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Key Points:
• This is the first geochemical evidence observed in intraplate basalts to support the magma-magma interaction in the mantle
• The magma-magma interaction can trigger the fractionation of garnet and clinopyroxene in the mantle
• The magma-magma interaction in the mantle is inferred to be a common petrogenetic model for Cenozoic basalts in eastern China

Supporting Information:
• Supporting Information S1

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Magma-magma interaction in the mantle beneath eastern China
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Abstract In addition to magma-rock and rock-rock reaction, magma-magma interaction at mantle depth has recently been proposed as an alternative mechanism to produce the compositional diversity of intraplate basalts. However, up to now no compelling geochemical evidence supports this novel hypothesis. Here we present geochemistry for the Longhai basalts from Fujian Province, southeastern China, which demonstrates the interaction between two types of magma at mantle depth. At Longhai, the basalts form two groups, low-Ti basalts (TiO2/MgO < 0.25) and high-Ti basalts (TiO2/MgO > 0.25). Calculated primary compositions of the low-Ti basalts have compositions close to L + Opx + Cpx + Grt cotectic, and they also have low CaO contents (7.1–8.1 wt %), suggesting a mainly pyroxenite source. Correlations of Ti/Gd and Zr/Hf with the Sm/Yb ratios, however, record binary mixing between the pyroxenite-derived melt and a second, subordinate source-derived melt. Melts from this secondary source component have low Ti/Gd and high Zr/Hf and Ca/Al ratios, thus likely representing a carbonated component. The Sr, Nd, Hf, and Pb isotopic compositions of the high-Ti basalts are close to the low-Ti basalts. The Sm/Yb ratio of the high-Ti basalts, however, is markedly elevated and characterized by crossing rare earth element patterns at Ho, suggesting that they have source components comparable to the low-Ti basalts, but that they have experienced garnet and clinopyroxene fractionation. We posit that mingling of SiO2-saturated tholeiitic magma with SiO2-undersaturated alkaline magma might trigger such fractionation. Therefore, the model of magma-magma interaction and associated deep evolution of magma in the mantle is proposed to explain the formation of Longhai basalts. It may, moreover, serve as a conceptual model for the formation of tholeiitic to alkaline intraplate basalts worldwide.

1. Introduction

Compositional variation of intraplate oceanic basalts is inferred to largely reflect chemical heterogeneity in the mantle, and this heterogeneous mantle composition is invoked to reflect variable contributions (components and amounts) of recycled oceanic crust [Armstrong and Harmon, 1981; Hofmann and White, 1982; Hofmann, 1997]. In addition to peridotite, crustal-derived components, i.e., eclogite and pyroxenite source rocks, are therefore considered to play important roles in the generation of intraplate oceanic basalts [Schulze, 1989; Yaxley and Green, 1998; Kogiso et al., 2003; Pertermann and Hirschmann, 2003; Keshav et al., 2004; Kogiso and Hirschmann, 2004; Pertermann et al., 2004; Mallik and Dasgupta, 2012, 2013]. An olivine-free, secondary pyroxenite, formed by the reaction between partial melts derived from recycled oceanic crust and mantle peridotite, has been proposed to be the source of SiO2-saturated basalts [Sobolev et al., 2005; Sobolev et al., 2007] as the melting of recycled crust is assumed to be prior to peridotite [e.g., Yasuda et al., 1994]. In addition to such melt-rock reaction, secondary pyroxenite may also form by rock-rock reaction at high-temperature and lower mantle conditions [Herzberg, 2011]. Subduction also transports carbonate components into the mantle [Yaxley and Green, 1994; Molina and Poli, 2000; Hammouda, 2003; Dasgupta et al., 2004]. CO2 released from these carbonates can induce peridotite or pyroxenite partial melting deep in the mantle, which generates SiO2-undersaturated, alkaline basaltic melts [Dasgupta and Hirschmann, 2006; Dasgupta et al., 2007; Gerbode and Dasgupta, 2010]. Interaction of such SiO2-undersaturated, alkaline basaltic melts and “common,” relatively SiO2-rich melts in the mantle has recently been proposed as a potential mechanism to explain compositional variation of intraplate basalts [Herzberg, 2011]. Here the chemical compositions of Cenozoic basalts from eastern China are used to test whether this mechanism has played a role in their evolution at mantle depth, and which geochemical signatures may be powerful tools for tracking interaction between magmas derived from common and carbonated mantle sources.

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Cenozoic basalts of eastern China are typical of intraplate basalts generated in an extensional continental setting [Zhou and Armstrong, 1982; Peng et al., 1986; Song et al., 1990; Zhi et al., 1990; Basu et al., 1991; Liu et al., 1994; Zou et al., 2000; Xu et al., 2005; Tang et al., 2006; Chen et al., 2009]. Eclogite and pyroxenite source components have been proposed to play an important role in the formation of these basalts, owing to their low CaO contents [Zeng et al., 2011], high Fe/Mn ratios [Liu et al., 2008], low H₂O contents [Chen et al., 2015; Liu et al., 2015b], high Eu/Eu* [Xu et al., 2012a], and low δ¹⁸O of their phenocryst [Zhang et al., 2009; Wang et al., 2011; Xu et al., 2012b; Liu et al., 2015b]. Such mafic components largely represent recycled oceanic crust or recycled continental crust, though it remains controversial. In addition to these crust-derived silicate components, carbonated components have also been suggested to be present in the mantle source of the intraplate basalts, based on their trace element [Zeng et al., 2010] and Mg, Zn isotope compositions [Huang et al., 2015; Liu et al., 2016; Tian et al., 2016; Yang et al., 2012]. The Cenozoic intraplate basalts of eastern China are therefore ideal targets for unravelling potential interaction process between different mantle melts and their compositional fingerprints. Here we focus on two series of flood basalt samples, high-Ti basalts and low-Ti basalts, from Fujian Province, southeastern China, and examine how they have evolved at mantle depth.

2. Geological Setting and Sample Description

Late Cenozoic basalts, which comprise dozens of small-scale flood basaltic fields [Yu et al., 2015a, 2015b] and a few monogenic basaltic fields, are common in Eastern China (inset in Figure 1a). They have oceanic island basalt (OIB)-like trace element signatures and are classified as typical intraplate, asthenosphere-derived basalts in a continental setting [e.g., Zou et al., 2000]. In southeastern China, Cenozoic basalts mainly occur along major trans-lithospheric faults in the Precambrian Cathaysia Block [Ho

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**Figure 1.** (a) Distribution of Cenozoic basalts in southeastern China [modified after Zeng et al., 2010] and in eastern China (embedded small map). (b) Distribution of Cenozoic basalts in Longhai county, Fujian province. Niutoushan is the only volcano in the Longhai basaltic field that contains abundant mantle xenoliths.
et al., 2003] (Figure 1a). The basalts studied here are from Longhai County in the Fujian Province (Figure 1b). Cenozoic basaltic magmatism in the Fujian Province took place at 17.1–14.8 Ma, ~11.9 Ma, and 2.2–0.9 Ma [Ho et al., 2003]. The Longhai basalts were predominantly emplaced during the earliest stage (at 17.1–14.8 Ma), composing a ~400 km² flood basalt field that is exposed east of the Changle-Nan’ao fault (Figure 1b). The Longhai basalts are mainly tholeiites with minor alkaline basalts. In addition, Niutoushan, a volcano of the Longhai flood basalt field, is composed of tholeiites and alkaline basalts. Most of its alkaline basalts contain abundant mantle xenoliths. Basalts from Niutoushan have been recently studied by Zou et al. (2000, 2004).

We have selected 13 Longhai basalts samples to measure their whole-rock geochemical composition. All samples are dark gray to rusty in color, showing a massive to vesicular structure. Most samples are fresh, but a few samples are slightly altered, in which olivine is partially to completely decomposed to iddingsite (Figure S1 in the supporting information). Based on the grain size of their mineral constituents, the Longhai basalts can be divided into two types: cryptocrystalline (Figure S1a) and phanerocrystalline (Figure S1c). Some of cryptocrystalline basalts are slightly porphyritic (Figure S1b). These basalts contain minor olivine phenocrysts (<5% modal abundance) set in a groundmass of olivine, clinopyroxene, plagioclase, Fe-Ti oxide, and glass. Pyroxene or plagioclase phenocrysts have not been observed (Figure S1b). The phanerocrystalline basalts mostly show equigranular texture, and they dominantly contain clinopyroxene and plagioclase. Pyroxene and plagioclase phenocrysts have not been observed in this sample (Figure S1d). All cryptocrystalline basalts belong to high-Ti basalts, while all phanerocrystalline basalts belong to the low-Ti basalts (details on the classification are provided in section 4.1 below). Mantle and crustal xenoliths are absent from the studied Longhai basalts except those from the Niutoushan volcano (samples 11FJ06 and 11FJ07).

Published data on Longhai basalts from the Niutoushan volcano [Zou et al., 2000, 2004] and Jieyang alkaline basalts from Guangdong province [Huang et al., 2013] were compiled for comparison.

### 3. Analytical Methods

Measurements of whole-rock major elements were performed at the State Key Laboratory for Mineral Deposits Research, Nanjing University, China, by using a Thermo Scientific ARL 9900 X-ray fluorescence spectrometer. Comparing the measured values of rock reference material GSR-3 to its preferred values [Xie et al., 1989], the uncertainties are less than 3% for Si, Ti, Al, Fe, Mn, Mg, Ca, and K and less than 6% for Na and P (Table S1 in the supporting information).

Measurements of whole-rock trace elements were made at the Department of Geology, Northwest University, China. Trace elements, including rare earth elements (REEs), were determined by using an ELAN 6100DRC inductively coupled plasma–mass spectrometer (ICP-MS) after acid digestion (HF + HNO₃) of samples in Teflon beakers. Analyses of U.S. Geological Survey rock reference materials (BHVO-2 and BCR-2) indicate precision and accuracy better than 6% for Ni, Pb, U, and Th and 3% for Sc, V, Cr, Co, Ni, Rb, Sr, Y, Zr, Nb, Ta, Cs, Ba, Pb, and most of REEs. The results of the analyses of these reference materials and blanks are summarized in Table S1.

Sr-Nd-Hf-Pb isotopes were analyzed at the State Key Laboratory for Mineral Deposits Research, Nanjing University. Sr-Nd isotopic analyses were performed by using a Finnigan Triton TI thermal ionization mass spectrometer, while Hf-Pb isotopic compositions were obtained by using a Neptune plus (Thermo Fisher Scientific) multicollector inductively coupled plasma-mass spectrometer (ICP-MS). Sample powders (~100 mg) were first dissolved in distilled HF–HNO₃–HClO₄ in Teflon capsules at 130°C. Separation of Sr and Nd was carried out on cation exchange resins (Bio-Rad 50WX8) following the analytical procedures given by Pu et al. [2005]. Four milliliters of 6 mol/L HCl was added to the column as a Sr elution, and 4.5 mL of 0.2 mol/L α-hydroxyisobutyric acid was added to the column as a Nd elution. Separation of Hf was carried out on Eichrom Ln Spec resins following the analytical procedures given by Yang et al. [2010], and 5 mL of 2 mol/L HF was added to the column as an Hf elution. Separation of Pb was carried out on anion exchange resins (Bio-Rad AG-1X8) following the analytical procedures given by Kuritani and Nakamura [2002], and 0.2 mL of water was added to the column as a Pb elution. Sr, Nd, and Hf isotopic compositions were normalized to ⁸⁶Sr/⁸⁶Sr = 0.1194, ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219, and ¹⁷⁹Hf/¹⁷⁷Hf = 0.7325, respectively. Measured Pb isotopic ratios were corrected for instrumental mass fractionation by reference to replicate analyses of the standard
the high-Ti basalts, the low-Ti basalts show weak positive Eu anomalies (Eu/Eu* = 1.03). LREE content decreases with increasing HREE content, showing a crossing REE pattern at Ho. Compared to high-Ti basalts are characterized by light REE (LREE) enrichment (La/Yb = 13.8), MgO (4.1–7.8 wt %) and TiO2 (1.3–2.6 wt %) contents. According to the nomenclature of Le Bas et al. [1986], they classify as basalts (tholeiitic) to trachybasalts (alkaline) (Figure 2a). We distinguish two groups, high-Ti (TiO2/MgO > 0.25) and low-Ti basalts (TiO2/MgO < 0.25) according to their TiO2/MgO ratios (Figure 2b).

The high-Ti basalts show lower MgO (4.1–6.3 wt %), CaO (6.5–8.3 wt %), and Ca/Al ratios (0.74–0.84) than the low-Ti basalts (MgO = 6.3–7.8 wt %, CaO = 8.5–9.5 wt %, and Ca/Al = 0.55–0.62) (Figure 2). According to this classification, the alkaline basalts from the Niutoushan volcano and the Jieyang alkaline basalts both belong to the high-Ti basalts group, while the tholeiites from the Niutoushan volcano belong to the low-Ti basalt group (Figure 2b).

The Ni contents of the two groups of basalts are similar to one another (not shown), but the high-Ti basalts show relatively lower concentrations of Cr and Sc (Figure 2d; Cr not shown) and higher concentrations of incompatible elements (Figure S2) than the low-Ti basalts. In general, the abundances of La, Nd, Sr, Pb, Th, and U are well correlated with Nb in both groups (Figure S2). The chondrite-normalized REE patterns of the high-Ti basalts are characterized by light REE (LREE) enrichment (La/Yb = 13.8–59.5), the lack of Eu anomalies, and pronounced medium REE/heavy REE (MREE/HREE) fractionation (Sm/Yb = 4.06–9.47) (Figure 3a). Their LREE content decreases with increasing HREE content, showing a crossing REE pattern at Ho. Compared to the high-Ti basalts, the low-Ti basalts show weak positive Eu anomalies (Eu/Eu* = 1.03–1.12; Eu/Eu* = EuN/(SmN × GdN)0.5), less enriched LREEs (La/Yb = 8.7–14.8), and less pronounced MREE/HREE fractionation (Sm/Yb = 2.63–3.42) (Figure 3a). On a primitive-mantle-normalized incompatible element diagram (Figure 3b), both groups resemble OIBs in terms of their enrichment in Nb and Ta and their depletion in Pb relative to the LREEs. The high-Ti basalts, however, show more pronounced negative Pb and Ti anomalies (Ce/Pb = 30.8–37.8, Ti/Gd = 1699–2182, Rb/Ba = 0.09–0.11, K/La = 360–426, Sr/Sr* = 0.91–0.98), while the low-Ti basalts have more pronounced depletion in Pb, K, and positive Sr anomalies (Sr/Sr* = 2 × SrN/(PrN + NdN)) (Ce/Pb = 21.3–26.3, Ti/Gd = 2220–2452, Rb/Ba = 0.01–0.08, K/La = 134–421, and Sr/Sr* = 1.11–1.46).

The variation in the Sr, Nd, Pb, and Hf isotopic compositions of both basalts groups is limited (87Sr/86Sr = 0.70356–0.70422, εNd = 4.0–7.5, and 206Pb/204Pb = 18.728–19.044) and less depleted than the composition of depleted mid-ocean ridge basalt (MORB) mantle (DMM) (87Sr/86Sr = 0.70263, εNd = 9.5, 206Pb/204Pb = 18.275) [Workman and Hart, 2005]. No obvious difference is observed in the Sr and Nd isotopic compositions of the two groups (Figure 4a), but the high-Ti basalts show slightly lower εNd values and higher 206Pb/204Pb and 208Pb/204Pb ratios than the low-Ti basalts (Figures 4b and 4c).
4.2. Mineral Composition

The composition of olivine phenocrysts and matrix crystals are shown in Table S3. The olivine crystals have a wide range of Fo value, varying from 83 to 52. All crystals have high CaO (0.12–0.34 wt %) and MnO (0.20–0.56 wt %) contents, which are negatively correlated with the Fo value (Figures S3a and S3b). The NiO content and Fo value of olivines, in contrast, show a positive correlation (Figure S3c). Most of the olivine phenocrysts plot within, or near, the olivine-melt equilibrium field (Figure S4a), which is constrained by the Fe-Mg exchange partition coefficient ($K_{D} = 0.30–0.34$) between olivine and basaltic liquid [Roeder and Emslie, 1970; Ulmer, 1989; Matzen et al., 2011]. Few olivine phenocrysts plot significantly below the equilibrium field, but they still show higher Fo values than the olivine matrix crystals (Figure S4a).

![Figure 2](image)

**Figure 2.** Variation in (a) Na$_2$O + K$_2$O versus SiO$_2$, (b) TiO$_2$ versus MgO, (c) Ca/Al versus MgO, and (d) Sc versus MgO for the Longhai basalts. The red circles and purple squares represent the high-Ti basalts and the low-Ti basalts of the Longhai basaltic field, which have been analyzed in this study. Published data for Niutoushan, the mantle xenolith-enriched basaltic rocks, are shown for comparison, including xenolith-rich, high-Ti basalts (red open triangles), and xenolith-free, low-Ti basalts (purple open triangles) [Zou et al., 2000, 2004]. The fractionation of olivine and clinopyroxene (green lines) was calculated by using the "Petrolog 3" software [Danyushevsky and Pyle, 2011] with a low-Ti basalt bulk-rock composition (11FJ01) as the liquid starting composition. Data for the Cenozoic alkaline basalts from Jieyang, Guangdong province (gray squares), are from Huang et al. [2013].

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![Figure 3](image)

**Figure 3.** (a) Chondrite-normalized REE patterns and (b) primitive-mantle-normalized incompatible element patterns for the Longhai basalts. The chondrite values and the primitive mantle values are from Anders and Grevesse [1989] and McDonough and Sun [1995], respectively. Data for the Cenozoic alkaline basalts of Jieyang, Guangdong province, are from Huang et al. [2013].
Clinopyroxenes form matrix crystals, while phenocrysts are absent. Their compositions are listed in Table S4. The crystals show low Mg# values (64.5–75.9), Al₂O₃ contents (1.3–3.4 wt %), and moderate to high MnO contents (0.13–0.30 wt %). Their Cr₂O₃ content positively correlates with their Mg# value (not shown). All clinopyroxene compositions plot below the clinopyroxene-melt equilibrium field (Figure S4b), which is constrained by the Fe-Mg exchange partition coefficient (K_D) between clinopyroxene and basaltic liquid, varying between 0.23 [Toplis and Carroll, 1995] and 0.27 [Putirka, 1999].

5. Discussion

As noted above, the basalts from Longhai can be divided into the low-Ti and high-Ti basalts, and they show obvious geochemical diversity (Figures 2 and 3), though their isotopic compositions are similar (Figure 4). In the elemental ratio plots (Figure 5), two arrays are composed of the low-Ti and high-Ti basalts, respectively. In the following sections, we shall discuss the cause of forming the arrays, which provide important clues for the genesis of Longhai basalts.

5.1. Postmagmatic Alteration, Crustal Contamination, and Low-Pressure Fractional Crystallization

The Longhai basalts show good correlations in the abundance of Nb and La, Nd, Sr, Pb, Th, and U (and other fluid-mobile elements) (Figure S2). These correlations highlight that even the most incompatible and fluid-mobile elements such as U were not affected by postmagmatic processes, e.g., by weathering. Furthermore, the Longhai basalts have OIB-like compositional characteristics such as negative Pb

![Figure 4. Variation in (a) εNd versus ⁸⁷Sr/⁸⁶Sr, (b) ²⁰⁶Pb/²⁰⁴Pb versus ²⁰⁶Pb/²⁰⁴Pb, and (c and d) εHf versus εNd for the Longhai basalts. εNd = [(¹⁴⁳Nd/¹⁴⁴Nd)sample/(¹⁴³Nd/¹⁴⁴Nd)CHUR] × 10⁴, where (¹⁴³Nd/¹⁴⁴Nd)CHUR = 0.512630 [Bouvier et al., 2008]; εHf = [(¹⁷⁶Hf/¹⁷⁷Hf)sample/(¹⁷⁶Hf/¹⁷⁷Hf)CHUR] × 10⁴, where (¹⁷⁶Hf/¹⁷⁷Hf)CHUR = 0.282785 [Bouvier et al., 2008]. Data for depleted MORB mantle (DMM) are from Workman and Hart [2005]. The terrestrial reference line is from Chauvel et al. [2008]. The Pacific MORB field is based on basalts from the East Pacific Rise. The data for HIMU (gray diamonds), EM-I (blue diamonds), EM-II (green diamonds), and basalts from the East Pacific Rise are from the GEOROC database (http://georoc.mpch-mainz.gwdg.de/georoc) and references therein. The HIMU field is defined by the HIMU-type basalts from St. Helena, Mangaia, Tubuai, Rurutu, Austral-Cook, and the Azores. The lithospheric mantle field is based on the composition of peridotite xenoliths from Cenozoic basalts of Mingxi, western Fujian [Tatsumoto et al., 1992; Qi et al., 1995]. The Nd-Hf isotopic compositions of recycled oceanic crust at various times are shown as evolution path (red line), which was calculated by using an average, present-day isotopic composition of MORB from the East Pacific Rise (6°N–18°N) [from Salters et al., 2011]. The green lines represent mixing curves between DMM and recycled oceanic crust at various times. Other symbols and data sources are the same as in Figure 2. The crystals show low Mg# values (64.5–75.9), Al₂O₃ contents (1.3–3.4 wt %), and moderate to high MnO contents (0.13–0.30 wt %). Their Cr₂O₃ content positively correlates with their Mg# value (not shown). All clinopyroxene compositions plot below the clinopyroxene-melt equilibrium field (Figure S4b), which is constrained by the Fe-Mg exchange partition coefficient (K_D) between clinopyroxene and basaltic liquid, varying between 0.23 [Toplis and Carroll, 1995] and 0.27 [Putirka, 1999].

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anomalies (high Ce/Pb ratios) and positive Nb and Ta anomalies (Figures 3b and 6a) and moderately depleted Sr-Nd-Hf isotopic compositions (Figures 4a and 4c), suggesting an asthenospheric origin with negligible crustal contamination. Most Cenozoic alkaline basalts elsewhere in eastern China have a comparable isotopic compositions, and they are also inferred to represent asthenosphere-derived melts that have experienced minor to no crustal contamination [e.g., Peng et al., 1986; Song et al., 1990; Zhi et al., 1990; Basu et al., 1991; Zou et al., 2000; Sakuyama et al., 2013].

Petrographic observation and whole-rock composition record fractional crystallization. The presence of olivine phenocrysts in some Longhai basalts (Figure S1) highlights a possible role of olivine fractionation of olivine from the basaltic melts. This proposal is also supported by the correlated Fo-NiO-MnO-CaO variations in olivine phenocryst compositions and their high CaO contents [Thompson and Gibson, 2000] (Figure S3). The low Ni contents (77.1–230.3 ppm) of the Longhai basalts and the positive correlation between MgO and Ni (not shown) are consistent with the fractionation of olivine. The absence of a negative Eu anomaly and the lack of plagioclase phenocrysts (Figure 3a) suggest that plagioclase fractionation did not occur.

We have also used the “Petrolog 3” software [Danyushevsky and Plechov, 2011] to model the Ca/Al compositional variation as a function of olivine and clinopyroxene removal for Longhai basalts. If the high-MgO samples (MgO = 10 wt %) approach the primary magma composition, high and constant Ca/Al ratios (Figure 2c) and Sc contents (Figure 2d) of the low-Ti basalts suggest that they have undergone the olivine fractionation alone because Ca and Sc are compatible in clinopyroxene (DCa = 1.57, DSc = 2.2) [Hill et al., 2011]. By comparison, fractional crystallization of clinopyroxene could account for the low Ca/Al ratios of the high-Ti basalts. But such clinopyroxene fractionation cannot explain the significant variation of Sm/Yb (from 4.06 to 9.47) and Ti/Gd (from 2182 to 1699) ratios that is characteristic for the high-Ti basalts (Figure 5a). Fractionation of 40 wt % olivine and clinopyroxene, for example, has a comparatively minor effect on the Sm/Yb and Ti/Gd ratios, changing them from 4.26 to 4.52 and from 1924 to 1856, respectively. Therefore, an additional process must be invoked to explain the chemical variation of the Longhai basalts.

Figure 5. Variation in Ti/Gd, Zr/Hf, Ca/Al, and MnO versus Sm/Yb for the Longhai basalts. The red and purple dashed lines with the correlation coefficients (R) are linear correlation trends for the Longhai high-Ti basalts and low-Ti basalts, respectively. Data for DMM are from Workman and Hart [2005]. Also shown are the fractionation vectors for clinopyroxene and olivine (”cpx and ol,” brown lines) and for clinopyroxene and garnet (”cpx and grt,” green lines). Phase proportions of the fractionates and partition coefficients used for the model paths (Sm, Yb, Ca, Al, and Mn) [Adam and Green, 2006; Pertermann et al., 2004] are provided in Table S6. The stars represent the two types of end-member magmas that we infer to have generated the compositional diversity of the Longhai basalts. Other symbols and data sources are the same as in Figure 2.
5.2. Mantle Partial Melting of a Single Mantle Source?

The low HREE concentrations of the Longhai basalts (Figure 3a) suggest that they are derived dominantly from partial melting at large depth, i.e., in the garnet facies because garnet has high HREE partition coefficients [e.g., Halliday et al., 1995; Klemme et al., 2002; Pertermann et al., 2004]. The Longhai basalts are therefore most likely derived from the asthenospheric mantle and not from the lithospheric mantle, which concurs with the notion that the bulk of magma in continental flood basalts comes from the asthenosphere [Arndt and Christensen, 1992].

With residual garnet in the source, increasing degrees of partial melting will result in decreasing Sm/Yb in the partial melts, and Sm/Yb ratios can thus be used to assess variations in the degree of partial melting [e.g., Klein and Langmuir, 1987]. The Longhai basalts have variable Sm/Yb composition, and they could therefore have originated from variable degrees of partial melting of a single mantle source. However, with an increasing degree of partial melting of a garnet-bearing source, both the Sm/Yb and the Ti/Gd ratios of the resulting melts should decrease, including melts derived from garnet peridotite, carbonated garnet peridotite, and eclogite/carbonated Eclogite (derived from recycled oceanic crust) (Figure 7a), because the partition coefficient for Ti between garnet and silicate melt is much smaller than that for Gd (DTi/DGd < 0.5) [Green et al., 2000; Klemme et al., 2002; Pertermann et al., 2004; Tuff and Gibson, 2007]. This is at odds with their negative correlation between the Sm/Yb and the Ti/Gd ratios. Because Ti is compatible in rutile, if rutile was a residual mineral in the source in addition to garnet, low-degree partial melting of eclogite would produce melts with high Sm/Yb ratios and low Ti/Gd, which could explain the negative correlation between the Ti/Gd and Sm/Yb ratios of the Longhai basalts. However, residual rutile would also induce the depletion of Nb and Ta in addition to Ti [Kessel et al., 2005], based on its high partition coefficients [Klemme et al., 2005], which is inconsistent with the Nb-enriched composition of the Longhai basalts (Figure 3b). We therefore posit that melting of a single mantle source at variable degrees cannot explain the compositional variation of the Longhai basalts.

5.3. Low-Ti Basalts: Mixing of Magmas Derived From Diverse Source Lithologies

Excluding the possibility of originating from a single source, we now explore if mixing between two compositionally contrasting melts from different lithologies at mantle depth can account for their compositional variation.
In order to assess the potential source lithology of Longhai low-Ti basalts, we have calculated their primary magma compositions, following Huang and Frey [2003] (Table S5). The low CaO content (7.1–8.1 wt %) inferred for the primary low-Ti magmas (Figure S6) indicates a pyroxenitic source because primary magmas derived from peridotite sources have significantly higher CaO content (~10 wt %) than those of pyroxenite, regardless of their degree of fertility of the peridotite being melted [Herzberg and Asimow, 2008]. Melts derived from pyroxenite sources are also inferred to have higher Fe/Mn ratios than peridotite-derived partial melt, because in clinopyroxene Mn is more compatible than Fe (D Mn = 1.11, DFe = 0.71), while in olivine Mn is less compatible than Fe (D Mn = 0.77, DFe = 1.06) [Le Roux et al., 2011]. High Fe/Mn ratios of low-Ti basalts (68.9–85.0), comparing to 54.0 ± 1.2 for primitive MORB [Qin and Humayun, 2008], also suggest that their source lithology is pyroxenite. In the normative Ol-Calcium Tschermak (CATS)-Qtz system, the primary melt compositions for the low-Ti basalts plot along the 3–4 GPa cotectic L + Opx + Cpx + Grt (Figure 8a), which supports the notion that pyroxenite is the main lithology in the mantle source.

Furthermore, an additional lithology (represented by “LITHOLOGY X” below for convenience) to pyroxenite is still not realized. Melt derived from LITHOLOGY X is inferred to have high Sm/Yb, Zr/Hf, and Ca/Al ratios and low Ti/Gd ratio based on the correlations observed in the element ratios of low-Ti basalts (Figure 5) because the pyroxenite-derived melts have low Ca/Al ratio. However, we cannot identify LITHOLOGY X on account of the compositions of the low-Ti basalts alone. Alkali olivine basalts from Jieyang, Guangdong province, which erupted during the Miocene (~20 Ma) [Huang et al., 2013], are plotted on the extending line of the mixing curve produced by low-Ti basalts of Longhai (Figure 5) and are close to LITHOLOGY X-derived melt. Like the Longhai basalts, the Jieyang basalts have OIB-like chemical compositions and they have also been interpreted to represent asthenosphere-derived melts [Huang et al., 2013]. It thus

![Figure 7](image-url)
seems possible that the Jieyang basalts are derived from a source which is compositionally comparable to LITHOLOGY \(X\). The Jieyang basalts show pronounced negative Zr, Hf, and Ti anomalies (Figure 3b) and superchondritic Zr/Hf and Ca/Al ratios (Figure 5). Experiments have shown that carbonatitic liquids with such compositional signatures can be produced at deep upper mantle partial melting conditions. The carbonatitic liquids have negative Zr, Hf, and Ti anomalies because the rare earth elements strongly partition into liquids compared to Zr, Hf, and Ti (\(D_{Zr} = 0.229\), \(D_{Hf} = 0.303\), \(D_{Ti} = 0.226\), and \(D_{Sm} = 0.032\) \cite{Dasgupta et al., 2009}). On the basis of their negative Zr, Hf, and Ti anomalies and high Ca/Al and Zr/Hf ratios, we have previously suggested that alkaline basalts from Shandong province, eastern China, have been derived from a carbonated source \cite{Zeng et al., 2010}. Light Mg isotopes and heavy Zn isotopes of Cenozoic basalts in eastern China also emphasize that recycled carbonates are an important mantle source component \cite{Huang et al., 2015; Liu et al., 2016; Tian et al., 2016; Yang et al., 2012}. Therefore, we proposed that LITHOLOGY \(X\) in the source of Longhai low-Ti basalts is a carbonated component. As above, we have calculated the primary magma composition for these Jieyang basalts. The low CaO contents of the estimated primary magma composition (Figure S6) and the high Fe/Mn ratios (53.8–63.7) of the Jieyang basalts indicate that they are most likely derived from a carbonated pyroxenite than a carbonated peridotite source. In the nominal Ol-CATS-Qtz system, the estimated primary melt compositions of the Jieyang alkaline basalts plot on the 3–4 Ga \([L + Ol + Cpx + Grt]\), \([L + Cpx + Grt + Opx]\), and \([L + Cpx + Grt]\) cotectics and the Thermal Divide are from \cite{Herzberg, 2011}. The estimated primary magma compositions of the low-Ti basalts (black squares and purple triangles for samples in this study and previous study, respectively), and the Jieyang basalts (gray squares with white rim) were calculated by adding olivine to bulk composition, following \cite{Huang and Frey, 2003}. Also shown are the compositional fields for experimental partial melting of pyroxenite \cite{Herzberg, 2011} and peridotite \cite{Walter, 1998; Grove et al., 2013}. The mantle xenolith-rich, high-Ti basalts from Niutoushan volcano, including samples in this study (samples 11FJ06 and 11FJ07) and elsewhere \cite{Zou et al., 2000}, are also plotted in this figure to identify the possible equilibrium mineral assemblages during the high-pressure fractionation. Other symbols and data sources are the same as in Figure 2. (b) Schematic pseudobinary olivine-silica diagram \citeafter{Herzberg, 2011} illustrating possible effects of magma-magma interaction at high pressure. The stars represent the two types of end-member magmas that we infer to have generated the compositional diversity of the Longhai basalts.

Figure 8. (a) Projections (mol %) of estimated primary magma/melt compositions for the low-Ti basalts from diopside onto the Olivine-Quartz-Calcium Tschermak’s (CATS) plane. The 3–6 Ga \([L + Ol + Cpx + Opx]\), \([L + Opx + Cpx + Grt]\), \([L + Cpx + Grt]\), and \([L + Opx + Cpx]\) cotectics and the Thermal Divide are from \cite{Herzberg, 2011}. The estimated primary magma compositions of the low-Ti basalts (black squares and purple triangles for samples in this study and previous study, respectively), and the Jieyang basalts (gray squares with white rim) were calculated by adding olivine to bulk composition, following \cite{Huang and Frey, 2003}. Also shown are the compositional fields for experimental partial melting of pyroxenite \cite{Herzberg, 2011} and peridotite \cite{Walter, 1998; Grove et al., 2013}. The mantle xenolith-rich, high-Ti basalts from Niutoushan volcano, including samples in this study (samples 11FJ06 and 11FJ07) and elsewhere \cite{Zou et al., 2000}, are also plotted in this figure to identify the possible equilibrium mineral assemblages during the high-pressure fractionation. Other symbols and data sources are the same as in Figure 2. (b) Schematic pseudobinary olivine-silica diagram \citeafter{Herzberg, 2011} illustrating possible effects of magma-magma interaction at high pressure. The stars represent the two types of end-member magmas that we infer to have generated the compositional diversity of the Longhai basalts.
that they are derived from an SiO₂-poor pyroxenite source. This interpretation is consistent with melting experiments on a carbonated MORB-like pyroxenite, which produced nephelinitic to basanitic melts with low SiO₂ contents of 44–47 wt % [Gerbode and Dasgupta, 2010]. We note, however, that reaction between pyroxenite-derived melts and peridotite in the presence of CO₂ may equally produce SiO₂-undersaturated alkaline basalts [Mallik and Dasgupta, 2014].

To further examine this hypothesis of magma mixing, we use the whole-rock Ti/Gd and Sm/Yb ratios for modeling partial melting of eclogite (recycled oceanic crust) at variably CO₂-rich conditions (i.e., at 0–9%). The modeling indicates that the Ti/Gd ratios of the melts decrease with an increasing proportion of carbonated component in the source. The melting of carbonated eclogite can produce melts with low Ti/Gd ratios and high Sm/Yb ratios; in contrast, melting of a CO₂-free eclogite produces melts with relatively high Ti/Gd ratios and low Sm/Yb ratios (Figure 7a). In other words, mixing between alkaline basaltic magma derived from carbonated eclogite and tholeiitic magma derived from a CO₂-free eclogite can quantitatively reproduce the chemical trends of the Longhai low-Ti basalts (Figure 7b).

5.4. Pyroxenite: Originated From Recycled Oceanic Crust

Excluding the potential influence of continental crust (section 5.1), the eclogite/pyroxenite in the mantle is most likely derived from oceanic crustal component, which has been suggested to be present in the mantle sources of Cenozoic basalts from eastern China [Xu et al., 2012a; Sakuyama et al., 2013; Xu, 2014]. Generally, oceanic crust consists of an upper portion of MORB-type pillow basalts and an underlying portion of gabbroic cumulates. The composition of the lower portion of the oceanic crust, i.e., its gabbroic cumulates, is suggested to have positive Sr and Eu anomalies reflecting plagioclase accumulation [Pietruszka et al., 2012]. Basalts that are derived from such recycled gabbroic cumulates inherit their characteristics [Chauvel and Hémond, 2000; Xu et al., 2012a]. The positive Eu and Sr anomalies of the low-Ti basalt (Figure 3) and the positive correlation between their Eu/Eu* and Sr/Sr* ratios (Figure 6b) indicate that the lower portion of oceanic crust might be an appropriate candidate for the CO₂-free eclogite component in the mantle source of the low-Ti basalts. The Jieyang basalts, in contrast, which we interpret to represent melts derived from a carbonated eclogite source, show negligible Eu and Sr anomalies (Figure 3), and their Sr/Sr* and Eu/Eu* ratios are close to 1 (Figure 6b). If such carbonated eclogite is also derived from the recycled oceanic crust, their compositional signatures are consistent with partial melting of the upper portion of oceanic crust (MORB-type pillow basalts). In fact, the carbonates are generally sequestered in the upper oceanic crust [Alt and Teagle, 1999; Jarrard, 2003]. We therefore infer that the Longhai low-Ti basalts are generated from the melting of recycled oceanic crust.

The Nd-Hf isotopic compositions of the Longhai basalts plot below the mantle array line (Figure 4c), indicating slight decoupling of εNd from εHf (Figure 4d). The Nd-Hf isotope variations have previously been inferred to be decoupled in MORB [Chauvel et al., 2008], and coincidently, Pacific MORB is generally located only on the unradiogenic Hf end of the MORB field (Figure 4b) [Salters et al., 2011], indicating an affinity between the Longhai basalts and Pacific crust. The calculated evolution path on which basalts derived from such a recycled oceanic crust component should lie (Figure 4d) also supports the recycling of ancient oceanic crust to account for the Nd-Hf isotopes of the Longhai basalts, which is consistent with recycling of oceanic crust as described in Chauvel et al. [2008].

5.5. High-Ti Basalts: High-Pressure Fractionation of Clinopyroxene and Garnet

The genesis of the Longhai high-Ti basalts may be similar to the low-Ti basalts, considering their equivalent isotopic compositions (Figure 4). The composition of the high-Ti basalts, however, significantly deviates from the mixing trend of the low-Ti basalts in their Ti/Gd, Zr/Hf, and Ca/Al ratios and MnO content versus the Sm/Yb ratio, with a lower Ca/Al ratio and MnO content for a given Sm/Yb ratio (Figure 5). The fractionation of clinopyroxene and olivine could explain their low Ca/Al ratios and MnO content, but it cannot account for their high Sm/Yb ratios. The high Sm/Yb signature could be attributed to the fractionation of garnet for its high HREE partition coefficients [e.g., Klemme et al., 2002; Pertermann et al., 2004]. As shown in Figures 5c and 5d, the fractionation of garnet with clinopyroxene can significantly increase the Sm/Yb ratios of the basalts and reproduce the composition of the high-Ti basalts (i.e., their low MnO content, low Ca/Al, and high Sm/Yb ratios). In addition, the crossing REE pattern at Ho for the high-Ti basalts can also be explained by the fractionation of garnet with clinopyroxene [Liu et al., 1992]. Assuming a low-Ti basalt
composition as the primary magma composition, fractional crystallization of 25% garnet and 75% clinopyroxene in different degrees yields magma compositions with crossing REE patterns at Ho (Figure S7b) similar to those of the Longhai high-Ti basalts (Figure S7a). In contrast, if the basaltic magmas undergo fractionation of olivine and clinopyroxene only, their REE concentrations increase simultaneously, without producing crossing REE patterns at Ho (Figure S7c). Furthermore, the presence of mantle xenoliths in high-Ti basalts from the Niutoushan volcano suggests that the magma ascended rapidly, without time to undergo low-pressure fractionation. In the normative Ol-CATS-Qtz system, these samples plot on cotectic L + Cpx + Grt. This indicates that the mineral assemblages in equilibrium with the high-Ti melts during the high-pressure fractionation are garnet and clinopyroxene, according with our proposal above.

The main question is at which conditions such fractionation can take place, because garnet does not crystallize at low pressure (<70 km) [Green and Ringwood, 1967]. Experimental results suggest that garnet and clinopyroxene are the predominant fractionation minerals at mantle depths of approximately 70–100 km [Green and Ringwood, 1967]. The present thickness of the lithosphere beneath the Southeastern China is only ~60–70 km [Zhou et al., 2012], which indicates that the fractionation of garnet and clinopyroxene may have taken place in the asthenospheric mantle. A study on Hawaiian shield stage lavas has previously proposed that the mingling of SiO2-poor melts derived from a peridotite source and SiO2-rich melts from derived from a pyroxenite source triggers crystallization of clinopyroxene and garnet at pressure of ~4 GPa [Herzberg, 2011]. Garnet-bearing, high-pressure cumulate xenoliths from Salt Lake Crater on the island of Oahu, Hawaii, are support of this interpretation [Keshav et al., 2007]. Megacrysts of clinopyroxene and garnet are common in alkaline basalts of eastern China, e.g., in exposures at Hannuoba and Kuanidian, which have also been proposed to have once been in equilibrium with basaltic melts [Zhi et al., 1990; Liu et al., 1992], and might represent the products of such fractional crystallization. We therefore commend that the Longhai high-Ti basalts are produced by the fractionation of garnet and clinopyroxene from a similar mantle source as the Longhai low-Ti basalts, which provides a viable and testable conceptual model for their evolution.

5.6. High-Pressure Magma-Magma Interaction Model: Genetic Link Between Low-Ti and High-Ti Basalts

We propose that both CO2 and eclogite source components played important roles in the formation of the Longhai basalts. Compared to dry peridotite [Hirschmann, 2000], eclogite partially melts at higher pressure [Yasuda et al., 1994] (Figure 9a), which is why an olivine-free pyroxenite has been suggested to be formed by reaction between partial melts of recycled oceanic crust and peridotite as the source of SiO2-saturated basaltic magmas [Sobolev et al., 2005; Sobolev et al., 2007]. However, the involvement of CO2, which is likely to originate from carbonate sequestered in the oceanic crust by hydrothermal alteration [Alt and Teagle, 1999; Jarrard, 2003], can induce the peridotite or eclogite/pyroxenite to melt deep (~4 GPa) in the mantle (Figure 9a). In contrast, CO2-free eclogite begins to melt at ~4 GPa [Yasuda et al., 1994], which is roughly consistent with the melting pressures we have estimated for the low-Ti primary magmas of the Longhai and Jieyang basalts (cf. Figure 8a). The simultaneous melting of both carbonated and CO2-free eclogite at this depth, as indicated by the estimated primary melt compositions (Figure 8a), likely resulted in their mingling at or close to this depth level. This magma-magma mingling in deep mantle sources has previously been inferred on the basis of melt inclusions in olivine from Cenozoic basalts of Hainan Island, southern China [Liu et al., 2015a]. For eastern China, we surmise that such magma-magma mingling in the deep mantle is a common process, as the erupted basalts generally show variable, but nevertheless negative correlations between Ti/Gd ratio and Sm/Yb ratio, similar to the Longhai low-Ti basalts. This also indicates that carbonated component and eclogite are widespread lithologies in the asthenospheric mantle.

Melting experiments further suggest that basaltic melts derived from carbonated peridotite and carbonated eclogite are SiO2-undersaturated [Dasgupta et al., 2007; Gerbode and Dasgupta, 2010]. Even if the melts were SiO2-saturated, they would react with surrounding dry peridotite in the presence of CO2 and thereby evolve into SiO2-undersaturated basaltic melts [Mallik and Dasgupta, 2014]. Mingling of such SiO2-undersaturated (alkaline) and SiO2-saturated (tholeiitic) magmas at high pressure (~4 GPa) may result in either mixing or crystallization (Figure 8b) [Herzberg, 2011]. If the mixture projects into the liquid area of pseudobinary Olivine-Silica diagram, mixing without crystallization ensues. This is the evolution we propose for the formation of the Longhai low-Ti basalts. If, in contrast, the mixture projects into the L + Px area (Figure 8b), then crystallization of garnet and clinopyroxene will ensue according to a reaction of the type:
SiO$_2$-saturated tholeiitic magma + SiO$_2$-undersaturated alkaline magma → SiO$_2$-saturated alkaline magma + garnet + clinopyroxene

This is the evolution we propose for the formation of the Longhai high-Ti basalts. It is noteworthy that such mingling-triggered crystallization can give rise to the transition from tholeiitic to alkaline magmas. Previous studies have proposed two processes to induce the transition between tholeiitic and alkaline magmas: (1) melting of a common mantle source at increasing degrees [Frey et al., 1978; Wilson et al., 1995; Caroff et al., 1997; Lustrino et al., 2002] and (2) reaction between nephelinitic or basanitic melt and peridotite [Lundstrom et al., 2000; Pilet et al., 2008]. Both models are suggested to transform the low-SiO$_2$ alkaline magma into high-SiO$_2$ tholeiitic magma. Our model with a transition from tholeiitic magma to SiO$_2$-rich alkaline magma is proposed to produce magma with high SiO$_2$ content, low Al$_2$O$_3$ content, low Ca/Al ratio, and high Sm/Yb ratio. Such evolution model at high pressure can also be observed in Cenozoic basalts from eastern China. The Ti/Gd and Sm/Yb ratios of those Cenozoic basalts with Sm/Yb $>$ 4.0 and Ca/Al $<$ 0.8 are lined with a shallower slope than other Cenozoic basalts in eastern China (Figure 7b), which is similar to that of the Longhai high-Ti basalts. Therefore, the magma-magma interaction in the mantle may also serve as an alternative or additional conceptual model for the generation of tholeiitic-alkaline magma successions worldwide.

The recycled oceanic crustal components that may generate the source melts for intraplate tholeiitic-alkaline basalts are likely stored in the mantle transition zone [e.g., Xu et al., 2012a; Sakuyama et al., 2013; Xu, 2014]. Mantle upwelling then transports the recycled crustal components into the upper mantle, and eclogite and carbonated lithologies are formed in close spatial association, which provides ample opportunity for mingling of their derivate melts (Figure 9b). Furthermore, previous studies have highlighted that secondary pyroxenite may be a key ingredient for producing the chemical heterogeneity observed in the intraplate basalts [Sobolev et al., 2005, 2007; Herzberg, 2011]. Magma-magma interaction can trigger the fractionation
of garnet and clinopyroxene at the mantle depth and therefore provides a potential mechanism to form such mafic lithology.

References


Dasgupta, R., M. M. Hirschmann, W. F. McDonough, M. Spiegelman, and A. C. Withers (2009), Trace element partitioning between garnet and carbonatite at 6.6 and 8.6 GPa with applications to the geochemistry of the mantle and of mantle-derived melts, Chem. Geol., 262, 57–77.


Ho, K. S., J. C. Chen, C. H. Lo, and H. L. Zhao (2003), 40Ar/39Ar dating and geochemo-
ical characteristics of late Cenozoic basaltic rocks from the Zhejiang-Fujian region, SE China: Eruption ages, magma evolution and petrogenesis, Chem. Geol., 197, 287–318.
Le Bas, M., R. Le Maitre, A. Streckeisen, and B. Zanettin (1986), A chemical classification of volcanic rocks based on the total alkali-silica diagram, J. Petrol., 27, 745–750.
Lustrino, M., L. Melluso, and V. Morra (2002), The transition from alkaline to tholeiitic magmas: A case study from the Ororeo-Dorgali Pleocene volcanic district (NE Sardinia, Italy), Lithos, 63, 83–113, doi:10.1016/S0024-4973(02)00113-5.


