



# Early Paleozoic crust–mantle interaction and lithosphere delamination in South China Block: Evidence from geochronology, geochemistry, and Sr–Nd–Hf isotopes of granites



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## ABSTRACT

The early Paleozoic orogen in South China Block is an intracontinental orogen, and synchronous magmatism (440–390 Ma) is mainly acidic with minor intermediate–mafic magmatism. Previous studies suggest that most of the early Paleozoic granites in South China belong to peraluminous S-type genesis while amphibole-bearing I-type granites are subordinate. However, our results indicate that considerable amounts of these early Paleozoic granites have characteristics of both S- and I-type granites. Thus, we propose to divide these granites into two groups: fewer of them are Group A with relatively high  $\varepsilon_{\text{Hf}}(t)$  values (clustering within  $-3.0$  to  $+9.0$ ) and  $\varepsilon_{\text{Nd}}(t)$  values ( $-5.2$  to  $+1.3$ ) as well as higher initial temperatures at 810–850 °C, and most of them are Group B with relatively low  $\varepsilon_{\text{Hf}}(t)$  values (clustering within  $-16.0$  to  $-1.0$ ) and  $\varepsilon_{\text{Nd}}(t)$  values ( $-13.2$  to  $-4.1$ ) as well as relatively low initial temperatures at 700–830 °C. The Xiawan monzogranite and Duntou granodiorite are typical Group A granitoids and yield zircon U–Pb ages of ca. 410 Ma. These two granites are characterized by high  $\text{SiO}_2$  (between 67.59 and 74.87 wt.%), metaluminous to peraluminous ( $A/\text{CNK} = 0.96$ – $1.48$ ) compositions, and a negative correlation between  $\text{P}_2\text{O}_5$  and  $\text{SiO}_2$ . Their biotites belong to magnesium biotites, indicating that they have partial features of either I- or S-type granites. Duntou granodiorites exhibit higher  $\varepsilon_{\text{Hf}}(t)$  values (clustering within  $+1$  to  $+8$ ) and  $\varepsilon_{\text{Nd}}(t)$  values ( $-3.0$  to  $+1.1$ ) while Xiawan monzogranites show relatively low  $\varepsilon_{\text{Hf}}(t)$  values (clustering within  $-1$  to  $+5$ ) and  $\varepsilon_{\text{Nd}}(t)$  values ( $-5.0$  to  $-3.7$ ). Group B granitoids are represented by the Miao'ershan–Yuechengling batholith, which are characterized by high  $\text{SiO}_2$  (between 64.57 and 77.37 wt.%), metaluminous compositions ( $A/\text{CNK} = 0.90$ – $1.24$ ), and a negative correlation between  $\text{P}_2\text{O}_5$  and  $\text{SiO}_2$ . Yuechengling porphyritic amphibole-bearing biotite granites in this batholith contain abundant amphibole, indicating that they are I-type granites. Miao'ershan–Yuechengling batholith also exhibits relatively low  $\varepsilon_{\text{Hf}}(t)$  values ( $-12.7$  to  $-1.8$ ) and  $\varepsilon_{\text{Nd}}(t)$  values ( $-8.9$  to  $-6.7$ ).

Geochemical and isotopic analyses on early Paleozoic granites, mafic enclaves and mafic to intermediate rocks demonstrate that the Group A granitoids including Xiawan and Duntou granites may be generated by AFC processes with interactions between asthenosphere-derived magma and metasedimentary rocks, and the Group B granitoids may be formed by AFC processes with interactions between synchronous basaltic magma and metamorphic basement. The post-collisional delamination and asthenospheric upwelling directly participate in the generation of Group A granitoids but indirectly induce the formation of Group B granitoids.

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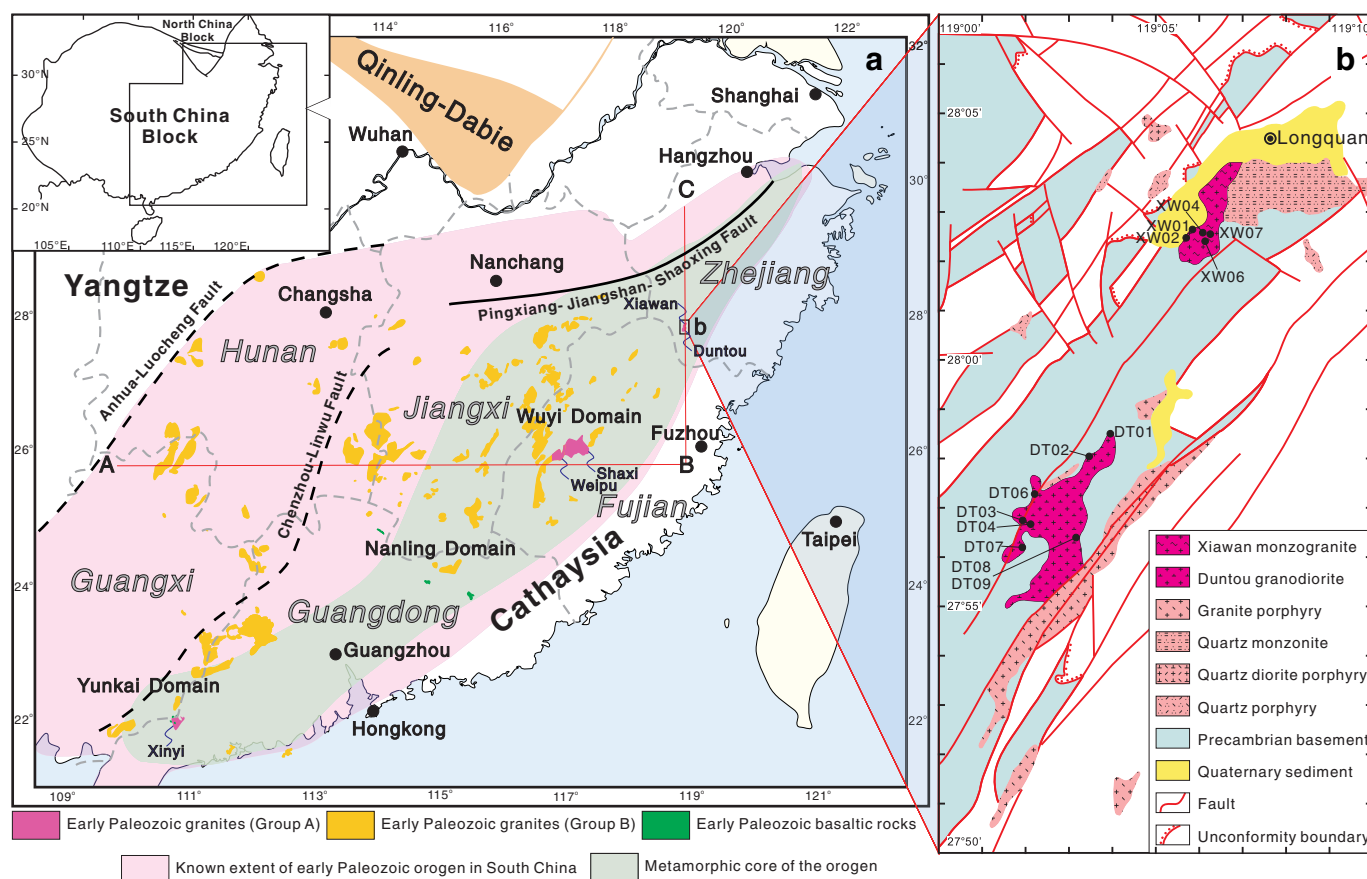
## 1. Introduction

The South China is tectonically divided into two major blocks: the Yangtze Block to the northwest and the Cathaysia Block to the southeast, which amalgamated during Neoproterozoic time (e.g., Charvet et al., 1996; Guo et al., 1985, 1989; Li, 1998; Li et al., 1995, 2002, 2008, 2009; Wang et al., 2006, 2007b, 2013a; Zhao and Cawood, 1999; Zhou et al., 2009). The boundary between the Yangtze

Block and Cathaysia Block is the northeasterly trending Pingxiang–Jiangshan–Shaoxing Fault, but the southwestern extension of this boundary is unclear because of poor exposure of outcrops and multiple intensive tectonic modifications. Either the Anhua–Luocheng Fault or the Chenzhou–Linwu Fault has been suggested as the SW boundary by different researchers (Fig. 1a, e.g., Chen and Jahn, 1998; Wang et al., 2008; Zhang et al., 2012; Zhao et al., 2013b). The South China was subsequently overprinted by at least three tectonothermal events in the early Paleozoic (Caledonian), Triassic (Indosinian) and Jurassic–Cretaceous (Yanshanian) (e.g., Charvet, 2013; Charvet et al., 1999, 2010; Faure et al., 2009; Li, 1998; Li and Li, 2007; Li et al., 2010c; Ren, 1991; Wang et al., 2005a, 2005b, 2011a, 2012a, 2013a; Xu et al., 2007).

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**Fig. 1.** (a) Schematic map showing the distribution of early Paleozoic igneous rocks in South China (modified after Li et al., 2010c; Sun, 2006; Wang et al., 2013b; Yao et al., 2012). (b) Geological map of Xiawan and Duntou granites. Sample locations are also indicated.

Contemporaneous with considerable granitic intrusions and coeval volcanism, the Yanshanian event has been systematically studied and interpreted as an extensional tectonics with large-scale mantle–crust interaction in response to the subduction of the Paleo-Pacific Plate (He and Xu, 2012; He et al., 2010a; Li and Li, 2007; Liu et al., 2012; Xie et al., 2006; Zhou et al., 2006). Owing to the lack of any synchronous intermediate-mafic volcanics, recent studies suggest that both the early Paleozoic and early Mesozoic (Indosinian) orogens are intra-continental (Charvet et al., 2010; Chu et al., 2012; Faure et al., 2009; Li, 1998; Li et al., 2010c; Yang et al., 2010; Wang et al., 2005b, 2012a). The widespread early Paleozoic and early Mesozoic granites in South China have been regarded as predominantly peraluminous, pure crust-derived S-type granites (Charvet, 2013; Li et al., 1989; Wang et al., 2011a, 2013a; Zhang et al., 2012; Zhou et al., 2006). However, the reports of Indosinian alkaline syenites and A-type granites indicate an extensional tectonic environment for South China during Triassic with possible basaltic magmatic underplating (Sun et al., 2011; Wang et al., 2005a; Xia et al., 2012; Zhao et al., 2013a).

Recently, Yao et al. (2012) and Wang et al. (2013b) reported the presence of high-Mg basalts, andesites, dacites (ca. 435 Ma) and gabbros (466–420 Ma) that may be related to lithosphere delamination, indicating the early Paleozoic mantle–crust interaction in South China (Fig. 1a). The early Paleozoic granites in South China Block can be divided into two groups: Group A in the center of metamorphic core of the orogen with relatively high  $\varepsilon_{\text{Hf}}(t)$  value ( $-9.0$  to  $+10.3$ , clustering within  $-3.0$  to  $+9.0$ ) and  $\varepsilon_{\text{Nd}}(t)$  ( $-5.2$  to  $+1.3$ ), suggesting the significant contribution of juvenile mantle-derived materials, and Group B widespread in orogen with relatively low  $\varepsilon_{\text{Hf}}(t)$  value ( $-35.4$  to  $+2.4$ , clustering within  $-16.0$  to  $-1.0$ ) and  $\varepsilon_{\text{Nd}}(t)$  ( $-13.2$  to  $-4.1$ ), suggesting an ancient recycled crustal source (see in Appendix Table 1 and related references in it). In addition, some of

the Group B granitoids also contain mafic enclaves, which suggests that even some Group B granites with low radiogenic Hf and Nd isotopes are not pure crust-derived but crust–mantle mixed source (e.g., Banshanpu, Hongxiaqiao, Daning, Shanzhuang, Hongjiang and Xuehuading; Cheng et al., 2009a; Lou et al., 2005; Sha and Yuan, 1991; Wu and Zhang, 2003; Xu et al., 2006; Zhang et al., 2012). In comparison with the intensively studied Group B granitoids, systematic studies of Group A granitoids lag far behind and consequently our understanding of the early Paleozoic magmatism in South China is at present highly incomplete. We thus conducted a detailed geochronological and petrological study of two early Paleozoic Group A granites in South China Block in order to better understand the tectonic environment of this early Paleozoic tectonothermal event and contemporary magmatism.

## 2. Geologic background and samples

The early Paleozoic orogenic belt spans the southeastern half of the South China Block (Fig. 1a), stretching for ~2000 km in a northeasterly direction (Ren et al., 1997), distributing from the Korean Peninsula (Charvet et al., 1999; Kim et al., 2006) to the Indochina block (Ren, 1991; Roger et al., 2007). The orogen was originally assigned to the Kwangsi orogeny (Ting, 1929), and was subsequently named South China Caledonian Fold Belt (Huang, 1978), Cathaysian or Huanan Caledonides (Chang, 1996; Charvet et al., 1999; Ren, 1991), Wuyishan–Yunkaidashan belt (Zhang et al., 1984), Wuyi–Yunkai tectonic zone (Zhang et al., 1991), early Paleozoic Orogen of the South China Block (Faure et al., 2009). Recently, Li et al. (2010c) interpreted it as the Wuyi–Yunkai orogeny. Wang et al. (2012a) used the previous Kwangsi orogeny to define the early Paleozoic event in South China.

With visible angular unconformity between pre-Devonian deformed rocks and Devonian strata (Grabau, 1924; Huang et al., 1980; Ren, 1964, 1991; Ting, 1929; Zhao et al., 1996), this orogen includes Neoproterozoic to Lower Paleozoic non-metamorphic or low-grade metamorphic sediments, Paleoproterozoic to Lower Neoproterozoic (Li, 1997; Li et al., 2002) high-grade metamorphic rocks, migmatites and granitoids. The high-grade metamorphic rocks which reach amphibolite to granulite facies occur mainly in the northeastern segment, including northern Fujian and southern Zhejiang provinces, and in the Nanling Domain (Fig. 1a) (e.g. FBGMR, 1985; Gan et al., 1993, 1995; Hu et al., 1991; Li, 1988, 1989; Li et al., 1993; Shui et al., 1988; Yu et al., 2006; ZBGMR, 1989; Zhao and Cawood, 1999). In the northern Wuyi Domain (Fig. 1a), amphibolite facies metamorphism occurred between ca. 460 and 445 Ma, whereas cooling below 500–300 °C took place by ca. 420 Ma (Li et al., 2010c). The orogen exhibits a near-isothermal decompression clockwise pressure–temperature (P–T) path and a maximum pressure of >0.8 GPa, which is revealed by the sequence of mineral assemblages and metamorphic reactions for schist, amphibolite and granulites (Li et al., 2010c; Yu et al., 2003a, 2003b, 2005b, 2006, 2007; Zhao and Cawood, 1999), indicating crustal thickening during the orogeny. In the southern Wuyi Domain (Fig. 1a), Yu et al. (2003a; 2005a, 2005b) reported the occurrence of the Taoxi pelitic granulites with the metamorphic age of 445–479 Ma, a peak metamorphic pressure of 1.0–1.1 GPa and temperatures of 835–878 °C. In the Yunkai Domain (Fig. 1a), garnet-bearing amphibolites occur as interlayers, lens and pods within the gneiss and schist in the Yunkai Complex or granulite enclave in the charnockite and cordierite granite (Chen and Zhuang, 1994; GBGMR, 1988; Peng et al., 2000), reflecting metamorphic temperatures of 780–880 °C and pressures of 0.53–0.71 GPa (Chen and Zhuang, 1994; Qin et al., 2006; Yu et al., 2007; Zhou et al., 1994a).

The Xiawan monzogranite and Duntou granodiorite are located at the southwest of Longquan city in southwestern Zhejiang Province, with an outcrop area of ~3 km<sup>2</sup> and ~16 km<sup>2</sup>, respectively. Both granites intrude into the Paleoproterozoic Badu complex. Samples were collected from Xiawan and Duntou granites for this study (Fig. 1b). Sampling locations (latitude and longitude) and mineral assemblages of the samples are listed in Table 1. Except that Xiawan monzogranite contains more K-feldspars than Duntou granodiorite, the two granites have similar mineral assemblages of quartz + K-feldspar + plagioclase + biotite ± muscovite. The plagioclases in Xiawan and Duntou granites have relatively high An contents (An<sub>15–30</sub> for Xiawan monzogranite and An<sub>25–35</sub> for Duntou granodiorite), implying a relatively high melt temperature (Dall'Agnol et al., 1999; Scaillet et al., 1995). It is noted that all muscovites are anhedral, suggesting they may be of secondary origin. Representative samples were analyzed for zircon U–Pb dating, Hf-isotope compositions and whole-rock major and trace element and Sr–Nd isotope compositions.

**Table 1**  
Lithologies and mineral assemblages of Xiawan and Duntou granites.

| Granitic complexes  | Main minerals       | Sample No. | Location (GPS position)       |
|---------------------|---------------------|------------|-------------------------------|
| Xiawan monzogranite | Quartz +            | XW01       | 28°02′38.9″N, 119°05′43.7″E   |
|                     | K-feldspar +        | XW02       | 28°02′26.5″N, 119°05′40.3″E   |
|                     | plagioclase +       | XW04       | 28°02′49.78″N, 119°06′10.10″E |
|                     | biotite ± muscovite | XW06       | 28°02′46.35″N, 119°06′15.13″E |
|                     |                     | XW07       | 28°02′47.82″N, 119°06′18.75″E |
|                     |                     | DT01       | 27°58′38.2″N, 119°03′50″E     |
|                     |                     | DT02       | 27°57′56.1″N, 119°03′17.3″E   |
| Duntou granodiorite | Plagioclase +       | DT03       | 27°56′36.2″N, 119°02′0.3″E    |
|                     | quartz +            | DT04       | 27°56′30.4″N, 119°02′12.4″E   |
|                     | K-feldspar +        | DT06       | 27°57′12.57″N, 119°02′23.95″E |
|                     | biotite ± muscovite | DT07       | 27°56′7.68″N, 119°02′16.18″E  |
|                     |                     | DT09       | 27°56′27.48″N, 119°03′15.75″E |

### 3. Analytical methods

#### 3.1. Major element compositions of minerals

All elemental analyses of minerals were obtained from polished thin sections using a JEOL JXA-8800 electron microprobe at State Key Laboratory for Mineral Deposits Research at Nanjing University, China. Element determinations (Si, Al, Fe<sup>T</sup>, Mg, Ti, Mn, Na, K, F and Cl) of biotites were carried out using a beam size of 1 µm, an accelerating potential voltage of 15 kV, and a probe current of 20 nA. The standards used were hornblende (for Si, Ti, Al, Fe, Ca, Mg, Na and K) and fayalite (for Mn). Matrix effects were corrected using the ZAF software provided by JEOL. The accuracy of the reported values for the analyses is 1%–5% depending on the abundance of the element.

#### 3.2. U–Pb dating of zircons

Zircons were extracted using standard density and magnetic separation techniques. Random zircon grains were handpicked under a binocular stereomicroscope and mounted in a 1.4 cm diameter epoxy disk, and polished to expose the central parts of the grains. In order to characterize the internal structures of the zircons and to choose appropriate target sites for U–Pb and Hf isotope analyses, cathodoluminescence (CL) imaging was done using a Quanta 400FEG environmental scanning electron microscope equipped with an Oxford energy dispersive spectroscopy system and a Gatan CL<sup>3+</sup> detector at the State Key Laboratory of Continental Dynamics, Northwest University, Xi'an for most of the samples, and Hitachi S2250-N scanning electron microscope at the Beijing SHRIMP Center, Chinese Academy of Geological Sciences for the rest. The operating conditions for the CL imaging were at 15 kV and 20 nA.

Zircon U–Pb dating were carried out using an Agilent 7500a ICP-MS equipped with a New Wave 213 nm laser sampler in the State Key Laboratory of Mineral Deposits Research, Nanjing University. Details of instrument settings and analytical procedures follow Jackson et al. (2004). Analyses were carried out with a beam diameter of 25 µm, 5 Hz repetition rate, and energy of 10–20 J/cm<sup>2</sup>. Data acquisition for each analysis took 100 s (40 s on background and 60 s on signal). The raw ICP-MS data were processed using GLITTER (Van Achterbergh et al., 2001). Common Pb was corrected according to the method proposed by Andersen (2002). The age calculations and plotting of concordia diagrams were made using Isoplot (ver. 3.23) (Ludwig, 2003).

#### 3.3. Hf-isotope analysis of zircon

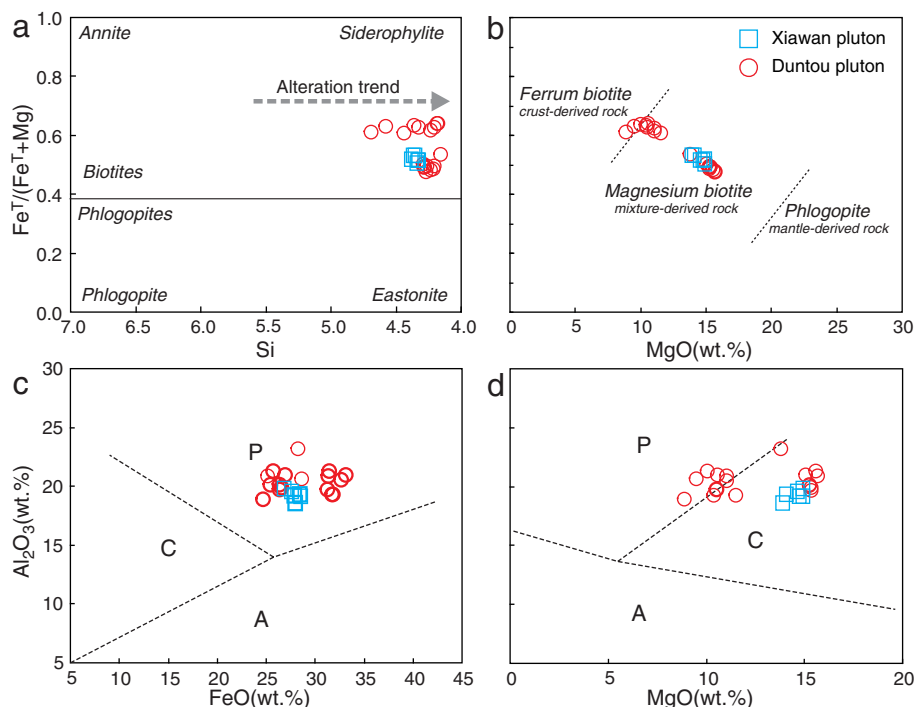
In situ Hf isotopic analysis of zircons were conducted using a Nu plasma MC-ICPMS, equipped with a 213 nm laser sampler at the Institute of Geochemistry, Chinese Academy of Sciences in Guiyang, China. The analysis was done with ablation pit of 60 µm in diameter, repetition rate of 10 Hz, ablation time of 60 s, and laser beam energy of 0.155 mJ/pulse. In order to evaluate the reliability of the data, zircon standard 91500 was analyzed during the course of this study and yielded a weighted mean <sup>176</sup>Hf/<sup>177</sup>Hf ratio of 0.282306 ± 24 (2σ), which is in good agreement with the solution analysis result (0.282306 ± 8; Woodhead et al., 2004). The analytical details and interference correction method of <sup>176</sup>Yb on <sup>176</sup>Hf are given in Tang et al. (2008). The measured <sup>176</sup>Lu/<sup>177</sup>Hf ratios and the <sup>176</sup>Lu decay constant of 1.867 × 10<sup>−11</sup> yr<sup>−1</sup> (Söderlund et al., 2004) were used to calculate initial <sup>176</sup>Hf/<sup>177</sup>Hf ratios. The chondritic values of <sup>176</sup>Lu/<sup>177</sup>Hf = 0.0336 ± 1 and <sup>176</sup>Hf/<sup>177</sup>Hf = 0.282785 ± 11 (2σ) (Bouvier et al., 2008) were used for calculating ε<sub>Hf</sub> values. The depleted mantle Hf model ages (T<sub>DM</sub>) were calculated using the measured <sup>176</sup>Lu/<sup>177</sup>Hf ratios based on the assumption that the depleted mantle reservoir has a linear isotopic growth from <sup>176</sup>Hf/<sup>177</sup>Hf = 0.279718 at 4.55 Ga to 0.283250 at present, with

**Table 2**  
Representative microprobe analyses of biotites in the Xiawan and Duntou granites.

| Sample                            | DT01  |       |       | DT04  |       |       |       |       |       |       |       |       | DT09  |       |       |       |       |       | XW07  |       |       |       |       |  |  |  |
|-----------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--|--|--|
| No.                               | 1     | 4     | 7     | 1     | 2     | 3     | 5     | 8     | 9     | 11    | 12    | 13    | 2     | 3     | 4     | 5     | 6     | 1     | 2     | 5     | 6     | 7     | 8     |  |  |  |
| SiO <sub>2</sub>                  | 26.03 | 26.43 | 25.56 | 27.87 | 25.09 | 28.77 | 25.31 | 26.82 | 24.98 | 24.97 | 25.15 | 24.38 | 25.65 | 25.15 | 25.20 | 26.11 | 26.08 | 26.68 | 26.01 | 25.98 | 26.18 | 25.85 | 25.49 |  |  |  |
| TiO <sub>2</sub>                  | 0.10  | 0.09  | 0.09  | 1.09  | 0.11  | 3.49  | 0.08  | 0.49  | 0.14  | 0.07  | 0.11  | 0.08  | 0.07  | 0.08  | 0.31  | 0.07  | 0.08  | 0.03  |       | 0.02  | 0.07  | 0.03  |       |  |  |  |
| Al <sub>2</sub> O <sub>3</sub>    | 23.18 | 20.94 | 19.67 | 20.61 | 19.69 | 18.89 | 19.27 | 19.26 | 20.94 | 20.49 | 20.84 | 21.28 | 19.87 | 20.09 | 20.13 | 20.86 | 21.29 | 19.12 | 19.31 | 19.56 | 19.81 | 19.15 | 18.57 |  |  |  |
| FeO <sup>T</sup>                  | 28.25 | 26.99 | 26.40 | 28.64 | 31.29 | 24.70 | 31.86 | 31.75 | 33.19 | 32.66 | 31.43 | 31.52 | 26.57 | 26.41 | 25.50 | 25.17 | 25.78 | 28.55 | 28.43 | 27.67 | 26.92 | 27.89 | 27.99 |  |  |  |
| MnO                               | 0.40  | 0.37  | 0.37  | 0.49  | 0.52  | 0.40  | 0.57  | 0.52  | 0.73  | 0.58  | 0.54  | 0.55  | 0.83  | 0.82  | 1.01  | 0.97  | 0.81  | 0.53  | 0.59  | 0.53  | 0.49  | 0.55  | 0.55  |  |  |  |
| MgO                               | 13.82 | 15.10 | 15.37 | 9.51  | 10.53 | 8.88  | 10.42 | 11.54 | 10.57 | 11.04 | 11.06 | 10.06 | 15.35 | 15.29 | 15.25 | 15.68 | 15.59 | 14.93 | 14.09 | 14.65 | 14.92 | 14.76 | 13.92 |  |  |  |
| CaO                               | 0.01  | 0.08  | 0.09  | 0.91  | 0.11  | 3.46  | 0.21  | 0.17  | 0.13  | 0.05  | 0.07  | 0.05  | 0.06  | 0.02  | 0.25  | 0.08  | 0.05  | 0.09  | 0.08  | 0.08  | 0.08  | 0.05  | 0.01  |  |  |  |
| Na <sub>2</sub> O                 | 0.04  | 0.00  |       | 0.05  | 0.02  | 0.02  | 0.00  | 0.06  |       |       |       | 0.00  |       |       | 0.00  | 0.03  |       | 0.03  | 0.01  |       | 0.07  | 0.01  | 0.01  |  |  |  |
| K <sub>2</sub> O                  | 0.02  | 0.01  | 0.02  | 0.94  | 0.09  | 1.30  | 0.04  | 0.26  | 0.02  | 0.02  | 0.07  | 0.27  | 0.00  |       | 0.04  | 0.02  | 0.02  | 0.00  | 0.01  | 0.00  | 0.06  | 0.00  | 0.01  |  |  |  |
| F                                 |       |       |       |       |       | 0.03  |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |  |  |  |
| H <sub>2</sub> O <sup>a</sup>     | 3.76  | 3.69  | 3.58  | 3.65  | 3.48  | 3.66  | 3.48  | 3.63  | 3.58  | 3.56  | 3.56  | 3.50  | 3.61  | 3.58  | 3.59  | 3.67  | 3.69  | 3.65  | 3.58  | 3.60  | 3.62  | 3.58  | 3.50  |  |  |  |
| Total                             | 95.62 | 93.71 | 91.14 | 93.77 | 90.92 | 93.62 | 91.25 | 94.50 | 94.30 | 93.45 | 92.82 | 91.68 | 92.01 | 91.44 | 91.27 | 92.65 | 93.40 | 93.61 | 92.12 | 92.08 | 92.23 | 91.87 | 90.06 |  |  |  |
| O = F,Cl                          | 0.00  | 0.00  | 0.00  | 0.01  | 0.00  | 0.01  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  |  |  |  |
| Total                             | 95.62 | 93.71 | 91.14 | 93.77 | 90.92 | 93.60 | 91.25 | 94.50 | 94.29 | 93.45 | 92.82 | 91.68 | 92.01 | 91.43 | 91.27 | 92.65 | 93.40 | 93.61 | 92.12 | 92.08 | 92.22 | 91.87 | 90.06 |  |  |  |
| Cations based on 22 oxygen anions |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |  |  |  |
| Si                                | 4.155 | 4.291 | 4.278 | 4.576 | 4.324 | 4.689 | 4.360 | 4.436 | 4.180 | 4.206 | 4.235 | 4.173 | 4.262 | 4.207 | 4.210 | 4.268 | 4.235 | 4.383 | 4.351 | 4.328 | 4.335 | 4.326 | 4.366 |  |  |  |
| Al <sup>IV</sup>                  | 3.845 | 3.709 | 3.722 | 3.424 | 3.676 | 3.311 | 3.640 | 3.564 | 3.820 | 3.794 | 3.765 | 3.827 | 3.738 | 3.793 | 3.790 | 3.732 | 3.765 | 3.617 | 3.649 | 3.672 | 3.665 | 3.674 | 3.634 |  |  |  |
| Al <sup>VI</sup>                  | 0.515 | 0.298 | 0.158 | 0.565 | 0.323 | 0.318 | 0.271 | 0.190 | 0.310 | 0.274 | 0.371 | 0.465 | 0.154 | 0.167 | 0.175 | 0.288 | 0.310 | 0.085 | 0.157 | 0.168 | 0.202 | 0.104 | 0.114 |  |  |  |
| Ti                                | 0.012 | 0.011 | 0.011 | 0.135 | 0.014 | 0.427 | 0.011 | 0.061 | 0.018 | 0.009 | 0.014 | 0.010 | 0.008 | 0.010 | 0.039 | 0.008 | 0.010 | 0.003 | 0.000 | 0.002 | 0.009 | 0.004 | 0.000 |  |  |  |
| Fe                                | 3.771 | 3.665 | 3.696 | 3.933 | 4.510 | 3.367 | 4.590 | 4.391 | 4.645 | 4.600 | 4.426 | 4.512 | 3.691 | 3.694 | 3.564 | 3.442 | 3.502 | 3.923 | 3.977 | 3.854 | 3.728 | 3.903 | 4.008 |  |  |  |
| Mn                                | 0.054 | 0.051 | 0.053 | 0.069 | 0.075 | 0.056 | 0.083 | 0.073 | 0.103 | 0.083 | 0.077 | 0.079 | 0.117 | 0.116 | 0.143 | 0.135 | 0.111 | 0.074 | 0.084 | 0.075 | 0.068 | 0.078 | 0.080 |  |  |  |
| Mg                                | 3.289 | 3.654 | 3.835 | 2.328 | 2.706 | 2.158 | 2.675 | 2.845 | 2.636 | 2.772 | 2.776 | 2.566 | 3.801 | 3.812 | 3.798 | 3.821 | 3.774 | 3.657 | 3.512 | 3.637 | 3.684 | 3.682 | 3.553 |  |  |  |
| Ca                                | 0.002 | 0.014 | 0.016 | 0.159 | 0.021 | 0.604 | 0.039 | 0.030 | 0.023 | 0.009 | 0.013 | 0.009 | 0.011 | 0.004 | 0.045 | 0.014 | 0.009 | 0.015 | 0.014 | 0.014 | 0.014 | 0.009 | 0.002 |  |  |  |
| Na                                | 0.012 | 0.001 | 0.000 | 0.014 | 0.008 | 0.005 | 0.001 | 0.019 | 0.000 | 0.000 | 0.000 | 0.001 | 0.000 | 0.001 | 0.001 | 0.008 | 0.000 | 0.009 | 0.002 | 0.000 | 0.021 | 0.002 | 0.004 |  |  |  |
| K                                 | 0.004 | 0.001 | 0.004 | 0.197 | 0.019 | 0.270 | 0.009 | 0.055 | 0.005 | 0.005 | 0.015 | 0.060 | 0.000 | 0.000 | 0.007 | 0.005 | 0.004 | 0.001 | 0.002 | 0.000 | 0.012 | 0.001 | 0.001 |  |  |  |
| OH <sup>a</sup>                   | 3.999 | 3.997 | 3.999 | 3.994 | 3.996 | 3.982 | 3.998 | 4.000 | 3.995 | 3.998 | 3.999 | 4.000 | 3.999 | 3.999 | 3.999 | 3.999 | 4.000 | 3.999 | 3.999 | 4.000 | 3.994 | 3.998 | 4.000 |  |  |  |
| F                                 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.014 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |  |  |  |
| Y total                           | 7.642 | 7.679 | 7.753 | 7.029 | 7.628 | 6.327 | 7.630 | 7.560 | 7.711 | 7.739 | 7.663 | 7.632 | 7.773 | 7.799 | 7.719 | 7.693 | 7.707 | 7.743 | 7.730 | 7.736 | 7.692 | 7.771 | 7.755 |  |  |  |
| X total                           | 0.019 | 0.016 | 0.020 | 0.371 | 0.048 | 0.880 | 0.049 | 0.104 | 0.028 | 0.014 | 0.027 | 0.069 | 0.011 | 0.005 | 0.054 | 0.027 | 0.013 | 0.025 | 0.018 | 0.014 | 0.047 | 0.012 | 0.007 |  |  |  |
| Al total                          | 4.360 | 4.007 | 3.880 | 3.989 | 3.999 | 3.629 | 3.912 | 3.754 | 4.129 | 4.068 | 4.136 | 4.293 | 3.892 | 3.960 | 3.965 | 4.020 | 4.075 | 3.703 | 3.807 | 3.840 | 3.867 | 3.778 | 3.748 |  |  |  |

<sup>a</sup> H<sub>2</sub>O calculations after Tindle and Webb, 1990.



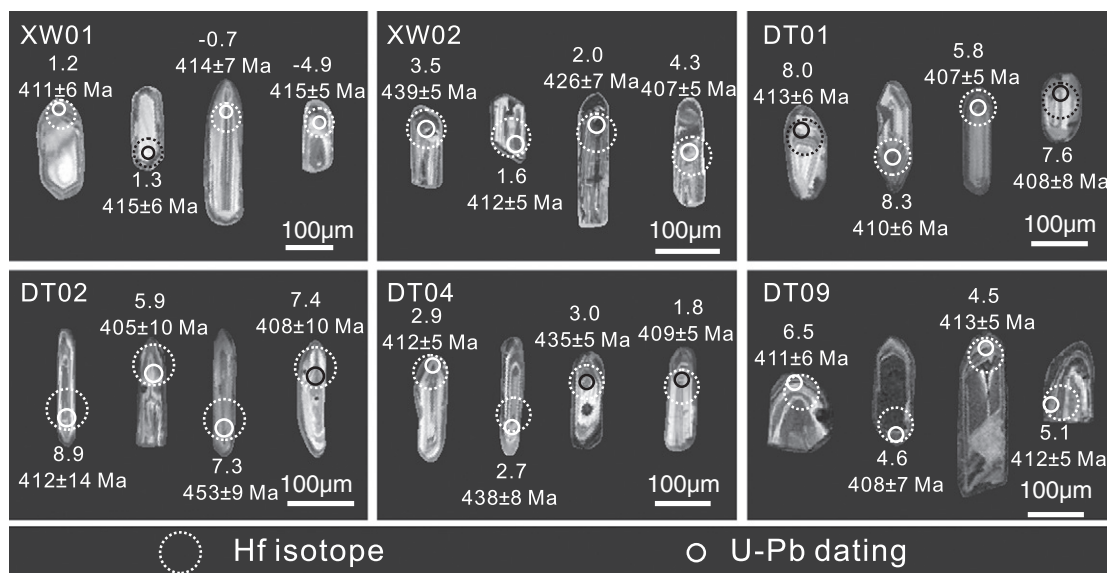


**Fig. 2.** (a)  $\text{Fe}^{\text{T}}/(\text{Fe}^{\text{T}} + \text{Mg})$  vs. Si diagram for biotite. (b)  $\text{Fe}^{\text{T}}/(\text{Fe}^{\text{T}} + \text{Mg})$  vs. MgO diagram for biotite (after Zhou, 1988). (c, d)  $\text{Al}_2\text{O}_3$  vs. FeO and MgO diagrams for biotite classification (after Abdel Rahman, 1994). A, biotite in anorogenic alkaline suites; P, biotite in peraluminous granites (S-type granites); C, biotite in metaluminous calc-alkaline granite suites (I-type granites).

$^{176}\text{Lu}/^{177}\text{Hf} = 0.0384$  (Griffin et al., 2000). The new continental crust Hf model ages ( $T_{\text{NC}}$ ) were calculated using the measured  $^{176}\text{Lu}/^{177}\text{Hf}$  ratios based on the assumption that the new continental crust reservoir (island arcs) has a linear isotopic growth from  $^{176}\text{Hf}/^{177}\text{Hf} = 0.279703$  at 4.55 Ga to 0.283145 at present, with  $^{176}\text{Lu}/^{177}\text{Hf} = 0.0375$  (Dhuime et al., 2011). The  $T_{\text{NC}}$  provides a better constraint than  $T_{\text{DM}}$  on when the continental crust generated (Dhuime et al., 2011). We also present a two-stage model age ( $T_{2\text{DM}}$  or  $T_{2\text{NC}}$ ) for each zircon, which assumes that its parental magma was produced from an average continental crust ( $^{176}\text{Lu}/^{177}\text{Hf} = 0.015$ ; Griffin et al., 2002) that was originally derived from the depleted mantle or island arcs.

### 3.4. Major and trace element analyses of whole-rocks

Bulk-rock major element analysis was performed using an ARL9800XP + X-ray fluorescence spectrometer (XRF) at the Center of Modern Analysis, NJU. The analytical precision is generally better than 2% for all elements. Trace element analyses were measured by ICPMS (Agilent 7500a) at Key Laboratory of Continental Dynamics, Northwest University, Xi'an. For trace element analysis, sample powders were digested using an HF + HNO<sub>3</sub> mixture in high-pressure Teflon bombs at 190 °C for 48 h. Analyses of rock standards BCR-2, BHVO-2 and AGV-2 indicate that precisions of trace element analyses are generally better than 5% and accuracies are better than 10%.



**Fig. 3.** CL images of representative zircons from Xiawan and Duntou granites. Small solid circles are spots for U–Pb isotope analyses, and big white dashed circles are spots for Hf isotope analyses.

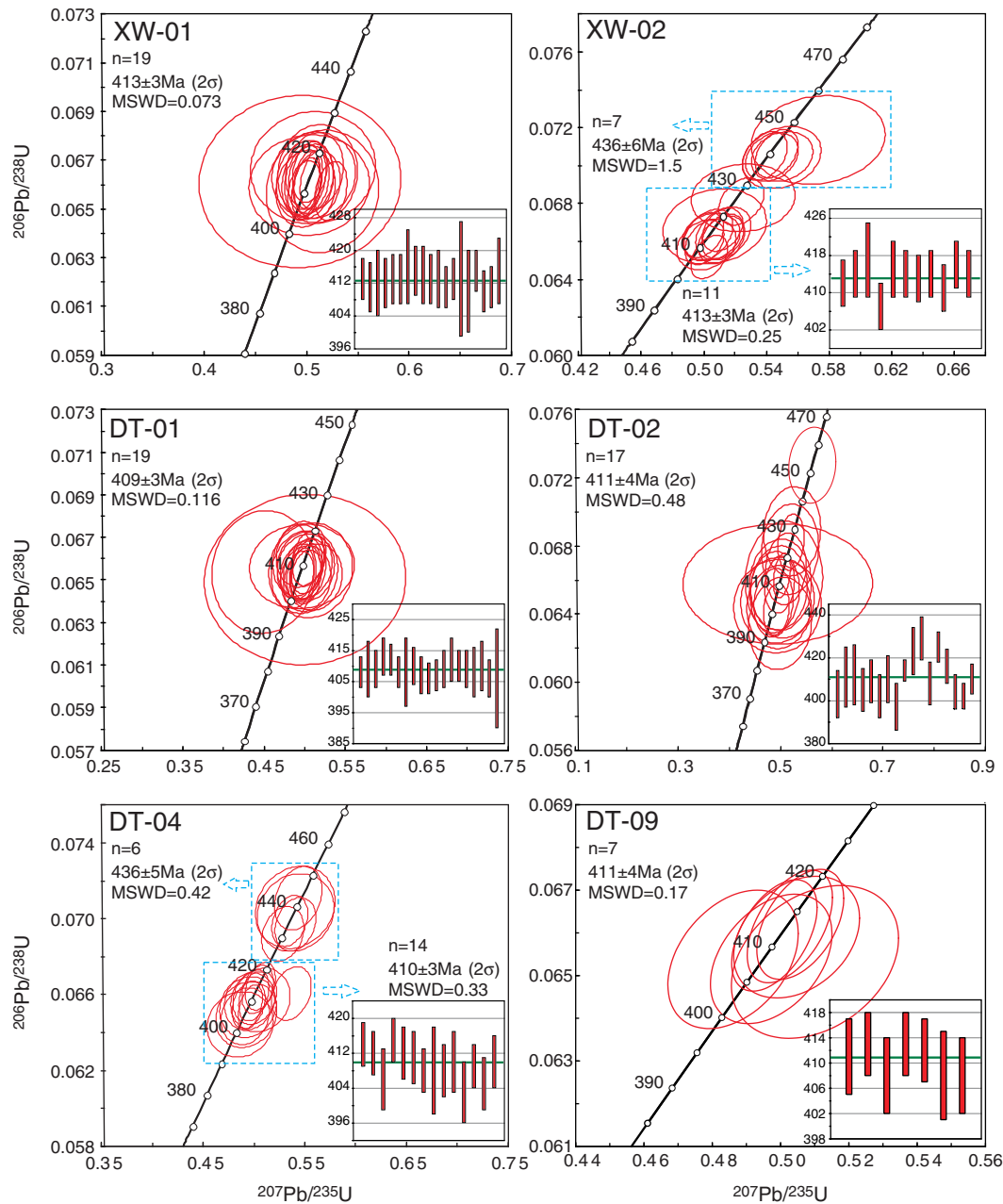


Fig. 4. U–Pb Concordia diagram of representative zircons from Xiawan and Duntou granites.

### 3.5. Sr–Nd isotope analysis of whole-rocks

All Rb–Sr and Sm–Nd isotope analyses were carried out at the Key Laboratory of Crust–Mantle Materials and Environments, University of Science and Technology of China. Following sample dissolution, Rb, Sr and the light rare-earth elements were isolated on quartz columns by conventional-ion exchange chromatography with a 5-ml resin bed of AG 50 W-X12 (200–400 mesh). Nd and Sm were separated from other rare earth elements on quartz columns using 1.7 ml Teflon powder coated with HDEHP, di(2-ethylhexyl) orthophosphoric acid, as cation exchange medium. Sr was loaded with a Ta–HF activator on pre-conditioned Ta filaments. Nd was loaded as phosphate on pre-conditioned Re filaments. Sr and Nd isotopic data were obtained using a Finnigan MAT-262 mass spectrometer. Sr and Nd isotopic ratios were corrected for mass fractionation relative to  $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$

and  $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ , respectively. Analyses on the standard solutions of NBS 987 and La Jolla yielded mean values of  $0.710249 \pm 0.000012$  ( $2\sigma$ ,  $n = 38$ ) for the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio and  $0.511869 \pm 0.000006$  ( $2\sigma$ ,  $n = 25$ ) for the  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio, during the course of this study. More details on analytical procedures are given in Chen et al. (2000) and Chen et al. (2007). For the calculation of  $(^{87}\text{Sr}/^{86}\text{Sr})_i$ ,  $\varepsilon_{\text{Nd}}(t)$  and Nd model ages, the following parameter were used:  $\lambda_{\text{Rb}} = 1.42 \times 10^{-11} \text{ year}^{-1}$  (Minster et al., 1982);  $\lambda_{\text{Sm}} = 6.54 \times 10^{-12} \text{ year}^{-1}$  (Lugmair and Marti, 1978);  $(^{147}\text{Sm}/^{144}\text{Nd})_{\text{CHUR}} = 0.1960 \pm 4$ ,  $(^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}} = 0.512630 \pm 11$  ( $2\sigma$ ) (Bouvier et al., 2008);  $(^{143}\text{Nd}/^{144}\text{Nd})_{\text{DM}} = 0.513151$ ,  $(^{147}\text{Sm}/^{144}\text{Nd})_{\text{DM}} = 0.2136$  (Liew and Hofmann, 1988). The  $^{147}\text{Sm}/^{144}\text{Nd}$  value of 0.118 for average continental crust (Jahn and Condie, 1995) was used for the mantle extraction model age ( $T_{2\text{DM}}$ ) for the source rocks of the magmas.

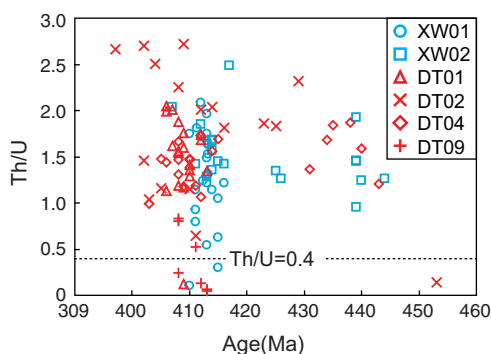


Fig. 5. Th/U vs Age diagram for zircons from Xiawan and Duntou granites.

## 4. Analytical results

### 4.1. Biotite compositions

The compositions of biotites in Xiawan monzogranite and Duntou granodiorite are shown in Table 2. Because of chloritization, the total major element contents are low without analyzing H<sub>2</sub>O. Watson and Harrison (1983) suggested that the chemical changes for the transformation from biotite to chlorite were as follows: large introductions of H<sub>2</sub>O and H<sup>+</sup>; relatively minor introductions of Mg and Fe; and major losses of K and Si. Since the major element composition of granitic chlorite is strongly influenced by the composition of the parent biotite (Dodge, 1973), the chlorites have similar FeO<sup>T</sup>/(FeO<sup>T</sup> + MgO) ratios to those of their host biotites (Tulloch, 1979). According to the revised mica classification (Rieder et al., 1998), all of the chloritic biotites in Xiawan and Duntou granites plot in between the Fe-rich siderophyllite end member and Mg-rich eastonite end member (Fig. 2a), and most of these chloritic biotites belong to magnesium biotites (Fig. 2b).

### 4.2. Zircons U–Pb geochronology

Two samples (XW01 and XW02) from Xiawan monzogranite and four samples (DT01, DT02, DT04 and DT09) from Duntou granodiorite are selected for zircon U–Pb dating and Hf isotope analyses. The locations of these 6 selected samples are shown in Fig. 1b. CL images of representative zircons are shown in Fig. 3. Zircons separated from

the selected samples are light yellow, prismatic or ellipsoidal in shape with aspect ratios of 1.5 to 4.0, and approximately 100 to 250 μm long with well-developed oscillatory zoning. Some euhedral zircons show prisms with {110} > {100} and pyramids with {211} > {101}, and others are ellipsoidal shape.

#### 4.2.1. Xiawan monzogranite (XW01 and XW02)

Nineteen U–Pb analyses of zircons from XW01 show variably high Th/U (0.11–2.09), indicating an igneous origin (Fig. 5). All the analyses are concordant, yielding a weighted mean <sup>206</sup>Pb/<sup>238</sup>U age of 413 ± 3 Ma (MSWD = 0.073; Appendix Table 2, Fig. 4).

Zircons from the XW02 have high and varying Th/U values (0.96 to 2.49) (Fig. 5). Of the 18 analyses, seven grains record older <sup>206</sup>Pb/<sup>238</sup>U ages of 436 ± 6 Ma (MSWD = 1.5; Appendix Table 2, Fig. 4). The remaining 11 analyses plot on the concordia curve and yield a weighted mean <sup>206</sup>Pb/<sup>238</sup>U age of 413 ± 3 Ma (MSWD = 0.25; Appendix Table 2, Fig. 4).

#### 4.2.2. Duntou granodiorite (DT01, DT02, DT04 and DT09)

A total of 19 analyses on 19 zircons from DT01 give high Th/U values (0.12 to 2.05) (Fig. 5). These analyses plot on or close to the concordia curve, yielding <sup>206</sup>Pb/<sup>238</sup>U ages of 406 ± 5 Ma to 413 ± 6 Ma with a weighted mean <sup>206</sup>Pb/<sup>238</sup>U age of 409 ± 3 Ma (MSWD = 0.116; Appendix Table 2, Fig. 4).

Zircons from DT02 show high Th/U values (0.14 to 2.72) and are consistent with their magmatic origin (Fig. 5). Eighteen analyses except for DT02-16 give <sup>206</sup>Pb/<sup>238</sup>U age of 453 ± 9 Ma, and other seventeen analyses yield <sup>206</sup>Pb/<sup>238</sup>U ages primarily between 397 ± 11 and 429 ± 10 Ma with a weighted mean <sup>206</sup>Pb/<sup>238</sup>U age of 411 ± 4 Ma (MSWD = 0.48; Appendix Table 2, Fig. 4).

Twenty analyses of 20 zircons from DT04 were obtained, showing high Th/U values (0.99–1.87) (Fig. 5). All the analyses are concordant. Six zircon grains exhibit older <sup>206</sup>Pb/<sup>238</sup>U ages ranging from 431 ± 6 Ma to 443 ± 7 Ma and give a weighted mean age of 436 ± 5 Ma (MSWD = 0.42; Appendix Table 2, Fig. 4). The other 14 zircon grains exhibit younger <sup>206</sup>Pb/<sup>238</sup>U ages ranging from 403 ± 7 Ma to 415 ± 5 Ma with a weighted mean age of 410 ± 3 Ma (MSWD = 0.33; Appendix Table 2, Fig. 4).

Seven analyses on seven grains from DT09 give high and varying Th/U values (0.05–0.84) (Fig. 5). The bulk of the analyses are grouped and concordant, defining a weighted mean <sup>206</sup>Pb/<sup>238</sup>U age of 411 ± 4 Ma (MSWD = 0.17; Appendix Table 2, Fig. 4).

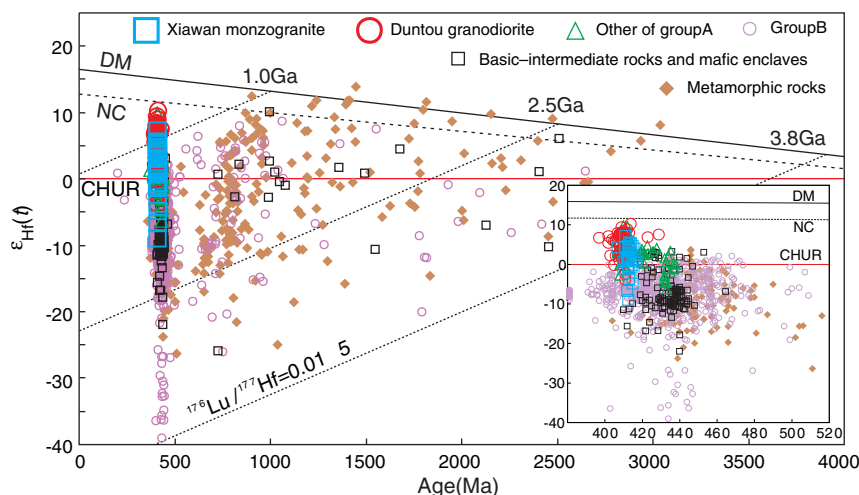


Fig. 6. Hf-isotope compositions of representative zircons from Xiawan and Duntou granites. Data sources are the same as in Appendix Table 1. Data of Hf-isotope are from the following references: Xu et al., 2005; Yu et al., 2005; Zeng et al., 2008; He et al., 2010b; Liu et al., 2010; Li et al., 2010a, 2010b, 2011; Chu et al., 2012; Guo et al., 2012; Nong et al., 2012; Yang, 2012; Yao et al., 2012; Zhang et al., 2010a, 2011a, 2011b, 2012; Wang et al., 2011a, 2013b; Zhao et al., 2013b and this study.

**Table 3**

Chemical compositions of representative samples from Xiawan and Duntou granites.

| Sample                             | Xiawan monzogranite |       |       |       | Duntou granodiorite |        |       |       |       |       |       |
|------------------------------------|---------------------|-------|-------|-------|---------------------|--------|-------|-------|-------|-------|-------|
|                                    | XW01                | XW04  | XW06  | XW07  | DT01                | DT02   | DT03  | DT04  | DT06  | DT07  | DT09  |
| SiO <sub>2</sub>                   | 73.19               | 72.97 | 72.44 | 72.25 | 67.59               | 68.89  | 74.36 | 73.51 | 74.87 | 72.95 | 74.63 |
| TiO <sub>2</sub>                   | 0.28                | 0.30  | 0.32  | 0.31  | 0.54                | 0.49   | 0.16  | 0.21  | 0.08  | 0.22  | 0.21  |
| Al <sub>2</sub> O <sub>3</sub>     | 13.43               | 13.47 | 13.17 | 13.58 | 15.69               | 16.23  | 13.54 | 13.85 | 12.59 | 13.94 | 13.26 |
| Fe <sub>2</sub> O <sub>3</sub>     | 2.04                | 2.22  | 2.32  | 2.15  | 3.51                | 3.23   | 1.28  | 1.95  | 0.60  | 1.86  | 1.80  |
| MnO                                | 0.03                | 0.02  | 0.03  | 0.04  | 0.05                | 0.04   | 0.03  | 0.03  | 0.04  | 0.04  | 0.05  |
| MgO                                | 0.39                | 0.41  | 0.54  | 0.77  | 1.52                | 1.15   | 0.24  | 0.54  | 0.13  | 0.40  | 0.72  |
| CaO                                | 0.61                | 0.19  | 0.82  | 0.97  | 1.09                | 0.45   | 0.16  | 1.00  | 1.62  | 1.03  | 1.34  |
| Na <sub>2</sub> O                  | 3.30                | 3.31  | 3.16  | 3.89  | 5.24                | 4.79   | 3.57  | 3.46  | 3.56  | 3.50  | 4.59  |
| K <sub>2</sub> O                   | 4.82                | 5.27  | 5.30  | 4.02  | 2.01                | 2.08   | 5.28  | 3.65  | 3.99  | 3.55  | 1.51  |
| P <sub>2</sub> O <sub>5</sub>      | 0.09                | 0.05  | 0.11  | 0.11  | 0.23                | 0.22   | 0.04  | 0.08  | 0.03  | 0.07  | 0.04  |
| LOI                                | 1.52                | 1.47  | 1.45  | 1.68  | 2.63                | 2.60   | 1.17  | 1.40  | 2.33  | 2.14  | 1.64  |
| SUM                                | 99.69               | 99.69 | 99.66 | 99.77 | 100.11              | 100.15 | 99.82 | 99.68 | 99.84 | 99.71 | 99.80 |
| ALK                                | 8.12                | 8.59  | 8.46  | 7.91  | 7.25                | 6.87   | 8.85  | 7.12  | 7.55  | 7.05  | 6.10  |
| A/CNK <sup>a</sup>                 | 1.14                | 1.17  | 1.06  | 1.09  | 1.23                | 1.48   | 1.14  | 1.21  | 0.96  | 1.22  | 1.14  |
| K <sub>2</sub> O/Na <sub>2</sub> O | 1.46                | 1.59  | 1.68  | 1.03  | 0.38                | 0.43   | 1.48  | 1.06  | 1.12  | 1.02  | 0.33  |
| Li                                 | 10.3                | 10.3  |       | 25.6  | 23.5                | 11.2   |       | 20.0  |       | 164.5 | 10.2  |
| Be                                 | 1.01                | 1.08  |       | 1.06  | 1.60                | 2.50   |       | 1.29  |       | 1.44  | 1.25  |
| Sc                                 | 3.16                | 3.45  |       | 3.77  | 3.40                | 3.53   |       | 2.64  |       | 2.77  | 2.23  |
| V                                  | 19.2                | 20.6  |       | 24.5  | 58.1                | 12.4   |       | 18.1  |       | 16.0  | 21.7  |
| Cr                                 | 4.70                | 8.47  |       | 6.60  | 14.1                | 2.13   |       | 6.50  |       | 2.75  | 6.00  |
| Co                                 | 2.57                | 1.61  |       | 2.82  | 8.12                | 1.46   |       | 2.69  |       | 2.30  | 2.87  |
| Ni                                 | 2.82                | 3.05  |       | 3.67  | 8.23                | 1.02   |       | 2.95  |       | 1.62  | 3.21  |
| Cu                                 | 13.77               | 5.98  |       | 4.62  | 8.52                | 2.87   |       | 3.16  |       | 2.09  | 3.34  |
| Zn                                 | 26.9                | 45.7  |       | 45.7  | 107                 | 47.6   |       | 34.9  |       | 37.2  | 46.2  |
| Ga                                 | 14.3                | 13.8  |       | 13.6  | 16.7                | 16.6   |       | 13.3  |       | 14.9  | 12.2  |
| Ge                                 | 0.78                | 0.71  |       | 0.58  | 0.62                | 1.34   |       | 0.91  |       | 0.77  | 0.84  |
| Rb                                 | 130                 | 125   |       | 147   | 101                 | 202    |       | 91.2  |       | 107   | 72.7  |
| Sr                                 | 151                 | 172   |       | 228   | 214                 | 137    |       | 327   |       | 151   | 225   |
| Y                                  | 7.79                | 7.79  |       | 7.74  | 8.31                | 24.4   |       | 7.55  |       | 9.35  | 5.22  |
| Zr                                 | 245                 | 276   |       | 220   | 219                 | 272    |       | 176   |       | 182   | 106   |
| Nb                                 | 9.61                | 10.6  |       | 9.66  | 8.07                | 19.3   |       | 4.59  |       | 11.5  | 3.48  |
| Cs                                 | 1.89                | 1.87  |       | 3.59  | 2.58                | 2.84   |       | 2.90  |       | 3.11  | 1.77  |
| Ba                                 | 1568                | 1888  |       | 1249  | 493                 | 881    |       | 2168  |       | 1079  | 262   |
| La                                 | 64.5                | 49.3  |       | 39.7  | 36.1                | 61.3   |       | 38.7  |       | 49.0  | 11.6  |
| Ce                                 | 106                 | 88.0  |       | 66.1  | 60.9                | 117    |       | 63.6  |       | 83.5  | 15    |
| Pr                                 | 11.1                | 10.1  |       | 6.39  | 6.38                | 13.5   |       | 6.22  |       | 8.01  | 1.98  |
| Nd                                 | 35.2                | 32.3  |       | 20.3  | 21.0                | 47.7   |       | 20.0  |       | 25.5  | 6.85  |
| Sm                                 | 4.86                | 4.49  |       | 2.95  | 2.95                | 8.18   |       | 2.98  |       | 3.79  | 1.17  |
| Eu                                 | 1.08                | 1.09  |       | 0.90  | 0.85                | 1.04   |       | 1.06  |       | 0.94  | 0.49  |
| Gd                                 | 3.33                | 3.02  |       | 2.18  | 2.15                | 6.61   |       | 2.19  |       | 2.88  | 1.04  |
| Tb                                 | 0.40                | 0.36  |       | 0.27  | 0.27                | 0.87   |       | 0.27  |       | 0.37  | 0.14  |
| Dy                                 | 1.83                | 1.75  |       | 1.43  | 1.41                | 4.79   |       | 1.40  |       | 1.80  | 0.82  |
| Ho                                 | 0.29                | 0.29  |       | 0.26  | 0.25                | 0.87   |       | 0.24  |       | 0.31  | 0.15  |
| Er                                 | 0.77                | 0.81  |       | 0.72  | 0.73                | 2.45   |       | 0.70  |       | 0.83  | 0.44  |
| Tm                                 | 0.10                | 0.11  |       | 0.10  | 0.10                | 0.35   |       | 0.10  |       | 0.11  | 0.07  |
| Yb                                 | 0.64                | 0.69  |       | 0.65  | 0.69                | 2.16   |       | 0.71  |       | 0.69  | 0.45  |
| Lu                                 | 0.10                | 0.11  |       | 0.11  | 0.10                | 0.32   |       | 0.11  |       | 0.11  | 0.07  |
| Hf                                 | 5.81                | 6.42  |       | 4.77  | 4.40                | 6.88   |       | 4.24  |       | 4.39  | 2.82  |
| Ta                                 | 0.36                | 0.29  |       | 0.34  | 0.68                | 1.04   |       | 0.38  |       | 0.74  | 0.15  |
| Pb                                 | 21.9                | 23.2  |       | 21.2  | 36.1                | 37.0   |       | 24.8  |       | 22.8  | 6.5   |
| Th                                 | 20.2                | 19.6  |       | 17.3  | 7.4                 | 23.2   |       | 15.7  |       | 15.3  | 3.7   |
| U                                  | 1.85                | 0.67  |       | 1.18  | 0.74                | 3.12   |       | 1.27  |       | 1.17  | 0.67  |
| Eu/Eu <sup>*b</sup>                | 0.78                | 0.86  |       | 1.04  | 0.98                | 0.42   |       | 1.21  |       | 0.84  | 1.33  |
| ΣREE                               | 230                 | 192   |       | 142   | 134                 | 267    |       | 138   |       | 178   | 41    |
| (La/Yb) <sub>N</sub>               | 68.3                | 48.0  |       | 41.0  | 35.5                | 19.1   |       | 36.9  |       | 47.7  | 17.6  |
| T (°C) <sup>c</sup>                | 836                 | 850   |       | 819   | 824                 | 865    |       | 811   |       | 815   | 763   |

<sup>a</sup> A/CNK = molar Al<sub>2</sub>O<sub>3</sub>/(CaO + Na<sub>2</sub>O + K<sub>2</sub>O).<sup>b</sup> Eu/Eu<sup>\*</sup> = 2 × Eu<sub>N</sub>/(Sm<sub>N</sub> + Gd<sub>N</sub>).<sup>c</sup> Temperature (°C) is calculated after Watson and Harrison (1983).

### 4.3. Zircons Hf-isotopes

The zircon Hf analyses were measured on the same grains used for U–Pb dating (Fig. 3). Analytical results of the Lu–Hf isotopic compositions are given in Appendix Table 3 and illustrated in Fig. 6.

#### 4.3.1. Xiawan monzogranite (XW01 and XW02)

Zircons from XW01 and XW02 show similar Hf-isotope compositions. The  $\varepsilon_{\text{Hf}}(t)$  and initial  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios for zircons in these two samples are relatively heterogeneous. The  $\varepsilon_{\text{Hf}}(t)$  values vary from  $-9.0$  to  $+7.2$ , clustering within the range of  $-1$  to  $+5$  (Fig. 5).

In addition, the initial  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios range from 0.282272 to 0.282730, corresponding to the two-stage depleted mantle Hf model ages ( $T_{2\text{DM}}$ ) of 0.92 Ga to 1.95 Ga or the two-stage new continental crust Hf model ages ( $T_{2\text{NC}}$ ) of 0.71 Ga to 1.78 Ga (Fig. 5).

#### 4.3.2. Duntou granodiorite (DT01, DT02, DT04 and DT09)

The zircons from DT01, DT02, DT04 and DT09 also exhibit similar  $\varepsilon_{\text{Hf}}(t)$  values and initial  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios. The  $\varepsilon_{\text{Hf}}(t)$  values vary from  $-3.9$  to  $+10.3$ , clustering within the range of  $+1$  to  $+8$  (Fig. 5). In addition, the initial  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios range from 0.282417 to 0.282814, corresponding to the two-stage depleted mantle Hf model



ages ( $T_{2DM}$ ) of 0.73 Ga to 1.63 Ga or the two-stage new continental crust Hf model ages ( $T_{2NC}$ ) of 0.51 Ga to 1.44 Ga (Fig. 5).

#### 4.4. Whole-rock major and trace elements

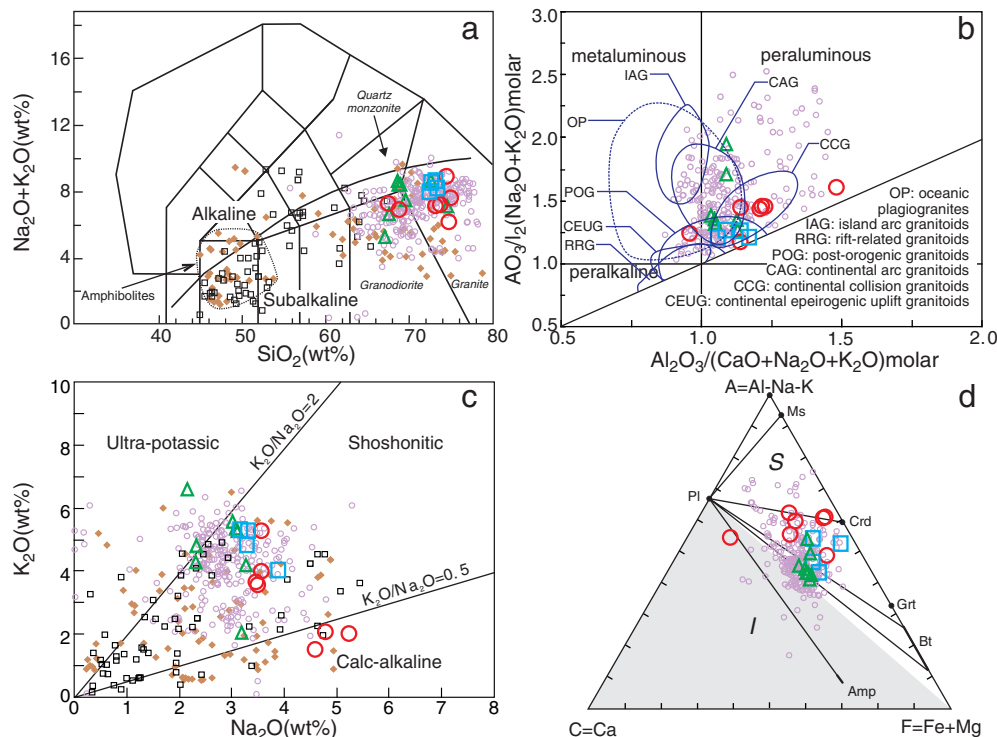
A complete data set of whole-rock major and trace element analyses for representative samples from the Xiawan monzogranite and Duntou granodiorite are listed in Table 3. All the samples of Xiawan and Duntou granites show high  $SiO_2$  (between 67.59 and 74.87 wt.%) and relatively high total alkalis ( $K_2O + Na_2O$ ) ranging from 6.10 to 8.85 wt.%, plotting in the granodiorite and granite fields on the total alkali-silica (TAS) diagram (Fig. 7a). Based on the molar ratios of  $Al_2O_3/(CaO + Na_2O + K_2O)$  (A/CNK) and  $Al_2O_3/(Na_2O + K_2O)$  (A/NK) (Fig. 7b), the Xiawan monzogranite is weakly to strongly peraluminous ( $A/CNK = 1.06–1.17$ ), plotting in the field of post-orogenic granitoids. The Duntou granodiorite is metaluminous to peraluminous ( $A/CNK = 0.96–1.48$ ), and most of the samples plot in the continental collision granitoids and post-orogenic granitoids field. In Fig. 7c, all samples of Xiawan and Duntou granites except for DT01, DT02 and DT09 have high  $K_2O$  (3.55–5.30 wt.%) and very high  $K_2O/Na_2O$  (1.02–1.68), characteristic mainly of crustal origin. The samples of DT01, DT02 and DT09 are distinct from other samples with its relatively low  $K_2O$  content (1.51–2.08 wt.%) and high  $Na_2O$  (4.59–5.24 wt.%), reaching to the field of Precambrian amphibolites, and show a likely mantle-derived magma involvement in Duntou granodiorite. Alternatively, the reduction of  $K_2O$  content in DT01, DT02 and DT09 may be caused by the alteration of biotite or other K-rich minerals, especially the LOI of DT01 and DT02 can reach more than 2.60 wt.% which is the highest of Duntou granodiorite. In  $K_2O-SiO_2$  (Fig. 8) and  $K_2O-Na_2O$  (Fig. 7c) diagrams, all samples of Xiawan and Duntou granites together with

other early Paleozoic granites in South China plot in the calc-alkaline to shoshonitic fields. In Harker diagrams (Fig. 8), Xiawan and Duntou granites show negative correlation between  $P_2O_5$  and  $SiO_2$ , characteristic of I-type granites. The  $P_2O_5$  and  $TiO_2$  saturation thermometer (Green and Pearson, 1986; Harrison and Watson, 1984) indicates that Xiawan and Duntou granites have high initial temperatures (Fig. 8), which is in accordance with their Zr saturation temperatures (763–865 °C, most higher than 810 °C; Table 3; Watson and Harrison, 1983).

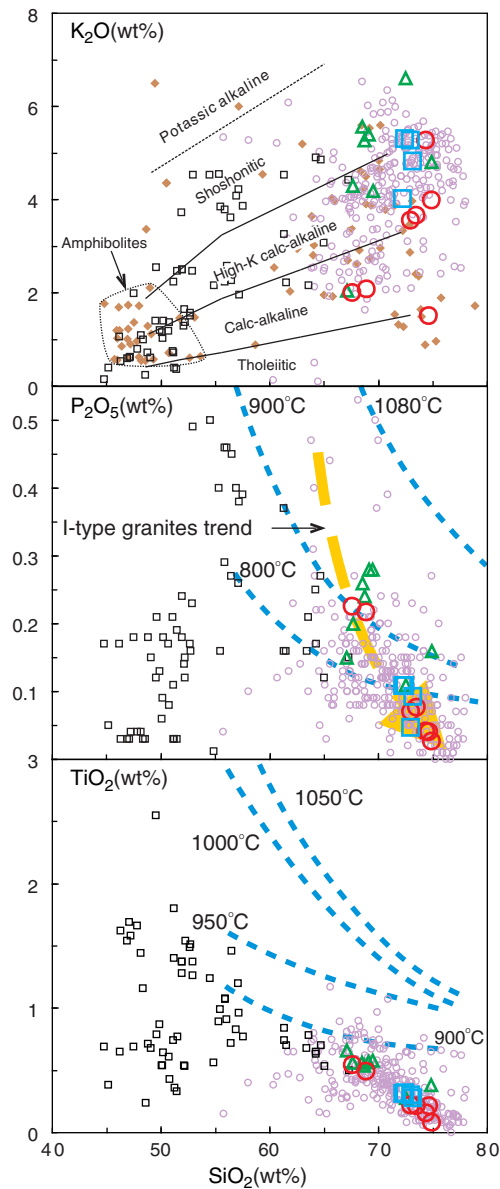
Xiawan and Duntou granites with total REE ranging from 41 to 267 ppm show similar chondrite-normalized REE patterns and relative enrichment of LREE over HREE without significant negative Eu anomalies ( $Eu/Eu^* = 0.42–1.33$ ), suggesting that the magma may be derived from lower crust or mantle-derived materials (Table 3, Fig. 9). The  $(La/Yb)_N$  values are higher in Xiawan monzogranite (41.0–68.3) than in Duntou granodiorite (17.6–47.7) (Table 3). In the primitive mantle-normalized trace element diagrams (Fig. 9), they are all characterized by positive Rb, Ba, Th, U and Pb and negative Nb and Ta anomalies and marked depletion in Sr, P and Ti. The negative P and Ti anomalies indicate that fractionation of apatite and Fe–Ti oxides also occurred during magma evolution. However, all the samples of Xiawan and Duntou together with other early Paleozoic granites in South China have REE patterns and trace element diagrams similar to Precambrian metamorphic basement rocks, suggesting the possibility that they are mainly derived from the crustal material.

#### 4.5. Sr–Nd isotopes

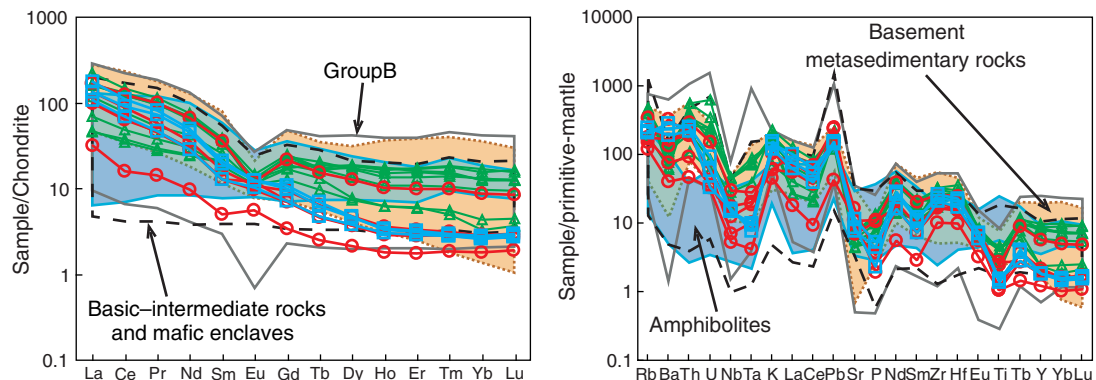
The whole-rock Nd isotopic data of Xiawan and Duntou granites are given in Table 4. Xiawan monzogranites have relatively lower initial  $^{87}Sr/^{86}Sr$  ranging from 0.70061 to 0.70419 and higher  $\epsilon_{Nd}(t)$  values



**Fig. 7.** (a) The total alkali vs. silica (TAS) diagram (after Middlemost, 1994) used for the classification of the Xiawan and Duntou samples. (b) Chemical compositions of the Xiawan and Duntou granites in terms of alumina saturation, the fields of granitoids from different tectonic environments are after Maniar and Piccoli (1989). (c)  $K_2O$  vs.  $Na_2O$  variation diagram (after Turner et al., 1996). (d) ACF diagram (after White and Chappell, 1977). Symbols are the same as in Fig. 6. Data of chemical compositions are from the following references: Chen et al., 2012; Cheng et al., 2009a, 2009b, 2012; Fu et al., 2004; Geng et al., 2006; He et al., 2010b; Li et al., 2006, 2010a, 2010b, 2010c, 2011; Liu et al., 2008; Lou et al., 2002; Lou et al., 2005; Peng et al., 2006a, 2006b; Sha and Yuan, 1991; Shen et al., 2008; Wan et al., 2010; Wang et al., 2011a, 2011b, 2013b; Wu and Zhang, 2003; Wu et al., 2008; Xu et al., 2006; Yao et al., 2012; Zeng et al., 2008; Zhang et al., 2010b, 2010c, 2012; Zhao et al., 2013b; Zhou et al., 1994b and this study.



**Fig. 8.** Harker diagram of major-element compositions of the Xiawan and Duntou samples: in  $K_2O$  vs.  $SiO_2$  diagram (after [Peccherillo and Taylor, 1976](#)), the dotted line represents the division between potassic alkaline and shoshonitic suites (after [Calanchi et al., 2002](#)); in  $P_2O_5$  vs.  $SiO_2$  (after [Harrison and Watson, 1984](#)), the I-type granites trend follows [Chappell \(1999\)](#); the  $TiO_2$  vs.  $SiO_2$  is after [Green and Pearson \(1986\)](#). Symbols and data sources are the same as in [Fig. 7](#).



**Fig. 9.** Chondrite-normalized REE patterns and Primitive mantle-normalized multiple trace element diagrams of the Xiawan and Duntou samples. The chondrite values are from [Taylor and McLennan \(1985\)](#). The primitive mantle values are from [McDonough and Sun \(1995\)](#). Symbols and data sources are the same as in [Fig. 7](#).

ranging from  $-5.0$  to  $-3.7$ . The initial  $^{87}Sr/^{86}Sr$  and  $\epsilon_{Nd}(t)$  of Duntou granodiorites vary from  $0.70249$  to  $0.70719$  and  $-3.0$  to  $+1.1$  respectively.

The Xiawan and Duntou granites and other granitoids of Group A have relatively higher radiogenic Nd than Group B granitoids but some still plot within the evolution domain of Precambrian basement in either Yangtze or Cathaysia ([Fig. 10a](#)). They are well distributed along the terrestrial array of  $\epsilon_{Nd}(t)$  vs.  $\epsilon_{Hf}(t)$  diagram ([Vervoort et al., 1999](#)), and most of the samples plot into the range of global lower crust ([Fig. 10b](#)).

## 5. Discussion

### 5.1. The chronology of early Paleozoic granites in South China

Numerous granitic bodies emplaced during the early Paleozoic to the east of the Anhua–Luocheng Fault in South China ([Fig. 1a](#)), covering an outcrop area over  $20,000 \text{ km}^2$  (e.g., [Shu et al., 2008a, 2008b](#); [Zhou et al., 2006](#)). Recently SHRIMP and LA-ICP-MS zircon U–Pb dating show that they were intruded mainly from  $381$  to  $467 \text{ Ma}$  ([Chen and Zhuang, 1994](#); [Chen et al., 2011](#); [Cheng et al., 2009a, 2009b, 2012](#); [Chu et al., 2012](#); [Fu et al., 2004](#); [Guo et al., 2012](#); [He et al., 2010b](#); [Li, 1991](#); [Li et al., 1989, 2010a, 2010b, 2010c](#); [Lou et al., 2005](#); [Nong et al., 2012](#); [Peng et al., 2000, 2006b](#); [Shen et al., 2008](#); [Tang and Li, 2003](#); [Wan et al., 2010](#); [Wang et al., 2011a, 2011b](#); [Wu and Zhang, 2003](#); [Wu et al., 2008](#); [Xu and Zhang, 1993](#); [Xu et al., 2006](#); [Zeng et al., 2008](#); [Zhang et al., 2010a, 2010b, 2010c, 2011b, 2012](#); [Zhao et al., 2013b](#) and this study; also see in [Appendix Table 1](#)), mostly between  $440$  and  $390 \text{ Ma}$ , systematically postdating the peak metamorphism (earlier than  $445 \text{ Ma}$ ; [Appendix Table 1](#); [Yu et al., 2005b, 2006, 2007](#); [Li et al., 2010c](#)), implying that they are not form in the syn-collision compressional environment. In addition, [Charvet et al. \(2010\)](#) reported ages of  $433 \pm 9 \text{ Ma}$  and  $437 \pm 5 \text{ Ma}$  (Early Silurian) for the main anatexis event, and a younger age of  $412 \pm 5 \text{ Ma}$  (Late Silurian–Early Devonian) for a late re-heating process by U–Th–Pb EPMA monazite dating. [England and Thompson \(1984\)](#) and [Thompson and Connolly \(1995\)](#) have argued that tens of millions of years may pass between a crustal thickening event and the subsequent melting/emplacement of syn-collisional granites. In fact, most of those granites are intruded into Paleoproterozoic to Neoproterozoic metamorphic basement (e.g., Mayuan, Badu, Zhoutan and Yunkai Complexes; see in [Appendix Table 1](#)), and a substantial proportion of granites develop gneissic structure with a strong magmatic orientation or a post-magmatic ductile deformational texture parallel to the schistosity of metamorphic wall rocks ([Wang et al., 2011a, 2013a](#); [Zhang et al., 2012](#)). Thus, all these available age data imply that early Paleozoic granites should belong to syn-collisional to post-collisional granites.

**Table 4**

Sr–Nd isotope compositions of representative samples from Xiawan and Duntou granites.

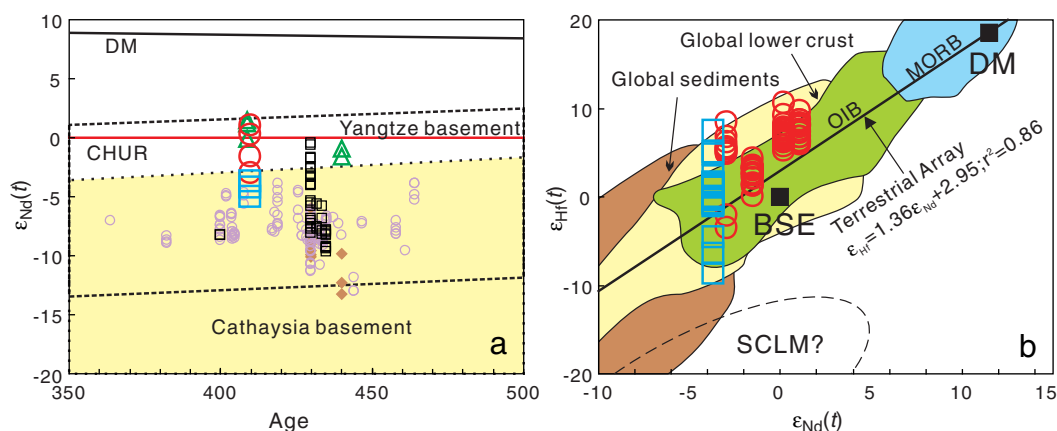
| Sample                     | Age (Ma) | Rb (ppm) | Sr (ppm) | $^{87}\text{Rb}/^{86}\text{Sr}$ | $^{87}\text{Sr}/^{86}\text{Sr}$ | $2\sigma$ | $^{87}\text{Sr}/^{86}\text{Sr}_i$ | Sm (ppm) | Nd (ppm) | $^{147}\text{Sm}/^{144}\text{Nd}$ | $^{143}\text{Nd}/^{144}\text{Nd}$ | $2\sigma$ | $\epsilon_{\text{Nd}}(t)$ | $T_{2\text{DM}}$ (Ga) |
|----------------------------|----------|----------|----------|---------------------------------|---------------------------------|-----------|-----------------------------------|----------|----------|-----------------------------------|-----------------------------------|-----------|---------------------------|-----------------------|
| <i>Duntou granodiorite</i> |          |          |          |                                 |                                 |           |                                   |          |          |                                   |                                   |           |                           |                       |
| DT01                       | 410      | 102      | 190      | 1.5526                          | 0.711557                        | 0.000016  | 0.70249                           | 3.36     | 22.9     | 0.0887                            | 0.5124                            | 0.000015  | 1.1                       | 1.08                  |
| DT02                       | 410      | 97.5     | 238      | 1.1868                          | 0.713814                        | 0.000017  | 0.70688                           | 2.69     | 16.9     | 0.0964                            | 0.5124                            | 0.000009  | 0.2                       | 1.15                  |
| DT04                       | 410      | 87.0     | 278      | 0.9055                          | 0.712438                        | 0.000017  | 0.70715                           | 3.21     | 20.7     | 0.0938                            | 0.5123                            | 0.000006  | −1.5                      | 1.29                  |
| DT09                       | 410      | 72.4     | 195      | 1.0751                          | 0.711977                        | 0.000017  | 0.70570                           | 1.32     | 7.20     | 0.1107                            | 0.5122                            | 0.000013  | −3.0                      | 1.41                  |
| <i>Xiawan monzogranite</i> |          |          |          |                                 |                                 |           |                                   |          |          |                                   |                                   |           |                           |                       |
| XW01                       | 410      | 119      | 132      | 2.6243                          | 0.715930                        | 0.000016  | 0.70061                           | 5.54     | 38.1     | 0.0879                            | 0.5121                            | 0.000015  | −3.7                      | 1.47                  |
| XW04                       | 410      | 125      | 172      | 2.0962                          | 0.715619                        | 0.000013  | 0.70338                           | 4.49     | 32.3     | 0.0839                            | 0.5121                            | 0.000010  | −5.0                      | 1.58                  |
| XW07                       | 410      | 147      | 228      | 1.8587                          | 0.715045                        | 0.000012  | 0.70419                           | 2.95     | 20.3     | 0.0878                            | 0.5121                            | 0.000005  | −4.2                      | 1.51                  |

Our geochronological results for six samples from Xiawan and Duntou granites give zircon U–Pb ages of ca. 410 Ma (Fig. 4). These ages can be interpreted as the crystallization ages of these granites. It is worth noting that a fraction of zircons reveal comparatively older ages in XW02, DT02 and DT04, and these older zircon grains give a weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  age of ca. 436 Ma in both XW02 and DT04 (Fig. 4). In addition, the Th/U values of such older zircons are magmatic origin, and the  $\epsilon_{\text{Hf}}(t)$  values of older zircons are fully consistent with younger ones, suggesting that all the 410 Ma and 436 Ma zircons are isogenic or crystallize from the same parental magma. Many studies have shown that multiple age populations could exist in one granite or a single zircon with different age domains. Hence the maximum age difference probably representing the duration of magma cooling–crystallization, may reach more than 50 Ma (Cheng et al., 2007; Gehrels et al., 2009; Lou et al., 2005; Wang et al., 2007a; Yu and Zhao, 2007). Thus, there might be a large magma chamber beneath Xiawan and Duntou granites, and the crystallization of zircons began when parental magma was still in the magma chamber. Asthenosphere-derived magma (see below) periodically heated the parental magma, and subsequent cooling events led to the crystallization process of zircons from Xiawan and Duntou granites lasting for 26 Ma from ca. 436 Ma to ca. 410 Ma. But de Saint Blanquat et al. (2011) indicates that the longevity of magma reservoirs may hardly exceed 10 Ma. Thus, Xiawan and Duntou granites may commonly form incrementally without large magma chamber and the growth of magma bodies is episodic (Annen, 2009; Annen et al., 2006; Glazner et al., 2004). Melt is converged by multiple batches of magma via several extraction events (Brown, 2013). Alternatively, these ca. 436 Ma zircons, which are also widely

observed in Mesozoic felsic lavas in SE China (Guo et al., 2012), are inherited from the melting source.

## 5.2. Melting temperature and pressure conditions

Many reports acknowledged a relationship between zircon crystallization and the interplay of temperature and melt chemistry in controlling zircon solubility. Watson and Harrison (1983) undertook synthesis experiments that showed zircon solubility to be a function of the zirconium concentration of the melt, temperature, and magma composition. We have applied this relationship to calculate the Zr saturation temperature of early Paleozoic granites in South China. The results show that, in contrast to group B granitoids, which display comparatively large temperature range from 609 °C to 884 °C (mostly on 700–830 °C) (Chen et al., 2012; Cheng et al., 2009a, 2009b, 2012; Fu et al., 2004; Geng et al., 2006; He et al., 2010b; Li et al., 2006, 2010a, 2010c, 2011; Liu et al., 2008; Lou et al., 2002, 2005; Peng et al., 2006a, 2006b; Shen et al., 2008; Wan et al., 2010; Wang et al., 2011a, 2012b, 2013b; Wu et al., 2008; Xu et al., 2006; Yao et al., 2012; Zeng et al., 2008; Zhang et al., 2010b, 2010c, 2012; Zhao et al., 2013b; Zhou et al., 1994b), the Group A granitoids, including the Xiawan and Duntou granites, generally record higher temperatures from 751 °C to 853 °C (mostly at 810–850 °C) (Wan et al., 2010; Li et al., 2010b and this study). This is likely due to the fact that the Group A granitoids form with more significant contributions of hot asthenosphere-derived materials (see below). An contents of plagioclases together with  $\text{P}_2\text{O}_5$  and  $\text{TiO}_2$  saturation thermometer of Xiawan and Duntou



**Fig. 10.** (a) Whole-rock Nd-isotope compositions of Xiawan and Duntou granites (the area of Yangtze and Cathaysia basement is after Chen and Jahn, 1998). (b)  $\epsilon_{\text{Nd}}(t)$  vs.  $\epsilon_{\text{Hf}}(t)$  diagram for the Xiawan and Duntou granites. The trend of the terrestrial array is from Vervoort et al. (1999). Fields for MORB, OIB and global sediments are from Vervoort et al. (1999), and for global lower crust from Vervoort et al. (2000). Bulk Silicate Earth (BSE) and Depleted Mantle (DM) from Blichert-Toft and Albarède (1997), a suggested field for the bulk cratonic (SCLM) from Griffin et al. (2000). Symbols are the same as in Fig. 6. Data sources are the same as in Appendix Table 1. Data of Sr–Nd isotope are from the following references: Cheng et al., 2009a, 2009b, 2012; Fu et al., 2004; Li, 1991; Li et al., 1989, 2010a, 2010b, 2010c; Peng et al., 2000; Peng et al., 2006a; Shen et al., 2008; Wan et al., 2010; Wang et al., 2011a, 2013b; Wu et al., 2008; Xu and Zhang, 1993; Xu et al., 2006; Yao et al., 2012; Zhang et al., 2010b, 2010c, 2012; Zhao et al., 2013b and this study.

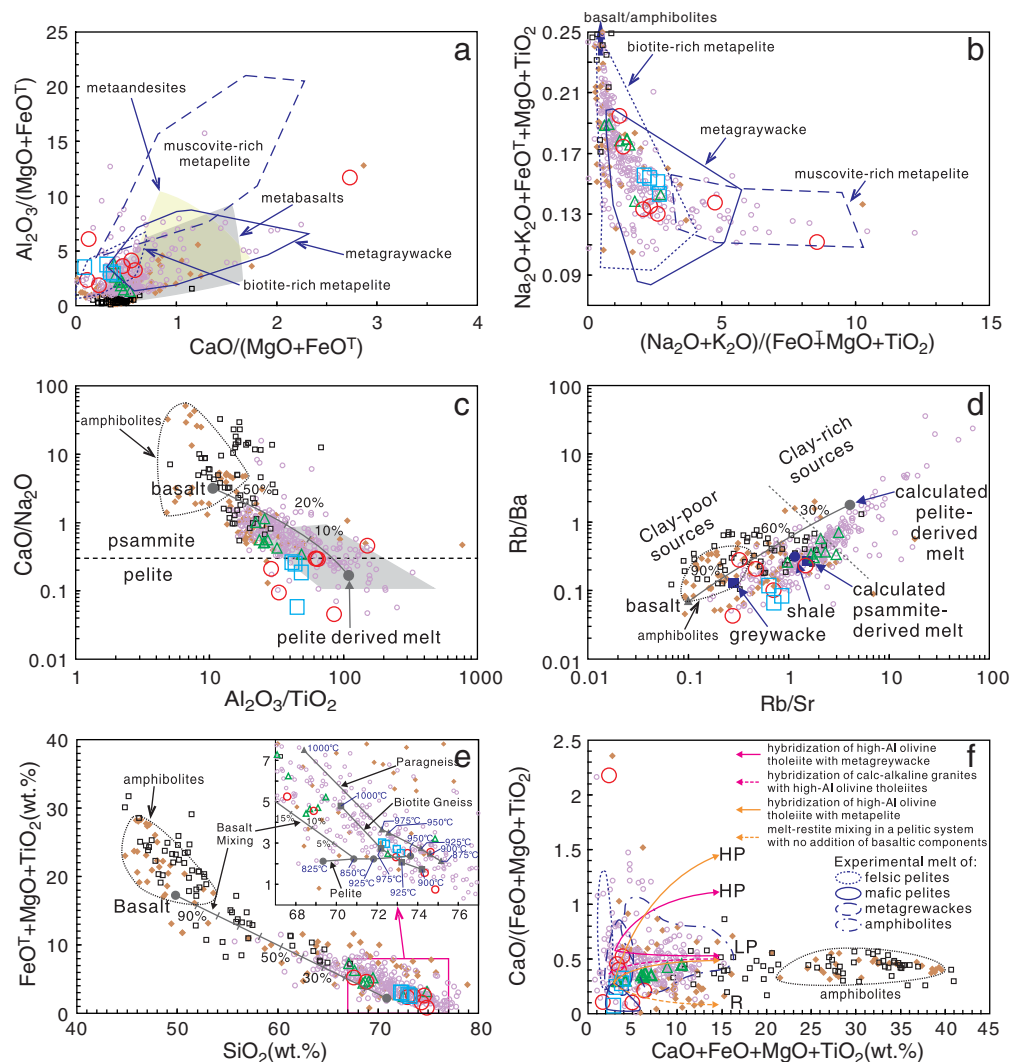
also support the result of zircon saturation temperatures (Fig. 8; Table 2).

As has been noted, the peak metamorphic pressure of the early Paleozoic orogen in South China Block was >0.8 GPa, reaching up to 1.0–1.1 GPa (Li et al., 2010c; Yu et al., 2003a, 2005a, 2005b, 2007), with the corresponding crustal thickness of 30–40 km. As syn-collisional to post-collisional granites, the stress relaxation process had begun when early Paleozoic granites started melting and emplacement. According to the experimental studies summarized by Patiño Douce (1999), the compositions of most early Paleozoic granites plot along the reaction curves that would be produced by the hybridization of high-Al olivine tholeiite with metapelite or metagreywacke at low pressure ( $\leq 0.5$  GPa) with the corresponding crustal thickness less than ca. 18 km (Fig. 11f), indicating fast crustal thinning after stress relaxation.

### 5.3. The geneses of early Paleozoic granites in South China

Based on the studies of Lachlan Fold Belt granitoids, Chappell and White (1974) classified them into S- and I-type. As per Chappell et al. (2012), S-type granites always contain more Al than is required to form feldspar, given the Na, K and Ca contents of the rock, and are therefore peraluminous. The excess Al is hosted in Al-rich biotite, generally accompanied by more Al-rich minerals such as cordierite or

muscovite. In contrast, I-type granites are metaluminous and always contain amphibole. Chappell (1984, 1999) argued that S-type granite was derived by partial melting of supracrustal rocks that have undergone some extents of weathering. On the other hand, I-type granite was derived by partial melting of mafic to intermediate meta-igneous crustal rocks that had not experienced surface processes. However, Gray (1984) proposed a two-component mixing model and Collins (1996) argued a three source-component mixing model which offers a better understanding of the genesis of granites between I- and S-type with partial characteristics of either I- or S-type and the linear isotopic array or chemical variation of the I–S type granitoids paragenetic assemblage. Recently, the integrated in situ U–Pb, Hf, and O isotope study of zircons from granites has also demonstrated that I-type granite may form by mixing of sedimentary materials and mantle-derived magmas instead of remelting ancient meta-igneous crustal rocks (He et al., 2010a; Kemp et al., 2007; Yang et al., 2012; Zhu et al., 2009). Clemens et al. (2011) also suspected that the S–I dichotomy in granite typology is unlikely to reflect simple sedimentary versus igneous sources. But Clemens (2003) argues that the isotopic variations between I- and S-granitoids could be caused by source heterogeneities, magma mixing, assimilation and even by isotopic disequilibrium. If source mixing, magma mixing and wall-rock assimilation do exist extensively, the intermediate types between I- and S-granitoids are probably not minor in volume.



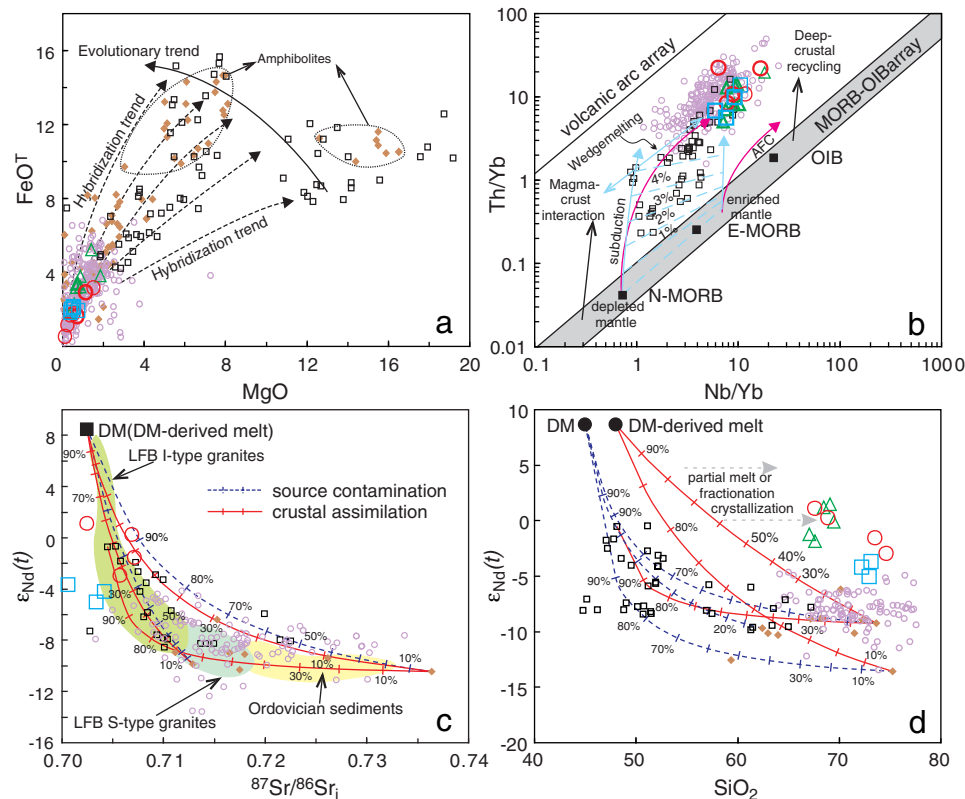
**Fig. 11.** Source discrimination diagrams for Xiawan and Duntou granites. (a) and (b) are after Lee et al. (2003) and Altherr and Siebel (2002). (c), (d) and (e) are after Sylvester (1998). (f) is after Patiño Douce (1999). Symbols and data sources are the same as in Fig. 7.



According to previous studies, except for a few granites that are considered as I-type granites (e.g., Hufang, Sibao, Maixie, Miao'ershan, Yuechengling, Hongjiang, Wugongshan, Shanzhuang, Sheshan and Daning; Chen et al., 2011, 2012; Li et al., 2010b, c; Lou et al., 2005; Nong et al., 2012; Sha and Yuan, 1991; Wu and Zhang, 2003; Zhao et al., 2013b), most early Paleozoic granites in South China belong to peraluminous S-type (Charvet, 2013). However, although most early Paleozoic granites are peraluminous, some of them are metaluminous (Fig. 7b) with relatively low  $K_2O/Na_2O$  values (Fig. 7c) and lack Al-rich cordierite or muscovite minerals. Some early Paleozoic granites have high  $P_2O_5$  that decreases with increasing  $SiO_2$  (Fig. 8) and show I-type granites affinity (Chappell, 1999). Thus, in ACF diagram (Fig. 7d) many early Paleozoic granites plot in the I-type field or straddle the boundary between I- and S-type fields. On the other side, those so-called I-type granites are always peraluminous with  $A/CNK = 0.93–1.40$  (most higher than 1.0). And except for a few granites like Yuechengling, Sheshan and Daning, those so-called I-type granites are generally amphibole-free. Therefore, the genetic type of early Paleozoic granites is not clear-cut, and many granites are transitional between S- and I-type, implying that source mixing, magma mixing or wall-rock assimilation instead of source heterogeneities may give rise to these granites (Clemens, 2003; Clemens et al., 2011). For example, lacking amphibole, Al-rich cordierite, or protogenic muscovite, Xiawan monzogranite and Duntou granodiorite are metaluminous to peraluminous ( $A/CNK = 0.96–1.48$ ) (Fig. 7b) with variable  $K_2O/Na_2O$  (Fig. 7c) and negative correlation between  $P_2O_5$  and  $SiO_2$  (Fig. 8), and most of them plot in the S-type field of ACF diagram (Fig. 7d). The compositions of biotites in Xiawan and Duntou granites plot in the fields of biotite in peraluminous granites (S-type granites) and biotite in metaluminous calc-alkaline

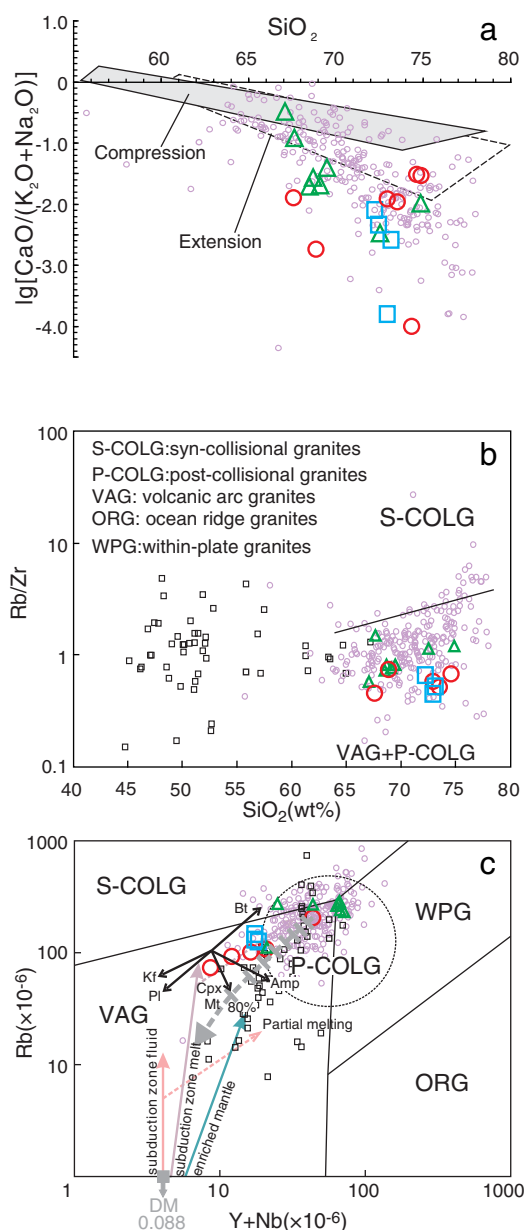
granite suites (I-type granites) (Fig. 2c, d). The Xiawan and Duntou granites exhibit high  $\varepsilon_{Hf}(t)$  and  $\varepsilon_{Nd}(t)$  values (Fig. 6, 10a) and their initial  $^{87}Sr/^{86}Sr$  and  $\varepsilon_{Nd}(t)$  are similar to Lachlan Fold Belt I-type granites (Fig. 12c), suggesting that Xiawan and Duntou granites are neither typical I- nor S-type granites but have partial characteristics of either I- or S-type granites. So it seems difficult to accurately classify early Paleozoic granites in South China following the classification of Lachlan Fold Belt granites into S- and I-type (Chappell and White, 1974). For the purpose of studying the genesis of early Paleozoic granites, we prefer to divide these granites into two Groups A and B using  $\varepsilon_{Hf}(t)$  and  $\varepsilon_{Nd}(t)$  values.

All the early Paleozoic granites in South China have similar REE and trace elements patterns to the metasedimentary rocks from Paleoproterozoic to Neoproterozoic metamorphic basement which are involved in early Paleozoic Orogen (Liu et al., 2008; Wan et al., 2010; Wang et al., 2011a; Zeng et al., 2008) (Fig. 9). Hf and Nd isotopic compositions of Group B granitoids are in accordance with the Paleoproterozoic to Neoproterozoic metamorphic basement while Hf and Nd isotopic compositions of Group A are higher (Appendix Table 1; Figs. 6, 10a). In source discrimination diagrams based on experimental studies of melting of metamorphic rocks, most of granitoids from both Group A and Group B plot in the biotite-rich metapelite field and the rest plot into muscovite-rich metapelite field, implying that most of the early Paleozoic granites are derived from the dehydration melting of biotite (Fig. 11a, b), which coincide with the temperature and pressure conditions for granitic magma generation (Dini et al., 2005). But the relatively high  $CaO/Na_2O$  ratios ( $>0.3$ ) and low  $SiO_2$  contents (part of samples  $<71$  wt.%) imply that these granites could be produced from psammitic sources or pelite-derived melts that



**Fig. 12.** (a)  $FeO$  vs.  $MgO$  diagram (after Zorpi et al., 1991). (b) Distribution of felsic igneous rocks from different tectonic settings on a  $Th/Yb$ – $Nb/Yb$  diagram (after Pearce, 2008). (c)  $\varepsilon_{Nd}(t)$  vs. initial  $^{87}Sr/^{86}Sr$  and (d)  $\varepsilon_{Nd}(t)$  vs.  $SiO_2$  diagrams at 410 Ma. The parameters of end-members are selected based on the literature (e.g., Niu and O'Hara, 2003; Wan et al., 2010; Wang et al., 2011a, 2013b; Workman and Hart, 2005 and reference therein). The depleted mantle is represented by  $SiO_2 = 45$  wt.%,  $Nd = 4.0$  ppm,  $Sr = 60$  ppm,  $^{87}Sr/^{86}Sr = 0.70246$  and  $\varepsilon_{Nd}(t) = +8.5$ , and depleted mantle-derived magma by  $SiO_2 = 48$  wt.%,  $Nd = 20$  ppm,  $Sr = 400$  ppm,  $^{87}Sr/^{86}Sr = 0.70246$  and  $\varepsilon_{Nd}(t) = +8.5$ . Four involved metasedimentary rocks are 09WG-32A1 ( $SiO_2 = 64$  wt.%,  $Nd = 30.2$  ppm,  $Sr = 97.6$  ppm,  $^{87}Sr/^{86}Sr = 0.73639$  and  $\varepsilon_{Nd}(t) = -10.5$ ), 09WG-32E ( $SiO_2 = 62.5$  wt.%,  $Nd = 19.0$  ppm,  $Sr = 131.9$  ppm,  $^{87}Sr/^{86}Sr = 0.71289$  and  $\varepsilon_{Nd}(t) = -9.4$ ), 09WG-32 g ( $SiO_2 = 73.7$  wt.%,  $Nd = 29.9$  ppm,  $Sr = 113.3$  ppm,  $^{87}Sr/^{86}Sr = 0.72617$  and  $\varepsilon_{Nd}(t) = -9.9$ ) and G0105-1 ( $SiO_2 = 75.3$  wt.%,  $Nd = 59.3$  ppm and  $\varepsilon_{Nd}(t) = -13.7$ ). Symbols and data sources are the same as in Figs. 7 and 10.





**Fig. 13.** Tectonic setting discrimination diagrams: (a)  $\lg[\text{CaO}/(\text{K}_2\text{O} + \text{Na}_2\text{O})]$  vs.  $\text{SiO}_2$  discrimination diagram is after Brown (1982); (b)  $\text{Rb/Zr}$  vs.  $\text{SiO}_2$  discrimination diagram is after Harris et al. (1986); (c)  $\text{Rb}$  vs.  $(\text{Y} + \text{Nb})$  discrimination diagram is after Pearce et al. (1984) and Pearce (1996). Symbols and data sources are the same as in Fig. 7.

interacted with mafic magmas (Sylvester, 1998) (Fig. 11c). However, Fig. 11d indicates that quite a number of the early Paleozoic granites have  $\text{Rb/Ba}$  and  $\text{Rb/Sr}$  ratios lower than psammite-derived melts. The  $\text{FeO}^T$ ,  $\text{MgO}$  and  $\text{TiO}_2$  contents of those granites demonstrate that if they are derived from partial melting of clay-poor sources, the initial temperatures must be higher than  $900^\circ\text{C}$  (Fig. 11e), which is highly unlikely according to the  $\text{P}_2\text{O}_5$  and  $\text{TiO}_2$  saturation thermometer and  $\text{Zr}$  saturation temperature of the early Paleozoic granites.

It's worth noting that early Paleozoic granites, mafic enclaves (Cheng et al., 2009a; Lou et al., 2005; Sha and Yuan, 1991; Wu and Zhang, 2003) and mafic to intermediate rocks (He et al., 2010b; Li et al., 2010a; Peng et al., 2006a; Wang et al., 2013b; Yao et al., 2012) or amphibolites (Li et al., 2011) always form a chemical array (Fig. 11c–f). Gray (1984) suggested that mafic enclaves are solidified basaltic dykes, which have been physically and chemically modified during ascent and emplacement of the granite magma. The  $\text{FeO}^T$  and  $\text{MgO}$  contents of these granites, mafic enclaves and mafic to intermediate rocks lie along

hybridization trend (Fig. 12a), implying some of early Paleozoic granites in South China form by mixing as previously proposed by Gray (1984). As for Xiaowan and Duntou granites, most of their biotites belong to magnesium biotites (Fig. 2b), which support the input of mantle source magma (Zhou, 1988). Therefore Figs. 11c–f, and 12a suggest the mixing of mafic and felsic components as the parent sources of these granites, but the relative proportions of each component for different granites vary. In addition, the mafic component of mixing model can either be mantle-derived magma or remelting of Paleoproterozoic to Neoproterozoic amphibolites (Li et al., 2011).

Granite generations are usually related with mantle-derived magmas underplating, and many researchers (e.g., Patiño Douce, 1999; Sylvester, 1998) believed that the interactions between the continental crust and underplated mafic magmas range from limited to mere heat transfer to chemical interactions. Although the early Paleozoic granites are most S-type, the peraluminous S-type granites also cannot completely rule out the input of mantle-derived magma. For instance, Barbarin (1996, 1999) have demonstrated that the peraluminous CPG-type granitoids generate where mantle-derived magma is injected into, or has been underplated. As mentioned above, the peak metamorphism of early Paleozoic orogen occurs earlier than 445 Ma and reaches to granulite facies with peak metamorphic pressure of 1.0–1.1 GPa and temperatures of  $835\text{--}878^\circ\text{C}$  (Yu et al., 2003a, 2005a, 2005b), followed by a phase of rapid cooling below  $500\text{--}300^\circ\text{C}$  which occurs by ca. 420 Ma (Li et al., 2010c). But those post-collisional granites were mainly produced between 440 and 390 Ma with melting temperatures in the range of  $609^\circ\text{C}$  to  $884^\circ\text{C}$  and pressure  $\leq 0.5$  GPa. Clemens (2003) also argued that normal geothermal gradients and crustal thickening likewise fail to provide sufficient heat for partial melting of the crust. Generally, the mantle must be the major heat source. Underplating of hot mantle-derived magmas heated and elevated temperature at significantly lower pressure. Thus, the early Paleozoic S-type granite can form by partial melting of meta-sedimentary rocks from Paleoproterozoic to Neoproterozoic metamorphic basement upon underplating or injection of mantle derived magmas.

Pearce (2008) suggested the  $\text{Th/Yb-Nb/Yb}$  diagram to highlight the crustal contamination. In the  $\text{Th/Yb-Nb/Yb}$  diagram, the variation trend of early Paleozoic granites, mafic enclaves and mafic to intermediate rocks indicates magma–crust interaction (contamination) due to wedge melting or assimilation fractional crystallization (AFC) (Fig. 12b). Given that the early Paleozoic tectothermal event is intracontinental, the generation of arc chemical signature may witness a paleo-subduction modified wedge column preserved from Neoproterozoic subduction (Wang et al., 2013b). The  $\text{Sr-Nd}$  isotopic array (Fig. 12c) also suggests a source contamination or crustal assimilation model, and excludes amphibolites as the mafic component. However, because granites cannot be directly derived from the mantle (Wyllie, 1984), contamination of depleted mantle and metasedimentary rocks from Paleoproterozoic to Neoproterozoic metamorphic basement may not account for the genesis of the early Paleozoic granites. As per the calculated binary mixing curves using  $\epsilon_{\text{Nd}}(t)$  values and  $\text{SiO}_2$  contents (Fig. 12d), the early Paleozoic mafic enclaves and mafic rocks form by contamination of depleted mantle by metasedimentary rocks from Paleoproterozoic to Neoproterozoic metamorphic basement while intermediate rocks and many early Paleozoic granites form by assimilation of mantle-derived magmas and metasedimentary rocks with some level of fractionation crystallization. It is hard to image that contamination of depleted mantle and metasedimentary rocks give rise the primary melt of the basaltic magmas, because no subduction took place in early Paleozoic Cathaysia block. The metasomatism must take place much earlier, as is the case for Jinan gabbroic intrusion from the North China Block (Guo et al., 2013). Therefore the basaltic magmas were likely derived from paleo-subduction metasomatized hydrated sub-continental lithosphere mantle (Wang et al., 2013b; Yao et al., 2012), whereas the intermediate to acidic magmas were the products of AFC

processes with interactions between the basaltic magmas and evolved crustal materials (Fig. 12b–d). With higher  $\varepsilon_{\text{Hf}}(t)$  and  $\varepsilon_{\text{Nd}}(t)$  values (Appendix Table 1; Figs. 6, 10a), the Group A granitoids including Xiawan and Duntou granites may be formed by mixing of more asthenosphere-derived magma with metasedimentary rocks. Parts of the Group B granitoids, mafic enclaves and mafic to intermediate rocks constitute fine assimilation (mixing of basaltic magma with metasedimentary rocks) curves, indicating that besides those purely crust-derived S-type granites, the Group B granitoids may be formed by mixing of synchronous basaltic magma with metamorphic crustal materials.

#### 5.4. Implications for geodynamics of early Paleozoic orogenesis and delamination in South China

In many tectonic settings discrimination diagrams (Brown, 1982; Harris et al., 1986; Pearce, 1996; Pearce et al., 1984), the early Paleozoic granites in South China show characteristics of granitoids produced in extensional environment (Fig. 13a), and most plot in the post-collisional and volcanic arc granites fields while the rest plot in the syn-collisional fields (Figs. 7b, 13b, c). As show in Fig. 13c, some early

Paleozoic granites including Xiawan and Duntou granites plot in the volcanic arc granites fields, as a result of fractional crystallization of K-feldspar and plagioclase, mixing of mantle-derived magmas or partial melting of subduction modified rocks. However, because Xiawan and Duntou granites show weak positive or negative Eu anomalies ( $\text{Eu}/\text{Eu}^* = 0.42\text{--}1.33$ ) and negative Sr anomalies, the fractional crystallization of K-feldspar and plagioclase must be insignificant (Table 3, Fig. 9). In fact, these tectonic setting discrimination diagrams have their own limitations, as pointed out by Förster et al. (1997) and Pearce et al. (1984), and granite compositions essentially depend on the nature of the source rocks, and are controlled only in the simplest cases by the tectonic setting. Thus as has been noted, the arc-like character may be derived from the remelting of paleo-subduction modified wedge column preserved from Neoproterozoic subduction (Wang et al., 2013b). Such a character was inherited by basaltic magmas that injected into, or underplated beneath, the crust and induced its melting to form the parental magma of early Paleozoic granites. Therefore, based on the geochronological studies and the formation of synchronous mafic rocks (Wang et al., 2013b; Yao et al., 2012), most of early Paleozoic granites belong to post-collisional granites and form in an extensional environment.

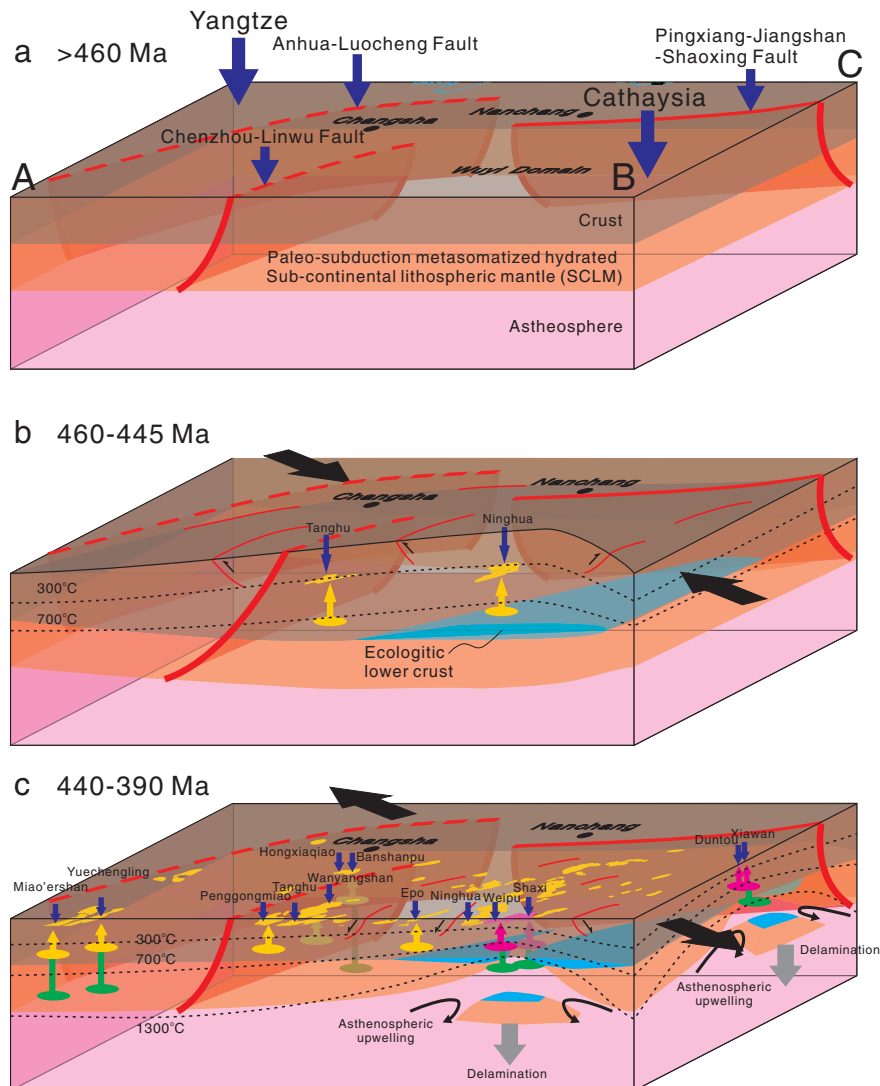


Fig. 14. Schematic cartoons showing the petrogenetic mechanism for early Paleozoic granites in South China as projected on cross section A–B and vertical section B–C in Fig. 1 (modified after Li et al., 2010c; Yao et al., 2012; Wang et al., 2013b).

The typical model of an orogenic cycle generally begins with crustal shortening leading to crust thickening, prograde metamorphism and high topography at the orogenic core. Subsequently the thickened crust resists further shortening and crustal root often experiences granulite or eclogite facies metamorphism. If the crustal root undergoes mineral equilibration under eclogite facies and becomes denser than the underlying mantle, it usually causes the delamination of both eclogitic lower crust and the attached lithospheric mantle (e.g., Kay and Kay, 1993). Finally, accompanying the decompression and retrograde metamorphism, late-orogenic tectonic collapse results from mantle–crust isostatic re-equilibrium (Arndt and Goldstein, 1989; Froidevaux and Ricard, 1987; Leech, 2001; Schott and Schmelting, 1998).

As discussed above, early Paleozoic granites form by partial melting of metasedimentary rocks from Paleoproterozoic to Neoproterozoic metamorphic basement induced by underplating or injection of hot mantle-derived magmas. The temperature and pressure evolution process of early Paleozoic orogenesis and magmatism also indicate fast crustal thinning and confirm that underplating of hot mantle-derived magmas heated and elevated temperature to induce the orogenic root melting and crust–mantle interaction. Nevertheless, lithosphere extension and decompression in the late-orogenic stage are not enough to trigger the subcontinental mantle melting, even if hydrated. This is because, at pressures less than about 2 GPa, ascent paths in the subcontinental mantle are nearly parallel to the basalt solidus, and so little melting occurs if the lithosphere is thinner than about 60 km (Harry and Leeman, 1995). Yao et al. (2012) suggested that the lower crust might undergo eclogite facies metamorphism. The Hf–Nd isotopic studies indicate the lower crust origin for Xiawan and Duntou granites (Fig. 10b). Some samples from these two granites exhibit weak positive Eu anomalies, implying that they may origin from mafic granulitic or eclogitic lower crust, yet portions with weak negative Eu anomalies may derive from the crust after mafic granulitic or eclogitic lower crust has delaminated (Gao et al., 1992, 1999a, 1999b, 2004; Gao and Wedepohl, 1995; Rudnick, 1995; Vanderhaeghe and Teyssier, 2001; Wedepohl, 1991) (Table 3, Fig. 9). Geochemical and isotopic analyses on the mafic enclaves and basic rocks indicate that the initial basaltic magmas were likely derived from a paleosubduction metasomatized hydrated sub-continental lithosphere mantle (SCLM) (Wang et al., 2013b; Yao et al., 2012) (Fig. 12b–d), and the melting temperature for the basaltic magmas and the calculated mantle potential temperature are both ca. 1300 °C, similar to that of a MORB-like asthenospheric mantle. This supports the hypothesis that the partially molten SCLM was heated up by upwelling asthenosphere triggered by the removal of the delaminated lithosphere (Yao et al., 2012). Yao et al. (2012) also predicted asthenospheric melts due to decompression after the delamination and suggested that such melts likely contributed to the basaltic underplating beneath the orogen. However, outcrop of such magmatism had not been identified. The Group A granitoids including Xiawan and Duntou granites form by AFC processes with interactions between asthenosphere-derived magma and metasedimentary rocks of metamorphic basement, which may serve as the evidence for the direct participation of asthenosphere.

Based on previous studies and this work, we try to elucidate the sequence of processes that occurred during the early Paleozoic in South China and improve the understanding of synchronous magmatisms:

- (1) The early Paleozoic Orogen in South China Block began at no later than 460 Ma (Middle Ordovician) (Li et al., 2010c) involved with paleo-subduction metasomatized hydrated SCLM (Wang et al., 2013b; Yao et al., 2012) and metasedimentary rocks from Paleoproterozoic to Neoproterozoic metamorphic basement (Fig. 14a).
- (2) At 460 to 445 Ma (Fig. 14b), with crustal shortening leading to crust thickening, prograde metamorphism attained the peak metamorphic pressure of 1.0–1.1 GPa and temperatures of 835–878 °C with a series of thrust faults developed (Li et al.,

2010c; Yu et al., 2003a, 2005a, 2005b, 2007), and a fraction of the metasedimentary rocks turned to melt and syn-collisional granites occurred (e.g., Tanghu, Ninghua and Hongjiang, Wu and Zhang, 2003; Zhang et al., 2010a, 2012). After peak metamorphism, metamorphic rocks rapid cooled down below 500–300 °C at ca. 420 Ma (Li et al., 2010c), owing to exhumation which caused by gravitational instability and collapsing or thermal relaxation. Anatexis of thickened crust is no longer the main way of granitic magmatism.

- (3) From 440 to 390 Ma (Fig. 14c), as the result of crust thickening, the crustal root underwent mineral equilibration under eclogite facies, causing the delamination of both the eclogitic lower crust and the attached lithospheric mantle with rapid unroofing and collapsing. The delaminated eclogitic lower crust, along with the attached SCLM, dropped into the hotter asthenosphere, promoting regional asthenospheric upwelling and the partial melting of paleo-subduction metasomatized hydrated SCLM (Li et al., 2010c; Yao et al., 2012; Wang et al., 2013b and this study). Due to the partial melting of the SCLM, basaltic magmas generated and underplated, then induced the partial melting of metasedimentary rocks and the AFC processes with interactions between the basaltic magmas and crustal materials to produce both pure crust-derived granitic magmas (e.g., Penggongmiao, Wanyangshan and Epo, Chu et al., 2012; Wu et al., 2008; Zhang et al., 2012) and crust–mantle hybridized granitic magmas (e.g., Miao'ershan, Yuechengling, Banshanpu and Hongxiaqiao, Chu et al., 2012; Xu and Zhang, 1993; Xu and Zhang, 1993; Xu et al., 2006; Yang et al., 2012; Zhang et al., 2012; Zhao et al., 2013b) of Group B. Meanwhile, the AFC processes with interactions between asthenosphere-derived magma and metasedimentary rocks of metamorphic basement produced granitic magmas of Group A (e.g., Weipu, shaxi, Xiawan and Duntou Li et al., 2010b and this study).

## 6. Conclusions

- (1) This study yields the crystallization age of Xiawan monzogranite and Duntou granodiorite of ca. 410 Ma. The older group ages of ca. 436 Ma found in both Xiawan and Duntou granites imply an incremental construction or episodic growth model or these older zircons are inherited from the melting source.
- (2) The early Paleozoic granites in South China generated mainly during 440 and 390 Ma are mostly post-collisional granites. With the exception of some typical S-type granites or I-type granites, many granites show petrological and geochemical characteristics of either I- or S-type. To avoid the ambiguous classification of I–S type, we prefer to divide all early Paleozoic granites into two groups: Group A with relatively high  $\varepsilon_{\text{Hf}}(t)$  and  $\varepsilon_{\text{Nd}}(t)$  values together with high initial temperatures, and Group B with relatively low  $\varepsilon_{\text{Hf}}(t)$  and  $\varepsilon_{\text{Nd}}(t)$  values together with low initial temperatures.
- (3) Geochemical and isotopic analyses on early Paleozoic granites and relative rocks demonstrate that the Group A granitoids including Xiawan and Duntou granites may form by AFC processes with interactions between asthenosphere-derived magma and metasedimentary rocks. Except for those pure crust-derived S-type granites, Group B granitoids may form by AFC processes with interactions between synchronous basaltic magma and metamorphic basement.
- (4) The Hf–Nd isotopic characteristics and weak positive or negative Eu anomalies in Xiawan and Duntou granites imply a delaminated eclogitic lower crust. Our petrogenetic studies of Group A granitoids also suggest the underplating of asthenospheric melts and support the delamination model. The delamination of eclogitic lower crust along with the attached SCLM at post-collisional stage triggered regional upwelling, and



led to partial melting of asthenosphere and of the paleo-subduction metasomatized hydrated SCLM, inducing the generations of Group A and Group B granitoids, respectively.

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