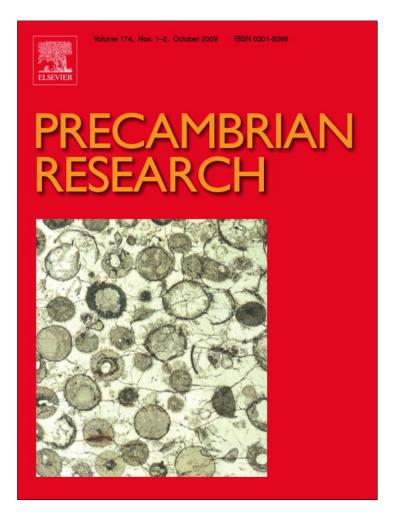
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Amalgamation between the Yangtze and Cathaysia Blocks in South China: Constraints from SHRIMP U–Pb zircon ages, geochemistry and Nd–Hf isotopes of the Shuangxiwu volcanic rocks

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ABSTRACT

South China was formed through the amalgamation of the Yangtze Block with the Cathaysia Block, but the timing of this amalgamation is controversial, ranging from Mesoproterozoic to Mesozoic. We report here SHRIMP U-Pb zircon ages, geochemistry and Nd-Hf isotopes of the Shuangxiwu Group volcanic rocks from the southeastern Yangtze Block. These rocks were strongly deformed, metamorphosed to greenschist-facies, intruded by 849 ± 7 Ma dolerites, and unconformably overlain by Neoproterozoic rift successions of no older than ca. 820 Ma. The Beiwu and Zhangcun volcanic rocks from the middle and uppermost Shuangxiwu Group were dated at 926 ± 15 Ma and 891 ± 12 Ma, respectively. All the studied rocks are characterized by highly positive $\varepsilon Nd(T)$ (5.4–8.7) and $\varepsilon Hf(T)$ (11.0–15.3) values. The Pingshui basaltic and andesitic rocks from the lower Shuangxiwu Group, which were previously dated at ca. 970 Ma, are high in Al₂O₃ (15–20%) but low in MgO (<8%), and are characterized by enrichments in Th and LREE but depletions in Nb, Ta, Zr, Hf and Ti, broadly similar to high-Al basaltic rocks in many volcanic arcs. The Beiwu andesitic to rhyolitic rocks have higher MgO than the experimental melts of basaltic rocks, and their Al₂O₃ content decreases with increasing SiO₂, similar to the regional coeval tonalites and granodiorites, suggesting their formation by crystal fractionation of basaltic parent magma. The Zhangcun volcanic rocks are high in SiO₂ (mostly >69%), low in MgO (0.35-1.2%), and have nearly constant Al₂O₃ contents of 14–15% and relatively uniform trace element concentrations. They were generated by remelting of juvenile mafic to intermediate arc rocks. Overall, the Shuangxiwu Group volcanic rocks and associated intrusive tonalites and granodiorites constitute a typical calc-alkaline magmatic assemblage of a 970-890 Ma active continental margin. These results and the 849 ± 7 Ma zircon U–Pb age for the undeformed doleritic dikes intruding the Shuangxiwu Group suggest that the tectonic regime of the study region transformed from plate convergence to intracontinental rifting in the time period between ca. 890 Ma and ca. 850 Ma. Previously reported 1.04-0.94 Ga metamorphic and deformation ages from the nearby Tianli Schists and evidence for the final closure of the back-arc basin at ca. 880 Ma (ophilitic obduction at Xiwan), further suggest that the amalgamation between the Yangtze and Cathaysia Blocks, likely through "soft docking" at the eastern segment of the Sibao orogen, was completed at ca. 880 Ma or soon after.

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1. Introduction

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It is widely accepted that the South China Block was formed through the amalgamation of the Yangtze Block with the Cathaysia Block, but the timing of the amalgamation has been a topic of debate. A number of studies in the late 1980s suggested that this occurred through a collisional orogenesis in South China during the early Mesozoic (Hsü et al., 1988, 1990) or early Paleozoic (Haynes, 1988). Because of the lack of geological evidence, such models were X.-H. Li et al. / Precambrian Research 174 (2009) 117-128

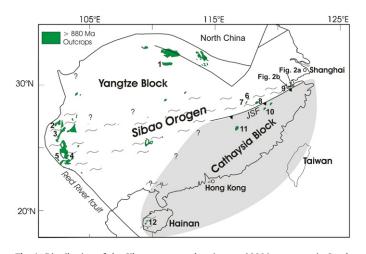


Fig. 1. Distribution of the Sibao orogen and major pre-880 Ma outcrops in South China (modified after Z.X. Li et al., 2007). Sources of information: 1: the Archean Kongling complex forming the oldest Yangtze basement (Gao et al., 1999; Qiu et al., 2000); 2: the tightly folded ca. 0.92 Ga Yanbian Group (Zhou et al., 2006; X.H. Li et al., 2006a); 3: the ca. 1.0 Ga Huiqinggou granitic gneiss and 1.0 Ga foreland-basin deposits (Z.X. Li et al., 2002); 4: the ca. 1.14-0.96 Ga Laowushan Formation and Kunyang foreland-basin deposits (Greentree et al., 2006); 5: the ca. 1.7 Ga Dahongshan Group (Hu et al., 1991; Greentree and Li, 2008); 6: the ca. 0.97 Ga Xiwan adakitic granite (X.H. Li et al., 1994; Li and Li, 2003); 7: the ca. 1.0 Ga Zhangshudun ultramafic complex within the NE Jiangxi Ophiolite (Chen et al., 1991); 8: the Tianli Schists that were deposited after 1.5 Ga and metamorphosed at 1.04–0.94 Ga (Z.X. Li et al., 2007); 9: the ca. 0.97-0.89 Ga Shuangxiwu arc (Ye et al., 2007; this study), with enlarged maps shown in Fig. 2; 10: the 1.83 Ga Danzhu gneissic granite (Li and Li, 2007); 11: the ca. 1.77 Ga Tianjingping amphibolite (Li, 1997); and 12: the Baoban complex that was intruded by ca. 1.43 Ga granites and metamorphosed at 1.3-1.0 Ga (Z.X. Li et al., 2002). JSF: Jiangshan-Shaoxing Fault.

challenged by subsequent studies (e.g., Chen et al., 1991; Charvet et al., 1996a,b; Li and McCulloch, 1996). Most researchers now believe that the two blocks amalgamated during the Proterozoic Sibao orogeny (also called the "Jiangnan" or "Jinning" orogeny by different authors in the literature), but the timing and evolution of the orogeny are still controversial. Some researchers suggested that the Sibao orogen belongs to part of the worldwide Grenvillian-aged orogenic events associated with the assembly of Rodinia (e.g., Z.X. Li et al., 1995, 2002, 2007, 2008; Greentree et al., 2006; X.H. Li et al., 2006a; Ye et al., 2007; W.X. Li et al., 2008a), whereas others considered that the Sibao orogeny lasted until ca. 0.82 Ga or even younger (e.g., Li, 1999; Zhao and Cawood, 1999; Zhou et al., 2006; Zheng et al., 2007).

Located at the southeastern margin of the Yangtze Block (Fig. 1), the Shuagxiwu anticline (Fig. 2b) consists of a suite of greenschistfacies, strongly deformed volcanic rocks overlain with an angular unconformity by middle Neoproterozoic rift volcano-sedimentary sequences. In this paper, we report SHRIMP U–Pb zircon ages and geochemical and Nd–Hf isotopic data for the Shuangxiwu calc-alkaline volcanic rocks. We demonstrate that the Shuangxiwu volcanic rocks represent an assemblage of arc volcanism formed on the eastern segment of the Sibao orogen at ca. 0.97–0.89 Ga, broadly coeval with regional metamorphism and deformation related to the Sibao orogeny (Z.X. Li et al., 2007) prior to the final amalgamation between the Yangtze and Cathaysia Blocks.

2. Geological background

The South China Block consists of the Yangtze Block and the Cathaysia Block, separated by the Sibao orogen (Fig. 1). Outcrops of pre-Neoproterozoic crystalline basement rocks are scarce in the Yangtze Block, with the oldest being the Kongling complex near the Yangtze Gorge Dam (marked as "1" in Fig. 1) consist-

ing of Archean to Paleoproterozoic high-grade metamorphic TTG (tonalite, trondhjemite and granodiorite) gneisses, metasedimentary rocks and amphibolites (e.g., Gao et al., 1999; Qiu et al., 2000). Variably deformed, low- to medium-grade metamorphic rocks of late Paleoproterozoic to early Neoproterozoic (≥900 Ma) ages are sporadically distributed around the margins of the Yangtze Block (Fig. 1). Some of them are well-dated, including, from west to east, the ca. 1.7 Ga Dahongshan Group in western Yunnan (Hu et al., 1991; Greentree and Li, 2008; "5" in Fig. 1), the 1.0 Ga Huiqinggou granitic gneiss (Z.X. Li et al., 2002; "3" in Fig. 1) and the 1.0-0.9 Ga Kunyang and Yanbian Groups and equivalents in western Yunnan and southern Sichuan (Greentree et al., 2006; X.H. Li et al., 2006a; "2" and "4" in Fig. 1), the Mesoproterozoic Tianli Schists (Z.X. Li et al., 2007; "8" in Fig. 1), the ca. 1.0 Ga ophiolites and the ca. 970 Ma Xiwan adakitic rocks in northeastern Jiangxi (Chen et al., 1991; Li and Li, 2003; "6" and "7" in Fig. 1), and the ca. 910 Ma Taohong and Xiqiu tonalite and granodiorite plutons in northeastern Zhejiang that intrude the Pingshui Formation of the lowest Shuangxiwu group (Ye et al., 2007; "9" in Fig. 1). The Jiangshan-

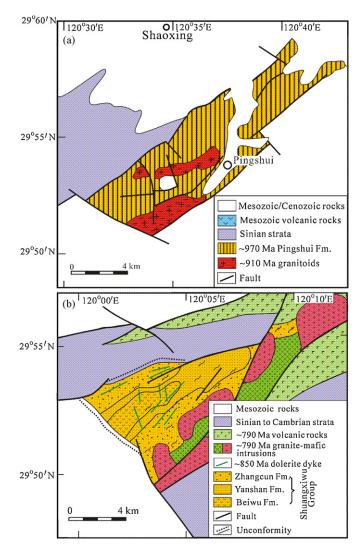


Fig. 2. Geological map of (a) the Pingshui area showing the distribution of the Pingshui Formation, the lower most unit of the Shuangxiwu Group, and (b) the Shuangxiwu area showing the Baiwu, Yanshan and Zhangcun Formations of the middle, upper and uppermost Shuangxiwu Group (simplified after the 1:200,000 geological map (ZPGST, 1975)). Ages for the ca. 970 Ma Pingshui Formation are from Zhang et al. (1990) and Chen et al. (2009); the ca. 910 Ma granitoids from Ye et al. (2007); the ca. 850 Ma dolerite dyke and ca. 790 Ma volcanic and granite-mafic intrusions from Z.X. Li et al. (2003) and X.H. Li et al. (2008).

Shaoxing Fault ("JSF" in Fig. 1) is considered a major boundary between the Yangtze and Cathaysia Blocks (Zhang et al., 2005), possibly partially truncating the eastern segment of the Sibao orogen during its Phanerozoic activations (Fig. 1).

The protolith of the Tianli Schists was a clastic sedimentary succession deposited sometime between 1.5 and 1.04 Ga (Z.X. Li et al., 2007). It underwent two major episodes of deformation and meta-morphism to upper greenschist-facies, at ca. 1.04–1.02 Ga and ca. 0.97–0.94 Ga, respectively, during the Sibao orogeny (Z.X. Li et al., 2007).

The Shuangxiwu Group consists predominantly of volcanic and pyroclastic rocks interbedded with felsic tuff and tuffaceous sandstones and siltstones that were strongly deformed and metamorphosed to greenschist-facies. It was divided into four formations according to lithologic characteristics, including, from bottom to top, the Pingshui, Beiwu, Yanshan and Zhangcun Formations (BGMRZJ, 1989). The Pingshui Formation, exposed around Pingshui (Fig. 2a), consists chiefly of altered basaltic to andesitic rocks. It is regarded as the lowest formation in the group, although it has no direct contact with the other three formations. The minimum age of the Pingshui Formation is constrained by the SHRIMP zircon U–Pb age of 913 ± 15 Ma for the Taohong pluton that intrudes the Pingshui basalts (Ye et al., 2007). Chen et al. (2009) recently reported LA-ICPMS U-Pb zircon analyses for two volcanic rocks from the Pingshui Formation. While the average ${}^{206}\text{Pb}/{}^{238}\text{Pb}$ ages of 904 ± 8 Ma and 906 ± 10 Ma were interpreted by the authors as the formation age of the Pingshui volcanic rocks, it is noted that their measured U-Pb data are highly discordant, with ²⁰⁶Pb/²³⁸Pb ages ranging from 878 to 999 Ma. On the other hand, the two dated samples have nearly identical $^{207}\text{Pb}/^{206}\text{Pb}$ ages within errors, with a mean of $965\pm12\,\text{Ma}.$ This Pb/Pb age, consistent with the Sm-Nd internal isochron age of 978 ± 44 Ma (Zhang et al., 1990), can be considered as the best estimate of the formation age of the Pingshui volcanic rocks.

The other three formations crop out in the Shuangxiwu anticline, ca. 50 km to the west of Pingshui, consisting of intermediate to felsic volcanic and volcaniclastic rocks with a total thickness of >1800 m (Fig. 2b). The lowermost Beiwu Formation, with a thickness of ca. 430 m, consists of andesite, dacite and rhyolite as well as volcaniclastic interbeds. Conformably overlying the Beiwu Formation is the Yanshan Formation, which consists mainly of felsic tuff, tuffaceous sandstones and siltstones with a thickness of ca. 470 m. At the top of the Shuangxiwu Group is the Zhangcun Formation that consists chiefly of felsic ignimbrite with a thickness of ca. 850 m. The Zhangcun Formation is unconformably overlain by basal conglomerates and bimodal volcanic rocks of the ~800 Ma rift successions (Z.X. Li et al., 2003; X.H. Li et al., 2008). Precise isotopic age has been lacking for the Shuangxiwu volcanic rocks except for a zircon evaporation Pb-Pb date of ca. 900 Ma for the uppermost Zhangcun rhyolite (Cheng, 1993). The minimum age of the Shuangxuwu volcanic rocks is constrained by the SHRIMP zircon U-Pb ages of 849 ± 7 Ma for the Shenwu dolerites that intrude the volcanic rocks (X.H. Li et al., 2008).

3. Analytical procedures

3.1. SHRIMP U–Pb zircon dating

Zircon concentrates were separated from ca. 5-kg samples using standard density and magnetic separation techniques. Zircon grains, together with zircon standard TEMORA (for sample 04ZJ67) and CZ3 (for sample 97Zh6), were mounted in epoxy mounts which were then polished to section the crystals in half for analysis. All zircons were documented with photomicrographs and cathodoluminescence (CL) images to reveal their internal structures. Measurements of U, Th, and Pb for sample 04ZJ67 were conducted using the SHRIMP II ion microprobe at the Beijing SHRIMP Center, Chinese Academy of Geological Sciences. U-Th-Pb ratios were determined relative to the TEMORA standard zircon (Black et al., 2004), and the absolute abundances were calibrated to the standard zircon SL13 (U = 238 ppm). Sample 97Zh6 was analyzed using the SHRIMP II(A) ion microprobe at Curtin University of Technology, with U-Th-Pb isotopic ratios and abundances being determined relative to the CZ3 standard (Nelson, 1997). Analyses of the standard zircons were interspersed with those of unknown grains. Measured compositions were corrected for common Pb using the measured ²⁰⁴Pb, and an average crustal composition (Cumming and Richards, 1975) appropriate to the age of the mineral was assumed. Because the common Pb is very low, the common Pb corrections were insensitive to the choice of common Pb compositions. U-Pb zircon data are listed in Table 1 (Appendix A). Uncertainties on individual analyses are reported at the 1σ level; mean ages for pooled ²⁰⁶Pb/²³⁸U results are quoted at the 95% confidence level.

3.2. Major and trace elements

After petrographic examination, the least-altered whole-rock samples were selected for geochemical and Nd-Hf isotopic analyses. Major element oxides were analyzed using a Rigaku RIX 2000 X-ray fluorescence spectrometer at the Guangzhou Institute of Geochemistry on fused glass beads. Calibration lines used in quantification were produced by bivariate regression of data from 36 reference materials encompassing a wide range of silicate compositions (X.H. Li et al., 2005), and analytical uncertainties are between 1% and 5%. Trace elements were analyzed using a PerkinElmer Sciex ELAN 6000 inductively coupled plasma mass spectrometer (ICP-MS) at the Guangzhou Institute of Geochemistry. Analytical procedures are similar to those described by X.H. Li et al. (2000). About 50 mg of each powdered sample was dissolved in a high-pressure Teflon bomb for 24 h using a HF+HNO₃ mixture. An internal standard solution containing the single element Rh was used to monitor signal drift during counting. A set of USGS and Chinese national rock standards including BHVO-1, W-2, AGV-1, G-2, GSR-1 and GSR-3 were chosen for calibrating element concentrations of unknowns, and analytical precision is typically 2-5%. Geochemical results are listed in Table 2 (Appendix A).

3.3. Whole-rock Nd–Hf isotopic compositions

Nd isotopic compositions were determined using a Micromass Isoprobe multi-collector ICP-MS at the Guangzhou Institute of Geochemistry, using analytical procedures described by X.H. Li et al. (2004). Nd fractions were separated by passing through cation columns followed by HDEHP columns. Measured ¹⁴³Nd/¹⁴⁴Nd ratios were normalized to 146 Nd/ 144 Nd = 0.7219, and the reported ¹⁴³Nd/¹⁴⁴Nd ratios were further adjusted relative to the Shin Etsu JNdi-1 standard of 0.512115. Separation of Hf from the matrix and rare earth elements was carried out using a combination of Eichrom RE and HDEHP columns. Hf isotopic compositions were determined using a Finnigan Neptune MC-ICP-MS at the Institute of Geology and Geophysics, using analytical procedures described by X.H. Li et al. (2007). The measured ¹⁷⁶Hf/¹⁷⁷Hf ratios were normalized to 179 Hf/ 177 Hf = 0.7325, and the reported 176 Hf/ 177 Hf ratios were further adjusted relative to the JMC 475 standard of 0.282160 (Nowell et al., 1998). Whole-rock Nd and Hf isotopic data are listed in Table 3 (Appendix A).

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4. Results

4.1. U–Pb zircon ages

Sample 04ZJ67 is a rhyolite collected from the Beiwu Formation (29°52'19"N, 120°02'35"E). Zircons are mostly euhedral to subhedral, transparent and colorless, ranging from 50 µm to 150 µm in length, and have length to width ratios between 2:1 and 3:1. Euhedral concentric zoning is common in most crystals in CL. Sixteen analyses of 16 zircons were obtained in sets of five scans during a single analytical session (Table 1, Appendix A). Th concentrations range from 4 ppm to 422 ppm, U from 70 to 3128 ppm, and Th/U ratios from 0.01 to 1.43. Common Pb is low; the proportions of common 206 Pb in total measured 206 Pb (f_{206} in Table 1, Appendix A) are mostly <0.5%. The measured ²⁰⁶Pb/²³⁸U ages vary from 227 Ma to 2330 Ma (Fig. 3a). Among them, two oval crystals (spots 4 and 5), display significantly old and discordant U–Pb results, with 207 Pb/ 206 Pb ages of 1935 ± 26 Ma (1 σ) and 2543 ± 10 Ma (1 σ), respectively. They are thus interpreted as xenocrysts. The dominant age population consists of eight analyses (spots 1, 2, 6, 7, 13, 14, 15 and 16) that have concordant U-Pb isotopic compositions with a weighted mean of ²⁰⁶Pb/²³⁸U age of 926 ± 15 Ma. This age is interpreted as the best estimate of the crys-

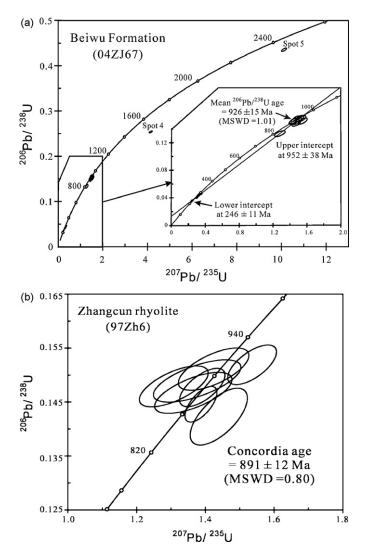


Fig. 3. U–Pb zircon concordia diagram for (a) rhyolite sample 04ZJ67 from the Baiwu Formation of the middle Shuangxiwu Group, and (b) rhyolite sample 97Zh6 from the Zhangcun Formation from the uppermost Shuangxiwu Group.

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tallization age for sample 04ZJ67. Spot 12 yields a slightly younger, discordant U–Pb age likely due to partial loss of radiogenic Pb. The remaining five analyses (spots 3, 8, 9, 10 and 11) are discordant, with 206 Pb/ 238 U age ranging from 227 to 289 Ma (Table 1, Appendix A). These zircons are relatively small and characterized by low Th/U ratios between 0.01 and 0.10, interpreted as metamorphic in origin. Apart from the two xenocrysts (spots 4 and 5), all other spots define a discordia with upper and lower intercepts at 952 ± 38 Ma and 246 ± 11 Ma, respectively (Fig. 3a). The latter is interpreted as the best estimate of the timing of metamorphism, comparable with the timing of the regional Indosinian orogenic magmatism and metamorphism (e.g. X.H. Li et al., 2006b; Li and Li, 2007).

Sample 97Zh6 is a rhyolite collected from the uppermost Zhangcun Formation ($29^{\circ}51'40''$ N, $120^{\circ}04'45''$ E). The zircons were mostly euhedral to subhedral, $100-150 \mu$ m in length with length to width ratios of about 2:1. Most zircons are transparent and colorless, with weak euhedral concentric zoning visible in CL. Eight analyses of 8 zircons were obtained (Table 1, Appendix A). These zircon grains have relatively low concentrations of U (73–232 ppm) and Th (24–224 ppm); Th/U ratio ranges from 0.33 to 0.97. All the analyses have indistinguishable U–Pb isotopic compositions within errors, which correspond to a single age population with a concordia 206 Pb/ 238 U age of 891 ± 12 Ma (Fig. 3b). This age is consistent with a previously reported zircon evaporation Pb–Pb date of ca. 900 Ma (Cheng, 1993), and is interpreted as the eruption age of the Zhangcun volcanic rocks.

4.2. Effects of alteration and metamorphism on chemical compositions

The studied volcanic rocks underwent greenschist-facies metamorphism and varying degrees of alteration. Their LOI (loss of ignition) values are highly variable, ranging from 4.2 to 8.0% for the Pingshui Formation rocks, 1.1 to 4.5% for the Beiwu Foramtion rocks, and 1.1 to 2.4% for the Zhangcun Formation rocks (Table 2, Appendix A). In general, the mafic rocks have higher LOI values than the felsic rocks. Thus, the effects of metamorphism and alteration on chemical compositions of these rocks need to be evaluated prior to any investigation of their geochemical characters. Zirconium in igneous rocks is generally considered to be the most immobile during low- to medium-grade metamorphism and alteration except for severe seafloor-hydrothermal alteration (e.g., Wood et al., 1979; Gibson et al., 1982). Fig. 4 shows the different geochemical behaviors of a number of elements against Zr contents.

The Zhangcun Formation rocks have the lowest LOI values and their major and trace elements show consistent variations with Zr, suggesting insignificant metamorphic and alteration effects on their geochemical composition. For rocks from the Pingshui and Beiwu Formations, alkaline (such as Rb) and alkaline earth (such as Sr) elements are overall scattered, implying varying degrees of mobility, whereas other elements are generally correlated with Zr, indicating that these elements are essentially immobile during metamorphism and alteration. In the following sections, only the immobile elements are used for rock classification and in petrogenetic discussions.

4.3. Geochemical characteristics

The Shuangxiwu volcanic rocks have a wide range of SiO₂ contents (between 53 and 74%). Most of the older, ca. 970 Ma rocks from the Pingshui Formation are basaltic to andesitic in composition (SiO₂ = 53–59%), whereas the younger, ca. 930–890 Ma rocks from the Beiwu and Zhangcun Formations are mainly andesitic to rhyolitic (SiO₂ = 57–74%). On the SiO₂ vs. Zr/TiO₂ diagram of Winchester and Floyd (1976), all the volcanic rocks plot into the sub-alkaline field (Fig. 5). Major elements (apart from K₂O and Na₂O) show con-

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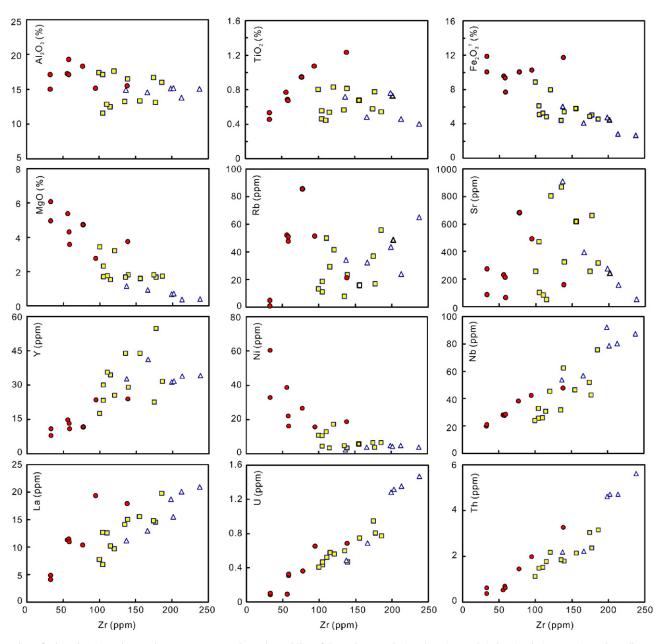


Fig. 4. Plots of selected major and trace elements vs. Zr to evaluate the mobility of these elements during alteration. Red circle: Pingshui Formation rocks; yellow square: Beiwu Formation rocks; blue triangle: Zhangcun Formation rocks. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

sistent variations in Harker diagrams (Fig. 6). The Pingshui basaltic to andesitic rocks show decreases in Al_2O_3 , MgO, $Fe_2O_3^T$ and CaO with increasing SiO₂, whereas TiO₂ and P₂O₅ increase until SiO₂ reaches ~58% and then decrease at higher SiO₂ contents. The Beiwu and Zhangcun felsic rocks display decreases in all these major elements with increasing SiO₂.

The chondrite-normalized REE patterns are illustrated in Fig. 7. All the rocks show moderate LREE-enriched patterns, and their total REE content increases with increasing SiO₂. The Pingshui basaltic and andesitic rocks and the Beiwu andesitic rocks have weak Eu anomalies, whereas the Beiwu and Zhangcun felsic rocks show distinct Eu anomalies (Eu/Eu* = 0.62–0.85). The Zhangcun felsic rocks have the most consistent REE abundances and patterns. In the primitive mantle-normalized spidergrams (Fig. 7d–f), all the volcanic rocks from the Shuangxiwu Group show "spiky" trace element patterns, with enrichment in Th and LREE and variable depletion in Nb, Ta, P, Ti, and to a lesser extent Eu. It is noteworthy that the basaltic and andesitic rocks from the Pingshui and the Beiwu Formations display strong Zr and Hf depletion relative to Nd and Sm, whereas such depletion is not shown in the felsic rocks from the Beiwu and Zhangcun Formations.

4.4. Nd-Hf isotopes

Despite variable chemical compositions (from basaltic andesite to rhyolite) and wide ranges of measured ¹⁴⁷ Sm/¹⁴⁴Nd (0.121–0.187) and ¹⁷⁶Lu/¹⁷⁷Hf (0.0094–0.0421) ratios, all the studied volcanic rocks have fairly constant initial Nd and Hf isotopic compositions, with ε Nd(T)=5.4–8.7 and ε Hf(T)=11.0–15.3, broadly similar to the Nd and Hf isotopic compositions of the associated Xiqiu and Taohong tonalite and granodiorite intrusions (Table 3, Appendix A). These rocks have Nd and Hf model ages mostly between 0.9 and 1.1 Ga, that are fairly close to their formation ages (Table 3, Appendix A). On the Hf–Nd isotopic plot

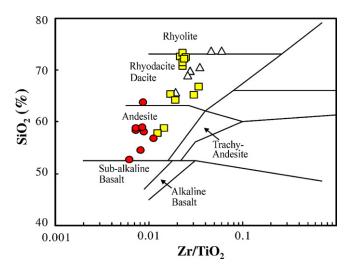


Fig. 5. SiO₂ vs. Zr/TiO₂ classification diagram of Winchester and Floyd (1976) Symbols are same as in Fig. 4.

(Fig. 8), their ε Hf and ε Nd values fall within the "Terrestrial Array" (Vervoort et al., 1999) between MORB and OIB, indicating that these rocks were derived predominantly from time-integrated depleted sources, and contributions from ancient continental crust played very little, if any, role in their origin.

5. Discussions

5.1. Petrogenesis

The Pingshui basaltic rocks are high in Al_2O_3 (15–20%), but low in MgO (<8%), and are characterized by enrichment of Th and LREE but depletion in high field strength elements (HFSE). They show pronounced negative Nb–Ta, Zr–Hf and Ti anomalies relative to the neighboring elements in the incompatible trace element spidergram (Fig. 7d) similar to those of arc basalts (McCulloch and Gamble, 1991; Tatsumi and Eggins, 1995). Although depletion in Nb, Ta and Ti can also be observed in some intraplate basalts due to either interaction with subcontinental lithospheric mantle or crustal contamination (Ellam and Cox, 1991; Hawkesworth et al., 1995; X.C. Wang et al., 2008), significant depletion in Zr and Hf relative to Nd and Sm is characteristic of basalts derived from mantle wedge metasomatized by subduction-related fluids (Fig. 9), as Zr and Hf typically display low solubility in fluids whereas they can show significant mobility in slab melts (e.g., La Flèche et al., 1998; Münker et al., 2004).

On the Zr-Ti discrimination diagram of Pearce (1982), the Pingshui basaltic rocks fall into the island-arc field (Fig. 10a), and are distinctive from the within-plate basalts. They are low in TiO₂ (0.5-1.2%) and have low Ti/V ratios (10-24), plotting in the arc basalts field on the Ti-V discrimination diagram of Shervais (1982) (Fig. 10b). The Pingshui basaltic rocks have characteristically low Mg# (<0.6), are low in Cr (<150 ppm) and Ni (<110 ppm), and have high ε Nd(T) and ε Hf(T) values, suggesting that they have undergone intensive olivine and clinopyroxene fractionation without appreciable involvement of continental crustal components. Insignificant to positive Eu anomalies (Fig. 7a) are consistent with a considerable delay of plagioclase crystallization to form high-alumina differentiates under high partial pressure of H₂O (e.g., Sisson and Grove, 1993; Schiano et al., 2004). Overall, the Pingshui basaltic rocks are similar in geochemistry to the high-Al basaltic rocks which are the most common rock type in many volcanic arcs (e.g., Crawford et al., 1987).

The Beiwu rocks are andesite to rhyolite in composition $(SiO_2 = 57.8-73.4\%)$, whereas the Zhangcun samples are dacite and rhyolite in composition $(SiO_2 = 65.8-73.7\%)$. They are mostly metaluminous to weakly peraluminous, with A/CNK [molar Al/(Ca+Na+K)]=0.75-1.1. A few samples have anomalously high A/CNK value of ~1.3 possible due to mobility of alkaline elements during alteration. All the samples are characterized by depleted mantle-like Nd and Hf isotopic compositions (ε Nd(T)>5.5 and ε Hf(T)>11), indicating inappreciable involvement of ancient continental components. All these geochemical and isotopic features suggest that these calc-alkaline, intermediate to felsic volcanic rocks are products of either fractional crystallization of mantle-derived calc-alkaline basaltic magma (e.g., Singer et al., 1992; Barth

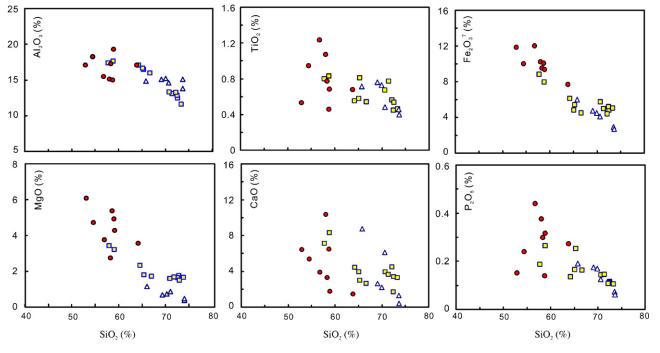


Fig. 6. Chemical variation Harker diagrams for the Shuangxiwu volcanic rocks. Symbols are same as in Fig. 4.

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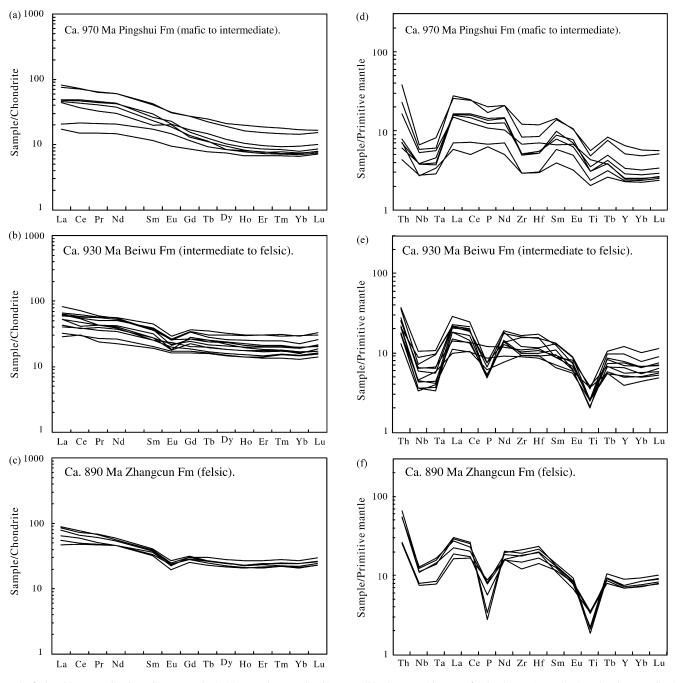


Fig. 7. (a–f) Chondrite-normalized REE diagrams and primitive mantle-normalized incompatible element spidergrams for the Shuangxiwu volcanic rocks. The normalization values are from Sun and McDonough (1989).

et al., 1995), or partial melting of juvenile sub-alkaline metabasaltic rocks (e.g., Drummond and Defant, 1990; Rushmer, 1991; Rapp and Watson, 1995). Despite similarities in Nd and Hf isotopic compositions, the Beiwu and Zhangcun rocks display distinct major element variation trends. At a given SiO₂ content, the Beiwu samples have overall higher MgO and lower Al₂O₃ contents than the Zhangcun samples (Fig. 6). Fig. 11 is a plot of MgO vs. SiO₂ showing the experimental liquids obtained by melting of basaltic protoliths. At a given SiO₂ content, the Beiwu rocks have MgO concentrations clearly higher than the experimental melts. Therefore, these rocks were unlikely to have been generated by melting of metabasaltic rocks. Although the Beiwu volcanic rocks have MgO concentrations similar to that of modern adakites produced by melting of subducted oceanic crust through interactions with the mantle (e.g. Drummond and Defant, 1990; Smithies, 2000), they are significantly lower in Sr/Y (1.4–31.6) but higher in Y (18–55 ppm) and HREE (such as Yb=2.5–5.1 ppm) than typical adakites (e.g., Defant and Drummond, 1993). Hence, they are different in origin from adakites. Two andesitic samples from the Beiwu Formation show Zr and Hf depletion relative to Sm (Fig. 7e), similar to the Pingshui basaltic to andesitic rocks. In general, the Beiwu volcanic rocks are very similar in geochemistry and Nd–Hf isotopes to the coeval Taohong and Xiqiu tonalite and granodiorite (Fig. 8) in the study area that were thought to be formed by crystal fractionation of basaltic magmas (Ye et al., 2007). All these features suggest that the Beiwu andesitic to rhyolitic rocks are likely formed by crystal fractionation of basaltic magmas. A distinct Eu negative anomaly and a sharp decrease of Al_2O_3 with increasing SiO₂ indicate that plagioclase was a predominant fractional phase.

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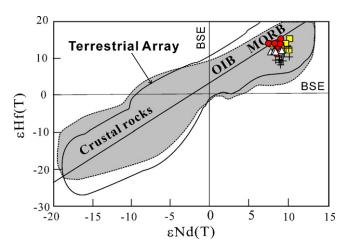


Fig. 8. Plot of ε Hf(T) vs. ε Nd(T) values for the Shuangxiwu volcanic rocks and the ca. 910 Ma tonalites and granodiorites that intruded the Pingshui Formation. "Terrestrial Array" indicates the Hf–Nd isotopic variation of present-day OIB, MORB and crustal clastic sediments and felsic igneous rocks (Vervort et al., 1999); Grey area shows the time-corrected "Terrestrial Array" at ca. 0.9 Ga. BSE: bulk silicate Earth; black crosses: the Xiqiu and Taohong tonalite and granodiorite intrusions; other symbols are same as in Fig. 4.

The Zhangcun rocks are high in silica (SiO₂ mostly >69%), yet low in MgO (0.35–1.2%), comparable to the experimental melts. All samples have a nearly constant Al_2O_3 content of 14–15% over the whole SiO₂ range, in contrast to the Beiwu rocks that show a decrease in Al_2O_3 with increasing SiO₂. Moreover, the Zhangcun rocks have relatively consistent REE and trace element abundances and patterns (Fig. 7c and f). All these geochemical features, in combination with their indistinguishable Nd and Hf isotopic compositions from the older Pingshui and Beiwu rocks, indicate remelting of a juvenile basaltic to andesitic arc crust (similar in comparison to the Pingshui and Beiwu rocks) at low pressure, similar to the silicic rocks in the Izu-Bonin and Tonga-Kermadec arcs (Tamura and Tasumi, 2002; Leat et al., 2007).

5.2. Tectonic implications

The timing of the Sibao orogeny and the final amalgamation between the Yangtze and Cathaysia Blocks is controversial, with two major competing viewpoints, i.e., late Mesoproterozoic to early Neoproterozoic (ca. 1.1–0.9 Ga) (e.g., Z.X. Li et al., 1995, 2002, 2007, 2008; Greentree et al., 2006; X.H. Li et al., 2006a; Ye et al., 2007;

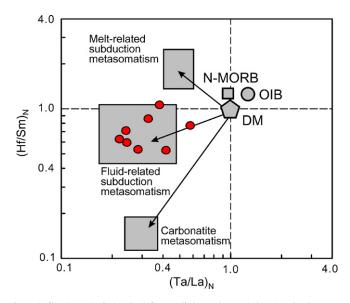


Fig. 9. $(Hf/Sm)_N vs. (Ta/La)_N plot (after La Flèche et al., 1998) showing the character$ istic depletion of Ta and Hf relative to La and Sm, respectively, for volcanic arc basaltsgenerated from a mantle source metasomatized by subduction-related processes. Itsuggests that the Pingshui basaltic rocks were likely derived from a mantle sourcemetasomatized by subduction-related fluids.

W.X. Li et al., 2008a) vs. middle Neoproterozoic (ca. 0.86-0.80 Ga or younger) (e.g., Li, 1999; Zhao and Cawood, 1999; Zhou et al., 2002, 2004; X.L. Wang et al., 2004, 2006, 2007, 2008; Wu et al., 2006; Zheng et al., 2007). Our present study demonstrates that the Shuangxiwu volcanic rocks, as well as the associated ca. 0.91 Ga syntectonic tonalite and granodiorite intrusions (Ye et al., 2007), are typical of arc magmatism along the active southeastern continental margin of the Yangtze Block (Fig. 12a and b). The oldest known arc magmatism here is represented by the ca. 970 Ma basaltic rocks of the Pingshui Formation (Sm-Nd internal isochron age of 978 ± 44 Ma, Zhang et al., 1990; LA-ICPMS Pb/Pb zircon age of 965 ± 12 Ma, Chen et al., 2009). Considering that metamorphism of the Tianli Schists, which are considered part of the SW-extension of the Shuangxiwu arc (marked as "9" and "8", respectively, in Fig. 1), started as early as 1042 ± 7 Ma (Z.X. Li et al., 2007), and that the NE Jiangxi ophiolite formed in the back-arc basin (Fig. 12a and b) at ca. 1.0 Ga (Chen et al., 1991), the initiation age of the Shuangxiwu arc likely occurred no later than 1.0 Ga (Fig. 12a).

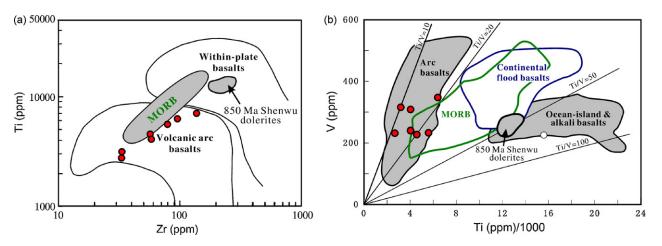


Fig. 10. (a) Ti vs. Zr discrimination diagram of Pearce (1982), and (b) V vs. Ti discrimination diagram of Shervais (1982) for the Pingshui basaltic rocks. The fields of arc basalts, MORB, continental flood basalts, and ocean-island and alkali basalts were drawn by Rollinson (1993) according to Shervais (1982). Data of the ca. 850 Ma Shenwu dolerites are from X.H. Li et al. (2008).

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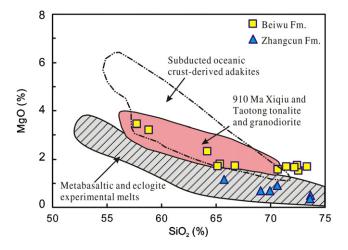


Fig. 11. MgO vs. SiO_2 for the Baiwu and Zhangcun volcanic rocks. The fields of metabasaltic and eclogite experimental melts are after a compilation by Q. Wang et al. (2006), and the fields of the ca. 910 Ma Xiqiu-Taohong tonalite and granodiorite are after Ye et al. (2007).

The youngest known arc magmatism, the Zhangcun Formation rhyolite, is dated at 891 ± 12 Ma (this study), and can be interpreted as the maximum age for the closure of the ocean between the Shuangxiwu arc and the Cathaysia Block. Subduction in the back-arc basin started from at least 968 ± 23 Ma as indicated by the occurrence of the Xiwan adakitic granites (Li and Li, 2003; Fig. 12b), and continued until ca. 880 Ma as indicated by the obduction of the Xiwan ophiolite onto the continent to form the

 880 ± 19 Ma obduction-type biotite granites (W.X. Li et al., 2008a; Fig. 12c). This ca. 880 Ma event marks the youngest recorded Neoproterozoic compressive tectonism in the eastern Sibao orogen (Fig. 12c).

The folded Shuangxiwu Group rocks were intruded at 849 ± 7 Ma by the Shenwu dolerites, that show close geochemical affinity to intraplate basalts formed in continental rifts (X.H. Li et al., 2008; Fig. 10). A similar zircon U–Pb age, 857 ± 13 Ma, was reported for the Guandaoshan pluton that intruded the strongly deformed, \geq 900 Ma Yanbian Group in the western Sibao orogen (X.H. Li et al., 2003a, 2006a; marked as "2" in Fig. 1). Overlying the Tianli Schists and the Shangxiwu magmatic arc with angular unconformities are the middle Neoproterozoic rift successions of the Nanhua Rift Basin that developed on both the Yangtze and Cathaysia Blocks since ca. 820 Ma (Wang and Li, 2003; Wang et al., 2003; W.X. Li et al., 2005, 2008b), most likely related to ca. 825 Ma mantle plume activities beneath South China (Z.X. Li et al., 1999, 2003; X.C. Wang et al., 2007; Fig. 12d).

The above observations suggest that the transition of the regional tectonic regime from interplate convergence to intracontinental rifting occurred between 880 ± 19 Ma and 849 ± 7 Ma in the eastern Sibao orogen.

In view of the lack of any exposed high-grade metamorphic rocks along the Sibao orogen other than the ca. 900 Ma Xiwan blueschists (location "6" in Fig. 1; Xu et al., 1992; Shu et al., 1993; Charvet et al., 1996a,b; Zhou, 1997) and the \geq 1.43 Ga Baoban complex in Hainan Island (marked as "12" in Fig. 1; Z.X. Li et al., 2002), the final docking between the Cathaysia and Yangtze blocks, particularly along the eastern Sibao orogen, was unlikely a collisional one. Such an intercontinental "soft docking" might be possible because of plate

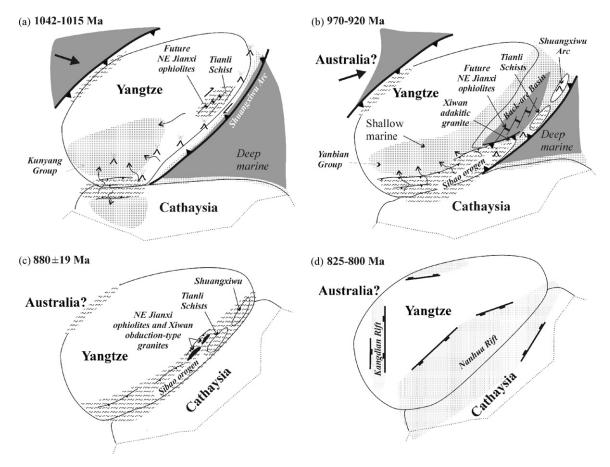


Fig. 12. (a-c) Cartons showing a magmatic arc and back-arc basin system evolving at the active continental margin of the southeastern Yangtze Block during the Sibao orogeny form ca. 1.04 Ga to ca. 0.88 Ga, and (d) subsequent continental rifting at ca. 820–800 Ma (modified after Z.X. Li et al., 2007).

geometry (i.e., regions protected by promontories) and kinematics (e.g., toward the end on an orogeny).

We note that different opinions exist regarding the Neoproterozoic tectonic environments of central and eastern South China, and existing models are constantly being challenged by new results. Rock units particularly relevant to this study are the Lengjiaxi and Sibao groups and their equivalents, that are traditionally thought to form a Mesoproterozoic "basement", as they were unconformably overlain by the middle Neoproterozoic rift successions (e.g., BGMRJX, 1984; BGMRGX, 1985; BGMRHN, 1988). However, recent U-Pb age determinations of detrital zircons from the Lengjiaxi and Sibao groups (X.L. Wang et al., 2007) display two major age peaks of ca. 940-890 Ma and ca. 865-850 Ma, and those authors interpret the rock formations as being formed in a ca. 860-800 Ma foreland basin. We consider such an interpretation inappropriate because the Shuangxiwu Group and the first phase of anorogenic magmatic rocks may be the sources for the above two populations of detrital zircons, respectively (Ye et al., 2007; X.H. Li et al., 2008, and this study). As discussed above, the Shuangxiwu arc appeared to have shut off after ca. 890 Ma and the back-arc basin closed by ca. 880 Ma. No Neoproterozoic metamorphic age younger than that has been reported to suggest the continued presence of an active margin or the closure of any ocean after ca. 880 Ma. The precise tectonic setting for the widespread ca. 850–820 Ma deposits is yet unclear. However, in view of the anorogenic nature of the ca. 850 Ma Shenwu dolorite dykes in eastern South China (X.H. Li et al., 2008) and the ca. 860 Ma Guandaoshan granitoid in western South China (X.H. Li et al., 2003a), and the occurrence of bimodal volcanic rocks in some of those successions (our unpublished results), we tentatively suggest that these rocks may represent an early phase of rifting as speculated by Z.X. Li et al. (2003, 2008).

X.L. Wang et al. (2008) also reported U-Pb zircon ages for two volcanic units in the Shuangqiaoshan Group in northern Jiangxi (regions surrounding "6" and "7" in Fig. 1). Although the authors assigned a major age population of ca. 0.88 Ga as the depositional age of the Shuangqiaoshan Group, a younger age population of ca. 0.77 Ga is also present in the two dated samples, indicating that the Shuangqiaoshan Group could be as young as <0.77 Ga. Those ca. 0.88 Ga zircons characteristically have high ε Hf(T) values varying from 3.3 to 18.8 (mostly between 8 and 15), very similar to those of the volcanic and intrusive rocks from the Shuangxiwu arc. It is highly likely that those 0.88 Ga zircons with such high ε Hf(T) values were derived from erosion of the Shuangxiwu magmatic arc during the middle Neoproterozoic. In addition, some ca. 0.82 Ga peraluminous granites from eastern Yangtze Block also contain ca. 0.88-0.91 Ga xenocryst zircons (X.H. Li et al., 2003b; Wu et al., 2006). It is thus likely that a greater magmatic arc with voluminous ca. 0.9 Ga silicic igneous rocks existed along the southeastern margin of the Yangtze Block, and acted as one of the major provenances for the sediments filling the middle Neoproterozoic basins.

6. Conclusions

- (1) New SHRIMP U–Pb zircon ages indicate that the Beiwu and Zhangcun volcanic rocks from the middle and uppermost Shuangxiwu Group were formed at 926 ± 15 Ma and 891 ± 12 Ma, respectively. In combination with previously published Sm–Nd and zircon Pb/Pb ages for the Pingshui volcanics, the ages for the Shuangxiwu Group volcanic rocks are constrained to be between ca. 970 Ma and ca. 890 Ma.
- (2) Geochemical and Nd–Hf isotopic results suggest that the Pingshui volcanic rocks are typical high-Al basaltic to andesitic rocks generated from partial melting of a mantle wedge matasomatized by subduction-related fluids. The Beiwu andesitic to rhyolitic rocks share isotopic similarities with the nearby, coeval tonalites and granodiorites formed by crystal fractionation of

basaltic rocks. The Zhangcun felsic volcanic rocks are likely remelting products of juvenile mafic to intermediate arc rocks. Overall, the Shuangxiwu igneous rocks constitute a typical calcalkaline arc assemblage formed at the active continental margin of the southeastern Yangtze Block during the earliest Neoproterozoic.

(3) The tectonic transition from plate convergence between the Yangtze and Cathaysia Blocks (the Sibao orogeny) to intracontinental rifting likely occurred at some time between 890 and 850 Ma. The final amalgamation between the Yangtze and Cathaysia blocks, possibly resulting from a "soft docking", likely took place at or soon after ca. 880 Ma, marking the end of the Sibao orogeny. Later, the Shuangxiwu magmatic arc became one of the major sedimentary source regions for middle Neoproterozoic sedimentary basins in South China.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.precamres.2009.07.004.

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