Multiple mantle metasomatism beneath the Leizhou Peninsula, South China: evidence from elemental and Sr-Nd-Pb-Hf isotope geochemistry of the late Cenozoic volcanic rocks

Pu Sun, Yaoling Niu, Pengyuan Guo, Shuo Chen, Meng Duan, Hongmei Gong, Xiaohong Wang and Yuanyuan Xiao

ABSTRACT
We analysed whole-rock major and trace elements and Sr-Nd-Pb-Hf isotopes of the late Cenozoic volcanic rocks in the Leizhou Peninsula, South China to investigate their mantle source characteristics. These volcanic rocks, collected from Jiujiang, Tianyang and Huoju areas of the Leizhou Peninsula, are characterized by incompatible element enrichment but variable isotopic depletion. The volcanic rocks from Jiujiang and Tianyang show prominent primitive-mantle-normalized positive Nb, Ta and Sr anomalies and depleted Sr-Nd-Pb-Hf isotope compositions, whereas those from Huoju show slight positive to negative Nb and Ta anomalies, a prominent positive Pb anomaly, and more enriched Sr-Nd-Pb-Hf isotope compositions. Two types of mantle metasomatism are required to explain the geochemical characteristics of these rocks. The Jiujiang and Tianyang samples were largely derived from a mantle source metasomatized recently by a low-F melt. Such low-F melt is generated within the asthenospheric mantle, which is enriched in volatiles and incompatible elements with positive Sr anomaly and depleted Sr-Nd-Pb-Hf isotope compositions. The Huoju samples were largely derived from a mantle source metasomatized by recycled upper continental crust material. These two types of mantle metasomatism beneath the Leizhou Peninsula are consistent with trace element characteristics of mantle mineralogy (e.g. clinopyroxene vs. amphibole), which reflects source evolution in space and time (e.g. tectonic setting change).

1. Introduction

Studies of oceanic basalts have revealed mantle chemical heterogeneity on all scales. Although the origin of mantle heterogeneity is controversial, seafloor subduction has long been inferred to be significant in causing the heterogeneity (e.g. Hofmann and White; Zindler and Hart; Hart; Farley; Stracke et al.; Willbold and Stracke). Seafloor subduction can carry terrigenous and pelagic sedimentary materials into the upper mantle, which has been inferred to be significant in forming geochemically enriched mantle sources (e.g. Weaver; Chauvel et al.; Farley; Jackson et al.). On the other hand, a low degree (low-F) melt derived within the seismic low velocity zone (LVZ) beneath oceanic lithosphere, which is highly enriched in volatiles, alkalis and incompatible elements, has been suggested to metasomatize the mantle source of intraplate volcanic rocks (Hanson; Wood; Halliday et al.; Niu et al., 1999, 2002, 2012; Niu and O’Hara; Niu et al., 2005, 2008, 2014; Pilet et al.). The presence of LVZ has also been observed beneath continental lithosphere of eastern Asia, eastern Australia and western America through seismic tomography (Ekström and Dziewonski), which has been thought to be significant in forming geochemically enriched continental intraplate basalts (e.g. Niu, 2005, 2014; Guo et al., 2016; Sun et al., 2017).

Late Cenozoic intraplate volcanic rocks are widespread in Southeast Asia (Figure 1(a)), including those in the South China Sea Basin (SCSB, Yan et al., 2006, 2015), in the Indochina Peninsula (Hoang and Flower), and in the Hainan Island and Leizhou Peninsula (Tu et al., 1991, 1992; Flower et al., 1992; Zhang et al., 1996; Ho et al., 2000; Xu et al., 2002; Zou and Fan, 2010; Pu Sun, Yaoling Niu, Pengyuan Guo, Shuo Chen, Meng Duan, Hongmei Gong, Xiaohong Wang and Yuanyuan Xiao

CONTACT Pu Sun, pu.sun@qdio.ac.cn; Yaoling Niu, yaoling.niu@durham.ac.uk

Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, China

Supplemental data for this article can be accessed here.

© 2018 Informa UK Limited, trading as Taylor & Francis Group
Wang et al. 2011, 2013; Liu et al. 2015). They are characterized by OIB (oceanic island basalts)-like incompatible element enrichment but varying extent of Sr-Nd isotope depletion with a Dupal-type Pb isotope signature (Tu et al. 1991, 1992; Flower et al. 1992; Hoang and Flower 1998; Chen et al. 2009; Zeng et al. 2013). Over the last decade, a mantle plume has been popularly invoked to explain the petrogenesis of these volcanic rocks, largely inferred from a mantle seismic tomography beneath the region (Lebedev and Nolet 2003; Zhao 2004; Yan and Shi 2007; Lei et al. 2009; Wang et al. 2011) although this interpretation remains debatable.

In this paper, we do not intend to discuss the plume debate, but focus on the mantle source heterogeneity of mantle metasomatic origin using bulk-rock major and trace elements and Sr-Nd-Pb-Hf isotopes of the late Cenozoic volcanic rocks from the Leizhou Peninsula. These rocks have been relatively poorly studied compared with other Cenozoic volcanic rocks in the Southeast Asia (Ho et al. 2000), which may provide new perspectives on the mantle source characteristics and mantle evolution histories beneath this area. We have identified two types of mantle metasomatism beneath this region: metasomatism genetically derived from melting of subducted terrigenous sediments (upper continental crust [UCC] material), and the metasomatism by an incompatible element enriched low-F melt derived from the asthenosphere.

2. Geological setting and samples

The Leizhou Peninsula is located at the geological transition between South China continental margin and the SCSB (Figure 1(a)). Southeast Asia is geologically considered as an assembly of exotic continental terranes fragmented from Gondwana with the amalgamation largely completed during the early Mesozoic (Lin et al. 1985; Metcalfe 1990; Tu et al. 1991; Chung et al. 1994; Zou et al. 2000). South China in the Mesozoic was characterized by having an active continental margin with extensive subduction-related granitoid magmatism (Jahn et al. 1990; Zhou and Li 2000; Li et al. 2012; Niu et al. 2015). The subduction was predicted to cease at ~100 Ma because of trench jam by an exotic micro-continent (Niu et al. 2015). The South China Sea is thought to open at ~32 Ma and spread until ~15.5 Ma (Taylor and Hayes 1983; Briais et al. 1993; Kido et al. 2001). The intraplate magmatism on the periphery of the SCSB contemporaneous with the SCSB spreading was limited, but extensively resumed after the cessation of the SCSB spreading (Yan et al. 2006; Huang et al. 2013).

The Ar-Ar and K-Ar dating gives erupting ages of 6.12 to 0.17 Ma for the volcanic rocks in the Leizhou Peninsula (Ho et al. 2000). Our samples were collected from Huoju, Jiujiang and Tianyang areas (Figure 1(b)). These volcanic lavas show layered structures (Figure 2(a)), caused by multiple episodes of eruptions (Ho et al. 2000). Porous and ropy structures can be observed at the surface of each lava layer (Figure 2(b)). These rocks show intergranular texture, with phenocrysts and microlites of olivine, clinopyroxene and magnetite aggregated between euhedral plagioclase laths (~0.5–1 mm; Figure 2(c,d)). Spinel peridotite mantle xenoliths and clinopyroxene megacrysts are present in volcanic rocks from Jiujiang and Tianyang (Yu et al. 2006; Huang et al. 2007).
3. Sample preparation and analytical procedures

We crushed fresh rocks to chips of ≤5 mm before repeatedly cleaned in Milli-Q water in an ultrasonic bath, dried and ground into ≥200 μm powders with an agate mill in a clean environment. Bulk-rock major elements were analysed at China University of Geosciences, Beijing (CUGB), using a Leeman Prodigy Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). Repeated analyses of USGS reference rock standards RCR-1, AGV-2 and national geological standard reference materials GSR-3 give analytical precision better than 1% for most elements except for TiO₂ (~1.5%) and P₂O₅ (~2.0%). The analytical details are given in Song et al. (2010). See Supplementary Table 1 for major element analytical results for USGS standard AGV-2.

Bulk-rock trace elements were analysed in the Institute of Oceanology, Chinese Academy of Sciences (IOCAS), using Agilent-7900 inductively coupled plasma mass spectrometer (ICP-MS). Fifty milligrams of each sample were dissolved with acid mix of distilled HCl + 3HNO₃ and HF in a high-pressure jacket equipped Teflon beaker at 190°C for 15 h, which was then dried and re-dissolved with 2 ml 3N HNO₃ for 2 h. The final sample solution was first loaded onto Sr-spec resin columns to separate Sr and Pb, with the eluted sample solution collected and then loaded onto AG 50W-X8 resin columns to separate REE. The eluted sample solution from AG 50W-X8 resin columns was collected and then loaded onto Ln-spec resin columns to collect Hf. The separated REE solution was dried and re-dissolved with 0.25 N HCl before being loaded onto Ln-spec resin columns to collect Nd. The above streamlined procedure was modified after Pin et al. (2014) and Yang et al. (2010). The measured ⁸⁷Sr/⁸⁶Sr, ¹⁴³Nd/¹⁴⁴Nd and ¹⁷⁶Hf/¹⁷⁷Hf isotope ratios were normalized for instrumental mass fraction using the exponential law to ⁸⁶Sr/⁸⁸Sr = 0.1194, ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219 and ¹⁷⁹Hf/¹⁷⁷Hf = 0.7325, respectively. International standards of NBS-987, JNd-1 and Alfa Hf were used as bracketing standards every five samples to monitor the instrument drift during the analysis of Sr,

Figure 2. (a) Layered structures of the volcanic lavas in the Leizhou Peninsula. (b) Porous and ropy structures at the surface of lava layers. (c, d) Photomicrographs showing intergranular textures, with phenocrysts and microlites of olivine, clinopyroxene and magnetite aggregated between euhedral plagioclase laths.
Nd and Hf isotopes, respectively. Repeated analysis for NBS-987 gives an average \(^{87}\text{Sr}/^{86}\text{Sr} = 0.710245 \pm 0.000012\) (n = 11, 20). Repeated analysis for JNdI-1 gives an average \(^{143}\text{Nd}/^{144}\text{Nd} = 0.512094 \pm 0.000008\) (n = 13, 20), and repeated analysis for Alfa Hf gives an average \(^{172}\text{Hf}/^{177}\text{Hf} = 0.282194 \pm 0.000007\) (n = 7, 20). Pb isotope ratios were normalized for instrumental mass fraction relative to NBS/SRM 997 \(^{203}\text{Ti}/^{205}\text{Ti} = 0.41891\). The international standard NBS-981 was used to monitor the instrument drift during the analysis of Pb isotopes. Repeated analysis of NBS-981 gives average \(^{206}\text{Pb}/^{204}\text{Pb} = 16.932 \pm 0.001\) (n = 10, 20), \(^{207}\text{Pb}/^{204}\text{Pb} = 15.489 \pm 0.003\) (n = 10, 20), and \(^{208}\text{Pb}/^{204}\text{Pb} = 36.684 \pm 0.013\) (n = 10, 20). See Supplementary Table 2 for the Sr-Nd-Pb-Hf isotopic results of USGS standards of BCR-2 and AGV-2.

4. Geochemistry

4.1 Major element compositions

The analytical data are given in Supplementary Table 1. For comparison, we also compiled major elements, trace elements and Sr-Nd-Pb isotope data of the Cenozoic basaltic rocks in the Hainan Island (Supplementary Table 3; Tu et al. 1991; Flower et al. 1992; Ho et al. 2000; Zou and Fan 2010; Wang et al. 2011). The volcanic rocks from the Leizhou Peninsula are mainly tholeiitic and show basaltic-andesitic SiO\(_2\) contents of 47.78–61.21 wt.% with Mg\(^\#\) of 53–65 (Figure 3(a)). The samples from Huoju have highly evolved SiO\(_2\) contents of 54.87–61.21 wt.% and 53–65 (Figure 3(a)). The samples from Huoju have highly evolved SiO\(_2\) contents of 54.87–61.21 wt.% and 53–65 (Figure 3(a)). The samples from Huoju have highly evolved SiO\(_2\) contents of 54.87–61.21 wt.% and 53–65 (Figure 3(a)).

4.2 Trace element compositions

Trace element data are given in Supplementary Table 1. These volcanic rocks show varying extents of light rare earth element (LREE) enrichment, with OIB-like [La/Yb]\(_{\text{N}}\) (chondrite normalized) of 6.0–12.9. They show REE abundances relatively less enriched than OIB, with slight positive Eu anomaly. One sample from Tianyang (ZC11-02) with negative Ce (Figure 4(a)), Zr and Hf anomalies (Figure 4(b)) and very high Ba/Zr (1.97) and Lu/Hf (0.11) ratios is best explained to reflect significant zircon crystallization because Ce\(^{4+}\) substitute Zr and Hf in zircon (Trail et al. 2012).

In the primitive-mantle-normalized multi-element spider diagram (Figure 4(b)), these volcanic rocks are enriched in incompatible elements, and tend to be more enriched in more incompatible elements, except for Nb, Ta, Pb and Sr, which are anomalous. The Huoju samples show varying Nb and Ta anomalies (from slight positive to negative), moderate positive Sr anomaly and prominent positive Pb anomaly. The samples from Jiujiang and Tianyang have positive Nb and Ta anomalies, weak to moderate positive Pb anomaly and significant positive Sr anomaly. The differences in Nb, Ta, Sr and Eu anomalies of these volcanic rocks are more apparent in Figure 5, with the ratios of [Nb/Th]\(_{\text{N}}\) and [Ta/U]\(_{\text{N}}\) falling between those of OIB and UCC, and Sr/ Sr* and Eu/Eu* higher than average OIB and most rocks from the Hainan Island. Furthermore, the samples from Huoju have lower [Nb/Th]\(_{\text{N}}\), [Ta/U]\(_{\text{N}}\), Sr/Sr* and Eu/Eu* compared with those from Jiujiang and Tianyang.

4.3. Sr-Nd-Pb-Hf isotopes

The Sr, Nd, Pb and Hf isotope data are given in Supplementary Table 2 and shown in Figure 6. In general, these rocks have more variable Sr-Nd-Pb isotopic compositions than rocks from the Hainan Island, and plot in the field of the Cenozoic basaltal s from SCSB (Figure 6(a,c,d)). They have generally depleted \(^{87}\text{Sr}/^{86}\text{Sr} (0.702955–0.704888), ^{143}\text{Nd}/^{144}\text{Nd} (0.512754–0.512998)\) and \(^{172}\text{Hf}/^{177}\text{Hf} (0.282939–0.283124)\), with \(\varepsilon_{\text{Nd}}\) of +2.3 to +7.0 and \(\varepsilon_{\text{Hf}}\) of +5.5 to +12.0, respectively. However, they have radiogenic \(^{207}\text{Pb}/^{204}\text{Pb} (15.530–15.666)\) and \(^{208}\text{Pb}/^{204}\text{Pb} (38.425–39.077)\) with intermediate \(^{206}\text{Pb}/^{204}\text{Pb} (18.454–18.727).

These rocks in Sr-Nd isotopic space define a negative trend (Figure 6(a)), which extends from the field of the depleted mid-ocean ridge basalts (MORB) to the most enriched OIB field. The positive Nd-Hf isotopic correlation is subparallel to the terrestrial array (Vervoort et al. 1999; Figure 6(b)). A high-angle trend away from the Northern Hemisphere Reference Line (NHRL; Hart 1984) in the \(^{207}\text{Pb}/^{204}\text{Pb} vs. ^{206}\text{Pb}/^{204}\text{Pb}\) diagram is significant (Figure 6(c)). In the \(^{208}\text{Pb}/^{204}\text{Pb} vs. ^{206}\text{Pb}/^{204}\text{Pb}\) diagram, they plot above and subparallel to the NHRL (Figure 6(d)), showing a Dupal signature (Hart 1984). Besides, there are a positive correlation between \(^{206}\text{Pb}/^{204}\text{Pb}\) and \(^{87}\text{Sr}/^{86}\text{Sr}\) and a negative correlation between \(^{206}\text{Pb}/^{204}\text{Pb}\) and \(^{143}\text{Nd}/^{144}\text{Nd}\) (Figure 6(e,f)).

The correlations of Sr-Nd-Pb-Hf isotope ratios of the volcanic rocks from the Leizhou Peninsula are to a first order consistent with two component-mixing in the mantle source region: an Indian-type depleted mantle component and an isotopically enriched component. Compared with samples from Jiujiang and Tianyang, the Huoju samples have higher \(^{87}\text{Sr}/^{86}\text{Sr}\) and \(^{206}\text{Pb}/^{204}\text{Pb}\) and lower \(^{143}\text{Nd}/^{144}\text{Nd}\) and \(^{176}\text{Hf}/^{177}\text{Hf}\) (Figure 6), indicating higher contribution of the isotopically enriched component in the mantle source region.
5. Discussion

5.1 Effect of fractional crystallization and crustal contamination on magma compositions

Compared with the samples from Jiujiang and Tianyang and the rocks from the Hainan Island, the samples from Huoju show relatively lower Mg#, CaO (Figure 3(e)), Ni (Figure 3(g)) and Cr (Figure 3(h)), reflecting their experiencing higher extent of fractional crystallization. The rocks from the Leizhou Peninsula show generally lower CaO/Al₂O₃ relative to the rocks from the Hainan Island, indicating their experiencing higher extent of crystallization of clinopyroxenes (Cpx; Figure 3(f)). According to the correlations of Mg# with Cr and Ni, these samples must have experienced olivine and Cpx-dominated fractional crystallization (Figure 3(g,h)).

Figure 3. TAS diagram (a) and selected Mg# variation diagrams (b–h). These volcanic rocks have experienced varying extent of fractional crystallization with the liquidus minerals dominated by olivine and clinopyroxene. The volcanic rocks from Huoju are more evolved with higher SiO₂ and lower Mg# than those from Jiujiang and Tianyang. For comparison, the compiled major element compositions and Cr and Ni contents of Cenozoic basaltic rocks from the Hainan Island are also plotted (Tu et al. 1991; Flower et al. 1992; Ho et al. 2000; Zou and Fan 2010; Wang et al. 2011).
Before using bulk-rock trace elements and Sr-Nd-Pb-Hf isotopes to infer source compositional characteristics, we need to evaluate the potential contribution of crustal contamination in the bulk-rock compositions of these volcanic rocks during their ascent to the surface. The continental crust materials are characterized by enriched SiO$_2$, radiogenic Sr isotopes and unradiogenic Nd isotopes. Therefore, involvement of the continental crust materials in the basaltic melt can increase both SiO$_2$ and $^{87}\text{Sr}/^{86}\text{Sr}$ values, while decrease $^{143}\text{Nd}/^{144}\text{Nd}$ values of the melt. Compared with the samples from Jiujiang and Tianyang, the samples from Huoju show generally higher SiO$_2$ (54.87–61.21 wt.%), and $^{87}\text{Sr}/^{86}\text{Sr}$ (0.703882–0.704888) (Figure 7). However, the higher SiO$_2$ and $^{87}\text{Sr}/^{86}\text{Sr}$ features of the Huoju samples should not be caused by crustal contamination, and their isotopic compositions were largely inherited from the source materials for the following reasons:

1. simple mixing calculation shows that to generate the Huoju samples with 54.87–61.21 wt.% SiO$_2$, as high as ~38–70% UCC materials are needed to assimilate with the assumed ‘primary’ basaltic melt. Even if such high extent of crustal assimilation was possible, it would generate melts with high $^{87}\text{Sr}/^{86}\text{Sr}$ values of

\[
\begin{align*}
&\text{UCC} \\
&\text{OIB} \\
&\text{Huoju} \\
&\text{Jiujiang & Tianyang}
\end{align*}
\]

Figure 4. (a) Chondrite-normalized REE patterns of the volcanic rocks from the Leizhou Peninsula. (b) Primitive mantle-normalized multiple incompatible element abundances of these rocks. For comparison, average compositions of present-day OIB (Sun and McDonough 1989) and upper continental crust (UCC) (Rudnick and Gao 2003) are plotted. The sample ZC11-02 with negative Ce anomaly also has negative Zr and Hf anomalies as the result of excess zircon crystallization.
Figure 5. Distinct [Nb/Th]N and [Ta/U]N (a) (primitive mantle normalized Nb/Th and Ta/U ratios to show the Nb and Ta anomalies) and Sr/ Sr* and Eu/Eu* (b) (Sr/Sr* = 2*SmPM/[PrPM + NdPM] and Eu/Eu* = 2*EuPM/[SmPM + GdPM] to show the Sr and Eu anomalies) between the samples from Huoju and Jiujiang and Tianyang. For comparison, the compositions of Cenozoic basalts from the Hainan Island (Tu et al. 1991; Flower et al. 1992; Ho et al. 2000; Zou and Fan 2010; Wang et al. 2011) and the average compositions of present-day OIB, both normal (N-type) and enriched (E-type) MORB (Sun and McDonough 1989) and UCC (Rudnick and Gao 2003) are also plotted.

~0.7071–0.7116 (Figure 7), much higher than the 87Sr/86Sr values (0.703882–0.704888) of the Huoju samples;

(2) there are no co-variations between SiO2 and 87Sr/86Sr values in the Huoju samples (Figure 7), indicating that the SiO2 and 87Sr/86Sr variations in the Huoju samples were controlled by different processes, rather than one common process of crustal contamination. The higher SiO2 contents were caused by high extent of fractional crystallization, while the higher 87Sr/86Sr values were likely inherited from the mantle source compositions;

(3) the Sr-Nd-Pb isotope compositions of the volcanic rocks in the Leizhou Peninsula plot in the field of Cenozoic basalts from the SCSB (Figure 6; Tu et al. 1992; Yan et al. 2008, Yan et al. 2015). These SCSB basalts were erupted through oceanic crust and experienced little continental crust contamination. Hence, the Sr-Nd-Pb isotope compositions of Cenozoic basalts from the SCSB and intraplate volcanic rocks in the periphery regions of the SCSB must reflect mantle signatures, which has been confirmed by studies of the Cenozoic volcanic rocks from Hainan Island (Tu et al. 1991), Vietnam (Hoang et al. 1996; Hoang and Flower 1998) and Southeast China (Sun et al. 2017, 2018).

5.2 Explanation of the positive Sr anomaly in the volcanic rocks from the Leizhou Peninsula

The volcanic rocks from the Leizhou Peninsula have a significant positive Sr anomaly (Figure 4(b)). Such positive Sr anomaly has also been observed in Cenozoic basalts from the Hainan Island (Figure 8), which was explained to result from the addition of recycled oceanic gabbro in the mantle source region (Wang et al. 2011), because plagioclase-rich oceanic gabbro has high Sr (Sobolev et al. 2000; Yaxley and Sobolev 2007; Stroncik and Devey 2011). Hence, the positive Sr anomaly in the Hainan basalts was suggested as evidence for the presence of recycled oceanic crust entrained by an upwelling mantle plume beneath this area (Wang et al. 2011). This explanation is possible and likely. However, this explanation is not suitable for the volcanic rocks in the Leizhou Peninsula, as reflected from the distinct correlation trends of Sr/Sr* with SiO2, [La/Sm]N, Nb/U and Zr/Hf between rocks from the Leizhou Peninsula and Hainan Island (Figure 8). This is because (1) partial melts from recycled gabbroic oceanic crust are characterized by both positive Sr anomaly and more silicic composition (Green and Ringwood 1968; Wyllie 1970; Yaxley and Sobolev 2007). However, the volcanic rocks from the Leizhou Peninsula show negative correlation between SiO2 and Sr/Sr* (Figure 8(a)); (2) recycled oceanic crust materials are depleted in incompatible elements with low [La/Sm]N (Niu et al. 2002, 2012; Niu and O’Hara 2003). However, the volcanic rocks from Jiujiang and Tianyang with higher Sr/Sr* have higher [La/Sm]N (primitive mantle normalized) of 2.5–3.3 than the average OIB (~2.4; Sun and McDonough 1989) (Figure 7(b)), reflecting an incompatible element enriched mantle source (Niu and Batiza 1997). Besides, these samples show Nb/U (38.2–61.3) similar to average OIB (47 ± 10; Hofmann et al. 1986) and super chondritic Zr/Hf ratios (38.3–43.3; Dupuy et al. 1992; Niu 2012) (Figure 8(c,d)). As the elements in each ratio
pair have similar incompatibility during mantle melting and magma evolution, these ratios thus largely reflect the source ratios (Hofmann et al. 1986; Niu and Batiza 1997). All the above characteristics suggest that the rocks from the Leizhou Peninsula with a significant positive Sr anomaly (especially those from Jiujiang and Tianyang) are derived from an incompatible element enriched mantle source.

The volcanic rocks from Jiujiang and Tianyang show generally depleted Sr-Nd-Pb-Hf isotope compositions (Figure 6), indicating their origin from an isotopically depleted asthenospheric mantle. As inferred from MORB, the asthenospheric mantle is incompatible element depleted, which is thought to result from continental crust extraction in the Earth’s early history (Gast 1968; O’Nions et al. 1979; Allègre et al. 1983). However, as inferred above, the mantle source of the Jiujiang and Tianyang samples is enriched, not depleted, in incompatible elements. Therefore, there must be a process that had re-enriched the incompatible elements in the asthenospheric mantle source of these volcanic rocks. Such process must also account for the significant positive Sr anomaly observed in these samples because of the positive correlations of Sr/Sr* with [La/Sm]N, Nb/U and Zr/Hf (Figure 8).

Figure 6. Sr-Nd-Pb-Hf isotope co-variations of the volcanic rocks from the Leizhou Peninsula. The terrestrial array in the Nd-Hf isotopic space is from Vervoort et al. (1999). Northern Hemisphere Reference Line (NHRL) is from Hart (1984). The Sr-Nd-Pb isotope compositions of Cenozoic basalts from the Hainan Island (Tu et al. 1991; Flower et al. 1992; Ho et al. 2000; Zou and Fan 2010; Wang et al. 2011) and the South China Sea Basin (SCSB; Tu et al. 1992; Yan et al. 2008, 2015), the Pb isotope compositions of the Central Indian Ridge (CIR) MORB (Mahoney et al. 1989) and average Java trench sediment that is largely mature continent derived (Plank and Langmuir 1998) are also plotted for comparison.
Figure 7. Modelling of crustal contamination in the SiO$_2$ vs. $^{87}$Sr/$^{86}$Sr diagram. The sample from Jiujiang with lowest SiO$_2$ (47.78 wt. %) was assumed as the basaltic melt unaffected by crustal contaminations. UCC material with 66.6 wt.% SiO$_2$, 327 ppm Sr (Rudnick and Gao 2003) and $^{87}$Sr/$^{86}$Sr value of 0.7173 (Plank and Langmuir 1998) is modelled to mix with the basaltic melt by variable extents. The modelling results show that the volcanic rocks in the Leizhou Peninsula are apparently off the mixing trend. To generate the Huoju samples with 54.87–61.21 wt.% SiO$_2$, as high as ~38–70% UCC materials are needed to assimilate with the basaltic melt, which would generate melts with high $^{87}$Sr/$^{86}$Sr values of ~0.7071–0.7116, much higher than the $^{87}$Sr/$^{86}$Sr values (0.703882–0.704888) of the Huoju samples.

Figure 8. In contrast with the positive correlation between Sr/Sr* and SiO$_2$ and negative correlations between Sr/Sr* and [La/Sm]$_N$, Nb/U and Zr/Hf in the Cenozoic volcanic rocks in the Hainan Island, the samples from the Leizhou Peninsula have negative correlation of Sr/Sr* with SiO$_2$, and positive correlations of Sr/Sr* with [La/Sm]$_N$, Nb/U and Zr/Hf. Hence, the positive Sr anomalies in the volcanic rocks from the Leizhou Peninsula cannot be explained by the involvement of the recycled oceanic crust materials in the mantle source region. The positive Sr anomalies (Sr/Sr* > 1) of the volcanic rocks from the Leizhou peninsula are consistent with the incompatible element enrichment in the mantle source (see text for details).
5.3 Low-F melt metasomatism in the mantle source region

Low-degree (low-F) melt metasomatism enriched in volatiles, alkalies and incompatible elements has long been considered significant in forming geochemically enriched mantle source (Halliday et al. 1995; Niu et al. 1996, 2002, 2012; Niu and O’Hara 2003; Workman et al. 2004; Niu 2005, 2008, 2014, Tang et al. 2006; Guo et al. 2016; Sun et al. 2017). Such low-F melt may develop within the LVZ and is inferred to be more enriched in the more incompatible elements (Niu et al. 1996, 2002, 2012; Niu and O’Hara 2003). Furthermore, during ascent through the lithosphere, the low-F melt can experience cooling-induced crystallization to form metasomatic amphibolite and/or pyroxenite veinlets (Hanson 1977; Wood 1979; Zanetti et al. 1996; Niu 2008; Pilet et al. 2008). Indeed, the presence of amphiboles, which occurs as interstitial grains in the mantle xenoliths entrained in these volcanic rocks indicates the existence of a modal mantle metasomatism (Yu et al. 2006). Furthermore, these mantle amphiboles are characterized by enriched incompatible elements and prominent positive Sr anomaly (Figure 9; Sr/Sr*= 1.71–3.96) (Yu et al. 2006). Although the partition coefficients of Sr/Sr* (D_{Sr/Sr*} = 2 \times D_Sr/[D_Pb + D_Nd]) between amphibole and basaltic melt are experimentally determined to be >1 (D_{Sr/Sr*} = 1.42, LaTourrette et al. 1995; also see the compilations in Dalpé and Baker (2000)), crystallization of the low-F melt with Sr/Sr* = 1 is still inadequate to form amphiboles with Sr/Sr* of 1.71–3.96. Therefore, it requires the metasomatic low-F melt having Sr/Sr* > 1 to crystallize the mantle amphiboles with prominent positive Sr anomalies. The volcanic rocks from Jiujiang and Tianyang derived from such low-F melt metasomatized mantle source thus show characteristics of enriched incompatible elements and positive Sr anomalies (Figure 9).

Because such low-F melt should have high Nd/Sm, U/Pb, Hf/Lu (the element on the numerator is more incompatible than that on the denominator in each ratio pair), it will develop long-time integrated Pb isotopes and unradiogenic Nd and Hf isotopes. However, the samples from Jiujiang and Tianyang with low ^{147}Sm/^{144}Nd and ^{176}Lu/^{177}Hf and high ^{238}U/^{206}Pb have high ^{143}Nd/^{144}Nd and ^{176}Hf/^{177}Hf and low ^{206}Pb/^{204}Pb (Figure 10(b–d)), which is inconsistent with the characteristics of the low-F melt after long-time decay. Therefore, we support a recent (or ‘current’) low-F melt metasomatism without enough time for isotope intergrowth, which is consistent with the understanding of the mantle metasomatism beneath eastern China (Niu et al. 2005, 2014; Guo et al. 2016; Sun et al. 2017, 2018). The positive correlation between ^{87}Rb/^{86}Sr and ^{87}Sr/^{86}Sr (Figure 10(a)) gives a pseudochron age of 1298 Ma. As the low-F melt metasomatism has been identified to be recent, this age has no geological significance, but is best explained by melting-induced mixing with the pseudochron slope controlled by the compositions of the two endmembers, i.e. a metasomatic low-F melt with relatively low Rb/Sr and depleted Sr isotope.

\[ \text{Figure 9. Distinct Pb/Ce and Sr/Sr* trends between Jiujiang/Tianyang and Huoju rock suites. For comparison, the compositions of Cenozoic basalts from the Hainan Island are also plotted (Tu et al. 1991; Flower et al. 1992; Ho et al. 2000; Zou and Fan 2010; Wang et al. 2011). The Jiujiang and Tianyang samples show low Pb/Ce but high Sr/Sr*, which is similar to the amphiboles in the mantle xenoliths (Yu et al. 2006) and is consistent with a low-F melt mantle metasomatism. The Huoju samples and rocks from the Hainan Island show high Pb/Ce and relative low Sr/Sr*, which is similar to the clinopyroxenes in the mantle xenoliths (Yu et al. 2006) and indicates a mantle metasomatism by recycled UCC materials.} \]
5.4 Recycled UCC material metasomatism in the mantle source region

The UCC material is characterized by enrichment in LILEs (large ion lithophile elements) and depletion in HFSEs (high field strength elements; e.g. Nb and Ta) with negative Sr and Eu anomalies, higher Pb/Ce than MORB and OIB and enriched Sr-Pb-Nd-Hf isotopes (Hofmann et al. 1986; Rudnick and Gao 2003; Jackson et al. 2007; Niu and O’Hara 2009). Therefore, contribution of the UCC material to the asthenospheric mantle or the mantle-derived melt will decrease the HFSE/LILE ratios (e.g. \([\text{Nb/Th}]_N\) and \([\text{Ta/U}]_N\), \(\text{Sr/Sr}^*\), \(\text{Eu/Eu}^*\), \(143\text{-Nd}/144\text{-Nd}\) and \(176\text{-Hf}/177\text{-Hf}\), but increase \(\text{Pb/Ce, } 87\text{Sr}/86\text{Sr}^*\) and \(206\text{Pb}/204\text{Pb}\) in the melt. The Huoju samples have low \([\text{Nb/Th}]_N\), \([\text{Ta/U}]_N\), \(\text{Sr/Sr}^*\) and \(\text{Eu/Eu}^*\) (Figure 5) and positive Pb anomaly (Figure 4) with more enriched Sr-Nd-Pb-Hf isotopes (Figure 6), which shows apparent crustal signatures. Furthermore, Sr-Pb-Nd-Hf isotope ratios show scattered yet significant correlations with [Nb/Th]_N, [Ta/U]_N, Sr/Sr* and Pb/Ce (see Supplementary Figure 1). With Sr-Pb-Nd-Hf isotopes being more enriched, [Nb/Th]_N, [Ta/U]_N and Sr/Sr* decrease while Pb/Ce increasing, which is most consistent with variable extent of incorporation of UCC material in the volcanic rocks in the Leizhou Peninsula.

As we have discussed above, such crustal signatures in these rocks cannot be attributed to the crustal contamination during melt ascent, and thus they must be inherited from the recycled UCC materials in the mantle source region. The UCC material present in the mantle source region was most likely originated from subducted terrigenous sediments. In Figure 6(c,d), the Pb isotope systematics indeed show trends from a CIR (Central Indian Ridge; Mahoney et al. 1989) MORB mantle component to a Java terrigenous sediment component (Plank and Langmuir 1998). The above inference confirms our previous interpretations that recycled UCC material must have added to the mantle source region of the Cenozoic basalts in Southeast China (Sun et al. 2017). The Huoju samples with more enriched Sr-Nd-Pb
10% recycled UCC materials were mixed in the mantle source region. Because clinopyroxene is an important host for incompatible elements in mantle minerals, its elemental and isotopic characteristics have been widely used to study the nature and intensity of the metasomatic event (e.g., Norman 1998; Xu et al. 2003; Niu 2004; Zheng et al. 2006; Tang et al. 2008; Wittig et al. 2009, 2010). Studies on the clinopyroxenes in the mantle xenoliths entrained in the Cenozoic volcanic rocks from the Leizhou peninsula show that some clinopyroxenes have high Pb/Ce with relatively low Sr/Sr* (Figure 9; Yu et al. 2006), which is consistent with trace element characteristics of the volcanic rocks from Huoju region and Hainan Island and UCC materials. This further substantiates the existence of recycled UCC material in the mantle source region beneath the Leizhou Peninsula and Hainan Island (Tu et al. 1991).

The recycling of UCC material into the asthenospheric mantle must be recent, because (1) ancient (e.g. >1Ga) recycled UCC materials with low U/Pb and Th/Pb ratios should have unradiogenic Pb isotope ratios (Stracke et al. 2003), which is in contrast with the radiogenic Pb isotopes of the Huoju samples; (2) the high angle Pb isotope trend away from the NHRL (Figure 6(c)) that is often observed in volcanic arc magmas (e.g. Cohen and O’Nions 1982; Woodhead and Fraser 1985; Vroon et al. 1993) is more consistent with a recent recycling of UCC material (Hart 1984; Tu et al. 1991). Trace element modelling shows that ~6–10% UCC materials were mixed in the first place with the depleted MORB mantle (DMM) materials. Such UCC material modified mantle source was then mixed by variable extents with the metasomatic low-F melt to form the ultimate mantle source of the volcanic rocks in the Leizhou Peninsula (Figure 11). Subduction of the Pacific plate in the Mesozoic along the present SE China coastline prior to opening of the South China Sea may have contributed this recycled UCC material as terrigenous sediment into the asthenospheric mantle beneath the Leizhou Peninsula (Figure 12(a); Tu et al. 1991). After the opening of the South China Sea, the tectonic setting of the Leizhou Peninsula changed from a subduction zone environment to an intraplate environment. The metasomatic agent in the asthenospheric mantle beneath the Leizhou Peninsula changed from recycled UCC material to a low-F melt derived within the asthenospheric mantle. Such low-F melt is enriched in incompatible elements and volatiles, which is buoyant and tends to ascend to metasomatize the overlying asthenospheric mantle and the base of the lithosphere (Figure 12(b)). The above inference may not be exact, but effectively captures the mantle evolution beneath the Leizhou Peninsula in space and time.

6. Conclusion

(1) The volcanic rocks in the Leizhou Peninsula show varying elemental and isotopic characteristics. The samples from Jiujiang and Tianyang show significant primitive-mantle-normalized positive Nb, Ta and Sr anomalies with depleted Sr-Nd-Pb-Hf isotope compositions, while some samples from Huoju show significant negative Nb and Ta anomalies, positive Pb anomaly and more enriched Sr-Nd-Pb-Hf isotope compositions.
(2) The positive Sr anomaly in the samples from Jiujiang and Tianyang is not evidence for the presence of recycled oceanic gabbro in the mantle source, but is consistent with the incompatible element enrichment of the mantle source materials.

(3) A low-F melt mantle metasomatism which is enriched in volatiles and incompatible elements is required to explain the incompatible element enrichment and positive Sr anomaly in these volcanic rocks. Such mantle metasomatism must take place recently to account for lacking isotope ingrowth in the mantle source regions.

(4) Presence of recycled UCC material in the mantle source region is also required to explain the trace element and isotope characteristics of the volcanic rocks from Huoju. These UCC

---

**Figure 12.** (a) The paleo-Pacific plate subducted along the present Southeast China coastline in the Mesozoic until exotic terranes (represented by the basement of continental shelf of East and South China Seas) jammed the trench and ceased the subduction activity at ~100 Ma (Niu et al. 2015). UCC material subducted as terrestrial sediment can melt and metasomatize the overlying asthenosphere in the mantle wedge (Johnson and Plank 2000). (b) After subduction cessation, the Leizhou Peninsula was in an intraplate environment. The asthenospheric mantle beneath Leizhou Peninsula experienced a low-F melt metasomatism. Such low-F melt enriched in incompatible elements and volatiles tended to rise (green arrows) due to buoyancy to metasomatize the overlying asthenospheric mantle that had been pre-modified by a recycling UCC material. The low-F melt can also metasomatize the overlying lithospheric mantle by crystallizing hydrous minerals (e.g. amphibole) and forming garnet pyroxenite, homblende-pyroxenite and hornblendite veins in the lithospheric mantle (Niu et al. 2002, 2012; Niu and O’Hara 2003; Niu 2005). Decompressional melting (red arrows) of such a multiply metasomatized asthenospherlic mantle formed the late Cenozoic volcanisms we studied.
materials, in the form of terrigenous sediments, may be subducted recently into the upper mantle.

**Article Highlight**

1. These rocks show incompatible element enrichment but variable isotopic depletion.
2. High bulk-rock Sr does not indicate recycled oceanic gabbro in the mantle source.
3. A low-F melt with high Sr enriched the incompatible elements of the mantle source.
4. A recently recycled UCC material is present in the mantle source region.

**Acknowledgments**

We are grateful to the constructive comments of two anonymous reviewers. This work was supported by the NSFC-Shandong Joint Fund for Marine Science Research Centers (U1606401), the National Natural Science Foundation of China (NSFC Grants 41776067, 41630968, 41130314, 91014003), Chinese Academy of Sciences (Innovation Grant Y42217101L), and grants from Qingdao National Laboratory for Marine Science and Technology (2015ASKJ03) and 111 Project (B18048).

**Disclosure statement**

No potential conflict of interest was reported by the authors.

**Funding**

This work was supported by the Chinese Academy of Sciences Innovation grant [Y42217101L]; National Natural Science Foundation of China [41130314, 41630968, 41776067, 91014003]; NSFC-Shandong Joint Fund for Marine Science Research Centers [U1606401]; 111 Project [B18048]; grants from Qingdao National Laboratory for Marine Science and Technology [2015ASKJ03].

**References**


