis incorporated a background acquisition of approximately 20–30 s (gas blank) followed by 30 s data acquisition from the sample. Off-line raw data selection and integration of background and analytical signals, and time-drift correction and quantitative calibration for U-Pb dating was performed by ICPMSDataCal (Liu et al., 2008). Zircon GJ-1 was used as external standard for U-Pb dating, and was analyzed twice every 5–10 analyses. Time-dependent drifts of U-Th-Pb isotopic ratios were corrected using a linear interpolation (with time) for every 5–10 analyses according to the variations of GJ-1 (i.e., 2 zircons GJ-1 + 5–10 samples + 2 zircons GJ-1) (Liu et al., 2008). Preferred U-Th-Pb isotopic ratios used for GJ-1 are from Jackson et al. (2004). The GJ-1 standard zircon has a crystallization age of  $608.5 \pm 0.4$  Ma, and there is no apparent banding visible in the zircon, which argues for a homo-geneous standard for in-situ analyses (Jackson et al. 2004). Uncertainty of preferred values for the external standard GJ-1 was propagated to the ultimate results of the samples. In all analyzed zircon grains the common Pb correction was not necessary due to the low signal of common  $^{204}\text{Pb}$  and high  $^{206}\text{Pb}/^{204}\text{Pb}$ . U, Th and Pb concentration was calibrated by zircon M-127 (with U: 923 ppm; Th: 439 ppm; Th/U: 0.475. Nasdala et al., 2008). Concordia diagrams and weighted mean calculations were made using Isoplot/Ex\_ver3. The zircon Plesovice is dated as unknown samples and yielded weighted mean

$^{206}\text{Pb}/^{238}\text{U}$  age of  $337.2 \pm 1.7$  Ma ( $2\sigma$ ,  $n=8$ ), which is in good agreement with the recommended  $^{206}\text{Pb}/^{238}\text{U}$  age of  $337.13 \pm 0.37$  Ma ( $2\sigma$ ) (Sláma et al., 2008).

### In situ zircon Hf isotopic analysis

The zircon Hf analyses of four samples (WS-92, DSC-11, HSQ-5 and NS-6) were done on the same grains as used for U-Pb dating. Zircon Hf isotope analysis was carried out in-situ using a Newwave UP 213 laser-ablation microprobe, attached to a Neptune multi-collector ICP-MS at MRL Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing. Instrumental conditions and data acquisition were comprehensively described by Hou et al. (2007) and Wu et al. (2006). A stationary spot was used for the present analyses, with a beam diameter of 55  $\mu\text{m}$  depending on the size of ablated domains. Helium was used as carrier gas to transport the ablated sample from the laser-ablation cell to the ICP-MS torch via a mixing chamber mixed with Argon. In order to correct the isobaric interferences of  $^{176}\text{Lu}$  and  $^{176}\text{Yb}$  on  $^{176}\text{Hf}$ ,  $^{176}\text{Lu}/^{175}\text{Lu} = 0.02658$  and  $^{176}\text{Yb}/^{173}\text{Yb} = 0.796218$  ratios were determined (Chu et al., 2002). For instrumental mass bias correction Yb isotope ratios were normalized to  $^{172}\text{Yb}/^{173}\text{Yb}$  of 1.35274 (Chu et al., 2002) and Hf isotope ratios to  $^{179}\text{Hf}/^{177}\text{Hf}$  of 0.7325 using an exponential law. The mass bias behavior of Lu was assumed to follow that of Yb, mass bias correction protocols details was described as Wu et al. (2006) and Hou et al. (2007). Zircon GJ-1 was used as the reference standard during our routine analyses, with a weighted mean  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio of  $0.282005 \pm 0.000016$  ( $2\sigma$ ,  $n=16$ ). It is not distinguishable from a weighted mean  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio of  $0.282000 \pm 0.000005$  ( $2\sigma$ ) using a solution analysis method by Morel et al. (2008).

## 4 Result

### 4.1 Zircon U-Pb ages

Zircons in the granodiorite porphyry (WS-92) at the Washan iron deposit with 100–150  $\mu\text{m}$  long and 50–100  $\mu\text{m}$  wide, are dominantly euhedral, prismatic, colorless with oscillatory zoning, showed in CL images (Fig. 5). Uranium and thorium concentrations range from 74.4 to 375.6 ppm, and from 74.3 to 284.6 ppm, respectively. Corresponding Th/U ratios are relatively high with ranging from 0.6 to 1.0, indicating their magmatic origin (Belousova et al., 2002; Hoskin and Black, 2000; Wang et al., 2011). 19 analyses of these zircons from the sample WS-92 were obtained and the LA-MC-ICP-MS U-Pb data of these zircons are summarized in Table 1. Of these 19 analyses yielded a weighted average age of  $126.1 \pm 0.5$  Ma



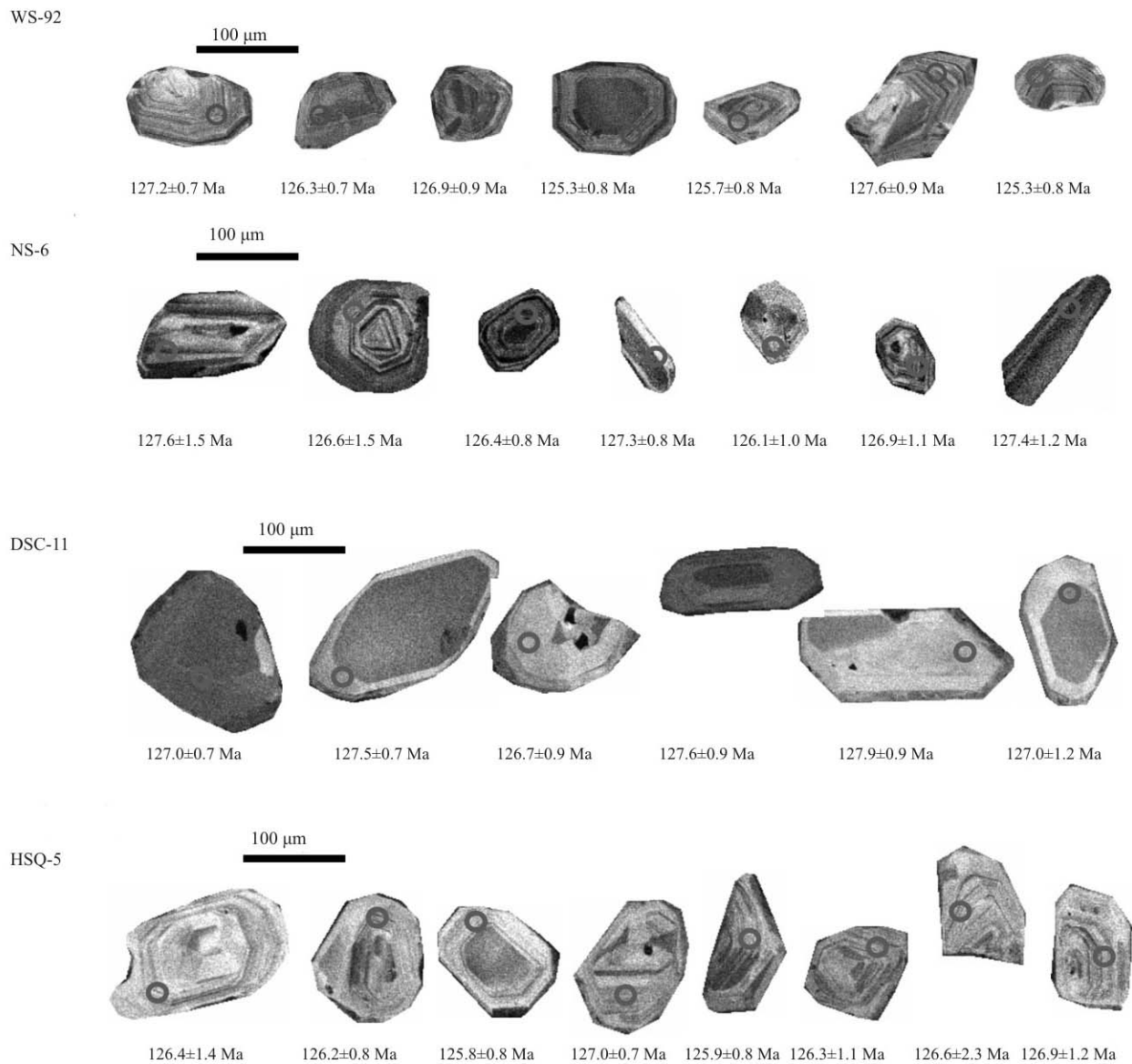


Fig. 5. Representative Cathodoluminescence (CL) images of zircons for intrusions with data of zircon U-Pb ages. The circles represent locations of zircon U-Pb and Hf isotopic analyses.

( $n=19$ , MSWD=1.7) (Fig. 6). This age is interpreted as the emplacement age of granodiorite porphyry at the Washan deposit.

Zircons in the granodiorite porphyry (NS-6) at the Nanshan iron deposit are 100–180 μm long and 50–100 μm wide, and are dominantly euhedral, prismatic, and colorless with oscillatory zoning (Fig. 5). Uranium and thorium concentrations range from 63.3 to 276.9 ppm, and from 61.1 to 273.2 ppm, respectively. Corresponding Th/U ratios are relatively high with ranging from 0.6 to 1.3 (Table 1). These indicate a magmatic genesis for the zircons (Belousova et al., 2002; Hoskin and Black, 2000; Wang et al., 2011). 19 analyses of these zircons from the sample NS-6 were obtained and the LA-MC-ICP-MS U-Pb data of these zircons are summarized in Table 1. Of these 19 analyses yielded a weighted average age of

126.8±0.5 Ma ( $n=19$ , MSWD=0.8) (Fig. 6). This age is interpreted to be the emplacement age of granodiorite porphyry at the Nanshan deposit.

Zircons in the granodiorite porphyry (DSC-11) at the Dongshan iron deposit are 120–250 μm long and 80–130 μm wide, and are dominantly euhedral, prismatic, and colorless with oscillatory zoning (Fig. 5). Uranium and thorium concentrations range from 26.3 to 160.2 ppm, and from 19.1 to 160.3 ppm, respectively. Corresponding Th/U ratios are relatively high with ranging from 0.6 to 1.1 (Table 1). These indicate a magmatic origin for the zircons (Belousova et al., 2002; Hoskin and Black, 2000; Wang et al., 2011). 19 analyses of these zircons from sample DSC-11 were obtained and the LA-MC-ICP-MS U-Pb data of these zircons are summarized in Table 1. Of these 19 analyses yielded a weighted average age of 127.3±0.5 Ma

Table 1 LA-MC-ICP-MS zircon U-Pb age of the granodiorite porphyries

| Sample    | Th    | U     | Th/U | $^{206}\text{Pb}/^{238}\text{U}$ |           |       | $^{207}\text{Pb}/^{206}\text{Pb}$ |           |         | $^{207}\text{Pb}/^{235}\text{U}$ |           |         |
|-----------|-------|-------|------|----------------------------------|-----------|-------|-----------------------------------|-----------|---------|----------------------------------|-----------|---------|
|           |       |       |      | age (Ma)                         | $1\sigma$ |       | age (Ma)                          | $1\sigma$ |         | age (Ma)                         | $1\sigma$ |         |
| WS-92     |       |       |      |                                  |           |       |                                   |           |         |                                  |           |         |
| WS-92-01  | 74.3  | 74.4  | 1.00 | 127.8                            | 1.0       | 83.4  | 32.4                              | 2.2       | 0.02002 | 125.9                            | 0.00016   | 0.04768 |
| WS-92-02  | 111.2 | 145.8 | 0.76 | 126.5                            | 0.9       | 168.6 | 24.1                              | 1.6       | 0.01982 | 128.8                            | 0.00014   | 0.04946 |
| WS-92-03  | 111.6 | 171.8 | 0.65 | 124.6                            | 0.7       | 87.1  | 30.6                              | 1.2       | 0.01952 | 122.6                            | 0.00012   | 0.04776 |
| WS-92-04  | 165.7 | 195.3 | 0.85 | 127.6                            | 0.8       | 235.3 | 63.9                              | 4.0       | 0.01998 | 134.0                            | 0.00013   | 0.05085 |
| WS-92-05  | 131.6 | 185.9 | 0.71 | 125.7                            | 0.8       | 127.9 | 24.1                              | 1.4       | 0.01969 | 125.8                            | 0.00013   | 0.04862 |
| WS-92-06  | 146.0 | 217.1 | 0.67 | 125.0                            | 0.9       | 183.4 | 23.1                              | 1.2       | 0.01959 | 128.1                            | 0.00014   | 0.04977 |
| WS-92-07  | 284.6 | 347.6 | 0.82 | 124.8                            | 0.9       | 168.6 | 25.9                              | 1.7       | 0.01955 | 127.2                            | 0.00014   | 0.04943 |
| WS-92-08  | 177.5 | 290.1 | 0.61 | 125.3                            | 0.8       | 187.1 | 43.5                              | 2.6       | 0.01963 | 128.8                            | 0.00012   | 0.04982 |
| WS-92-09  | 271.0 | 342.5 | 0.79 | 126.9                            | 0.9       | 176.0 | 24.1                              | 1.5       | 0.01988 | 129.4                            | 0.00014   | 0.04958 |
| WS-92-10  | 142.5 | 249.6 | 0.57 | 124.6                            | 0.9       | 166.8 | 27.8                              | 1.8       | 0.01952 | 126.4                            | 0.00015   | 0.04924 |
| WS-92-11  | 164.9 | 251.5 | 0.66 | 127.4                            | 0.8       | 183.4 | 14.8                              | 1.1       | 0.01996 | 130.2                            | 0.00013   | 0.04976 |
| WS-92-12  | 140.0 | 204.8 | 0.68 | 127.2                            | 0.7       | 209.3 | 33.3                              | 2.0       | 0.01993 | 131.5                            | 0.00012   | 0.05032 |
| WS-92-13  | 116.6 | 203.2 | 0.57 | 126.6                            | 0.7       | 209.3 | 18.5                              | 1.2       | 0.01983 | 130.9                            | 0.00010   | 0.05031 |
| WS-92-14  | 138.7 | 202.3 | 0.69 | 126.3                            | 0.7       | 168.6 | 20.4                              | 1.3       | 0.01979 | 128.4                            | 0.00011   | 0.04941 |
| WS-92-15  | 132.4 | 231.1 | 0.57 | 126.6                            | 0.9       | 239.0 | 52.8                              | 3.8       | 0.01984 | 133.1                            | 0.00014   | 0.05094 |
| WS-92-16  | 143.4 | 180.4 | 0.79 | 125.3                            | 0.8       | 72.3  | 31.5                              | 1.6       | 0.01962 | 122.6                            | 0.00012   | 0.04745 |
| WS-92-17  | 133.0 | 142.8 | 0.93 | 125.3                            | 1.0       | 109.4 | 52.8                              | 2.8       | 0.01963 | 124.9                            | 0.00016   | 0.04823 |
| WS-92-18  | 157.5 | 240.2 | 0.66 | 125.1                            | 0.7       | 161.2 | 14.8                              | 1.0       | 0.01960 | 127.0                            | 0.00011   | 0.04928 |
| WS-92-19  | 276.8 | 375.6 | 0.74 | 127.6                            | 0.9       | 220.4 | 14.8                              | 1.2       | 0.01999 | 132.6                            | 0.00015   | 0.05058 |
| NS-6      |       |       |      |                                  |           |       |                                   |           |         |                                  |           |         |
| NS-6-2    | 224.6 | 207.3 | 1.08 | 127.6                            | 1.5       | 166.8 | 77.8                              | 5.3       | 0.01999 | 130.0                            | 0.00024   | 0.04920 |
| NS-6-3    | 136.8 | 216.2 | 0.63 | 126.6                            | 1.5       | 64.9  | 59.3                              | 3.4       | 0.01984 | 123.7                            | 0.00024   | 0.04732 |
| NS-6-4    | 96.3  | 163.0 | 0.59 | 126.8                            | 1.2       | 150.1 | 70.4                              | 4.3       | 0.01987 | 128.7                            | 0.00020   | 0.04908 |
| NS-6-5    | 64.0  | 86.0  | 0.74 | 126.1                            | 0.9       | 116.8 | 75.9                              | 5.0       | 0.01976 | 126.3                            | 0.00015   | 0.04836 |
| NS-6-6    | 185.0 | 270.2 | 0.68 | 126.4                            | 0.8       | 400.1 | -366.6                            | 1.2       | 0.01980 | 120.3                            | 0.00012   | 0.04612 |
| NS-6-7    | 67.0  | 91.6  | 0.73 | 127.6                            | 0.9       | 101.9 | 85.2                              | 6.2       | 0.01999 | 127.7                            | 0.00014   | 0.04807 |
| NS-6-8    | 88.7  | 122.3 | 0.73 | 125.9                            | 1.3       | 50.1  | 55.6                              | 4.4       | 0.01972 | 123.7                            | 0.00020   | 0.04703 |
| NS-6-9    | 61.6  | 76.0  | 0.81 | 125.7                            | 0.8       | 127.9 | 44.4                              | 2.6       | 0.01969 | 125.9                            | 0.00013   | 0.04859 |
| NS-6-10   | 72.7  | 91.4  | 0.79 | 126.1                            | 1.0       | 87.1  | 100.0                             | 8.0       | 0.01975 | 127.3                            | 0.00016   | 0.04776 |
| NS-6-11   | 273.2 | 211.9 | 1.29 | 126.1                            | 1.2       | 150.1 | 70.4                              | 4.9       | 0.01975 | 129.1                            | 0.00018   | 0.04908 |
| NS-6-12   | 157.4 | 172.5 | 0.91 | 125.6                            | 1.0       | 122.3 | 27.8                              | 2.3       | 0.01967 | 125.6                            | 0.00016   | 0.04832 |
| NS-6-13   | 161.0 | 276.9 | 0.58 | 126.9                            | 1.1       | 127.9 | 34.3                              | 2.5       | 0.01987 | 127.7                            | 0.00017   | 0.04862 |
| NS-6-14   | 119.4 | 148.7 | 0.80 | 128.0                            | 0.8       | 105.6 | 83.3                              | 5.9       | 0.02005 | 128.5                            | 0.00013   | 0.04814 |
| NS-6-15   | 70.6  | 107.0 | 0.66 | 126.1                            | 0.9       | 146.4 | 77.8                              | 3.6       | 0.01975 | 126.8                            | 0.00014   | 0.04897 |
| NS-6-16   | 147.9 | 210.9 | 0.70 | 128.6                            | 1.2       | 79.7  | 61.1                              | 4.7       | 0.02015 | 128.7                            | 0.00019   | 0.04760 |
| NS-6-17   | 252.7 | 200.1 | 1.26 | 127.3                            | 0.8       | 150.1 | 36.1                              | 1.9       | 0.01994 | 128.5                            | 0.00013   | 0.04904 |
| NS-6-18   | 61.1  | 63.3  | 0.97 | 126.5                            | 1.3       | 200.1 | 55.6                              | 5.7       | 0.01982 | 129.1                            | 0.00020   | 0.04871 |
| NS-6-19   | 82.7  | 89.8  | 0.92 | 127.8                            | 0.9       | 166.8 | 82.4                              | 5.2       | 0.02002 | 129.7                            | 0.00014   | 0.04919 |
| NS-6-20   | 130.6 | 118.1 | 1.11 | 127.4                            | 1.2       | 164.9 | 64.8                              | 4.5       | 0.01997 | 130.8                            | 0.00018   | 0.04936 |
| DSC-11    |       |       |      |                                  |           |       |                                   |           |         |                                  |           |         |
| DSC-11-1  | 41.0  | 53.0  | 0.77 | 126.9                            | 0.9       | 120.5 | 66.7                              | 4.1       | 0.01988 | 126.9                            | 0.00014   | 0.04847 |
| DSC-11-2  | 19.1  | 26.3  | 0.73 | 127.4                            | 1.7       | 13.1  | 137.0                             | 14.4      | 0.01996 | 128.9                            | 0.00027   | 0.04633 |
| DSC-11-3  | 33.7  | 45.0  | 0.75 | 127.5                            | 2.9       | 298.2 | 159.2                             | 5.5       | 0.01998 | 128.8                            | 0.00046   | 0.05227 |
| DSC-11-4  | 37.4  | 50.5  | 0.74 | 127.4                            | 0.9       | 200.1 | 77.8                              | 4.0       | 0.01995 | 127.5                            | 0.00014   | 0.04872 |
| DSC-11-5  | 160.3 | 160.2 | 1.00 | 127.0                            | 0.7       | 101.9 | 62.0                              | 4.0       | 0.01989 | 126.5                            | 0.00011   | 0.04804 |
| DSC-11-6  | 65.5  | 78.8  | 0.83 | 127.5                            | 0.7       | 127.9 | 38.9                              | 1.9       | 0.01997 | 127.0                            | 0.00012   | 0.04856 |
| DSC-11-7  | 29.5  | 45.9  | 0.64 | 127.8                            | 1.3       | 211.2 | 66.7                              | 3.3       | 0.02002 | 131.5                            | 0.00021   | 0.05020 |
| DSC-11-8  | 29.1  | 46.2  | 0.63 | 128.3                            | 1.2       | 139.0 | 65.7                              | 3.6       | 0.02010 | 128.6                            | 0.00019   | 0.04885 |
| DSC-11-9  | 53.0  | 62.5  | 0.85 | 128.1                            | 1.2       | 200.1 | 73.1                              | 3.6       | 0.02008 | 128.2                            | 0.00019   | 0.04872 |
| DSC-11-10 | 25.9  | 42.8  | 0.60 | 127.5                            | 1.1       | 142.7 | 53.7                              | 2.7       | 0.01998 | 127.9                            | 0.00017   | 0.04886 |
| DSC-11-11 | 46.4  | 51.4  | 0.90 | 126.7                            | 0.9       | 127.9 | 66.7                              | 3.7       | 0.01985 | 126.6                            | 0.00015   | 0.04862 |
| DSC-11-12 | 55.5  | 54.2  | 1.02 | 127.2                            | 1.0       | 124.2 | 84.2                              | 4.8       | 0.01993 | 127.3                            | 0.00015   | 0.04853 |
| DSC-11-13 | 71.0  | 72.2  | 0.98 | 127.9                            | 0.9       | 166.8 | 57.4                              | 2.9       | 0.02003 | 128.6                            | 0.00014   | 0.04918 |



Table 1 Continued

| Sample    | Th    | U     | Th/U | $^{206}\text{Pb}/^{238}\text{U}$ |            |       | $^{207}\text{Pb}/^{235}\text{U}$ |            |         | $^{206}\text{Pb}/^{238}\text{U}$ |            |         | $^{207}\text{Pb}/^{235}\text{U}$ |            |  | $^{207}\text{Pb}/^{206}\text{Pb}$ |            |  | $^{207}\text{Pb}/^{235}\text{U}$ |            |  |          |            |
|-----------|-------|-------|------|----------------------------------|------------|-------|----------------------------------|------------|---------|----------------------------------|------------|---------|----------------------------------|------------|--|-----------------------------------|------------|--|----------------------------------|------------|--|----------|------------|
|           |       |       |      | age (Ma)                         | 1 $\sigma$ |       | age (Ma)                         | 1 $\sigma$ |         | age (Ma)                         | 1 $\sigma$ |         | age (Ma)                         | 1 $\sigma$ |  | age (Ma)                          | 1 $\sigma$ |  | age (Ma)                         | 1 $\sigma$ |  | age (Ma) | 1 $\sigma$ |
| DSC-11-14 | 40.5  | 51.1  | 0.79 | 127.6                            | 0.9        | 142.7 | 130.0                            | 6.1        | 0.02000 | 0.00015                          | 0.04888    | 0.00169 | 0.13656                          | 0.00687    |  |                                   |            |  |                                  |            |  |          |            |
| DSC-11-16 | 29.4  | 33.8  | 0.87 | 127.0                            | 1.2        | 109.4 | 127.0                            | 6.4        | 0.01989 | 0.00019                          | 0.04823    | 0.00228 | 0.13318                          | 0.00716    |  |                                   |            |  |                                  |            |  |          |            |
| DSC-11-17 | 34.8  | 54.4  | 0.64 | 126.3                            | 0.9        | 79.7  | 124.0                            | 3.1        | 0.01979 | 0.00014                          | 0.04758    | 0.00113 | 0.12989                          | 0.00345    |  |                                   |            |  |                                  |            |  |          |            |
| DSC-11-18 | 37.5  | 34.4  | 1.09 | 126.9                            | 1.5        | 57.5  | 122.2                            | 5.7        | 0.01987 | 0.00023                          | 0.04719    | 0.00233 | 0.12788                          | 0.00633    |  |                                   |            |  |                                  |            |  |          |            |
| DSC-11-19 | 22.2  | 30.5  | 0.73 | 127.7                            | 1.0        | 231.6 | 132.8                            | 3.9        | 0.02001 | 0.00016                          | 0.05076    | 0.00152 | 0.13971                          | 0.00443    |  |                                   |            |  |                                  |            |  |          |            |
| DSC-11-20 | 48.4  | 66.3  | 0.73 | 128.6                            | 1.8        | 76.0  | 128.9                            | 7.2        | 0.02015 | 0.00029                          | 0.04754    | 0.00195 | 0.13534                          | 0.00801    |  |                                   |            |  |                                  |            |  |          |            |
| HSQ-5     |       |       |      |                                  |            |       |                                  |            |         |                                  |            |         |                                  |            |  |                                   |            |  |                                  |            |  |          |            |
| HSQ-5-1   | 97.3  | 132.6 | 0.73 | 126.4                            | 1.4        | 13.1  | 126.5                            | 11.8       | 0.01980 | 0.00022                          | 0.04631    | 0.00221 | 0.13268                          | 0.01316    |  |                                   |            |  |                                  |            |  |          |            |
| HSQ-5-2   | 123.6 | 180.9 | 0.68 | 126.6                            | 1.0        | 20.5  | 121.4                            | 5.2        | 0.01983 | 0.00016                          | 0.04647    | 0.00064 | 0.12699                          | 0.00207    |  |                                   |            |  |                                  |            |  |          |            |
| HSQ-5-3   | 128.8 | 177.5 | 0.73 | 126.2                            | 0.8        | 20.5  | 122.3                            | 5.2        | 0.01977 | 0.00013                          | 0.04646    | 0.00155 | 0.12804                          | 0.00573    |  |                                   |            |  |                                  |            |  |          |            |
| HSQ-5-4   | 80.5  | 122.3 | 0.66 | 125.7                            | 0.9        | 20.5  | 121.3                            | 3.3        | 0.01969 | 0.00014                          | 0.04647    | 0.00098 | 0.12694                          | 0.00364    |  |                                   |            |  |                                  |            |  |          |            |
| HSQ-5-5   | 105.4 | 135.7 | 0.78 | 125.8                            | 0.8        | 101.9 | 125.6                            | 4.8        | 0.01971 | 0.00012                          | 0.04802    | 0.00153 | 0.13165                          | 0.00532    |  |                                   |            |  |                                  |            |  |          |            |
| HSQ-5-6   | 123.9 | 137.4 | 0.90 | 125.8                            | 0.8        | 77.9  | 123.3                            | 3.6        | 0.01971 | 0.00012                          | 0.04735    | 0.00114 | 0.12914                          | 0.00396    |  |                                   |            |  |                                  |            |  |          |            |
| HSQ-5-7   | 90.2  | 117.7 | 0.77 | 128.3                            | 1.0        | 5.7   | 123.7                            | 6.8        | 0.02010 | 0.00015                          | 0.04615    | 0.00189 | 0.12951                          | 0.00756    |  |                                   |            |  |                                  |            |  |          |            |
| HSQ-5-8   | 90.4  | 134.9 | 0.67 | 127.0                            | 0.7        | 87.1  | 125.7                            | 4.1        | 0.01989 | 0.00012                          | 0.04776    | 0.00137 | 0.13180                          | 0.00461    |  |                                   |            |  |                                  |            |  |          |            |
| HSQ-5-9   | 202.9 | 224.6 | 0.90 | 127.2                            | 0.7        | 400.1 | 121.3                            | 2.8        | 0.01993 | 0.00011                          | 0.04606    | 0.00095 | 0.12691                          | 0.00313    |  |                                   |            |  |                                  |            |  |          |            |
| HSQ-5-10  | 85.4  | 132.8 | 0.64 | 125.9                            | 0.8        | 101.9 | 124.6                            | 2.5        | 0.01973 | 0.00012                          | 0.04806    | 0.00097 | 0.13058                          | 0.00278    |  |                                   |            |  |                                  |            |  |          |            |
| HSQ-5-11  | 81.3  | 119.0 | 0.68 | 126.3                            | 1.1        | 116.8 | 127.5                            | 4.5        | 0.01979 | 0.00017                          | 0.04836    | 0.00129 | 0.13377                          | 0.00503    |  |                                   |            |  |                                  |            |  |          |            |
| HSQ-5-13  | 104.5 | 128.0 | 0.82 | 125.9                            | 0.9        | 120.5 | 125.9                            | 3.5        | 0.01972 | 0.00014                          | 0.04843    | 0.00123 | 0.13200                          | 0.00386    |  |                                   |            |  |                                  |            |  |          |            |
| HSQ-5-14  | 81.1  | 111.5 | 0.73 | 126.5                            | 1.3        | 100.1 | 131.6                            | 13.0       | 0.01982 | 0.00020                          | 0.04789    | 0.00235 | 0.13841                          | 0.01459    |  |                                   |            |  |                                  |            |  |          |            |
| HSQ-5-15  | 108.3 | 143.4 | 0.76 | 126.6                            | 2.3        | 16.8  | 126.8                            | 8.3        | 0.01983 | 0.00037                          | 0.04633    | 0.00145 | 0.13299                          | 0.00926    |  |                                   |            |  |                                  |            |  |          |            |
| HSQ-5-16  | 152.3 | 187.9 | 0.81 | 125.9                            | 1.5        | 122.3 | 128.7                            | 4.3        | 0.01972 | 0.00024                          | 0.04831    | 0.00092 | 0.13518                          | 0.00480    |  |                                   |            |  |                                  |            |  |          |            |
| HSQ-5-17  | 160.1 | 150.1 | 1.07 | 125.1                            | 0.7        | 25.9  | 119.0                            | 1.3        | 0.01959 | 0.00011                          | 0.04617    | 0.00050 | 0.12437                          | 0.00139    |  |                                   |            |  |                                  |            |  |          |            |
| HSQ-5-18  | 80.6  | 110.8 | 0.73 | 126.2                            | 0.9        | 16.8  | 120.6                            | 1.9        | 0.01977 | 0.00015                          | 0.04634    | 0.00069 | 0.12610                          | 0.00211    |  |                                   |            |  |                                  |            |  |          |            |
| HSQ-5-19  | 155.9 | 244.0 | 0.64 | 127.3                            | 1.1        | 76.0  | 126.0                            | 4.8        | 0.01994 | 0.00017                          | 0.04754    | 0.00136 | 0.13211                          | 0.00535    |  |                                   |            |  |                                  |            |  |          |            |
| HSQ-5-20  | 206.4 | 214.3 | 0.96 | 126.9                            | 1.2        | 79.7  | 125.0                            | 3.9        | 0.01988 | 0.00019                          | 0.04758    | 0.00124 | 0.13106                          | 0.00430    |  |                                   |            |  |                                  |            |  |          |            |

( $n=19$ , MSWD=0.3) (Fig. 6). This age is interpreted to be the emplacement age of granodiorite porphyry at the Dongshan deposit.

Zircons in the granite (HSQ-5) at the Heshangqiao iron deposit are 120–200  $\mu\text{m}$  long and 80–130  $\mu\text{m}$  wide, and are dominantly euhedral, prismatic, and colorless with oscillatory zoning (Fig. 5). Uranium and thorium concentrations range from 110.8 to 244.0 ppm, and from 80.5 to 206.4 ppm, respectively. Corresponding Th/U ratios are relatively high with ranging from 0.6 to 1.1 (Table 1). These indicate a magmatic origin for the zircons (Belousova et al., 2002; Hoskin and Black, 2000; Wang et al., 2011). 19 analyses of these zircons from sample HSQ-5 were obtained and the LA-MC-ICP-MS U-Pb data of these zircons are summarized in Table 1. Of these 19 analyses yielded a weighted average age of  $126.3\pm 0.4\text{Ma}$  ( $n=19$ , MSWD=0.7) (Fig. 6). This age is interpreted to be the emplacement age of granite at the Heshangqiao deposit.

#### 4.2 In situ zircon Hf isotope

The zircon grains used for U-Pb dating were large enough to be analyzed for Hf isotope compositions. As expected for zircons,  $^{176}\text{Lu}/^{177}\text{Hf}$  ratios of them are very low, ranging from 0.000485 to 0.003908 (mean value 0.001054). Thus, following the time of zircon crystallization, there was virtually not change in zircon  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios, but a relatively strong change in  $\varepsilon_{\text{Hf}}(t)$  values due to the increase in chondritic  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios over this period (Siebel and Chen, 2010). This is evident from the differences between the measured and initial  $^{176}\text{Hf}/^{177}\text{Hf}$  values for Late Mesozoic zircons (Table 2).

The zircon grains chosen from the four samples for Hf isotope analysis yield a narrow range of  $\varepsilon_{\text{Hf}}(t)$  value (−0.4 to −10.4) (Fig. 7). However, there are a little of data beyond of the range. Zircons from the granodiorite porphyry (WS-92) at the Washan mine were analyzed, giving the  $\varepsilon_{\text{Hf}}(t)$  value range from −2.2 to −6.8. Seventeen of nineteen Hf isotopic spot analyses were obtained for sample NS-6 from the Nanshan mine, yielding the most of  $\varepsilon_{\text{Hf}}(t)$  values between −0.4 to −7.8. The other two is 7.17 and 1.56. The sample from the Dongshan mine (DSC-11) yields the  $\varepsilon_{\text{Hf}}(t)$  value, whose range is −1.9 to −10.4. Most of zircon analysis data from sample of the Heshangqiao mine (HSQ-5) shows a similar  $\varepsilon_{\text{Hf}}(t)$  value range of −3.1 to −6.5 to WS-92, except one (−37.4). All spots have mainly  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios of 0.282401 to 0.282687, yielding two-stage Hf model ages of 1207 Ma to 1844 Ma with a mean age of 1493 Ma, except three grains with  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios of 0.282904, 0.282747 and 0.281637, and two-stage Hf model ages of 724 Ma, 1083 Ma and 3535 Ma respectively.

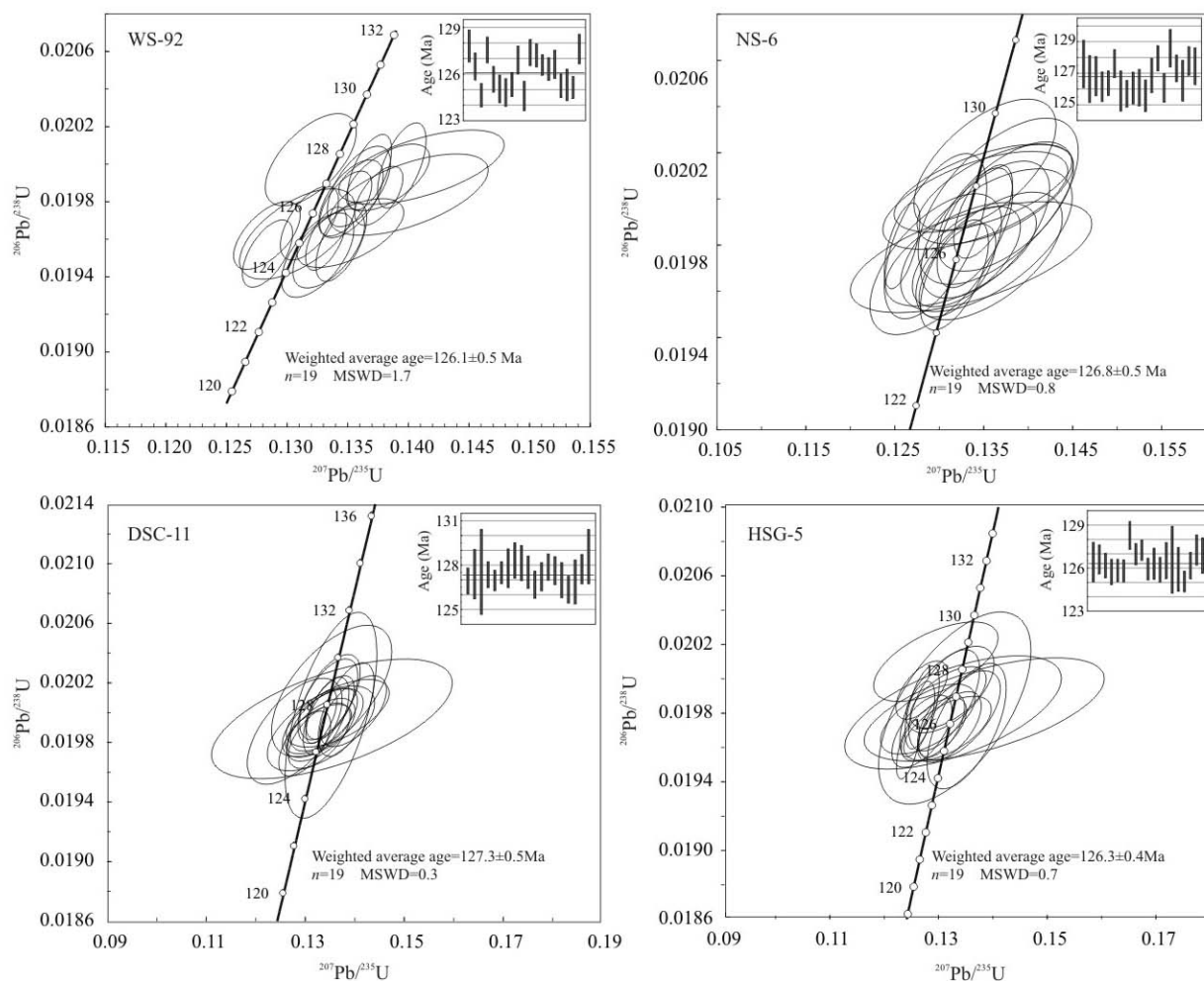


Fig. 6. LA-MC-ICP-MS zircon U-Pb concordia diagrams of intrusions.

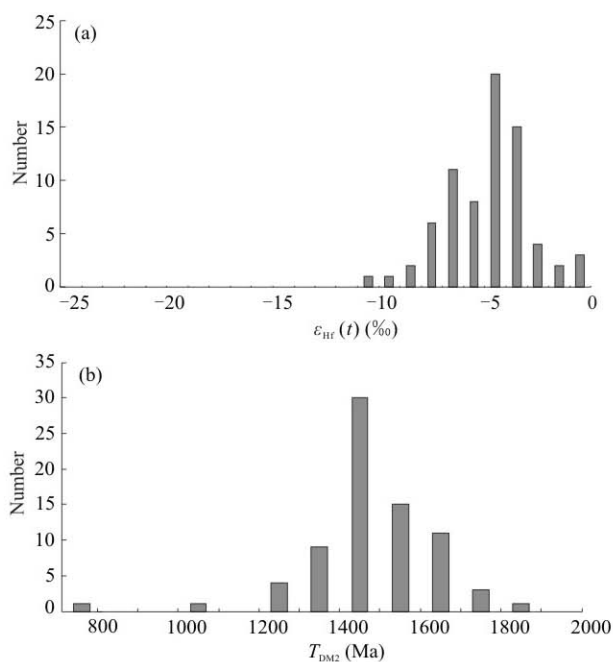


Fig. 7. Histogram of Zircon  $\epsilon_{\text{Hf}}(t)$  values (a) and two-stage model ages (b) of intrusions.

## 5 Discussion

### 5.1 Geochronology

The Ningwu volcanic basin is an important ore district in the MLYRB, endowed with numerous large iron deposits and some copper or/and gold deposits. Previous researches have indicated that subvolcanic rocks, especially diorite porphyrite, are associated with the iron deposits (NRG, 1978; Yu and Mao, 2002; Yu et al., 2007, 2008; Hou et al., 2010; Tu et al., 2010).

Timing of these magmatism and mineralization has long been an interesting topic and attracted great attention. In the 1970s and 1980s, the ages of those ore deposits and related granodioritic stocks were yielded by the traditional K-Ar and Rb-Sr isochron methods. The commonly accepted ages are 126.8–125.3 Ma for the Longwangshan Formation, 120.2–121.4 Ma for the Dawangshan Formation, 114.0–109.7 Ma for the Gushan Formation and 105.5–91.0 Ma for the Niangniangshan Formation. The ages of iron mineralization and subvolcanic rocks are 93.1–118.8 Ma and 120.1–125.1 Ma, respectively (NRG, 1978; IGCAS, 1987). These age data provide constraints



on the timing of these magmatism and mineralization in the study area.

In the past ten years, precise SHRIMP zircon U-Pb, LA-ICP-MS zircon U-Pb and Ar-Ar age dating have been applied to constraining the magmatism and mineralization, and a geochron frame of volcanic rocks has been found, as illustrated in Fig. 3. Geochronology of subvolcanic rocks (diorite porphyrite) associated with iron deposits (i.e. the host rock) has been systemically measured, and the age range is 131.1–128.2 Ma (Fan et al., 2010; Hou and Yuan, 2010; Xue et al., 2010). However, ages of magnetite-apatite deposits obtained show a wide geochronological range of 122.9–134.9 Ma. Yu and Mao (2004) gained an age of  $122.9 \pm 0.2$  Ma for the Meishan deposit and  $124.9 \pm 0.3$  Ma for the Gaocun (Taocun) deposit with albite Ar-Ar dating, and an age of  $126.7 \pm 0.2$  Ma for the Zhongjiu deposit with phlogopite Ar-Ar dating. Ma et al. (2010) obtained an age of 126–129 Ma for the Dongshan iron deposit with in situ Ar-Ar dating on actinolite. Yuan et al. (2010) obtained ages of  $134.9 \pm 1.1$  Ma,  $132.9 \pm 1.1$  Ma and  $>128$  Ma with Ar-Ar dating on phlogopite for the Baixiangshan, Hemushan and Gaocun (Taocun) iron deposits, respectively. However, whether the mineralization activity (134.9–122.9 Ma) continued throughout the whole volcanic period (134.8–126.6 Ma) has not been revealed yet.

Detailed field investigations conducted by the authors show that disseminated, massive, breccia, stockwork ore and hydrothermal vein ores of iron deposits occur in subvolcanic rocks or surrounding volcanic rocks (the Dawangshan Formation). And the breccia ore consists of a matrix of magnetite with actinolite and minor apatite, hosting diorite porphyrite fragments. The fragments are mostly poorly rounded with alteration in the rim. The above geological facts suggest that iron mineralization occurred later than the cooling of subvolcanic rocks, i.e. 131.1–128.2 Ma (Fan et al., 2010; Hou and Yuan, 2010; Xue et al., 2010). In the mining areas, minor granodioritic rocks occurring as rock stocks, cut across ore bodies without magnetite mineralization (Fig. 4). We collected such rock samples in the Washan, Nanshan, Dongshan and Heshangqiao iron deposits and obtained new zircon LA-MC-ICP-MS U-Pb ages of 127.3–126.1 Ma for granodioritic rocks, which also suggests the lower limit of the timing of mineralization, 127 Ma.

Compared with the ages of volcanic rocks from the four volcanic formations, the data obtained in this study are close to those of the Niangniangshan Formation or/and the Gushan Formation within the error ranges. However, the ages provided by different authors by means of different methods with different experimental errors are slightly different. As stated above, field evidence demonstrates

that the diorite porphyrite was formed in the late of Dawangshan Formation. In addition, the NRG (1978) suggested that rubbles of diorite porphyrite and the iron ore in the Gushan Formation in the Zhonggu orefield and Meishan mining area, and the iron mineralization should be earlier than the occurrence of the Gushan Formation. The data we obtained, which are consistent with one another, further confirm this understanding and constrain the iron mineralization in a very short period of 131–127 Ma.

In the late stage of volcanic activity, hydrothermal vein-type copper and/or gold deposits occurred in part of the Ningwu ore district (e.g. Tongjing copper-gold deposit, Dapingshan copper deposit), which are considered to be closely related with the Niangniangshan Formation (NRG, 1978). The ages of the granodioritic stocks are similar to that of the volcanic rocks of the Niangniangshan cycle. Therefore, further research is needed to study the possibility that granodioritic stocks are related to copper and/or gold mineralization.

## 5.2 Magma source

In this study, the  $^{176}\text{Lu}/^{177}\text{Hf}$  ratios of zircons gained from granodioritic stocks are quite low, which shows that there is little or no accumulation of radiogenic Hf, and the  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios obtained in this study can basically represent the Hf isotopic composition of the magma system during its formation (Wu et al., 2007). As shown in Table 2, Fig. 7 and Fig. 8, the Hf compositions of the late Mesozoic granodioritic stocks crossing the iron ore bodies are characterized by  $^{176}\text{Lu}/^{177}\text{Hf} = 0.000485\text{--}0.003908$ ,  $^{176}\text{Hf}/^{177}\text{Hf} = 0.281637\text{--}0.282904$  and  $\varepsilon_{\text{Hf}}(t) = -37.43$  to  $7.17$ , centered on  $0.0008\text{--}0.0021$ ,  $0.28245\text{--}0.28265$  and  $-3$  to  $-8$  respectively. The data are clearly different from the composition of the MORB ( $^{176}\text{Hf}/^{177}\text{Hf}$  ratio: Pacific MORB,  $0.28313\text{--}0.28326$ ; Atlantic MORB,  $0.28302\text{--}0.28335$ ; Indian MORB, about  $0.2832$ ; Patchett and Tatsumoto, 1980; Patchett, 1983; Salters, 1996; Slaters and White, 1998; Chauvel and Blichert-Toft, 2001), as well as those of oceanic basalts worldwide ( $\varepsilon_{\text{Hf}}(t) > 0$ ) (Salters and Hart, 1991; Hamelin et al., 2010), and are obviously higher than the  $\varepsilon_{\text{Hf}}(t)$  value of the lower crust in the Yangtze Craton ( $-62.7$ ,  $t = 126$  Ma, 4.0 Ga crust and about  $-20$ ,  $t = 126$  Ma, 1.9 Ga crust, Zhang et al., 2006; Zhang and Zheng, 2007) and lower than the  $^{176}\text{Lu}/^{177}\text{Hf}$  ratio of the crust (average crust:  $0.015$ , Griffin et al., 2002; lower crust:  $0.022$ , and upper crust:  $0.0093$ , Amelin et al., 1999), reflecting that the rocks could not be directly derived by partial melting of the most prominent components at the surface of the Earth, the depleted mantle, the OIB-enriched mantle and the crust. In Fig. 8, the plotted points of the Hf isotopic composition of the

**Table 2 In situ zircon Hf isotope compositions of the granodioritic stocks**

| Sample    | <i>t</i> (Ma) | <sup>176</sup> Yb/ <sup>177</sup> Hf | 2σ       | <sup>176</sup> Lu/ <sup>177</sup> Hf | 2σ       | <sup>176</sup> Hf/ <sup>177</sup> Hf | 2σ       | ε <sub>Hf</sub> (0) | ε <sub>Hf</sub> ( <i>t</i> ) | <i>T</i> <sub>DM1</sub> (Ma) | <i>T</i> <sub>DM2</sub> (Ma) | <i>f</i> <sub>LW/Hf</sub> |
|-----------|---------------|--------------------------------------|----------|--------------------------------------|----------|--------------------------------------|----------|---------------------|------------------------------|------------------------------|------------------------------|---------------------------|
| WS-92-1   | 127.8         | 0.072729                             | 0.000264 | 0.001116                             | 0.000011 | 0.282502                             | 0.000016 | -9.53               | -6.82                        | 1063                         | 1617                         | -0.97                     |
| WS-92-2   | 126.5         | 0.115177                             | 0.003166 | 0.001604                             | 0.000041 | 0.282635                             | 0.000022 | -4.86               | -2.21                        | 888                          | 1323                         | -0.95                     |
| WS-92-3   | 124.6         | 0.081302                             | 0.000282 | 0.001307                             | 0.000003 | 0.282570                             | 0.000020 | -7.14               | -4.52                        | 973                          | 1468                         | -0.96                     |
| WS-92-4   | 127.6         | 0.074687                             | 0.000490 | 0.001266                             | 0.000009 | 0.282526                             | 0.000020 | -8.70               | -6.00                        | 1034                         | 1565                         | -0.96                     |
| WS-92-5   | 125.7         | 0.083864                             | 0.001112 | 0.001699                             | 0.000031 | 0.282595                             | 0.000019 | -6.26               | -3.64                        | 947                          | 1413                         | -0.95                     |
| WS-92-6   | 125.0         | 0.091571                             | 0.001240 | 0.001538                             | 0.000018 | 0.282586                             | 0.000017 | -6.59               | -3.98                        | 956                          | 1434                         | -0.95                     |
| WS-92-7   | 124.8         | 0.069093                             | 0.000847 | 0.001178                             | 0.000011 | 0.282582                             | 0.000017 | -6.71               | -4.07                        | 952                          | 1440                         | -0.96                     |
| WS-92-8   | 125.3         | 0.102590                             | 0.000306 | 0.001807                             | 0.000006 | 0.282574                             | 0.000019 | -6.99               | -4.39                        | 980                          | 1461                         | -0.95                     |
| WS-92-9   | 126.9         | 0.084486                             | 0.000604 | 0.001491                             | 0.000009 | 0.282555                             | 0.000018 | -7.66               | -5.00                        | 998                          | 1501                         | -0.96                     |
| WS-92-10  | 124.6         | 0.051786                             | 0.000449 | 0.000891                             | 0.000007 | 0.282545                             | 0.000017 | -8.04               | -5.38                        | 997                          | 1523                         | -0.97                     |
| WS-92-11  | 127.4         | 0.063532                             | 0.000470 | 0.001306                             | 0.000005 | 0.282570                             | 0.000014 | -7.14               | -4.45                        | 972                          | 1466                         | -0.96                     |
| WS-92-12  | 127.2         | 0.049542                             | 0.000241 | 0.000952                             | 0.000015 | 0.282557                             | 0.000017 | -7.62               | -4.91                        | 982                          | 1495                         | -0.97                     |
| WS-92-13  | 126.6         | 0.058599                             | 0.000334 | 0.001085                             | 0.000004 | 0.282594                             | 0.000019 | -6.29               | -3.61                        | 933                          | 1412                         | -0.97                     |
| WS-92-15  | 126.3         | 0.084359                             | 0.000632 | 0.001603                             | 0.000009 | 0.282571                             | 0.000018 | -7.11               | -4.47                        | 979                          | 1467                         | -0.95                     |
| WS-92-16  | 126.6         | 0.093598                             | 0.000385 | 0.001664                             | 0.000009 | 0.282634                             | 0.000018 | -4.87               | -2.23                        | 890                          | 1324                         | -0.95                     |
| WS-92-17  | 125.3         | 0.073109                             | 0.001028 | 0.001278                             | 0.000017 | 0.282593                             | 0.000018 | -6.34               | -3.70                        | 940                          | 1417                         | -0.96                     |
| WS-92-18  | 125.3         | 0.085523                             | 0.000153 | 0.001469                             | 0.000002 | 0.282600                             | 0.000019 | -6.07               | -3.44                        | 934                          | 1401                         | -0.96                     |
| WS-92-19  | 125.1         | 0.066205                             | 0.001019 | 0.001135                             | 0.000015 | 0.282541                             | 0.000018 | -8.16               | -5.51                        | 1009                         | 1531                         | -0.97                     |
| WS-92-20  | 127.6         | 0.075886                             | 0.001168 | 0.001371                             | 0.000020 | 0.282556                             | 0.000018 | -7.63               | -4.95                        | 994                          | 1498                         | -0.96                     |
| NS-6-2    | 127.6         | 0.116202                             | 0.004428 | 0.001893                             | 0.000093 | 0.282687                             | 0.000020 | -3.02               | -0.38                        | 820                          | 1207                         | -0.94                     |
| NS-6-3    | 126.6         | 0.073898                             | 0.001726 | 0.001419                             | 0.000054 | 0.282539                             | 0.000019 | -8.25               | -5.59                        | 1020                         | 1538                         | -0.96                     |
| NS-6-4    | 126.8         | 0.071679                             | 0.000359 | 0.001285                             | 0.000003 | 0.282476                             | 0.000018 | -10.48              | -7.80                        | 1105                         | 1678                         | -0.96                     |
| NS-6-5    | 126.1         | 0.090751                             | 0.001252 | 0.001703                             | 0.000020 | 0.282670                             | 0.000018 | -3.62               | -0.99                        | 840                          | 1245                         | -0.95                     |
| NS-6-6    | 126.4         | 0.090992                             | 0.000596 | 0.001566                             | 0.000007 | 0.282587                             | 0.000022 | -6.55               | -3.91                        | 955                          | 1431                         | -0.95                     |
| NS-6-7    | 127.6         | 0.069043                             | 0.001305 | 0.001145                             | 0.000019 | 0.282584                             | 0.000026 | -6.65               | -3.95                        | 949                          | 1435                         | -0.97                     |
| NS-6-8    | 125.9         | 0.098499                             | 0.000731 | 0.001553                             | 0.000014 | 0.282589                             | 0.000021 | -6.47               | -3.83                        | 952                          | 1426                         | -0.95                     |
| NS-6-9    | 125.7         | 0.091282                             | 0.000989 | 0.001454                             | 0.000013 | 0.282602                             | 0.000023 | -6.00               | -3.36                        | 930                          | 1396                         | -0.96                     |
| NS-6-10   | 126.1         | 0.079755                             | 0.000939 | 0.001427                             | 0.000021 | 0.282625                             | 0.000021 | -5.21               | -2.56                        | 898                          | 1345                         | -0.96                     |
| NS-6-11   | 126.1         | 0.219897                             | 0.003902 | 0.003180                             | 0.000053 | 0.282904                             | 0.000027 | 4.66                | 7.17                         | 524                          | 724                          | -0.90                     |
| NS-6-12   | 125.6         | 0.201006                             | 0.003296 | 0.003908                             | 0.000045 | 0.282747                             | 0.000028 | -0.88               | 1.55                         | 775                          | 1083                         | -0.88                     |
| NS-6-13   | 126.9         | 0.096178                             | 0.000909 | 0.001629                             | 0.000010 | 0.282508                             | 0.000020 | -9.32               | -6.67                        | 1069                         | 1607                         | -0.95                     |
| NS-6-14   | 128.0         | 0.050038                             | 0.000232 | 0.001016                             | 0.000005 | 0.282605                             | 0.000016 | -5.91               | -3.19                        | 916                          | 1386                         | -0.97                     |
| NS-6-15   | 126.1         | 0.112771                             | 0.001246 | 0.002111                             | 0.000035 | 0.282624                             | 0.000016 | -5.22               | -2.63                        | 915                          | 1349                         | -0.94                     |
| NS-6-16   | 128.6         | 0.067368                             | 0.001186 | 0.001410                             | 0.000027 | 0.282515                             | 0.000017 | -9.10               | -6.40                        | 1054                         | 1591                         | -0.96                     |
| NS-6-17   | 127.3         | 0.171627                             | 0.000711 | 0.003430                             | 0.000010 | 0.282657                             | 0.000025 | -4.06               | -1.56                        | 900                          | 1282                         | -0.90                     |
| NS-6-18   | 126.5         | 0.061183                             | 0.000557 | 0.001055                             | 0.000010 | 0.282523                             | 0.000020 | -8.80               | -6.11                        | 1032                         | 1571                         | -0.97                     |
| NS-6-19   | 127.8         | 0.100281                             | 0.000330 | 0.001561                             | 0.000003 | 0.282559                             | 0.000022 | -7.54               | -4.87                        | 995                          | 1493                         | -0.95                     |
| NS-6-20   | 127.4         | 0.104088                             | 0.001036 | 0.001622                             | 0.000031 | 0.282675                             | 0.000021 | -3.43               | -0.77                        | 831                          | 1232                         | -0.95                     |
| DSC-11-1  | 126.9         | 0.037824                             | 0.000424 | 0.000598                             | 0.000005 | 0.282489                             | 0.000019 | -10.01              | -7.28                        | 1067                         | 1646                         | -0.98                     |
| DSC-11-2  | 127.4         | 0.063352                             | 0.000508 | 0.000981                             | 0.000009 | 0.282510                             | 0.000018 | -9.28               | -6.57                        | 1049                         | 1600                         | -0.97                     |
| DSC-11-3  | 127.5         | 0.055924                             | 0.000278 | 0.000851                             | 0.000003 | 0.282480                             | 0.000019 | -10.34              | -7.61                        | 1087                         | 1667                         | -0.97                     |
| DSC-11-4  | 127.4         | 0.057248                             | 0.000211 | 0.000917                             | 0.000003 | 0.282523                             | 0.000015 | -8.80               | -6.08                        | 1028                         | 1570                         | -0.97                     |
| DSC-11-5  | 127.0         | 0.162684                             | 0.000269 | 0.002537                             | 0.000009 | 0.282647                             | 0.000020 | -4.42               | -1.85                        | 893                          | 1300                         | -0.92                     |
| DSC-11-6  | 127.5         | 0.071082                             | 0.000608 | 0.001060                             | 0.000006 | 0.282523                             | 0.000018 | -8.81               | -6.10                        | 1032                         | 1571                         | -0.97                     |
| DSC-11-7  | 127.8         | 0.074300                             | 0.000546 | 0.001087                             | 0.000004 | 0.282552                             | 0.000016 | -7.78               | -5.07                        | 992                          | 1506                         | -0.97                     |
| DSC-11-8  | 128.3         | 0.119490                             | 0.005976 | 0.001754                             | 0.000091 | 0.282570                             | 0.000022 | -7.14               | -4.47                        | 984                          | 1468                         | -0.95                     |
| DSC-11-9  | 128.1         | 0.041737                             | 0.000511 | 0.000598                             | 0.000005 | 0.282474                             | 0.000019 | -10.54              | -7.77                        | 1088                         | 1678                         | -0.98                     |
| DSC-11-10 | 127.5         | 0.042027                             | 0.000206 | 0.000629                             | 0.000002 | 0.282458                             | 0.000020 | -11.09              | -8.35                        | 1111                         | 1714                         | -0.98                     |
| DSC-11-11 | 126.7         | 0.063600                             | 0.000493 | 0.000947                             | 0.000008 | 0.282401                             | 0.000022 | -13.12              | -10.42                       | 1200                         | 1844                         | -0.97                     |
| DSC-11-12 | 127.2         | 0.064818                             | 0.001265 | 0.000932                             | 0.000016 | 0.282490                             | 0.000021 | -9.96               | -7.25                        | 1075                         | 1644                         | -0.97                     |
| DSC-11-13 | 127.9         | 0.068897                             | 0.001266 | 0.001014                             | 0.000019 | 0.282496                             | 0.000021 | -9.76               | -7.04                        | 1069                         | 1631                         | -0.97                     |
| DSC-11-14 | 127.6         | 0.063643                             | 0.000092 | 0.000971                             | 0.000002 | 0.282508                             | 0.000024 | -9.33               | -6.61                        | 1051                         | 1604                         | -0.97                     |
| DSC-11-16 | 127.0         | 0.067715                             | 0.000547 | 0.001030                             | 0.000005 | 0.282428                             | 0.000022 | -12.16              | -9.46                        | 1165                         | 1783                         | -0.97                     |
| DSC-11-17 | 126.3         | 0.071273                             | 0.000228 | 0.001205                             | 0.000002 | 0.282462                             | 0.000024 | -10.98              | -8.31                        | 1123                         | 1710                         | -0.96                     |
| DSC-11-18 | 126.9         | 0.063111                             | 0.000816 | 0.001001                             | 0.000011 | 0.282506                             | 0.000021 | -9.40               | -6.70                        | 1054                         | 1608                         | -0.97                     |
| DSC-11-19 | 127.7         | 0.053536                             | 0.000435 | 0.000971                             | 0.000008 | 0.282563                             | 0.000021 | -7.38               | -4.66                        | 973                          | 1480                         | -0.97                     |
| DSC-11-20 | 128.6         | 0.082249                             | 0.001025 | 0.001376                             | 0.000017 | 0.282569                             | 0.000021 | -7.18               | -4.48                        | 976                          | 1469                         | -0.96                     |
| HSQ-5-1   | 126.4         | 0.053038                             | 0.000352 | 0.000856                             | 0.000007 | 0.282564                             | 0.000014 | -7.35               | -4.64                        | 969                          | 1478                         | -0.97                     |
| HSQ-5-2   | 126.6         | 0.069150                             | 0.000833 | 0.001130                             | 0.000015 | 0.282555                             | 0.000017 | -7.67               | -4.99                        | 989                          | 1500                         | -0.97                     |
| HSQ-5-3   | 126.2         | 0.081105                             | 0.000823 | 0.001309                             | 0.000018 | 0.282552                             | 0.000018 | -7.79               | -5.13                        | 999                          | 1509                         | -0.96                     |
| HSQ-5-4   | 125.7         | 0.051869                             | 0.000819 | 0.000845                             | 0.000015 | 0.282570                             | 0.000017 | -7.13               | -4.45                        | 960                          | 1465                         | -0.97                     |
| HSQ-5-5   | 125.8         | 0.090218                             | 0.000654 | 0.001632                             | 0.000013 | 0.282572                             | 0.000018 | -7.08               | -4.46                        | 979                          | 1465                         | -0.95                     |
| HSQ-5-6   | 125.8         | 0.053427                             | 0.000121 | 0.000839                             | 0.000003 | 0.282608                             | 0.000019 | -5.81               | -3.12                        | 908                          | 1380                         | -0.97                     |
| HSQ-5-7   | 128.3         | 0.045712                             | 0.000281 | 0.000738                             | 0.000005 | 0.282511                             | 0.000020 | -9.22               | -6.47                        | 1040                         | 1595                         | -0.98                     |
| HSQ-5-8   | 127.0         | 0.051382                             | 0.000128 | 0.000820                             | 0.000004 | 0.282532                             | 0.000021 | -8.47               | -5.76                        | 1013                         | 1549                         | -0.98                     |
| HSQ-5-9   | 127.2         | 0.101513                             | 0.001034 | 0.002061                             | 0.000029 | 0.282590                             | 0.000024 | -6.45               | -3.83                        | 964                          | 1426                         | -0.94                     |
| HSQ-5-10  | 125.9         | 0.066626                             | 0.000364 | 0.001026                             | 0.000004 | 0.282594                             | 0.000022 | -6.30               | -3.62                        | 932                          | 1413                         | -0.97                     |
| HSQ-5-11  | 126.3         | 0.056580                             | 0.000196 | 0.000919                             | 0.000003 | 0.282566                             | 0.000020 | -7.27               | -4.58                        | 968                          | 1473                         | -0.97                     |
| HSQ-5-13  | 125.9         | 0.057929                             | 0.000580 | 0.001032                             | 0.000007 | 0.282557                             | 0.000019 | -7.59               | -4.92                        | 983                          | 1495                         | -0.97                     |
| HSQ-5-14  | 126.5         | 0.047506                             | 0.000711 | 0.000847                             | 0.000014 | 0.282551                             | 0.000020 | -7.80               | -5.10                        | 987                          | 1507                         | -0.97                     |
| HSQ-5-15  | 126.6         | 0.060705                             | 0.000486 | 0.001089                             | 0.000009 | 0.282564                             | 0.000016 | -7.34               | -4.66                        | 975                          | 1479                         | -0.97                     |
| HSQ-5-16  | 125.9         | 0.027131                             | 0.000248 | 0.000485                             | 0.000004 | 0.281637                             | 0.000020 | -40.15              | -37.43                       | 2231                         | 3535                         | -0.99                     |
| HSQ-5-17  | 125.1         | 0.093646                             | 0.003929 | 0.001609                             | 0.000068 | 0.282610                             | 0.000020 | -5.75               | -3.13                        | 924                          | 1381                         | -0.95                     |
| HSQ-5-18  | 126.2         | 0.048050                             | 0.000243 | 0.000797                             | 0.000005 | 0.282557                             | 0.000020 | -7.61               | -4.91                        | 978                          | 1495                         | -0.98                     |



Table 2 Continued

| Sample   | <i>t</i> (Ma) | <sup>176</sup> Yb/ <sup>177</sup> Hf | 2σ       | <sup>176</sup> Lu/ <sup>177</sup> Hf | 2σ       | <sup>176</sup> Hf/ <sup>177</sup> Hf | 2σ       | $\varepsilon_{\text{Hf}}(0)$ | $\varepsilon_{\text{Hf}}(t)(\text{‰})$ | <i>T</i> <sub>DM1</sub> (Ma) | <i>T</i> <sub>DM2</sub> (Ma) | <i>f</i> <sub>Lu/Hf</sub> |
|----------|---------------|--------------------------------------|----------|--------------------------------------|----------|--------------------------------------|----------|------------------------------|----------------------------------------|------------------------------|------------------------------|---------------------------|
| HSQ-5-19 | 127.3         | 0.069928                             | 0.000458 | 0.001289                             | 0.000016 | 0.282596                             | 0.000018 | -6.23                        | -3.55                                  | 935                          | 1409                         | -0.96                     |
| HSQ-5-20 | 126.9         | 0.062552                             | 0.000561 | 0.001024                             | 0.000011 | 0.282544                             | 0.000020 | -8.08                        | -5.38                                  | 1002                         | 1525                         | -0.97                     |

$$\varepsilon_{\text{Hf}}(0) = ((^{176}\text{Hf}/^{177}\text{Hf})_{\text{S}} / (^{176}\text{Hf}/^{177}\text{Hf})_{\text{CHUR},0} - 1) \times 10000,$$

$$\varepsilon_{\text{Hf}}(t) = ((^{176}\text{Hf}/^{177}\text{Hf})_{\text{S}} - (^{176}\text{Lu}/^{177}\text{Hf})_{\text{S}}(e^{\lambda t} - 1)) / ((^{176}\text{Hf}/^{177}\text{Hf})_{\text{CHUR},0} - (^{176}\text{Lu}/^{177}\text{Hf})_{\text{CHUR},0}(e^{\lambda t} - 1)) \times 10000,$$

$$T_{\text{DM1}} = 1/\lambda \times \ln\{1 + ((^{176}\text{Hf}/^{177}\text{Hf})_{\text{S}} - (^{176}\text{Hf}/^{177}\text{Hf})_{\text{DM}}) / [(^{176}\text{Lu}/^{177}\text{Hf})_{\text{S}} - (^{176}\text{Lu}/^{177}\text{Hf})_{\text{DM}}]\},$$

$$T_{\text{DM2}} = T_{\text{DM1}} - (T_{\text{DM1}} - t) \times ((f_{\text{CC}} - f_{\text{S}}) / (f_{\text{CC}} - f_{\text{DM}})),$$

$$f_{\text{S}} = (^{176}\text{Lu}/^{177}\text{Hf})_{\text{S}} / (^{176}\text{Lu}/^{177}\text{Hf})_{\text{CHUR},0}, f_{\text{CC}} = (^{176}\text{Lu}/^{177}\text{Hf})_{\text{C}} / (^{176}\text{Lu}/^{177}\text{Hf})_{\text{CHUR},0}, f_{\text{DM}} = (^{176}\text{Lu}/^{177}\text{Hf})_{\text{DM}} / (^{176}\text{Lu}/^{177}\text{Hf})_{\text{CHUR},0},$$

$$(^{176}\text{Lu}/^{177}\text{Hf})_{\text{S}} \text{ and } (^{176}\text{Hf}/^{177}\text{Hf})_{\text{S}} \text{ are test values, } (^{176}\text{Lu}/^{177}\text{Hf})_{\text{CHUR},0} = 0.03321, (^{176}\text{Hf}/^{177}\text{Hf})_{\text{CHUR},0} = 0.282772, (^{176}\text{Lu}/^{177}\text{Hf})_{\text{DM}} = 0.03842, (^{176}\text{Hf}/^{177}\text{Hf})_{\text{DM}} = 0.28325$$

$$(\text{Blichert-Toft and Albarede, 1997}), (^{176}\text{Lu}/^{177}\text{Hf})_{\text{C}} = 0.015 (\text{Griffin et al., 2002}), t \text{ is the formation time of the sample, } \lambda_{\text{Lu}} = 1.867 \times 10^{-11} \text{ year}^{-1} (\text{Soderlund et al., 2004}).$$

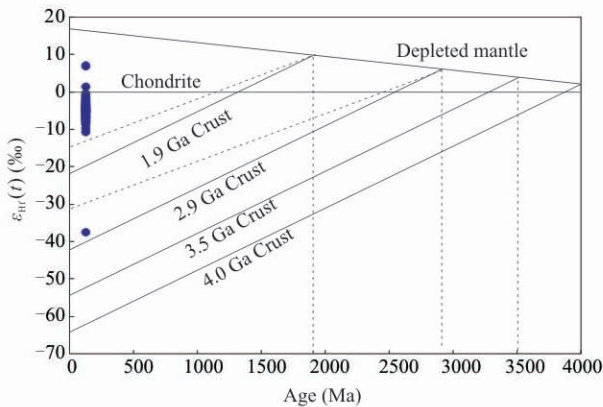


Fig. 8. Hf isotope evolution diagram of zircon of intrusions.

The DM line denotes the evolution of the depleted mantle with a present-day  $^{176}\text{Hf}/^{177}\text{Hf}=0.28325$  and  $^{176}\text{Lu}/^{177}\text{Hf}=0.0384$  (Griffin et al., 2004). The corresponding solid lines of 1.9Ga, 2.9Ga, 3.5Ga and 4.0Ga lower crust evolution in the Liantu and Kongling Formation, which represent the peak ages of crust growth of Yangtze Craton, are calculated by assuming the  $^{176}\text{Lu}/^{177}\text{Hf}$  ratio of 0.009 for average continental crust from the Yangtze Craton (Zhang et al., 2006; Zhang and Zheng, 2007). The dashed lines were drawn assuming that crust growth occurred respectively at continental crust at 1.9Ga and 2.9Ga with  $^{176}\text{Lu}/^{177}\text{Hf}$  ratio of 0.015 for average continental crust (Griffin et al., 2002).

rock stocks (i.e. the distribution of zircons) are above the evolution line of the crust in the Yangtze Craton (Zhang et al., 2006; Zhang and Zheng, 2007) in the intermediate zone connecting the chondrite line to the crustal curve (1.9

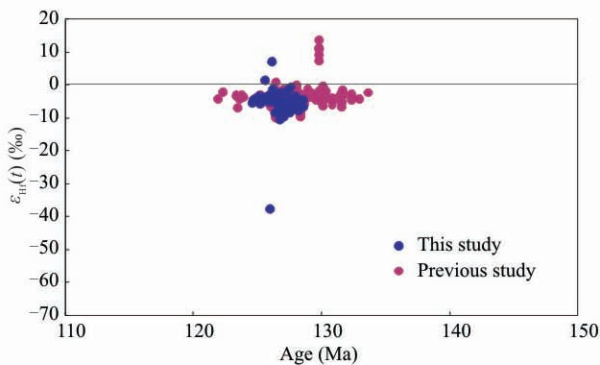


Fig. 9. Plot of the zircon Hf isotopes vs. zircon U-Pb ages for volcanic-subvolcanic rocks and intrusions in Ningwu ore district.

Data are from this study, Hou and Yuan (2010) and Yuan et al. (2011). The zircon Hf isotopes of lower crust are from Kongling metamorphic rocks in the Yangtze Craton (Zhang et al., 2006).

Ga). In addition, there is one zircon grain with much lower  $\varepsilon_{\text{Hf}}(t)$  value (-37.43) and higher  $T_{\text{DM2}}$  age (3535 Ma), which is similar to those of the initial stage of the Yangtze craton (Zhang et al., 2006), and two zircon grains with higher  $\varepsilon_{\text{Hf}}(t)$  values (1.55 and 7.17) and lower  $T_{\text{DM2}}$  ages (1083 Ma and 724 Ma) are consistent with the higher  $\varepsilon_{\text{Hf}}(t)$  values (7.64 to 13.91) and younger  $T_{\text{DM2}}$  (294 Ma to 581 Ma) of the five grain zircons from the samples of the Gushan intrusion obtained by Yuan et al. (2011). The observation also indicates that the granodioritic stocks will not have only one end member source. Furthermore, Münker et al. (2004) and Hanyu et al. (2002) conformed that the Hf element as high-field strength element can affect the composition of the rock by slab melts that originate from subducted oceanic crust. Nebel et al. (2011) presented that  $^{176}\text{Hf}/^{177}\text{Hf}$  decreases from 0.28314 to 0.28268 in the Banda arc, East Indonesia, with an increasing in the involvement of subducted crustal material in the magma source. The Hf isotopic data gained in this study have similar compositions to the end member of involved more crustal signatures. The evidence above reflects dynamic geological evolution which strongly suggests that the source of the rocks was not formed only from one single component end member, and crust material had been assimilated into the source magma generation during its ascent. By reviewing previous studies, one can see that almost all of the Hf isotopic compositions of granodioritic stocks are concordant with those of volcanic rocks and diorite porphyrite (associated with iron ore deposits) in the Ningwu basin with the  $\varepsilon_{\text{Hf}}(t)$  values concentrated in a range of -1‰ to -9‰ (Fig. 9). Combined with previous studies on Nd-Sr-Pb isotopic characteristics (Xing, 1996; Xing and Xu, 1999; Wang et al., 2001a; Hou et al., 2010; Yuan et al. 2011), we therefore consider that granodioritic stocks might share a similar source with volcanic rocks and diorite porphyrite. Granodioritic rocks occurred in the Ningwu ore district have a close original relationship with dioritic rocks.

### 5.3 Geodynamic background

It is generally accepted that the magmatism and mineralization in the MLYRB, occurring during the Mesozoic (145–120Ma), has two major episodes: (1) 156–

137 Ma high-K calc-alkaline granitoids associated with 148–135 Ma porphyry-skarn-stratabound Cu-Au-Mo-Fe deposits; (2) 135–123 Ma shoshonitic series associated with 135–123 Ma magnetite-apatite deposits and other small-scale economic deposits (Cu, Au, Pb-Zn) (Chang et al., 1991; Zhai et al., 1992a; Mao et al., 2006, 2009, 2011; Pan and Dong, 1999; NRG, 1978; Ren et al., 1991; Zhou et al., 2008a, 2010). And A-type granitoids (126.5–124.8 Ma) are associated with Au and U mineralization, occurring on the two sides of the lower reaches of Yangtze River (Zhang et al., 1988; Tang et al., 1998; Xing and Xu, 1999; Fan et al., 2008). During that period of time, the tectonic regime underwent significant shift, with the main structural pattern converted from nearly E-W to NE-NNE (Tao et al., 1998; Qi et al., 2000; Dong et al., 2007), possibly experiencing crust thickening, delamination of the lower crust, extension of the tectonic regime, lithospheric thinning, asthenosphere upwelling and crust-mantle interaction (Mao et al., 2005, 2011; Li, 2010a, b; Zhou et al., 2008a; Xie et al., 2006a; Lü et al., 2004; Wang et al., 2001a, b, 2003; Zhang et al., 2001). It is commonly considered that these tectonizations are associated with oblique subduction of the Izanagi plate, which tore up the low-angle subducted slab and the overlying crust along the ore belt due to disharmonious movement of the Yangtze craton and the North China craton beside it (Mao et al., 2011; Zhu et al., 2003, 2010; Sun et al., 2007; Li, 2000; Deng et al., 1992; Qiu et al., 1981).

In the second episode, the geochron of volcanic-subvolcanic rocks and intrusions is concentrated in 135–125 Ma, belonging to the Early Cretaceous, in the MLYRB, mainly including the Ningwu basin (135–126Ma, Zhang et al., 2003; Hou and Yuan, 2010; Xue et al., 2010; Fan et al., 2010; Zhou et al., 2011; Yuan et al., 2011), the Luzong basin (135–127Ma, Zhou et al., 2008b, 2010; Xue et al., 2010; Qin et al., 2010; Zeng et al., 2010), the Jinniu basin (130–125Ma, Xie et al., 2006b, 2011), and the Fanchang basin (134–128Ma, Lou and Du, 2006; Yu and Xu, 2009; Yan et al., 2009; Yuan et al., 2010). We present that the age of iron mineralization in the Ningwu ore district also varies in a narrow range of 131–127 Ma, being consistent with that of the earlier volcanic activity (the Dawangshan Formation). When the oblique subduction of the Izanagi plate transformed its moving direction to NE-NNE and tore up the low-angle subducted slab (Mao et al., 2008, 2011; Zhou et al., 2008a, 2011; Xie et al., 2006b, 2008a, 2008b; Yuan et al., 2008; Xing and Xu, 1999). Based on geochemical and geochronological studies, Xie et al. (2011), Yuan et al. (2008, 2010) and Yan et al. (2009) suggested that volcanic rocks in the Fanchang basin, Jinniu basin and part of the Luzong basin are characterized by bimodal volcanic rocks, occurring in

the same period. Besides, A-type granite occurred partially and transitorily during 126.5–124.8 Ma (Fan et al., 2008), slightly later than iron mineralization in the MLYRB. The above discussion provides evidence that Early Cretaceous volcanic rocks and the porphyry iron mineralization in the MLYRB were developed in an extensional tectonic regime induced by the Izanagi plate while transforming its moving direction to NE-NNE and the low-angle subducted slab tearing up (Mao et al., 2005, 2008, 2011; Zhou et al., 2008a; Xie et al., 2011), and the previous subducted slab remaining in the asthenosphere might have contributed to the rock-forming process. Magmatism and mineralization of porphyry iron deposits in the Ningwu ore district occurred also in an extensional tectonic regime.

## 6 Conclusions

Based on the above analyses and discussion, the following conclusions can be reached:

(1) Emplacement and crystallization (typically for zircons) of the granodioritic stocks in the study area occurred at an age range of 126–127 Ma, and the age of the iron mineralization in the Ningwu ore district is in a very short period of 131–127 Ma.

(2) Granodioritic rocks occurring in the Ningwu ore district have a close original relationship with dioritic rocks.

(3) Magmatism and mineralization of porphyry iron deposits in the Ningwu ore district occurred in an extensional tectonic regime induced as the Izanagi plate transformed its moving direction to NE-NNE.

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