Jurassic metasomatised lithospheric mantle beneath South China and its implications: Geochemical and Sr-Nd isotopic evidence from the Late Jurassic shoshonitic rocks

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Abstract

It is well established that the Late Jurassic magmatism in the southeastern area of the South China Block (SCB) is associated with an extensional event. However, the triggering mechanism for this event remains unclear, with models commonly invoking either the back-arc extension or intra-continental extension in response to the slab roll-back of the Pacific plate or the asthenospheric upwelling. The key issue about these models revolves around whether the subducted Pacific slab contributed to mantle source beneath the SCB during the Jurassic, or not. The basalts can provide significant clues for probing the nature of the lithospheric mantle and underlying convective mantle. In this study, we present the detailed zircon U-Pb geochronological, whole-rock elemental and Sr-Nd isotopic data for the Late Jurassic trachybasalt and trachyandesite from the Mashan Complex, and provide new constrains on the condition of the lithospheric mantle and the mantle dynamic of the SCB during the Jurassic. LA-ICP-MS zircon U-Pb dating suggests that these volcanic rocks erupted in the Late Jurassic (~158 Ma). All volcanic samples have shoshonitic geochemical affinities with high K_2O (2.03-4.89 wt.%) and K_2O/Na_2O (0.55-2.50). They are strongly enriched in LILE and LREE with positive K anomalies, positive $\varepsilon Nd_{(t)}$ values (from +0.8 to +3.0) and moderate Dy/Yb (1.98-2.36), low Ba/La (11.1-30.7), Th/Yb (2.29-5.77), U/Th (0.18-0.35), Th/Nb (0.16-0.27) and Th/Ce (0.08-0.15) ratios. Such geochemical signatures suggest that the Mashan volcanic rocks were derived from low-degree (1-5%) partial melting of a metasomatised lithospheric mantle with poor evidence for supporting the involvement of the Pacific

slab-derived components. The synthesis of the available data shows that the Jurassic shoshonitic and mafic rocks have higher $\varepsilon Nd_{(t)}$ values (mostly positive $\varepsilon Nd_{(t)}$ values) than the Triassic shoshonitic and mafic rocks ($\varepsilon Nd_{(t)}<0$), reflecting the source transformation from the Triassic enriched lithospheric mantle to the Jurassic depleted source. The metasomatism of the lithospheric mantle is likely to be associated with the asthenospheric upwelling prior to the Late Jurassic. The asthenosphere-lithosphere interaction might have produced a new metasomatised zone within the lowermost segment of the lithospheric mantle. It is inferred that the Jurassic magmatism in the southeast of the SCB might be associated with the asthenospheric upwelling in an intra-continental extension setting.

Keywords: Late Jurassic shoshonitic rock; Intra-continental extension; Asthenospheric upwelling; Mashan Complex; South China Block

1. Introduction

The Yanshanian (Late Mesozoic) magmatism is intensive and widespread in the southeast of the South China Block (SCB) (Fig. 1; e.g., Sun, 2006; Zhou et al., 2006b; Wang et al., 2013a). Available data showed that the Late Yanshanian (Cretaceous) magmatism in the southeastern SCB is significantly influenced by the Pacific subduction, as evidenced by the NE-trending Cretaceous igneous rocks along the coastal regions of South China (Fig. 1b; Sun, 2006; Zhou et al., 2006b; Li and Li, 2007; Wang et al., 2013a; Jiang et al., 2015). However, there is no consensus on whether the Early Yanshanian (Jurassic) magmatic activities in this region are also directly dominated by the Pacific subduction (e.g., Zhou and Li, 2000; Zhou et al., 2006b; Li and Li, 2007; Chen et al., 2008; Jiang et al., 2009, 2015; Wang et al., 2013a; Gan et al., 2016, 2017a, b;). The debate around the Jurassic magmatism focuses on two key aspects, of which one is in regards to the contribution of the subducted Pacific slab-derived components and the other is the timing. If the subducted Pacific slab had contributed to mantle source beneath the southeastern SCB, the mantle-derived rocks (e.g., mafic rocks and shoshonitic rocks) should record the important information on the potential interaction process among the slab, lithospheric mantle and asthenosphere, and in turn help us to understand the initial timing of such process.

Shoshonitic rocks are mainly characterized by high K_2O contents (>3 wt.%), K_2O/Na_2O ratios (>0.5) and high incompatible elemental concentrations (e.g., Foley, 1992). They have been documented in various tectonic regimes involving oceanic, continental and within-plate settings (e.g., Müller et al., 1992; Rogers et al., 1992; Chung et al., 2001; Hunt et al., 2012). The mantle-derived shoshonitic rocks, as well as mafic rocks, are important carriers for exploring the mantle components, and they can also bring new insights into the nature of the mantle and geodynamic process. In the southeast of the SCB, the Jurassic shoshonitic rocks are mainly distributed in the eastern Guangxi, western Guangdong and southern Jiangxi Provinces, at which is far away from the coastal regions of South China with a long distance of >500 km (Fig. 1b). Previous studies have focused on the intrusive shoshonitic rocks, however, poor attentions have been paid to the synchronous volcanic rocks (e.g., Li et al., 1999, 2000, 2001, 2003, 2004; Zhu et al., 2005; He et al., 2010; Chen et al., 2013; Lao et al., 2015). The Mashan Complex in the eastern Guangxi Province consists of intrusive and volcanic shoshonitic rocks and is a large and typical shoshonitic complex in the southeastern SCB (Fig. 2a-b) (e.g., Guangxi BGMR, 1985; Li et al., 2004; Duan et al., 2013; Wang, 2013; Lao et al., 2015). Thus, we herein present a series of new detailed geochronological, whole-rock chemical and Sr-Nd isotopic data for the Late Jurassic volcanic rocks from the Mashan Complex. The chief aims of this study are: (1) to constrain the timing of the shoshonitic magmatism; (2) to explore the mantle source of the shoshonitic rocks and assess the subduction contribution to the source; and (3) to provide a better constraint on the Jurassic tectonic setting of the southeastern SCB.

2. Geological background and petrology

The SCB is bounded by the North China Craton to the north, the Tibetan Block to the west, the Indochina Block to the southwest and the Pacific plate to the east (Fig. 1a; Zhou et al., 2006b; Wang et al., 2013a). It was formed by the amalgamation of the Yangtze Block with the Cathaysia Block along the Jiangnan Orogen during the early Neoproterozoic (Fig. 1a; Zhao and Cawood, 2012; Zhang et al., 2012b; Zhang and Wang, 2016). Since the amalgamation, the SCB has undergone three Phanerozoic thermal-tectonic events involving the Kwangsian (also named as the Caledonian in Chinese literature, Early Paleozoic), Indosinian (Early Mesozoic) and Yanshanian (Late Mesozoic), accompanied with extensive and widespread igneous rocks in the southeastern SCB (e.g., Wang et al., 2003, 2005b, 2008, 2010, 2013a; Zhou et al., 2006b; Li and Li, 2007; Zhang et al., 2012a; Jiang et al., 2015). The Yanshanian igneous rocks are the most widespread in the southeast of South China and are closely associated with numerous precious metal ore deposits (e.g., Zhou et al., 2006b; Wang et al., 2013a). The Early Yanshanian igneous rocks mainly occur in the interior of the SCB, whereas the Late Yanshanian ones are distributed along the coastal regions of South China (Fig. 1b; e.g., Zhou and Li, 2000; Wang et al., 2003, 2005b, 2008, 2013a; Zhou et al. 2006b; Li and Li, 2007; Jiang et al., 2009, 2015). Such spatial distribution appears to suggest that the Yanshanian igneous rocks have a younging trend towards the southeast, from inland to coast (Zhou et al., 2006b). However, this younging trend does not extend systematically from the Jurassic to Cretaceous due to the occurrence of the Late Jurassic granitoids within the coastal regions (e.g., Guo et al., 2012; Huang et al., 2013; Zhang et al., 2015b).

The Jurassic igneous rocks mainly consist of granites, minor mafic-intermediate intrusions, along with the synchronous basalt and rhyolite that form part of a bimodal volcanic suite within sedimentary basins (e.g., Li et al., 2003, 2004; Wang et al., 2003, 2008, 2013a; Zhou et al., 2006a, b; He et al., 2010; Meng et al., 2012; Chen et al., 2013; Jiang et al., 2015; Cen et al., 2016; Gan et al., 2016, 2017a, b). Some Jurassic igneous rocks have shoshonitic geochemical affinities and mainly occur in the eastern Guangxi, western Guangdong and southern Jiangxi Provinces (Figs. 1b and 2a), such as the Mashan shoshonitic Complex (153.8 ± 0.6 Ma; Lao et al., 2015), Nandu syenite pluton (162 ± 1 Ma; Chen et al., 2013), Niumiao syenite pluton (160 ± 4 Ma; Zhu et al., 2005) and Tabei and Quannan syenite plutons (~178 Ma; He et al., 2010). The Mashan Complex is special amongst these Jurassic shoshonitic intrusions, and it is the only multi-phased one which is composed of separated mafic, intermediate and acid igneous rocks (Fig. 2a-b; e.g., Guangxi BGMR, 1985; Duan et al., 2013; Wang, 2013; Lao et al., 2015).

The Mashan Complex is located in the Shuangqiao-Jinshi-Mashan areas with a total acreage of ~93 km^2 (Fig. 2b; Guangxi BGMR, 1985). The complex intrudes the Triassic Darongshan granite (230-260 Ma) to the east (Chen et al., 2011; Jiao et al., 2015) and the Cambrian-Devonian strata to the southwest (Fig. 2b), and it is contacted with the Cambrian-Devonian strata via the fault in the north (Fig. 2b; Guangxi BGMR, 1985). The Mashan Complex consists of a suite of intrusive rocks and corresponding volcanic succession. The intrusive rocks are mainly composed of monzonite, diorite and syenite, and the volcanic rocks are marked by trachybasaltic and trachyandesitic rocks (e.g., Guangxi BGMR, 1985; Duan et al., 2013; Wang, 2013; Lao et al., 2015). The volcanic samples in this study were collected from the Shuangqiao village and Shiniuling quarry (Fig. 2b). Trachybasalt samples contained abundant phenocrysts (<10%) (Fig. 3a-b), and trachyandesitic samples had only a small percentage (<3%) of phenocrysts. The phenocryst is mainly dominated by pyroxene glomerocrysts, and the groundmass consists of plagioclase microlites and minor pyroxene (Fig. 3a-b).

3. Analytical methods

3.1. Zircon U-Pb analyses

The standard density and magnetic separation techniques were both applied to separation of zircon grains from trachyandesitic samples SQ-10 and MZ-1C2. The separated zircon grains were then handpicked under a binocular microscope, mounted in epoxy resin, polished to about half thickness and finally vacuum-coated with high purity gold. The internal textures of the zircon grains were checked by using transmitted and reflected light micrographs and cathode-luminescence (CL) imaging at Sun Yat-sen University, China.

Zircon U-Pb analyses for Sample SQ-10 were carried out using a Nu Plasma multi-collector inductively-coupled-plasma mass-spectrometer (MC-ICP-MS) coupled with a Resonetics RESOlution M-50-HR Excimer Laser Ablation System at Department of Earth Sciences, the University of Hong Kong. Helium gas, as an additional diatomic gas to enhance sensitivity, was mixed with argon and nitrogen gases. Details of instrument parameters and analytical procedures were reported by Xia et al. (2011). A laser repetition rate of 6 Hz with a spot size of 30 μm was used for ablating zircons. U-Th-Pb ratios and their absolute abundances were calibrated against standard zircon 91500 (1062.4 ± 0.6 Ma, Wiedenbeck et al., 1995). All uncertainties were calibrated against standard zircon 91500, and zircon GJ-1 (608.53 ± 0.37 Ma, Jackson et al., 2004) was used as a secondary standard. Zircon U-Pb dating for Sample MZ-1C2 was undertaken on an Agilent 7500a ICP-MS coupled with a 193 nm Geolas 2005M laser-ablation system at the China University of Geosciences (Wuhan).

Particular operating conditions for instruments and detailed analytical procedures are described by Liu et al. (2008). Helium was applied as a carrier gas to enhance the transport efficiency of the ablated material. A laser spot size of 32 μm and a laser repetition of 6 Hz was used for ablating zircons during these analyses. Standard zircon 91500 was used as an external standard and analyzed twice every 8 analyses. Fractionation correction and quantitative calibration were performed by the software of ICPMSDataCal (Liu et al., 2010). Concordia diagrams for zircon U-Pb results and weighted mean calculations were calculated using the Isoplot program (Ludwig, 2009).

3.2. Whole-rock major oxides, elemental and Sr-Nd isotopic analyses

All rock samples were crushed into mm-scale grain size after removing the weathered rims. The grains were first washed with purified water in an ultrasonic bath and then powdered into 200-mesh grain size using an agate ring mill. All whole-rock geochemical analyses were carried out at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. A wavelength X-ray fluorescence spectrometer was used to measure major oxide contents. Detailed description of analytical procedures was given in Li et al. (2005). Elemental analyses were obtained using a Perkin-Elmer Sciex ELAN 6000 ICP-MS, following the procedures of Liu et al. (1996). The analytical accuracy was better than 5% for most trace elements (Liu et al., 1996). Strontium (Sr) and Neodymium (Nd) isotopic ratios were measured on a Neptune MC-ICP-MS, and the sample preparation and chemical separation procedures were described by Wei et al. (2002) and Liang et al. (2003). The measured $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios were calibrated to $^{86}Sr/^{88}Sr$ = 0.1194 and $^{146}Nd/^{144}Nd$ = 0.7219, respectively.

4. Results

4.1 Zircon U-Pb dating results

Zircon U-Pb dating was conducted on two trachyandesitic samples: MZ-1C2 from the Shiniuling quarry (22°45′54.7″N, 109°34′27.6″E) and SQ-10 from the Shuangqiao village (22°42′43.4″N, 109°33′19.8″E). The analytical results are listed in Table 1 and shown in Fig. 4.

The zircon grains from MZ-1C2 are euhedral and transparent with oscillatory zoning (Fig. 4a). The thirteenth analytical spot with low Th/U ratio (0.3) shows an apparent $^{206}Pb/^{238}U$ age of 311.9 ± 10.7 Ma (Fig. 4a). The remaining fifteen spots on 15 grains display high Th/U ratios of 0.8-1.6 and yield a weighted mean $^{206}Pb/^{238}U$ age of 158.4 ± 1.1 Ma with MSWD=0.4 (Fig. 4a). This age can be interpreted as the eruption age of the volcanic rocks from the Mashan Complex.

Most of the zircon grains from SQ-10 are subhedral and rounded (Fig. 4b), and eight zircon grains show euhedral and obvious oscillatory zoning in CL imaging (Fig. 4b) with Th/U ratios of 0.5-1.0. Eight analytical spots on the eight euhedral grains yield a weighted mean $^{206}Pb/^{238}U$ age of 158.6 ± 3.0 Ma with MSWD = 0.7 (Fig. 4b), which is in agreement with that of MZ-1C2. The remaining seventeen zircon grains show older apparent $^{206}Pb/^{238}U$ ages ranging from 179 Ma to 1236 Ma, interpreted as captured grains (Fig. 4b).

4.2 Geochemical characteristics

Major oxides and trace element results for the volcanic samples from the Mashan Complex are listed in Table 2. All samples, including other literatures' data (e.g., Guo et al., 2001; Wu and Li, 2011; Duan et al., 2013; Wang, 2013), are illustrated in Figs. 5-7. Most of major oxides show insignificant linear correlations with the loss on ignition (not shown), and all major oxide contents are recalculated to 100% (accounting for loss on ignition) and used in below description and diagrams. The volcanic samples show SiO_2 = 48.92-57.96 wt.%, Al_2O_3 = 13.14-16.74 wt.%, MgO = 2.35-6.98 wt.%, CaO = 4.17-11.19 wt.%, TiO_2 = 1.20-2.53 wt.% and Fe_2O_{3t} = 7.42-12.29 wt.%. They plot into the fields of alkaline basalt and trachyandesite (Fig. 5a) and high-K calc-alkaline and/or shoshonite series (Fig. 5b). These samples have high total alkaline (5.29-9.08 wt.%), K_2O (2.03-4.89 wt.%) and K_2O/Na_2O (0.55-2.50), showing shoshonitic geochemical affinities (Fig. 5c-d). CaO/Al_2O_3, FeO_t, CaO and MgO are negatively correlated with SiO_2 (Fig. 6a-d), and Ni and Cr show positive correlations with MgO (Fig. 6g-h).

The volcanic samples show similar rare earth element (REE) and multi-elemental normalized patterns (Fig. 7a-b). They are strongly enriched in light REE (LREE) and depleted in high REE (HREE) with insignificant Eu anomalies (Fig. 7a). $(La/Yb)_{CN}$ (where CN means chondrite normalized) ratios range from 10.1 to 16.8 and $(Dy/Yb)_{CN}$ from 1.32 to 1.58. These samples are mainly characterized by pronounced enrichment in large ion lithophile elements (LILE) and depletion in high field strength elements (HFSE) with negative Nb-Ta, Ti and significantly positive K anomalies in Fig. 7b. Such REE and multi-elemental normalized patterns are similar to those of the synchronous intrusive rocks in the Mashan Complex and the Jurassic (~178 Ma) Quannan and Taibei syenites (Fig. 7a-b; Li et al., 2003; He et al., 2010; Duan et al., 2013; Wang, 2013; Lao et al., 2015).

Our Sr-Nd isotopic data, along with previously-reported data for the volcanic rocks from the Mashan Complex, are presented in Table 3 and shown in Fig. 8a-b. The measured $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios range from 0.70564 to 0.70820 and from 0.51259 to 0.51271, respectively. The corresponding initial $^{87}Sr/^{86}Sr$ ratios are in range of 0.70452-0.70693 with $\varepsilon Nd_{(t)}$ values ranging from +0.8 to +3.0 (Table 3). The Sr-Nd isotopic compositions of these volcanic rocks are similar to those of the Jurassic shoshonitic rocks, but distinct from those of the Triassic shoshonitic rocks in the southeastern SCB (Fig. 8a-b; Li et al., 2003, 2004; Wang et al., 2005a; He et al., 2010; Mao et al., 2013).

5. Discussion

5.1 Formation age of the Mashan Complex

There is no consensus on the formation time of the Mashan Complex, especially the volcanic rocks (Table 4; Guangxi BGMR, 1985; Li et al., 2004; Duan et al., 2013; Wang, 2013; Lao et al., 2015). The previous study proposed that the Mashan Complex formed over a protracted time with multiple magmatic phases (Guangxi BGMR, 1985). Wang (2013) reported zircon U-Pb ages of 162~165 Ma for the syenite, diorite and monzonite from the Mashan Complex (Table 4). Wu and Li (2011) considered the basalts from this complex erupting at the Triassic, and Wang (2013) obtained a zircon U-Pb age of 246.7 ± 1.5 Ma for these basalts. However, zircon grains sorted from the basalts were euhedral with obvious oscillatory zoning (Wang, 2013), similar to those from the Triassic Darongshan granite (230-260 Ma) that was intruded by the Mashan Complex in morphological signatures, Th/U ratios and apparent ages (Chen et al., 2011; Jiao et al., 2015). Such signatures suggest that zircon grains hosted in the basalts were most likely to be captured. A diorite porphyry sample from the Mashan Complex yielded a $^{40}Ar/^{39}Ar$ plateau age of 153.8 ± 0.6 Ma (Lao et al., 2015). Our two trachyandesitic samples from this complex yield weighted mean $^{206}Pb/^{238}U$ ages of 158.4 ± 1.1 Ma (MZ-1C2) and 158.6 ± 3.0 Ma (SQ-10) (Fig. 4a-b), interpreted as the eruption ages of volcanic rocks, which are in good agreement with those of the intrusive rocks from this complex. In summary, the Mashan Complex formed in the Late Jurassic of ~154-159 Ma.

5.2 Assessment of crustal contamination and fractional crystallization

Given that the volcanic rocks from the Mashan Complex erupted in a continental setting, there is a strong likelihood that crustal contamination could have occurred during magma ascent (e.g., Castillo et al., 1999). The crustal contamination is posible due to the presence of inherited zircons in Fig. 4b. However, for elemental and isotopic ratios, the effects of crustal contamination might be relatively limited. Firstly, the volcanic samples are characterized by positive $\varepsilon Nd_{(t)}$ values (from +0.8 to +3.0) and low initial $^{87}Sr/^{86}Sr$ ratios (from 0.70452 to 0.70693), suggesting minor crustal contamination. Secondly, the lack of positive correlation between $\varepsilon Nd_{(t)}$ and MgO (Fig. 9a) and the negative correlation of Nb/La with La/Sm (Fig. 9c) is also consistent with minimal crustal contamination. Thirdly, the samples show variable Nb/La ratios regardless of MgO content (Fig. 9b), and also have much higher Nb/U (12.4-31.8) and Nb/La (0.78-1.05) ratios than average values for continent crust (3.91 and 0.40, respectively) in Fig. 9d (Rudnick and Gao, 2003). More importantly, simple Sr-Nd modeling results (Fig. 8a) show that about 20-30% SCB crustal components into the depleted mantle-derived melt are required to achieve the Nd isotope of the Mashan volcanic samples. However, such high proportional crustal components are not consistent with their major oxides, trace elemental and Sr isotopic compositions.

The relatively large variation of MgO and SiO_2 contents for the Mashan volcanic samples demonstrates that they are not the representative of primary magmas, and may have undergone significant fractional crystallization. Olivine fractionation is supported by the negative correlation of SiO_2 with MgO (Fig. 6c) and the positive correlations of MgO with Cr and Ni (Fig. 6g-h). Decreasing CaO/Al_2O_3 with increasing SiO_2 (Fig. 6a) suggests the fractional crystallization of clinopyroxene. The negative correlation between SiO_2 and FeO_t (Fig. 6d) might be a consequence of hornblende fractionation, which is also supported by the depletion in middle REE (Fig. 7a). However, slightly negative Eu and Sr anomalies (Fig. 7a-b) preclude significant plagioclase fractionation. The fractionation of Ti-Fe oxides and apatite appears to be minor in terms of TiO_2 and P_2O_5 variations with increasing SiO_2 (Fig. 6e-f).

5.3 Origin of volcanic rocks from the Mashan Complex

The volcanic samples from the Mashan Complex are strongly enriched in LILE and LREE, resembling ocean island basalt (OIB) compositions (Fig. 7a-b). However, they show higher initial $^{87}Sr/^{86}Sr$ and lower $\varepsilon Nd_{(t)}$ than the Ningyuan (~175 Ma) and Antang (~168 Ma) asthenosphere-derived basalts with OIB-like geochemical signatures in the southeastern SCB (Fig. 8a-b; e.g., Wang et al., 2003, 2004; Li et al., 2004; Jiang et al., 2009; Meng et al., 2012). The Mashan volcanic samples have much lower Nb/U (12.4-31.8) and Ce/Pb (4.99-15.0) ratios than average MORB or OIB (47 and 25, respectively; Fig. 9d; Hofmann et al., 1986). These samples are also characterized by negative Nb-Ta and significantly positive K anomalies (Fig. 7a), distinct from those of OIB (Sun and McDonough, 1989). In contrast, Their REE and multi-elemental normalized patterns (Fig. 7a-b) are similar to those of the Jurassic (~178 Ma) Quannan and Tabei syenites that have been interpreted as derivation from a lithospheric mantle source (e.g., Li et al., 2003; He et al., 2010). The Sr-Nd isotopic compositions (Fig. 8a-b) for these volcanic samples also coincide with those of other Jurassic shoshonitic rocks in the southeastern SCB (e.g., Li et al., 1999, 2000, 2004; Zhu et al., 2005; He et al., 2010; Chen et al., 2013). Thus, parental magmas for the Mashan volcanic samples might have originated from lithospheric rather than asthenospheric mantle.

The mineralogy of the lithospheric mantle have pronounced effects on the composition of primary melts (e.g., Barry et al., 2003; Hunt et al., 2012; Sheldrick et al., 2018), potentially explaining geochemical signatures of the Mashan volcanic samples. These samples have high K_2O (2.03-4.89 wt.%) contents and K_2O/Na_2O (0.55-2.50) ratios with significantly positive K anomalies (Fig. 7a), suggesting that the potassium in the source is enriched relative to nearby incompatible elements (e.g., Ta and La) and that a potassic mineral phase contributed to the final melt compositions. Phlogopite and amphibole, as common accessory phases in the mantle source, are the most likely candidates (e.g., Condamine and Médard, 2014). Partition coefficient (*D*) data suggest that Rb and Ba are compatible, and Sr is incompatible in phlogopite (D^{Ba}_{phl}=2.9, D^{Rb}_{phl}=5.8, D^{Sr}_{phl}=0.16; Adam et al., 1993; LaTourette et al., 1995; Spath et al., 2001), and these elements behave more similar to one another regarding amphibole compatibility (D^{Ba}_{amp}=0.5, D^{Rb}_{amp}=0.3, D^{Sr}_{amp}=0.3; Adam et al., 1993; LaTourette et al., 1995). Melts in equilibrium with phlogopite are expected to have significantly high Rb/Sr (>0.1) and low Ba/Rb (<20) ratios, but melts derived from an amphibole-bearing source may have high Ba concentrations and Ba/Rb ratios (Furman and Graham, 1999). The Mashan volcanic samples have relatively high Rb/Sr (0.08-0.25) and low Ba/Rb (4.99-11.3) ratios (Fig. 10a), suggestive of phlogopite in the source. Furthermore, these samples are characterized by high LILE and LREE (Fig. 7a-b). Partial melting of either garnet or spinel peridotite will preferentially lead to enrichment of LREE due to the retention of HREE in the source (e.g., McKenzie and O'Nions, 1991). However, the distribution coefficients of HREE in garnet are higher than those in spinel, leading melts in equilibrium with garnet to have high Dy/Yb ratios (e.g., McKenzie and O'Nions, 1991; LaTourette et al., 1995; Blundy et al., 1998). The Mashan volcanic samples show large variations of Dy/Yb ratios (1.98-2.36), suggesting perhaps both garnet and spinel as residual phases in the source (Fig. 10b, e.g., McKenzie and O'Nions, 1991; Blundy et al., 1998; Duggen et al., 2005). The presence of garnet in the source is further supported by the relatively strong depletion in HREE (Fig. 7b). To place constraints on the proportion of garnet and spinel in the mantle source, these samples are plotted on a diagram of $(Tb/Yb)_P$ (where P stands for primitive mantle-normalized) versus $(Yb/Sm)_P$ (Fig. 10c; Zhang et al., 2006), which are consistent with a 10-80% contribution from melting in the presence of garnet with low-degree (1-5%) partial melting. Interestingly, these samples have similar Sm/Yb and Ce/Yb ratios with the Emeishan low-Ti and high-Ti basalts (Fig. 10d) that were interpreted as being generated within the spinel-garnet transition zone and garnet stability field (Xu et al., 2001a), respectively.

The Fe_2O_{3t} and TiO_2 contents of the Mashan volcanic samples are higher than those of the Triassic shoshonitic rocks, and are plotted in the field between the depleted peridotite and fertile peridotite in Fig. 11 (Falloon et al., 1988), suggesting that the mantle source for these volcanic samples might have been metasomatically enriched. Enrichment in LILE and LREE for these volcanic samples supports the hypothesis that the mantle source had undergone metasomatism related to the infiltration of hydrous fluids/melts (e.g., McKenzie, 1989; Pilet et al., 2008). Likewise, phlogopite in the mantle is usually associated with the interaction between the lithospheric mantle and the ascending fluids/melts (e.g., Menzies et al, 1987). The origin of different metasomatic fluids has a prominent effect on the geochemical compositions of lithospheric mantle. Metasomatic fluids derived from subducted sediments, for example, are likely to have greatly different elemental and isotopic compositions from the host lithospheric mantle and the asthenosphere-derived melts (e.g., Rogers et al., 1992; Zhang et al., 2002). The samples from the Mashan Complex are marked by low Ba/La (11.1-30.7), Th/Yb (2.29-5.77), U/Th (0.18-0.35), Th/Nb (0.16-0.27) and Th/Ce (0.08-0.15) ratios, ruling out the subduction-derived fluids or melts (Class et al., 2000). The Early Mesozoic subduction-related igneous rocks have poorly been discovered in the southeastern SCB so far (e.g., Wang et al., 2013a; Gan et al., 2017a), and the Mashan Complex would have been >500 km away from either the Neotethyan or the Pacific trenches. Instead, the Mashan volcanic samples are characterized by depleted Sr-Nd isotopes (Fig. 8a), reflecting some degree of the asthenospheric contribution. This is also in agreement with Sr-Nd-Pb isotopic compositions on diorites from the Mashan Complex (Lao et al., 2015). In addition, simple modeling calculations support that the Sr-Nd isotopic compositions of the Mashan volcanic samples can be balanced by the interaction of lithospheric mantle with 20-30% asthenosphere-derived melts (Fig. 8a). Thus, it is concluded that the volcanic rocks from the Mashan Complex were most likely to be derived from low-degree (1-5%) partial melting of a phlogopite-bearing peridotite around the spinel-garnet transition zone (60-80 km; e.g., Ellam, 1992; McKenzie and O'Nions, 1991) previously metasomatised by the asthenosphere-derived fluids/melts.

5.4 Tectonic implications

As discussed above, the volcanic samples from the Mashan Complex were derived from partial melting of a metasomatised lithospheric mantle. The question arises to when and why the metasomatic enrichment of lithospheric mantle occurred. The metasomatic event might not be caused by an ancient enrichement based on the following evidence. (1) The initial $^{87}Sr/^{86}Sr$ ratios of the Mashan volcanic samples are not particularly elevated (Fig. 8a). (2) These volcanic samples, along with other Jurassic shoshonitic and mafic rocks, have distinct Sr-Nd isotopic compositions from the Triassic shoshonitic and Early Paleozoic mafic rocks that were derived from an ancient metasomatised lithospheric mantle (Fig. 8a-b; Wang et al., 2005a, 2013b; Yao et al., 2012; Mao et al., 2013; Zhang et al., 2015a). (3) The Late Jurassic (~160 Ma) Qinghu monzonite has high $\varepsilon Hf_{(t)}$ (~11.6) and mantle-like $\delta^{18}O$ (~5.4) values, interpreted as derivation from a recently metasomatised lithospheric mantle (Li et al., 2009). In addition, studies on the mantle xenolithos hosted in the Ningyuan basalts suggest a juvenile sub-continental lithospheric mantle beneath the SCB (Liu et al., 2012). Available data show that the Triassic shoshonitic and Early Paleozoic mafic rocks are marked by negative $\varepsilon Nd_{(t)}$ values ($\varepsilon Nd_{(t)}<0$), whereas the majority of the Jurassic mafic and shoshonitic rocks show positive $\varepsilon Nd_{(t)}$ values ($\varepsilon Nd_{(t)}>0$; Fig. 8b). Such a contrasting change of $\varepsilon Nd_{(t)}$ values reflects the transition of lithosphere mantle from enriched (Triassic) to depleted (Jurassic), suggesting the metasomatic enrichment occurred after the Triassic, prior to the Late Jurassic. This metasomatised lithospheric mantle was likely to be characterized by enriched elemental and depleted

Sr-Nd isotopic compositions.

During the Jurassic period, across the southeast of the SCB, there experienced multiple episodes of lithospheric extensional events marked by A-type granites and bimodal volcanic rocks (e.g., Chen et al., 2008; Wang et al., 2013a; Jiang et al., 2015; Cen et al., 2016; Gan et al., 2016, 2017a, b). The mechanism for triggering these extensional events remains highly disputed (e.g., Zhou et al., 2006b; Li and Li, 2007; Wang et al., 2013a; Jiang et al., 2009, 2015), involving the mechanisms of back-arc extension (caused by the slab roll-back of the Pacific plate) or intra-continental extension (in response to the asthenospheric upwelling). However, the synchronous subduction-related rocks have poorly been reported in this region (e.g., Wang et al., 2003, 2005b, 2008, 2013a; Chen et al., 2008), and the spatial distribution of the Jurassic magmatism is significantly distinct from that of the Cretaceous magmatism (Fig. 1b). Moreover, the Jurassic mafic rocks in the inland of the SCB show distinct Sr-Nd-Pb isotopic compositions from the Cretaceous mafic rocks along the coastal regions of South China that were usually interpreted as the derivation from mantle sources metasomatised by the Pacific slab-derived components (Chen et al., 2008). As previously mentioned, the geochemical signatures of the Late Jurassic volcanic rocks from the Mashan Complex suggest that the mantle source had poorly been influenced by slab-derived components. In contrast, numerous geological observations support asthenospheric upwelling during the Jurassic (note, we use the term “asthenospheric upwelling” here to mean perturbations within the shallowest part of the upper mantle, and not a deep-rooted mantle plume), including (1) the calculated mantle potential temperatures of the Early Jurassic Xialan gabbroic and Changpu basaltic samples (~190 Ma) range from 1341 *°C* to 1407 *°C* (Cen et al., 2016; Gan et al., 2017a). Such mantle potential temperatures are close to those of modern MORB ambient mantle (~1350 ± 50 °C; e.g., Herzberg et al., 2007; Lee et al., 2009) and the western Basin and Range Province of United States (1350-1450 *°C*; Wang et al., 2002), indicative of large-scale asthenospheric upwelling during the Early Jurassic; (2) the Ningyuan (~175 Ma) and Antang (~168 Ma) basalts in Hunan and Jiangxi Provinces show OIB-like geochemical affinities that were regarded as derivation from asthenospheric mantle (e.g., Wang et al., 2003, 2004; Jiang et al., 2009; Meng et al., 2012); and (3) the mafic microgranular enclaves (160-163 Ma) hosted in Huashan and Qitianling granites (160-163 Ma) are also responsible for the asthenospheric upwelling (Zhu et al., 2005; Zhao et al., 2012). The $\varepsilon Nd_{(t)}$ and Nb/La ratios of the Jurassic mafic rocks in the southeast of the SCB are plotted along the asthenosphere-lithosphere mixing trend (Chen et al., 2008; Meng et al., 2012; Gan et al., 2017a). Thus, it is inferred that the metasomatic enrichment event is most likely to be geodynamically associated with the asthenospheric upwelling. Admittedly, the far-field effects of the Pacific subduction on the asthenospheric upwelling can not be entirely excluded from such a model, as slab dynamics could have influenced the mantle flow pattern beneath the SCB. More detailed work needs to be done in the future to evaluate whether the asthenospheric upwelling is triggered by the far-field effects of the Pacific subduction. Considering that the slab-derived components from the Pacific plate have poorly contributed to the mantle source of the Jurassic shoshonitic and mafic rocks, this study prefers to suggest that the Jurassic magmatism in the southeast of the SCB was likely to be associated with the asthenospheric upwelling in an intra-continental extension setting.

Decompression partial melting of asthenospheric mantle can produce mafic rocks with OIB-like geochemical signatures (e.g., the Ningyuan and Antang basalts; Wang et al., 2003, 2004; Jiang et al., 2009; Meng et al., 2012). Asthenosphere-derived melts interact with the overlying lithospheric mantle, giving rise to a metasomatised zone within the lowermost segment of lithospheric mantle (Fig. 12), which is characterized by depleted Sr-Nd isotopic compositions. Partial melting of this metasomatised mantle could then generate the Late Jurassic shoshonitic rocks in the southeast of the SCB. Simultaneously, continual heating by upwelling asthenosphere can result in partial melting of the overlying ancient lithospheric mantle, causing magma mixing, which in turn could have generated other Jurassic mafic rocks (e.g., the Xialan (~190 Ma) and Chebu (173 Ma) gabbros; Li et al., 2003; He et al., 2010; Zhu et al., 2010; Wang et al., 2013a; Gan et al., 2017a). The injection of mafic magmas into crust will produce a large-scale crustal melting and the crust-mantle interaction, leading to the huge volume Late Jurassic granitoids (~64,100 km^2), as well as mafic microgranular enclaves (Zhu et al., 2005; Sun, 2006; Zhao et al., 2012).

Conclusions

(1) The trachybasaltic and trachyandesitic rocks from the Mashan Complex have shoshonitic geochemical affinities and the trachyandesitic rocks are dated at ~158 Ma.

(2) They were derived from partial melting of a newly metasomatised mantle

within spinel-garnet transition zone.

(3) The metasomatism enrichment of lithospheric mantle was associated with asthenosphere-derived melts.

(4) This metasomatism was likely to have occurred during the Jurassic, and the Jurassic magmatism in the southeast of the SCB was related to asthenospheric upwelling in an intra-continental extension setting.

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Figure captions

Fig. 1 (a) A simplified map of the South China Block (SCB). (b) Distribution of the Late Mesozoic igneous rocks in southeastern SCB (modified after Sun, 2006).

Fig. 2 (a) Distribution of the Late Mesozoic igneous rocks in the eastern Guangxi and western Guangdong Provinces, showing distribution of the Late Jurassic shoshonitic rocks. (b) Geological map of the Mashan Complex with locations of samples collected in this study (revised after Wang, 2013).

Fig. 3 Field geological characteristics and photomicrographs of the volcanic rocks from the Mashan Complex. Abbreviation: Pyr, pyroxene; Pl, plagioclase.

Fig. 4 Zircon CL images and U-Pb concordia diagrams for trachyandesite from the Mashan Complex.

Fig. 5 (a) Nb/Y vs. SiO_2 (Winchester and Floyd, 1977), (b) Co vs. Th (Hastie et al., 2007), (c) SiO_2 vs. K_2O (solid line is from Peccerillo and Taylor (1976)) and (d) K_2O vs. Na_2O for volcanic samples from the Mashan Complex. Data of volcanic rock (previous study) and intrusive rock are from Guo et al. (2001); Wu and Li (2011); Duan et al. (2013); Wang (2013) and Lao et al. (2015).

Fig. 6 SiO_2 vs. (a) CaO/Al_2O_3, (b) CaO, (c) MgO, (d) FeOt, (e) TiO_2 and (f) P_2O_5, and

MgO vs. (g) Cr and (h) Ni for volcanic samples from the Mashan Complex. The symbols and cited data of volcanic rocks are the same as in Fig. 5.

Fig. 7 Chondrite-normalized REE patterns (a) and primitive mantle-normalized spidergram (b) for volcanic samples from the Mashan Complex. Primitive mantle- and chondrite-normalized values, OIB and E-MORB are from Sun and McDonough (1989). Data of volcanic rock (previous study) and intrusive rock are from Guo et al. (2001); Wu and Li (2011); Duan et al. (2013); Wang (2013) and Lao et al. (2015), the Quannan and Tabei syenites from Li et al. (2003) and He et al. (2010), the Triassic shoshonitic rock from Wang et al. (2005a) and Mao et al. (2013).

Fig. 8 (a) $(^{87}Sr/^{86}Sr)_i$ vs. $\varepsilon Nd_{(t)}$ and (b) t(Ma) vs. $\varepsilon Nd_{(t)}$ for volcanic samples from the Mashan Complex. The carmine line in (a) notes the source contamination of lithospheric mantle with depleted mantle (DM)-derived metls, and the black line represents the assimilation of the DM-derived melts with the SCB crustal rocks. The number in (a) represents the percentage of the DM-derived melts. The lithospheric mantle is represented by Nd = 3.0 ppm, Sr = 48 ppm, $(^{87}Sr/^{86}Sr)_i$ =0.71220, $\varepsilon Nd_{(t)}$ = -9.9 (Tieshan-Yangfang syenite (Wang et al., 2005a)), the SCB crustal rocks by Nd = 26.3 ppm, Sr = 206 ppm, $(^{87}Sr/^{86}Sr)_i$ =0.7130, $\varepsilon Nd_{(t)}$ = -15. The DM is represented by Nd = 4.0 ppm, Sr = 60 ppm, $(^{87}Sr/^{86}Sr)_i$ = 0.703000 and $\varepsilon Nd_{(t)}$ = +8.0, and the DM-derived melts by Nd = 20 ppm, Sr = 400 ppm, $(^{87}Sr/^{86}Sr)_i$ = 0.70300, $\varepsilon Nd_{(t)}$ = +8.0. Data of the Early Paleozoic mafic rocks are from Yao et al. (2012), Wang et al.

(2013b) and Zhang et al. (2015a), Triassic shoshonitic and mafic rocks from Wang et al. (2005a), Mao et al. (2013) and Jiang et al. (2015), Jurassic mafic and shoshonitic rocks from Li et al. (1999, 2000, 2001, 2003, 2004), Wang et al. (2003, 2005b, 2008), Zhu et al. (2005, 2010), Zhou et al. (2006a), Jiang et al. (2009), He et al. (2010), Meng et al. (2012), Chen et al. (2013), Cen et al. (2016) and Gan et al. (2017a), Ningyuan and Antang basalts from Wang et al. (2008), Jiang et al. (2009) and Meng et al. (2012). The symbols and cited data of volcanic rocks are the same as in Fig. 5.

Fig. 9 (a) MgO vs. $\varepsilon Nd_{(t)}$, (b) MgO vs. Nb/La, (c) Nb/La vs. La/Sm and (d) Nb/U vs. Ce/Pb for volcanic samples from the Mashan Complex. Nb/U and Ce/Pb ratios of continent crust and OIB&MORB in (d) are from Rudnick and Gao (2003) and Hofmann et al. (1986), respectively. The field of the Antang basalt is after Meng et al. (2012). The symbols and cited data of volcanic rocks are the same as in Fig. 5.

Fig. 10 (a) Ba/Rb vs. Rb/Sr (Furman and Graham, 1999), (b) La/Yb vs. Dy/Yb (Xu et al., 2001b), (c) $(Tb/Yb)_P$ vs. $(Yb/Sm)_P$ and (d) Sm/Yb vs. Ce/Yb for volcanic samples from the Mashan Complex. The field of primitive mantle (PM) in (a) is from Sun and McDonough (1989). Melting model and partition coefficients in (b) are after Xu et al. (2001b) and references therein. In figure (c), the grid shows the range of model melt compositions by different proportions (1%, 5%, 10% and 15%) of partial melting of model source; the proportions of melt contribution from garnet-facies peridotite (Gar) are shown by the dashed gray lines, e.g., Gar 0 represents melt from spinel peridotite;

the bold lines indicate the constant melt fraction; and the details of model source and model curves are after Zhang et al. (2006) and references therein. The partial melting modeling in (d) was conducted according to Ellam (1992) and the field of Emeishan low Ti and high Ti basalts are from Xu et al. (2001a). The symbols and cited data of volcanic rocks are the same as in Fig. 5.

Fig. 11 Fe_2O_{3t} vs. TiO_2 for volcanic samples from the Mashan Complex. The field of peridotitic melts is after Falloon et al. (1988), and Triassic shoshonitic rock from Wang et al. (2005a) and Mao et al. (2013). The symbols and cited data of volcanic rocks are the same as in Fig. 5.

Fig. 12 Schematic cartoon of petrogenetic mechanism for Late Jurassic magmatic activities in southeastern SCB. See text in details.

Table captions

Table 1 LA-ICP-MS zircon U-Pb dating results for volcanic samples from the Mashan Complex

Table 2 Major oxides (wt.%) and trace elemental (ppm) compositions for volcanic samples from the Mashan Complex

Table 3 Sr-Nd isotopic compositions for volcanic samples from the Mashan Complex

Table 4 Synthesis of the formation age of the Mashan Complex