Magmatic record of Prototethyan evolution in SW Yunnan, China: Geochemical, zircon U–Pb geochronological and Lu–Hf isotopic evidence from the Huimin metavolcanic rocks in the southern Lancangjiang zone

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Abstract

The Huimin metavolcanic rocks, consisting mainly of basalt, andesite, and dacite, are exposed predominantly in the Huimin area of the southern Lancangjiang zone, SW Yunnan. Three metavolcanic rock samples yielded zircon U–Pb ages of 456 ± 3 Ma, 456 ± 7 Ma and 459 ± 14 Ma, suggesting the eruption occurred in the Late Ordovician. These metavolcanics are characterized by sub-alkaline rocks, with high Al_2O_3 (12.45–17.68 wt%) and low TiO_2 (0.60–0.96 wt%). The rocks are enriched in LREEs and LILEs with weakly negative Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.37\text{--}0.99$) and depleted in HFSEs, which is geochemically similar to typical subduction-related arc volcanic rocks. Zircons with Late Ordovician magmatic ages (~ 456 Ma) have homogeneous Lu–Hf isotopic compositions with in-situ $\varepsilon_{\text{Hf}}(t)$ values of $-4.36\text{--}-3.30$ and Hf model ages of 1.51–1.55 Ga, indicating that the Huimin metavolcanic rocks might have originated from a metasomatic mantle source. Our data provide reliable evidence for the presence of Ordovician magmatism in the Sanjiang area, represent the magmatic record of Prototethyan evolution in SW Yunnan, and identify a hitherto unknown early subduction event at the northeastern Gondwana margin.

Keywords: Southern Lancangjiang zone; Late Ordovician; Metavolcanic rocks; Prototethyan evolution; SW Yunnan

1 Introduction

A commonly accepted view in past decades is that the Tethys Ocean developed from the Alps through Afghanistan to southwestern China and Peninsular Malaysia (Bullard et al., 1965; Hsu and Bernoulli, 1978; Sengor and Hsu, 1984; Metcalfe, 1996, 2002, 2013; Acharyya, 1998; Hennig et al., 2009; Wang et al., 2010). Available data show that the Tethyan evolution can be temporally divided into Prototethyan (Late Sinian–Silurian), Paleotethyan (Devonian–Triassic), and Neotethyan (since Cretaceous) stages (Li et al., 1990; Pan et al., 1997). The Nujiang–Lancangjiang–Jinshajiang (Sanjiang) area in SW Yunnan, China, preserves abundant records of the Tethyan evolution and is a critical area for studying Proto-, Paleo-, and Neotethyan tectonic patterns. Nevertheless, most work

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44 focused on a Paleotethyan tectonic reconstruction using petrological, geochronological, and
45 geochemical analyses for magmatic rocks and associated sedimentary rocks. These data revealed that
46 the Changning-Menglian Belt and its southern extension, the Chiangmai zone in Thailand, have been
47 regarded as the major sutures of the main Paleotethyan oceanic basin and the collisional boundary of
48 the Sibumasu and Indochina-Yangtze blocks (Metcalf, 1996, 2011; Zhong, 1998).

49 An Early Paleozoic ophiolite suite and associated magmatic rocks are recorded in Qinghai-Tibet
50 and SW Yunnan (Chen et al., 2007; Liu et al., 2009; Mao et al., 2012; Wang et al., 2013), occurring
51 with a series of lithotectonic blocks (North Qiangtang, Simao, Indochina and South China) that
52 originated from the northeastern Gondwana margin (Feng, 2002; Metcalf, 1996; Zhong, 1998).
53 However, less attention has been paid to these Prototethyan geological records, and the tectonic
54 implications of a Gondwana reconstruction are still unknown. We present a set of field investigations,
55 including new U–Pb and Lu–Hf zircon isotopic data as well as whole-rock elemental results of the
56 Huimin metavolcanic rocks in the southern Lancangjiang zone, SW Yunnan, to unravel the rocks'
57 origin and constrain the Prototethyan tectonic evolution and the tectonic setting of the Gondwana
58 margin.

59 **2 Geological background and petrography**

60 Southwestern Yunnan is located in the junction of two tectonopaleogeographic domains involving
61 the South China and Sibumasu blocks. From east to west, it can be divided into the Ailaoshan Belt, the
62 Simao Block, the Lancangjiang zone, the Changning–Menglian Belt, the Baoshan Block, the Nuijiang
63 Belt, and the Tengchong Block (Liu et al., 1991; Zhong, 1998; Wang et al., 2006; Fig. 1). The Simao
64 Block is bounded by the Lancangjiang zone to the west and the Ailaoshan ophiolitic zone to the east
65 (Fig. 1). It is believed to have a connection to the Yangtze Block (Liu, 1993; Zhong, 1998) or to
66 represent the northern segment of the Indochina Block (Metcalf, 1996). The Lancangjiang tectonic
67 zone is composed of an arc magmatic zone, the Lincang granite batholith and the Damenglong and
68 Lancang metamorphic rocks (Fig. 1). It is divided into the northern, central, and southern Lancangjiang
69 zones (Fig. 1). The Changning–Menglian Belt is considered to be the closure boundary of the main
70 Paleotethyan Ocean. The Baoshan and Tengchong blocks are commonly accepted as fragments of the
71 Sibumasu continent with stratigraphic and paleontological similarities to Gondwana (Fan and Zhang,
72 1994; Metcalf, 1996, 2002; Zhong, 1998; Feng, 2002; Fontaine, 2002). The basement of the Baoshan
73 Block comprises the Proterozoic granulite–amphibolite facies metamorphic rocks, including the
74 Ximeng, Chongshan and Gaoligong groups (Yunnan BGMR, 1990, 1996; Liu et al., 1991; Mo et al.,
75 1993; Fang et al., 1996; Zhong, 1998).

76
77
78 [Insert Figure 1]
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80 Our study area is located in the southern Lancangjiang zone (see locations in Fig. 1). In this area,
81 the metamorphic rocks are mainly characterized by low-grade metamorphic volcanic–sedimentary
82 rocks, which are defined as the Lancang Group and are covered by the Lower Carboniferous Nanduan
83 Formation with an angular unconformity (Jia, 1994; Feng et al., 1996). The Lancang Group could be
84 subdivided into the Nanmuling, Mengjingshan, Manlai, and Huimin formations from the bottom up.
85 The Nanmuling Formation is dominated by carbonaceous quartz schist. The Mengjingshan Formation

is mainly composed of sericite schist and sericite quartz schist. The Manlai Formation includes predominantly sericite quartz schist and mica schist. The Huimin Formation, which has a strata-thickness of 300–1000 m, consists mainly of a metamorphic basalt–andesite association and an andesitic and rhyolitic tuff with interlayers of slate, phyllite, and siderite (Wei et al., 1984; Wu et al., 1984; Yang et al., 2013; Fig. 2).

[Insert Figure 2]

The Huimin metavolcanic sequence, which was previously mapped as Proterozoic or Early Paleozoic rocks (Yunnan BGMR, 1990; Zhong, 1998; Zhai et al., 1990; Shen et al., 2008), contains two volcanic–sedimentary cycles (Fig. 2). The metavolcanic rocks in this study were commonly metamorphosed as greenschists with dark-green colors. Their mineral compositions are chlorite, albite, and epidote along with minor amounts of sphene, apatite, zircon and Fe–Ti oxides. Samples D008 and D009 from Cycle I are albite–chlorite schist. These samples show blastoporphyritic textures and have main mineral compositions of 55–60 % flaky blastic chlorite and 40–45 % grain blastic albite. Samples D010 and D011 from Cycle II are albite–epidote–chlorite schist. These samples show palimpsest hyalopilitic textures and mainly consist of flaky blastic chlorite (15–20 %), grained blastic epidote (15–20%) and grained blastic albite (10–15%). The sample locations are illustrated in Fig. 2.

3 Analytical methods

Zircon grains were separated from the samples by using conventional heavy liquid and magnetic techniques and purified by handpicking under a binocular microscope. The grains were mounted in an epoxy resin, polished and coated with gold, and then photographed in transmitted and reflected light. The internal textures of the zircons were examined by using a cathodoluminescence (CL) imaging technique prior to the U–Pb isotopic analyses. U–Pb isotope analysis was conducted with a LA–ICP–MS at the State Key Laboratory of Geological Processes and Mineral Resources (GPMR), China University of Geosciences (Wuhan). The detailed analytical procedure is described in Liu et al. (2008, 2010). The standard GJ-1 and 91500 zircons were used to determine the elemental fractionation that occurs during sputter ionization. The off-line selection and integration of background and signals, time-drift correction and quantitative calibration were conducted through ICPMSDataCal (Liu et al., 2010). The zircon U–Pb age concordia and weighted average plots were made by Isoplot/Ex_ver3 (Ludwig, 2003). The analytical results are listed in Table 1.

[Insert Table 1]

Zircon in-situ Lu–Hf isotopic ratio analysis was conducted by a Neptune Plus MC–ICP–MS (Thermo Fisher Scientific, Germany) in combination with a Geolas 2005 excimer ArF laser ablation system (Lambda Physik, Göttingen, Germany) at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences (Wuhan). Helium was used as the carrier gas to transport the ablated sample. The spot size was 44 µm. The instrumental conditions and detailed analysis of the process were performed according to Hu et al. (2012). The Hf isotopic data were collected on some of the same zircons analyzed for U–Pb and in similar domains as identified in the CL/BSE images.

The interference of ^{176}Yb on ^{176}Hf was corrected by measuring the interference-free ^{173}Yb isotope and using the ratio $^{176}\text{Yb}/^{173}\text{Yb}=0.79381$ (Segal et al., 2003) to calculate $^{176}\text{Yb}/^{177}\text{Hf}$. Similarly, the relatively minor interference of ^{176}Lu on ^{176}Hf was corrected by measuring the intensity of the interference-free ^{175}Lu isotope and using the recommended ratio $^{176}\text{Lu}/^{175}\text{Lu}=0.02656$ (Blichert-Toft and Albarede, 1997) to calculate $^{176}\text{Lu}/^{177}\text{Hf}$. The calculation of the initial Hf isotope values used the ^{176}Lu decay constant of $1.865\times 10^{-11} \text{ a}^{-1}$ (Scherer et al., 2001). The calculated model ages (T_{DM}) are based on the depleted mantle model described by Griffin et al. (2000). The analytical data are illustrated in Table 2.

[Insert Table 2]

The samples were crushed and powdered to less than 200 mesh for whole-rock geochemical analysis. Major oxides were determined through XRF–1800 spectrometry at the State Key Laboratory of Geological Processes and Mineral Resources (GPMR), China University of Geosciences (Wuhan). The analytical error is usually $< 1\%$ and the detection limit is $< 0.05\%$ for most major elements. For trace elements, the rock powders were first digested by $\text{HF}+\text{HNO}_3$ in Teflon bombs and then analyzed by an Agilent 7500a ICP–MS at the GPMR. The analytical precision is generally better than 5% for most elements. The detailed sample-processing digesting procedure and the analytical precision and accuracy for major and trace elements are described by Ma et al. (2012) and Liu et al. (2008), respectively. The analytical results are shown in Table 3.

[Insert Table 3]

4 Results

4.1 Zircon U–Pb geochronology

Thirty-three analyses on 33 grains from samples D008, D009 and D010 are listed in Table 1 and shown in Fig. 4.

[Insert Figure 3]

These zircons are mostly euhedral and short-columnar in morphology, transparent and colorless in color, and generally small in size (60–100 μm , 1:1–2:1). The analyses of twenty-six spots gave a wide range of U (160–2224 ppm) and Th (152–1987 ppm) concentrations. The Th/U ratios are in the range of 0.38 to 1.23 (Table 1). The CL images reveal oscillatory zonation with low to variable luminescence (Fig. 3), indicative of an igneous origin (Hoskin and Black, 2000; Wu and Zheng, 2004). Three samples for D008, D009 and D010 have an obvious age peak at $\sim 456 \text{ Ma}$, yielding a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of $456\pm 3 \text{ Ma}$ with $\text{MSWD}=0.58$ ($n=14$), $456\pm 7 \text{ Ma}$ with $\text{MSWD}=1.9$ ($n=7$) and $459\pm 14 \text{ Ma}$ with $\text{MSWD}=2.5$ ($n=5$). In combination with the Th/U ratios and CL image, these ages can be interpreted as the crystallization ages of the samples, representing the formation time of the Huimin metavolcanic rocks.

[Insert Figure 4]

Meanwhile, samples D008 and D009 also preserved some signatures of Mesoproterozoic (1.44 to

1.05 Ga), Neoproterozoic (~900 Ma) and Cambrian (~500 Ma) inherited and/or captured zircon ages. The captured Proterozoic and Cambrian zircons were probably from the Proterozoic basement materials and earlier magmatic activities in the Simao Block.

4.2 Geochemical characteristics

All of the samples (D008, D009, D010 and D011) have relatively high loss on ignition (LOI) varying from 3.30 wt% to 7.92 wt% (Table 3), suggesting that these rocks might have undergone some degree of alteration (Rolland et al., 2002). Thus, we mainly use the immobile elements (HFSEs and REEs) to classify and discuss their tectonic setting and petrogenesis.

The studied metavolcanic rocks have 48.67–65.96 wt% SiO₂, 3.42–8.43 wt% MgO and 0.13–0.67 wt% P₂O₅ and are characterized by low TiO₂ (0.60–0.96 wt%) and high Al₂O₃ content (12.45–17.68 wt%), similar to typical island arc volcanic rocks (Bailey, 1981). Al₂O₃, FeOt, and MgO generally show a negative correlation with SiO₂, but little correlation exists between CaO or P₂O₅ and SiO₂. Their *mg*-numbers (atomic Mg/(Mg+ΣFe)) range from 0.38 to 0.59. In the SiO₂ versus K₂O+Na₂O diagram (Le Maitre et al., 1989; Fig. 5a), the samples fall into the fields of sub-alkaline basalt to dacite.

In the diagrams of Nb/Y versus Zr/TiO₂ (Winchester and Floyd, 1977; Fig. 5b) and SiO₂ versus FeOt/MgO (Miyashiro, 1974; Fig. 5c), most samples fall in the fields of calc-alkaline andesites and basaltic andesites, analogous to the continental island arc volcanic association.

[Insert Figure 5]

The samples show similar chondrite-normalized REE patterns (Fig. 6a) and have moderately fractionated light rare earth elements (LREEs) relative to heavy rare earth elements (HREEs), with TREOs (Total Rare Earth Oxides) of 91.60–308.90 ppm and (La/Yb)_{cn} of 4.15–8.88. All of the samples show weakly negative Eu anomalies (Eu/Eu* = 0.37–0.99), which suggests the magma source contained a variable number of residual plagioclases. The REE patterns are characterized by right-sloping curves with an enrichment of LREEs and lack of HREEs, similar to typical island arc volcanic rocks (Bailey, 1981).

[Insert Figure 6]

On the primitive mantle-normalized incompatible element spidergram (Fig. 6b), the samples are characterized by subparallel spiky patterns with enrichment in LILEs and depletion in HFSEs (Fig. 6b), exhibiting high LILE/HFSE ratios similar to those of island arc related volcanic rocks (Tatsumi and Maruyama, 1989). The (Nb/La)_{cn} ratios are in the range of 0.23–0.74, exhibiting a geochemical connection to arc volcanic rocks. Negative Ti anomalies are also apparent in Fig. 6b. In contrast, the samples have lower Nb and Ta contents and higher Th/Nb, Th/Yb and La/Yb ratios than those of average MORBs. However, compared with those of typical island arc volcanic rocks from the Sunda arc in Indonesia (Gertisser and Keller, 2003), Barren Island in the NE Indian Ocean (Luhr and Haldar, 2006) and the Japan arc (Kimura and Yoshida, 2006), the rocks exhibit higher TREOs and lower Nb/La (0.24–0.76) and Nb/U (2.99–6.81) ratios.

4.3 Zircon in-situ Lu-Hf isotopic compositions

To figure out the magma source of the Huimin metavolcanic rocks, the Lu–Hf isotopic compositions of a set of representative zircons (~456 Ma) were analyzed. Because the zircons therein were very small (60–100 μm), only 4 zircons from sample D008 could be used for the Hf isotope analysis. The beam positions are shown in Fig. 3, and the analytical results are listed in Table 2.

The $^{176}\text{Yb}/^{177}\text{Hf}$ ratios of the zircons range from 0.03301 to 0.05100. The $^{176}\text{Lu}/^{177}\text{Hf}$ ratios range from 0.00089 to 0.00132 and are much smaller than 0.002, indicating that only a small amount of radiogenic Hf accumulated after the zircons crystallized (Griffin et al., 2000). Therefore, the initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratio can also be used to represent the final $^{176}\text{Hf}/^{177}\text{Hf}$ ratio when the zircons initially formed (Wu et al., 2007). The $f_{\text{Lu/Hf}}$ values ranged from -0.9602 to -0.9732 (-0.9680 on average), significantly less than that of the mafic (0.34, Amelin et al., 2000) and salic crust (-0.72, Vervoort et al., 1996). Thus, the two-stage Hf model ages (T_{DM2}) are more accurate for the time when the source materials were derived from the depleted mantle. The zircon in-situ Lu–Hf isotopic compositions of the Huimin metavolcanic rocks are homogenous with similar ϵHf (t) (-4.36– -3.30) and T_{DM2} values (1.51–1.55 Ma).

5 Discussions

5.1 The eruption ages of the Huimin metavolcanic rocks

Different opinions exist about the age of the Huimin metavolcanic rocks. In 1:200,000 Geological Maps of Jinghong and Menghai, the rocks were mapped as the Neoproterozoic sequence (Yunnan BGMR, 1990). On the basis of its whole-rock Sm–Nd isochron age of 1982 ± 41 Ma, the sequence was proposed as “the Yangtze basement” (Zhong, 1998). However, Zhai et al. (1990) obtained a whole-rock Rb–Sr isochron age of 519 Ma and believed that these rocks erupted during the Early Paleozoic. In addition, Shen et al. (2008) believed that the Huimin volcanic sequence formed before the Devonian.

In this paper, we initially report the precise zircon U–Pb ages of the Huimin metavolcanic rocks. Three samples have their weighted mean $^{206}\text{Pb}/^{238}\text{U}$ ages of 456 ± 3 Ma, 456 ± 7 Ma and 459 ± 14 Ma besides a few captured zircons. These ages indicate that the Huimin metavolcanic rocks erupted around 456 Ma in the Late Ordovician.

5.2 Tectonic setting and source characteristics

As mentioned above, the Huimin metavolcanic rocks in the study area exhibit typical arc-like geochemical signatures (Bailey, 1981), such as lower TiO_2 , Ni and Cr contents, higher Al_2O_3 contents, a marked enrichment in LILEs and LREEs and a pronounced depletion in HFSEs, suggesting that they were products of an island–arc setting.

[Insert Figure 7]

In the ω (FeOt/MgO)– ω (TiO_2) and the ATK discrimination diagrams, the vast majority of samples plot in the field of island arc basalts (Glassley, 1974, Fig. 7a; Zhao, 1989; Fig. 7b). In the $\text{Ti}/100\text{--Zr--}3^*\text{Y}$ and the $\text{Hf}/3\text{--Th--Ta}$ diagrams, the samples plot in the field of calc-alkaline arc volcanic rocks (Wood, 1980, Fig. 8). All of these features suggest an arc setting for the generation of the Huimin basic to medium–acidic metavolcanic rocks in the southern Lancangjiang zone, which is consistent with previous considerations (Zhou and Lin, 1982; Li et al., 1991; Shen et al., 2008).

[Insert Figure 8]

Recently, Mao et al. (2012) obtained LA-ICP-MS zircon U–Pb ages of 421 ± 1 Ma and 418 ± 5 Ma for the medium–basic to medium–acidic continental island arc volcanic rocks, which were formerly mapped as the Lower Carboniferous, on the western edge of Simao Block (Fig. 10c), and zircon U–Pb ages of 444–439 Ma for ophiolitic mélangé were obtained in the Changning–Menglian Belt (Wang et al., 2013; Fig. 10c). All of these observations suggest an evolution of the Prototethyan Ocean in the Sanjiang area.

In addition, the mineral $^{40}\text{Ar}/^{39}\text{Ar}$ age of 418 ± 10 Ma for the granodiorite was obtained at Biluo Snow Mountain in the central Lancangjiang zone (Dai et al., 1986; Fig. 10c). Medium–basic to medium–acidic island arc volcanic rocks from the Lower Paleozoic Youxi Formation were separated from the Precambrian Jitang Formation, and a whole-rock Rb–Sr isochron age of 371 ± 50 Ma for dacite was reported in the northern Lancangjiang zone (Yong et al., 1990; Fig. 10c). As approximately coeval arc-like volcanic rocks are also presented in the central and northern Lancangjiang zones, the Late Ordovician Huimin metavolcanic rocks in the southern Lancangjiang zone may have been generated in the subduction zone that ultimately resulted in the closure of the Prototethyan Ocean.

The samples show enrichment in LILEs and depletion in HFSEs with pronounced negative Nb–Ta and Zr–Hf anomalies (Fig. 6), and they are characterized by relatively low $(\text{Nb/La})_{\text{cn}}$ ($0.23\text{--}0.74$, < 1.0) and high Th/Ta ($9.68\text{--}22.63$) and Th/Nb ($0.65\text{--}1.65$) ratios. These signatures suggest the involvement of components with a crustal signature (Wilson, 1989; Elliott et al., 1997).

The very low Nb/Th ($0.60\text{--}1.54$) ratios indicate the presence of a Ti-rich residual phase that holds Nb (e.g., rutile) during partial melting. The samples have higher Ni contents than the expected range of normal, primarily mantle-derived melt and plot in the fields of subduction-related metasomatic lithospheric mantle and orogenic volcanism in the diagrams of Nb/Yb versus Th/Yb, La/Nb versus La/Ba and Nb/Zr versus Th/Zr (Fig. 9a–c), which is suggestive of subduction-related metasomatic enrichment (Saunders et al., 1992; Woodhead et al., 2001; Wang et al., 2013b).

[Insert Figure 9]

Zircon Lu–Hf isotopic compositions have been widely applied to determine the sources of different geochemical domains, such as depleted mantle, chondrite, and crust (Wu et al., 2007). Zircons in the representative sample have similar Hf isotopic compositions with ϵ_{Hf} (456 Ma) values of $-4.36\text{--}-3.30$ and T_{DM2} model ages of $1.51\text{--}1.55$ Ga, with four spots falling slightly below the CHUR reference curve (Blichert-Toft and Albarede, 1997) on the age (Ga) versus ϵ_{Hf} (456 Ma) diagram (Fig. 9d). This observation indicates derivation from an anciently metasomatized source. As a result, an alternative scenario can be proposed stating that the subcontinental lithosphere was anciently (prior to the Mesoproterozoic) metasomatized by slab- plus sediment-derived fluids and melts.

5.3 Evidence of Prototethyan subduction

In recent years, many researchers have tried to shed light on subjects regarding the Prototethys within the Qinghai–Tibet and Sanjiang areas. Available data show that the

Sanjiang area in western Yunnan, where Proto/Paleo-Tethyan remnants are well preserved, is an important component of orogenic zones associated with the final closure of the Proto/Paleo-Tethyan Ocean (Zhang et al., 1985; Cong et al., 1993; Zhong, 1998).

Li et al. (2008), Wang et al. (2008), Zhai et al. (2010) and Wu (2013) reported that SHRIMP zircon U–Pb ages for cumulate gabbro in the Longmucuo–Shuanghu Belt range from 467±4 Ma to 432±7 Ma (Fig. 10c). Wang et al. (2013) obtained LA–ICP–MS zircon U–Pb ages of 444±4 Ma and 439±2 Ma for cumulate gabbro and gabbro in the Changning–Menglian Belt (Fig. 10c). These data suggest the existence of the Prototethyan Ocean in the middle–late Early Paleozoic.

We have obtained the first reliable zircon U–Pb ages of the Huimin metavolcanic rocks at ~456 Ma. This definitive age has significant implications for understanding the evolution of the Prototethyan Ocean and the northern margin of East Gondwana. The basalt-basaltic andesite-andesite sequence with minor dacite and rhyolite has a geochemical arc signature. The Huimin metavolcanic rocks suggest a continental island arc scenario in a contractional setting.

[Insert Figure 10]

The paleogeographic reconstruction for East Gondwana in the Late Ordovician is shown in Fig. 10a and b. The Simao Block, which includes the Huimin area, is part of the South China-Indochina composite terrane (Cathaysian Province, the yellow area in Fig. 10c) in modern SE Asia. The Early Paleozoic location of the Simao Block is unknown, but it must be close to or part of the larger South China or Indochina blocks. The occurrence of continental island arc volcanic rocks in the Huimin area suggests that there was an active convergent margin in the Late Ordovician along the northwestern part of East Gondwana. The Early Paleozoic island arc volcanic rocks are also exposed in the northern and central Langcangjiang zones (Yong et al., 1990; Dai et al., 1986; Fig. 10c). The Late Silurian medium–basic to medium–acidic island arc volcanics were reported in the Dazhonghe area approximately 100 km to the northeast of the Huimin area (Mao et al., 2012; Fig. 10c). All of these rocks are products of continental island arc magmatism.

Additionally, a zircon U–Pb age of 429±2 Ma and Re–Os isotopic ages of 429±6 Ma and 442±6 Ma for two molybdenite samples were obtained at the Dapingzhang dacite-hosted volcanogenic massive sulfide deposit in the southern Lancangjiang zone (Li et al., 2010; Lehmann et al., 2013; Fig. 10c). The massive sulfide ore was interpreted as a product of island arc magmatism in back-arc volcanic settings within an overall contractional environment (Huston et al., 2010; Lehmann et al., 2013). Indications for Early Paleozoic rifting are also seen in Cambro-Ordovician deep water sedimentary rocks along the margins of the Tarim and Indochina blocks (Metcalf, 1998, 2011).

The formation of these island arc or back-arc basins during the Late Ordovician–Late Silurian may be attributed to northern subduction of the Prototethyan Ocean beneath the Pan-Cathaysian landmass group along an active continental margin of East Gondwana (Fig. 10b and c).

Along with the breakup of Rodinia, the North China, South China, and Tarim blocks and a series of relatively small blocks, including the Simao, North Qiangtang and Indochina blocks, were successively rifted and migrated northward from the northern margin of the East Gondwana

supercontinent during the late Neoproterozoic (Metcalf, 1998, 2011). A certain size of Prototethyan Ocean occurred between these blocks and East Gondwana (Stampfli and Borel, 2004; Fig. 10ab). Our data in this study provide reliable evidence for the subduction of the Early Paleozoic Prototethyan Ocean that ultimately resulted in its subsequent closure. We propose an extensive early subduction event beneath the Pan-Cathaysian landmass group (Li et al., 1995; including North Qiangtang, Simao, Indochina and South China) at the northern margin of East Gondwana.

The reconstruction of the exact paleogeographic location of the Simao block within the Gondwana margin is still difficult due to the complex amalgamation history of SE Asia and the Cenozoic transformation caused by the India-Asia collision. Remnants of this paleo-active margin may also be found within the microcontinental collage of western Yunnan and the Tibetan Plateau, where poorly-defined Early Paleozoic subduction-related rocks are known (Zhu et al., 2013).

Incorporating all of the data above, tectonic relics of the Prototethyan ocean crust are also preserved along the Paleotethyan tectonic zone in the Sanjiang area (Fig. 10c). In the stage of Prototethyan evolution, the tectonic paleogeographic pattern is possibly similar to that of the Paleotethyan evolution in SW Yunnan, indicating a spatial connection between the Early Paleozoic Prototethyan and the Late Paleozoic Paleotethyan. Further study needs to be conducted on their internal relationship, especially on the tectonic transform during the Silurian, Devonian, and Carboniferous.

6 Conclusions

Petrological, geochronological, and geochemical data (including zircon Lu-Hf isotopic data) for the Huimin metavolcanic rocks in the southern Lancangjiang zone allow us to reach the following conclusions:

(1) The Huimin metavolcanic rocks have a LA-ICP-MS zircon U-Pb age of ~456 Ma, falling within the Late Ordovician.

(2) These rocks are highly enriched in LREEs and LILEs and depleted in HFSEs, with high Al_2O_3 , low TiO_2 , and weakly negative Eu anomalies ($\text{Eu}/\text{Eu}^*=0.37\text{--}0.99$), notably similar to typical subduction-related arc volcanic rocks. These data and the zircon Lu-Hf isotopic compositions are consistent with derivation from an anciently metasomatized mantle source.

(3) These data, together with other studies, suggest that there are tectonic relics of the Prototethyan continental margin in the southern Lancangjiang zone, SW Yunnan, which reveals that the subduction of the Prototethyan Ocean beneath the Pan-Cathaysian landmass group occurred in the Late Ordovician along the northern margin of East Gondwana. There is solid evidence for investigating the evolution of the Prototethyan Ocean and the reconstruction of East Gondwana in SW Yunnan.

7 Acknowledgements

We are grateful to Profs. J-B Zhou and another anonymous reviewer for their critical and constructive reviews and comments on this paper. We would like to thank Prof. Y-B Wu for his help during the writing. This study was financially supported by projects from the China Natural Science Foundation (41172202 and 41190073) and the China Geological Survey (1212011121256). This is a contribution to State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences (Wuhan).

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622

Figure Captions

Fig. 1 Simplified geological map of the Lancangjiang zone in SW China (revised from Yunnan BGMR, 1990; Wang et al., 2010), showing the locations of the Huimin metavolcanic rocks

Fig. 2 Lithological column of the Huimin Formation in the Huimin area (SW Yunnan), showing the locations of the collected samples

Fig. 3 Cathodoluminescence images (CL) of the representative zircons for the Huimin metavolcanic rocks. The red and blue circles show the locations of zircon U-Pb geochronological analysis and Zircon in-situ Lu-Hf isotopic ratio analysis, respectively.

Fig. 4 Zircon U-Pb concordia and weighted mean plots for the representative samples (a: D008, b: D009, and c: D010) of the Huimin metavolcanic rocks

Fig. 5 (a) $\omega(\text{Na}_2\text{O})+\omega(\text{K}_2\text{O})-\omega(\text{SiO}_2)$, (b) $\text{Zr}/\text{TiO}_2\text{-Nb/Y}$, and (c) $\omega(\text{FeO}^*)/\omega(\text{MgO})-\omega(\text{SiO}_2)$ diagrams of the Huimin metavolcanic rocks

(a) Le Maitre et al., 1989; Pc-picro/basalt; B-basalt; O₁-basaltic andesite; O₂-andesite; O₃-dacite; S₁-trachy basalt; S₂-basaltic trachyandesite; S₃-trachyandesite; T-trachyte/trachydacite; R-rhyolite; U₁-tephrite/basanite; U₂-phonotephrite; U₃-tephriphonolite; Ph-phonolite; F-foidite; (b) Winchester and Floyd, 1977; (c) Miyashiro, 1974. The green triangles and red squares are the plotting spots of the basic volcanic rocks and the medium-acidic volcanic rocks, respectively.

Fig. 6 (a) Chondrite-normalized REE and (b) primitive mantle-normalized incompatible element patterns for the Huimin metavolcanic rocks

Normalized values for chondrite and primitive mantle are from Taylor and McLennan (1985) and Sun and McDonough (1989), respectively. The data of N-MORB and E-MORB are from Sun and McDonough (1989). The data of arc volcanic rocks are from Luhr and Haldar (2006) and Kimura and Yoshida (2006). The meaning of the green triangles and red squares is described in Fig. 5.

Fig. 7 (a) $\omega(\text{FeO}^*)/\omega(\text{MgO})-\omega(\text{TiO}_2)$ and (b) ATK diagrams

(a) Glassley, 1974; IAB-island arc basalt; MORB-Oceanic ridge basalt; OIB-oceanic island basalt; (b) Zhao, 1989; I-oceanic basalt zone; II-continental basalt zone; III- island-arc, orogenic-belt basalt andesite zone. The meaning of the green triangles and red squares is described in Fig. 5.

Fig. 8 $\text{Ti}/100\text{-Zr-}3^*\text{Y}$ and $\text{Hf}/3\text{-Th-Ta}$ diagrams of the Huimin metavolcanic rocks (after Wood, 1980)

The meaning of the green triangles and red squares is described in Fig. 5.

Fig. 9 (a) Nb/Yb vs Th/Yb , (b) La/Nb vs La/Ba , (c) Nb^*100/Zr vs Th^*100/Zr diagrams and (d) Age (Ga) vs ϵHf (456 Ma) diagram for zircons separated from Sample D008 of the Huimin metavolcanic

rocks

Fig. 10 (a) Global paleogeographic map for the Late Ordovician (Blakey, 2011); (b) reconstruction of northeastern Gondwana for the Late Ordovician, showing the postulated positions of the East and Southeast Asian blocks, the distribution of land and sea, and the subduction zone; and (c) the distribution of the principal continental blocks and sutures of East and Southeast Asia, showing the Gondwana and Cathaysian Provinces and the locations of the Early Paleozoic magmatic rocks.

Table Captions

Table 1 LA-ICP-MS zircon U-Pb dating data of the Huimin metavolcanic rocks

Table 2 Zircon in-situ Lu-Hf isotopic compositions of the representative sample

Table 3 Major oxides (wt%) and element abundances (ppm) for the Huimin metavolcanic rocks (Samples with * are from Shen et al. (2008))

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Table

Table 1 LA-ICP-MS zircon U-Pb dating data of the Huimin metavolcanic rocks

Spot	Pb	Th	U	Th/U	²⁰⁷ Pb/ ²⁰⁶ Pb		²⁰⁷ Pb/ ²³⁵ U		²⁰⁶ Pb/ ²³⁸ U		²⁰⁷ Pb/ ²⁰⁶ Pb		²⁰⁶ Pb/ ²³⁵ U		²⁰⁶ Pb/ ²³⁸ U	
	ppm				Ratio	1σ	Ratio	1σ	Ratio	1σ	Age (Ma)	1σ	Age (Ma)	1σ	Age (Ma)	1σ
D008																
1	392	438	705	0.62	0.0583	0.0039	0.5842	0.0386	0.0726	0.0010	542	152	467	25	452	6
2	325	367	645	0.57	0.0576	0.0026	0.5897	0.0265	0.0740	0.0011	514	74	471	17	460	6
3	547	651	857	0.76	0.0618	0.0025	0.6298	0.0248	0.0737	0.0010	667	62	496	15	458	6
4	359	404	644	0.63	0.0626	0.0031	0.6327	0.0324	0.0731	0.0011	695	84	498	20	455	6
5	441	540	715	0.76	0.0573	0.0029	0.5850	0.0289	0.0736	0.0010	503	84	468	18	458	6
6	332	389	647	0.60	0.06	0.0028	0.5948	0.0248	0.0730	0.0010	602	67	474	16	454	6
7	1067	1414	1148	1.23	0.0597	0.0028	0.6006	0.0294	0.0728	0.0011	592	79	478	19	453	7
8	447	523	757	0.69	0.0616	0.0028	0.6215	0.0288	0.0728	0.0009	660	79	491	18	453	5
9	451	519	787	0.66	0.0641	0.0043	0.6465	0.0405	0.0738	0.0011	743	107	506	25	459	7
10	320	359	620	0.58	0.0612	0.0032	0.619	0.0322	0.0735	0.0013	646	82	489	20	457	8
11	280	257	520	0.49	0.0598	0.0031	0.6573	0.0344	0.0796	0.0011	595	89	513	21	494	7
12	4500	1682	1526	1.10	0.0874	0.0021	3.0300	0.0716	0.2498	0.0023	1368	32	1415	18	1437	12
13	532	610	987	0.62	0.0562	0.0020	0.6418	0.0235	0.0826	0.0013	459	52	503	15	512	8
14	424	458	748	0.61	0.0592	0.0029	0.5927	0.0262	0.0739	0.0012	574	69	473	17	459	7
15	599	756	828	0.91	0.0542	0.0024	0.5363	0.0231	0.0718	0.0010	380	71	436	15	447	6
16	757	257	1127	0.23	0.0809	0.0024	2.2001	0.0677	0.1954	0.0023	1218	42	1181	21	1151	13
17	536	618	919	0.67	0.0546	0.0025	0.5523	0.0246	0.0738	0.0010	396	76	446	16	459	6
18	547	629	813	0.77	0.0549	0.0023	0.5678	0.0231	0.0754	0.0011	409	65	457	15	468	7
19	395	200	525	0.38	0.0699	0.0025	1.5162	0.0539	0.1571	0.0019	925	53	937	22	941	11
20	3838	2379	1888	1.26	0.0762	0.0020	1.5730	0.0486	0.1489	0.0028	1100	33	960	19	895	16
D009																
1	481	944	832	1.13	0.0662	0.0063	0.6732	0.0629	0.0737	0.0012	813	206	523	38	459	7

2	896	1987	1979	1.00	0.0595	0.0023	0.6113	0.0233	0.0740	0.0009	585	61	484	15	460	5
3	584	400	1545	0.26	0.0714	0.0024	1.6044	0.0510	0.1631	0.0016	968	70	972	20	974	9
4	322	514	1271	0.4	0.0607	0.0033	0.6167	0.0326	0.0737	0.0010	629	121	488	20	458	6
5	344	724	1311	0.55	0.0599	0.0023	0.5899	0.0213	0.0709	0.0009	599	56	471	14	441	5
6	469	837	2224	0.38	0.0579	0.0021	0.5956	0.0213	0.0736	0.0009	527	58	474	14	458	5
7	280	587	838	0.70	0.0605	0.0030	0.6211	0.0301	0.0739	0.0011	621	78	491	19	459	7
8	628	506	1182	0.43	0.0719	0.0020	1.7801	0.0515	0.1770	0.0020	984	40	1038	19	1050	11
9	440	328	914	0.36	0.0783	0.0024	1.932	0.0579	0.1776	0.0024	1154	38	1092	20	1054	13
10	590	1152	1495	0.77	0.0601	0.0038	0.6174	0.0384	0.0745	0.0009	606	141	488	24	463	6
D010																
1	128	290	380	0.76	0.0553	0.0026	0.5717	0.0273	0.0738	0.001	424	82	459	18	459	6
2	142	343	318	1.08	0.0592	0.0030	0.5907	0.0294	0.0724	0.0013	575	77	471	19	451	8
3	66	152	160	0.95	0.0665	0.0050	0.669	0.0483	0.0738	0.0015	821	117	520	29	459	9
4	122	220	338	0.65	0.0737	0.0031	0.7796	0.0325	0.0767	0.0012	1034	58	585	19	476	7
5	325	659	1013	0.65	0.0574	0.0051	0.5656	0.0488	0.0714	0.0013	508	201	455	32	445	8

Table 2 Zircon in-situ Lu-Hf isotopic compositions of the representative sample

Spot	age (Ma)	$^{176}\text{Hf}/^{177}\text{Hf}$	1 σ	$^{176}\text{Yb}/^{177}\text{Hf}$	1 σ	$^{176}\text{Lu}/^{177}\text{Hf}$	1 σ	$\varepsilon\text{Hf}(0)$	$\varepsilon\text{Hf}(t)$	T _{DM1} (Ma)	T _{DM2}	f _{Lu/Hf}
D008-1	452	0.282398	0.000038	0.039741	0.000996	0.001094	0.000024	-13.23	-3.61	1209	1506	-0.97
D008-7	494	0.282379	0.000044	0.033013	0.000821	0.000890	0.000015	-13.88	-3.30	1228	1522	-0.97
D008-8	453	0.282375	0.000042	0.033647	0.000339	0.000939	0.000011	-14.05	-4.36	1237	1548	-0.97
D008-11	453	0.282397	0.000037	0.050999	0.000740	0.001322	0.000024	-13.25	-3.68	1217	1511	-0.96

Table 3 Major oxides (wt%) and element (ppm) abundances for the Huimin metavolcanic rocks

Samples	Huimin (this study)				Huimin			Manlai	
	D008	D009	D010	D011	H2*	H4*	H5*	H9*	H10*
SiO ₂	58.36	61.39	51.50	51.10	48.67	60.68	57.06	50.79	65.96
TiO ₂	0.60	0.73	0.69	0.69	0.90	0.96	0.93	0.85	0.86
Al ₂ O ₃	13.32	16.43	13.11	13.05	17.68	16.14	14.66	17.35	12.45
CaO	5.82	0.48	9.60	9.46	0.82	0.50	7.41	0.18	0.98
FeOt	5.76	6.90	10.82	11.12	22.77	7.86	8.63	12.24	8.22
MgO	3.42	3.93	6.98	7.23	6.62	4.19	4.13	8.43	3.59
K ₂ O	2.93	4.03	1.27	1.29	0.14	0.75	1.55	1.25	2.15
Na ₂ O	0.94	0.33	1.24	1.08	0.02	4.33	0.84	0.97	0.47
MnO	0.08	0.06	0.15	0.15	1.76	0.13	0.15	0.23	0.11
P ₂ O ₅	0.14	0.15	0.22	0.21	0.29	0.25	0.33	0.13	0.67
LOI	7.92	4.38	3.30	3.36	0.00	3.87	3.51	6.81	3.90
Total	99.29	98.81	98.88	98.74	99.67	99.66	99.20	99.23	99.36
mg-number	55.47	54.42	57.49	57.69	37.87	52.80	50.09	59.09	47.82
A/NK	2.82	3.35	3.84	4.11	95.88	2.03	4.79	5.89	4.02
A/CNK	0.87	2.84	0.63	0.64	10.55	1.82	0.89	5.30	2.55
Sc	16.85	22.31	37.28	37.39	41.80	47.40	47.10	51.50	36.20
V	89.3	117	222	223	215	308	340	380	303
Cr	161	197	546	551	192	357	106	1236	971
Co	35.8	46.6	84.4	91.5	42.2	48.1	40.1	107	72.0
Ni	63.3	75.4	172	181	46.7	73.2	167	597	337
Rb	110	164	64.8	66.0	41.0	99.6	2.93	86.6	134
Sr	93.5	9.81	535	538	58.3	436	47.1	55.3	69.5
Y	25.25	27.06	21.47	21.92	43.70	37.50	16.60	15.20	27.10
Zr	141	161	90.5	89.8	233	180	164	170	137
Nb	10.45	12.46	5.36	5.38	13.00	11.20	18.40	8.27	7.62
Ba	594	882	659	804	279	693	16.5	1124	2075
La	21.51	22.89	15.26	15.62	54.50	32.00	24.10	14.30	23.30
Ce	46.61	51.22	31.80	32.66	101.00	63.90	60.90	28.70	38.60
Pr	5.21	5.80	3.94	3.98	13.50	7.78	6.04	3.55	6.44
Nd	20.80	23.07	16.26	16.64	54.10	32.20	23.40	14.20	27.70
Sm	4.42	4.99	3.62	3.79	10.10	6.97	4.20	3.16	6.11
Eu	0.94	0.98	0.98	1.01	2.12	1.64	0.48	0.99	1.91
Gd	4.35	4.61	3.62	3.79	8.71	6.69	3.51	2.85	5.45
Tb	0.73	0.77	0.59	0.62	1.43	1.13	0.49	0.44	0.89
Dy	4.46	4.70	3.68	3.92	7.84	6.50	2.81	2.65	5.10
Ho	0.90	0.98	0.75	0.78	1.60	1.31	0.58	0.57	1.00
Er	2.60	2.92	2.25	2.42	4.56	3.79	1.76	1.83	2.74
Tm	0.40	0.45	0.36	0.38	0.67	0.54	0.30	0.28	0.38
Yb	2.52	2.76	2.35	2.43	4.40	3.61	2.14	2.47	2.49
Lu	0.36	0.40	0.34	0.34	0.67	0.51	0.35	0.41	0.39

Hf	4.02	4.80	2.52	2.48	6.79	4.97	4.87	4.94	3.91
Ta	0.88	1.09	0.43	0.43	0.95	0.75	1.17	0.49	0.37
Pb	6.13	3.53	35.73	35.62	6.09	7.13	6.09	12.50	13.40
Th	11.77	14.46	6.60	6.61	21.50	7.26	21.50	7.26	7.59
U	2.51	2.83	1.61	1.64	3.73	3.75	2.70	1.78	2.23
Eu/Eu*	0.65	0.61	0.82	0.80	0.67	0.72	0.37	0.99	0.99
Σ REE	141.08	153.6	107.2	110.3	308.9	206.0	147.6	91.6	149.6
(La/Yb) _{cn}	6.12	5.94	4.66	4.60	8.88	6.36	8.08	4.15	6.71
(Gd/Yb) _{cn}	1.43	1.38	1.28	1.29	1.64	1.53	1.36	0.95	1.81

Samples with * are from Shen et al. (2008)