Geochemistry and Mantle Potential Temperature of Late Cenozoic Basaltic Rocks from the Northern and Western Continental Margins of the South China Sea

Xiaobo Yuan¹,*, Wang Ding²

¹Institute of Marine Science, Hebei Normal University of Science and Technology, Qinhuangdao, China
²Graduate School of Life and Environmental Sciences, University of Tsukuba, Tsukuba, Japan

Email address:
yuanxiaobo2011@163.com (Xiaobo Yuan), dingwang@geol.tsukuba.ac.jp (Wang Ding)

*Corresponding author

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Abstract: Deep dynamic processes of the evolution of the South China Sea (SCS) are recorded by the large-scale magmatism in the SCS and its surrounding regions. The geochemical analysis of whole-rock and olivine phenocryst was conducted on the Late Cenozoic basaltic rocks, which are exposed in the continental margins of the northern (the Leiqiong Area) and western (the Kontum Area) SCS. Consistent geochemical characteristics were shown on the basaltic rocks based on the results, which are similar to OIB from intra-plate environment. Mantle potential temperature ($T_p$) was measured by MgO of parental magma compositions and by olivine-liquid equilibria thermometry, with an average of 1489°C beneath the Leizhou Peninsula, 1555°C beneath the Northern Hainan and 1458°C beneath the Kontum Area. Compared with $T_p$ of SCS MORB, the mantle excess temperature is about 78–175°C in the studied areas. The highest excess temperature within typical plume-affected regions. Our results provide the evidence based on temperature for the existence of the Hainan Plume. The data of highest $T_p$ under the North Hainan may indicate the upper reaches of mantle plume. The mantle source of post-spreading magmatism in SCS and its surrounding region is likely to be correlated to that of pre-spreading volcanic activities in the northern continental margins.

Keywords: Hainan Plume, Mantle Potential Temperature, Geochemistry, The South China Sea, Post-Spreading

1. Introduction

The Cenozoic basaltic rocks are widely covered in the South China Sea (SCS) and its surrounding region. In relation to the evolution of the SCS [1–2], the temporal and spatial distribution of Cenozoic magmatism in the areas can be divided into three stages [3–4]. Firstly the pre-spreading stage (>~32 Ma), when scattered around the northern continental margin, magmatism erupted bimodal rift volcanic rocks [5–7]; Secondly the SCS basin spreading (~32~15.5 Ma), magmatism concentrated in the ocean basin, produced mainly middle-ocean ridge basalts (MORBs) [8–9]; Thirdly the post-spreading stage (~<15 Ma), intraplate magmatism expanded largely into the Leiqiong and adjacent areas in the South China, the Indochina Peninsula, and the SCS basin itself (Figure 1). Such temporal-spatial changes of magmatism have undoubtedly reveal the important signs about the evolution of the SCS and related deep dynamics.

There are several studies focusing on the post-spreading basaltic rocks from continental margins of the northern and western SCS [10–20]. Ocean Island Basalt-like (OIB-like) geochemical characteristics were shown on these basaltic rocks, originated from the mixture of the Depleted MORB Mantle (DMM) with Enriched Mantle 2 (EM-2) [20–21]. However, there are some debates about the origin of EM-2 like source. Some researchers considered continental lithospheric mantle [13–14], while others suggested a deep mantle plume source [19–20, 22]. Therefore, the question about the existence of mantle plume becomes more important. In recent years, the Hainan Plume underlying the SCS region was proposed based on geophysical investigation [23–26]. A low-velocity column beneath the northern part of Hainan Island has extended from the shallow depths down to mantle transition zone [24]. Although geophysical studies suggested the existence of the Hainan Plume, the features of magmatism in this region are still slightly different.
from that in typical plume-affected regions. More evidence should be presented for the existence of Hainan plume. Furthermore, the detail of thermal structure of the Hainan Plume and its effect on post-spreading magmatism are still unclear.

The mantle potential temperature ($T_p$) was used to distinguish between the mantle plume-related thermal anomalies and ambient mantle [27–31]. Considering the wide distribution of basaltic rocks in Late Cenozoic times, the data of $T_p$ in different locations is helpful for a better understanding of the thermal structure of mantle plume.

In this study, we collected the Late Cenozoic basaltic rocks from the Leiqiong Area in South China and the Kontum Area in Central Vietnam to carry out a geochemical analysis on whole-rock and olivine composition for the estimation of the $T_p$. Based on the results, we constrain the mantle plume structure and its possible influence on the evolution of the SCS.

2. Geological Background and Sampling

In the continental margin of northern SCS, basaltic rocks covered mainly in the northern part of Hainan Island and the adjacent Leizhou Peninsula (Leiqiong Area), being over 4000 km$^2$ in areas and up to over 100 m in thickness [10]. Volcanic activities during the Late Cenozoic times in Leiqiong Area were divided into two stages [10]: The early stage (late Tertiary, >3.5 Ma) dominated by flood type fissure eruption of quartz- or olivine-tholeiites, and the later phase (Quaternary, <2 Ma) characterized by central type eruption of alkali olivine basalts and olivine tholeiites. Three samples from Leizhou Peninsula were collected respectively from Huguangyan area, Yingfengling Mountain, and at Xuwen town with an eruptive period no more than 0.1 Ma. Eight samples were obtained in northern part of Hainan Island: three from Maanling Mountain and Jinniling Mountain in Haikou city, the eruption period no more than 0.1 Ma; five from Penglai Town, erupted at about 3.57–4.80 Ma (Figure 1) (Table 1).

Occurred in the Indochina Peninsula, the Late Cenozoic magmatism formed scattered volcanic centers (Figure 1). We collected samples from the Kong Plong and Pleiku volcanic centers around the Kontum Area in Central Vietnam (Figure 1) (Table 1). The Kong Plong volcanic center erupted during 10.5–16.5 Ma and 7.0–8.2 Ma, the basaltic rocks are interbedded with sandstone, siltstone, and claystone [32]. The magmatism in the Pleiku were later than in the Kong Plong, which preserved two eruptive episodes: the early episodes (6.5–3.4 Ma) dominated by quartz- or olivine- tholeiite and the later episodes (2.4–0.2 Ma) erupted olivine tholeiite, alkali basalt, and basanite [17]. Therefore, the ages of samples from Kong Plong and Pleiku are in the range between 16.5–7.0 Ma and 6.5–0.2 Ma, respectively.

All samples are fresh without any significant alterations. Porphyritic textures and vesicular structure were displayed in different rocks. The phenocrysts are mainly olivine, clinopyroxene and plagioclase. Plagioclase crystals are
3. Analytical Methods

The samples were worn off and ground to ~200 mesh for whole-rock geochemical analyses.

The analysis on whole rock for its major and trace elements were performed at the Regional Geology and Minerals Survey of Hebei Province, Langfang, Hebei Province. The analysis of major elements was conducted by X-ray fluorescence (XRF) (RIKAGU RIX 2100), with standard GBW07105 and BCR-2 were used to monitor drift during measurements, and its analytical precision is 5% better. The analysis of trace elements, including rare earth elements (REE), were carried out by an inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 7500a) and monitored by the GBW07105 (GSR-3). The accuracy of ICP-MS for trace elements is 5–10% better depending on the concentration of the given element. The experimental procedures can refer to [7].

Six samples (three Leiqiong basaltic rocks and three Kontum basaltic rocks) were one-side polished to make thin sections for microscopic observation and electron probe micro analyses (EPMA). Analyses on the major element analyses of olivine were carried out by using SHIMADZU EPMA-1720 instrument at the Experimental Center of China University of Geosciences, Beijing. Operating conditions were as follows: 15 kV accelerating voltage, 10 nA beam current, and a beam spot diameter of 1 µm. Counting times were 50 s for all elements. The data were regressed by oxide-ZAF correction methods.

4. Results

4.1. Major and Trace Element Compositions

Results of whole-rock major elements and trace elements of samples from the Leiqiong and Kontum Areas are listed in Table 1.

The SiO₂ contents of the Leiqiong basaltic rocks range from 48.86–54.39% with an average of 51.10%; samples from the Kontum Area show slightly lower SiO₂ contents varying 44.31–50.76% (average 46.58%). Total alkalis (Na₂O+K₂O) are higher than 3.1% for all samples. In a total alkalis-silica (TAS) diagram (Figure 2), samples from the Leiqiong Area are classified as basalt, basaltic andesite, trachybasalt, and basaltic trachyandesite, varying from alkaline to cale-alkaline series, while samples from the Kontum Area belong to the alkaline series with one exception (VN024-1). The Mg# values (Mg#=100*Mg/(Mg+Fe²⁺)) of Leiqiong basaltic rocks show the ranges of 53.40–63.15 (average 57.29), similar to the range of Kontum basaltic rocks (47.92–60.17, average 57.54).

In the distribution pattern of primitive mantle-normalized trace element (Figure 3a), a typical OIB-like pattern is shown in all samples, which are featured by enriched in large ion lithophile elements (LILE) and high field strength elements (HFSE), without negative Pb anomalies. The Ni, Co, Cr of samples from Leiqiong Area are 86.9–361.5 ppm, 39.2–46.9 ppm, and 234–472.2 ppm, respectively. Those of rocks from Kontum Plateau are 167–252 ppm, 50.7–69.6 ppm and 234–287 ppm, respectively. The Mg# values and the Ni and Cr contents of all samples are far lower than those for partial melts from peridotite mantle (Mg#>70, Ni>400–500 ppm, Cr>1000 ppm; [35–36]).

Figure 2. A rock classification diagram of the basaltic rocks from this study, according to their Na₂O+K₂O and SiO₂ contents. The dashed line separating alkaline and sub-alkaline basalts is from [33].

Figure 3. (a) Primitive mantle-normalized spider grams for basaltic rocks from Leiqiong Area and Kontum Plateau. Data for the primitive mantle and OIBs are from [34]. (b) Chondrite-normalized spider grams for basaltic rocks from Leiqiong Area and Kontum Plateau. Data for the chondrite and OIBs are from [34].
In the Leiqiong basaltic rocks, total REE contents (ΣREE) are shown in a range of 59.38–263.33 ppm, while the Kontum basaltic rocks display larger range of 126.55–338.88 ppm. From the chondrite-normalized REE diagram (Figure 3b), a light rare earth element (LREE) enriched pattern is shown in all samples. The LREE/HREE are 3.71–10.50 for the Leiqiong basaltic rocks and 5.61–10.99 for the Kontum basaltic rocks, indicating the high degree of fractionation between LREE and HREE. The Leiqiong basaltic rocks show a slightly positive anomaly of Eu (δEu=1.05–1.16), while no Eu anomaly (δEu=0.98–1.07) in the Kontum basaltic rocks (Figure 3b). Both rocks, however, show enrichment of (La/Yb)N (4.44–18.99 and 8.47–23.31, respectively).

4.2. Mineral Chemical Characteristics

Table 2 listed the results of the analyses on electron probe

| Area         | Leiqiong Area |
|--------------|---------------|
| Location     | N             | N             | N             | N             | N             | N             |
| GPS Position | 21°08′30.43″N | 20°34′51.10″N | 20°16′38.56″N | 19°55′50.48″N | 19°30′11.66″N | 19°34′41.24″N |
| Sample No.   | M128-1        | M330-2        | M332-1        | H001-1        | HK01-2        | HK02-2        |
|              | 50.86         | 14.90         | 14.86         | 14.23         | 13.78         | 13.84         |
|              | 1.49          | 1.97          | 1.49          | 1.38          | 1.94          | 1.94          |
|              | 1.05          | 1.47          | 1.04          | 0.86          | 1.97          | 1.97          |
|              | 0.48          | 2.26          | 2.38          | 2.06          | 1.23          | 1.23          |
|              | 0.79          | 7.22          | 6.58          | 7.90          | 1.11          | 0.86          |
|              | 5.50          | 14.90         | 14.86         | 14.23         | 13.78         | 13.84         |
|              | 0.95          | 1.94          | 1.38          | 1.94          | 1.94          | 1.94          |
|              | 0.86          | 1.97          | 1.23          | 1.23          | 1.97          | 1.97          |
|              | 2.06          | 2.26          | 2.38          | 2.06          | 1.23          | 1.23          |
|              | 7.90          | 14.90         | 14.86         | 14.23         | 13.78         | 13.84         |
|              | 1.11          | 0.86          | 1.23          | 1.23          | 1.97          | 1.97          |
|              | 0.86          | 1.97          | 1.23          | 1.23          | 1.97          | 1.97          |
|              | 2.06          | 2.26          | 2.38          | 2.06          | 1.23          | 1.23          |
|              | 7.90          | 14.90         | 14.86         | 14.23         | 13.78         | 13.84         |
|              | 1.11          | 0.86          | 1.23          | 1.23          | 1.97          | 1.97          |
|              | 0.86          | 1.97          | 1.23          | 1.23          | 1.97          | 1.97          |
|              | 2.06          | 2.26          | 2.38          | 2.06          | 1.23          | 1.23          |
|              | 7.90          | 14.90         | 14.86         | 14.23         | 13.78         | 13.84         |
|              | 1.11          | 0.86          | 1.23          | 1.23          | 1.97          | 1.97          |
|              | 0.86          | 1.97          | 1.23          | 1.23          | 1.97          | 1.97          |
|              | 2.06          | 2.26          | 2.38          | 2.06          | 1.23          | 1.23          |
|              | 7.90          | 14.90         | 14.86         | 14.23         | 13.78         | 13.84         |
|              | 1.11          | 0.86          | 1.23          | 1.23          | 1.97          | 1.97          |
|              | 0.86          | 1.97          | 1.23          | 1.23          | 1.97          | 1.97          |
|              | 2.06          | 2.26          | 2.38          | 2.06          | 1.23          | 1.23          |
|              | 7.90          | 14.90         | 14.86         | 14.23         | 13.78         | 13.84         |
|              | 1.11          | 0.86          | 1.23          | 1.23          | 1.97          | 1.97          |
|              | 0.86          | 1.97          | 1.23          | 1.23          | 1.97          | 1.97          |
|              | 2.06          | 2.26          | 2.38          | 2.06          | 1.23          | 1.23          |
|              | 7.90          | 14.90         | 14.86         | 14.23         | 13.78         | 13.84         |
|              | 1.11          | 0.86          | 1.23          | 1.23          | 1.97          | 1.97          |
|              | 0.86          | 1.97          | 1.23          | 1.23          | 1.97          | 1.97          |
|              | 2.06          | 2.26          | 2.38          | 2.06          | 1.23          | 1.23          |
|              | 7.90          | 14.90         | 14.86         | 14.23         | 13.78         | 13.84         |
|              | 1.11          | 0.86          | 1.23          | 1.23          | 1.97          | 1.97          |
|              | 0.86          | 1.97          | 1.23          | 1.23          | 1.97          | 1.97          |
|              | 2.06          | 2.26          | 2.38          | 2.06          | 1.23          | 1.23          |
|              | 7.90          | 14.90         | 14.86         | 14.23         | 13.78         | 13.84         |
|              | 1.11          | 0.86          | 1.23          | 1.23          | 1.97          | 1.97          |
| Total        | 99.77         | 99.83         | 99.83         | 99.75         | 99.73         | 99.73         |
| Mg#          | 61.69         | 57.03         | 60.25         | 53.4          | 54.46         | 54.08         |

Table 1. Whole-rock major elements and trace elements of basaltic rocks from the Leiqiong and Kontum Areas.
Table 1. Continued.

| Area          | Leiqiong Area                  | Location | Leizhou Peninsula | Northern Hainan |
|---------------|--------------------------------|----------|-------------------|-----------------|
| GPS Position  | N 21°08′30.43″ E 110°16′13.35″ | E        | E                 | E               |
| Sample No.    | MM21-1                         | MM32-1   | MM32-2            | MM32-3          |
| Cu            | 54.35                          | 50.39    | 51.06             | 43.73           |
| Zn            | 88.43                          | 90.88    | 86.14             | 114.7           |
| Ga            | 18.91                          | 16.88    | 16.95             | 21.68           |
| Rb            | 33.11                          | 7.51     | 12.8              | 25.56           |
| Sr            | 575.5                          | 266.2    | 308               | 554.4           |
| Zr            | 163.08                         | 91.12    | 82.59             | 205.48          |
| Nb            | 35.61                          | 10.7     | 13.19             | 33.19           |
| Mo            | 1.32                           | 0.6       | 0.68              | 1.66            |
| In            | 0.05                           | 0.05     | 0.04              | 0.05            |
| Ti             | 0.12                           | 0.07     | 0.07              | 0.06            |
| Pb             | 6.43                           | 4.74     | 4.82              | 6.04            |
| Bi             | 0.02                           | 0.02     | 0.03              | 0.02            |
| Th             | 7.01                           | 2.16     | 2.16              | 4.24            |
| U               | 1.09                           | 0.41     | 0.46              | 0.97            |
| Cs              | 0.99                           | 0.21     | 0.35              | 0.38            |
| Ba            | 439.4                          | 113      | 146.4             | 436.3           |
| Hf             | 4.13                           | 2.68     | 2.36              | 5.67            |
| Ta             | 2.73                           | 0.78     | 0.85              | 2.49            |
| W              | 0.55                           | 0.26     | 0.24              | 0.53            |
| Th              | 0.12                           | 0.07     | 0.07              | 0.06            |
| Pb             | 6.43                           | 4.74     | 4.82              | 6.04            |
| Bi             | 0.02                           | 0.02     | 0.03              | 0.02            |
| Th             | 7.01                           | 2.16     | 2.16              | 4.24            |
| U               | 1.09                           | 0.41     | 0.46              | 0.97            |

| Area          | Kontum Area                   | Location | Kong Pong | Pleiku |
|---------------|--------------------------------|----------|-----------|--------|
| GPS Position  | N 14°42′16.07″ E 108°27′43.33″ | E        | E         | E      |
| Sample No.    | VN15-1                         | VN23-1   | VN23-2   | VN24-1 |
| Major Oxides (wt.%) | SiO₂ 50.24 | 44.31 | 45.32 | 50.76 |
|                | Al₂O₃ 15.32 | 12.39 | 12.68 | 13.56 |
|                | TiO₂ 1.84 | 3 | 2.93 | 1.88 |
|                | Fe₂O₃ 6.96 | 2.4 | 3.02 | 3.18 |
|                | FeO 3.81 | 9.53 | 8.69 | 9.21 |
|                | CaO 6.63 | 8.5 | 8.16 | 8.47 |
|                | MgO 5.2 | 9.78 | 9.6 | 7.66 |
|                | K₂O 2.01 | 2.78 | 2.98 | 1.15 |
|                | Na₂O 3.52 | 2.74 | 2.43 | 3.11 |
|                | MnO 0.12 | 0.17 | 0.18 | 0.17 |
|                | P₂O₅ 0.51 | 0.95 | 0.93 | 0.93 |
|                | LOI 3.67 | 3.12 | 2.75 | 2.66 |
| Total          | 99.81 | 99.66 | 99.68 | 99.73 |
| Mg#            | 47.92 | 59.85 | 59.99 | 55.67 |
| Trace elements (ppm) | Y 23.28 | 31.53 | 32.18 | 23.72 |
|                | La 38.27 | 71.58 | 64.33 | 24.19 |
|                | Ce 65.82 | 126.27 | 121.95 | 43.22 |
|                | Pr 8.27 | 16.17 | 14.31 | 5.81 |
|                | Nd 33.45 | 67.2 | 59.84 | 25.9 |
|                | Sm 7.12 | 12.93 | 11.31 | 6.13 |
|                | Eu 2.27 | 3.99 | 3.48 | 2.15 |
|                | Gd 6.37 | 11.06 | 9.74 | 6.03 |
|                | Tb 1.03 | 1.6 | 1.41 | 1.03 |
|                | Dy 5.34 | 7.8 | 7.21 | 5.69 |
|                | Ho 0.92 | 1.25 | 1.17 | 0.98 |
|                | Er 2.38 | 3.04 | 2.87 | 2.49 |
|                | Tm 0.34 | 0.44 | 0.2 | 0.38 |
|                | Yb 1.98 | 2.2 | 2.02 | 2.05 |
|                | Lu 0.61 | 0.78 | 0.29 | 0.51 |
|                | Li 8.34 | 6.98 | 4.82 | 4.46 |
|                | Be 1.59 | 2.61 | 2.79 | 1.14 |
Electron probe analyses of olivines in the basaltic rocks from Leiqiong Area and Kontum Area.

Table 2. Electron probe analyses of olivines in the basaltic rocks from Leiqiong Area and Kontum Area.

| Location   | Sample No. | Location | Analytical Point | Host Rock | MM28-1 | HK05-2 |
|------------|------------|----------|------------------|-----------|---------|--------|
| Leizhou Peninsula | VN15-1 | Kong Plong | 1.44 | MM28-1 | 4.37 | 10.87 |
|            | VN15-2 |            | 1.56 |          | 4.47 | 10.97 |
|            | VN23-1 |            | 1.44 |          | 4.37 | 10.87 |
|            | VN23-2 |            | 1.56 |          | 4.47 | 10.97 |
|            | VN24-1 |            | 1.44 |          | 4.37 | 10.87 |
|            | VN24-2 |            | 1.56 |          | 4.47 | 10.97 |
|            | VN25-1 |            | 1.44 |          | 4.37 | 10.87 |
|            | VN25-2 |            | 1.56 |          | 4.47 | 10.97 |
|            | VN25-3 |            | 1.44 |          | 4.37 | 10.87 |

Note: (1) Mg# = 100×Mg/(Mg+Fe), Fe²⁺/Fe³⁺=0.8998, cation ratio; (2) LOI = loss on ignition.
In figure 5, the Fo values of olivines are shown as a function of Mg# of the host basaltic rocks. The Fe-Mg exchange partition coefficients between the olivine and the basaltic melt (KD=[Fe/Mg]eq/[Fe/Mg]liq) are well constrained by the experiments, varying from 0.30 at 1 atm to 0.31–0.34 at 5–15 kbar [41]. No olivine falls within the equilibrium. Olivine in VN024-1 and MM28-1 are significantly lower than the equilibrium, suggesting the analysed olivine are laterally crystallizing matrix grain. Samples HK05-2, VN25-1, VN23-1 and HN05-1 contains olivine above the equilibrium field, indicating that they formed early in the process of magma evolution. The highest Fo values in the Leiqiong and Kontum Areas are 90.88 and 89.27, indicating the Mg# of 75 and 71.5 are required for olivine-liquid equilibrium (Figure 5).

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**Table 2. Continued.**

| Location        | Northern Hainan | Kontum Area |VN23-1 |VN24-1 |VN25-1 |
|-----------------|-----------------|-------------|--------|--------|--------|
| **Host Rock**   | HK05-7          |             |        |        |        |
| **Analytical Point** | 2-1c            | 2-2m        | 2-3r   | 4-1c   | 1-1c   |
| **Silicon (SiO₂)** | 40.71           | 40.25       | 37.77  | 41     | 38.65  |
| **Aluminum (Al₂O₃)** | 0.01            | 0.02        | 0.03   | 0.01   | 0.02   |
| **Titanium (TiO₂)** | 0              | 0.08        | 0      | 0      | 0.04   |
| **Cr₂O₃** | 0.04            | 0.04        | 0      | 0      | 0.04   |
| **Iron (FeO)** | 9.22            | 9.15        | 23.25  | 8.72   | 23.57  |
| **Manganese (MnO)** | 0.21            | 0.09        | 0.34   | 0.14   | 0.28   |
| **Nickel (NiO)** | 0.44            | 0.47        | 0.31   | 0.44   | 0.03   |
| **Magnesium (MgO)** | 49.8            | 48.47       | 37.16  | 48.77  | 35.76  |
| **Calcium (CaO)** | 2.07            | 0.08        | 0      | 0.07   | 0.28   |
| **Sodium (NaO)** | 0.06            | 0.08        | 0.28   | 0.09   | 0.24   |
| **K₂O** | 0.04            | 0.04        | 0      | 0.04   | 0.02   |
| **CoO** | 0.01            | 0.02        | 0.11   | 0      | 0.02   |
| **P₂O₅** | 0              | 0.04        | 0      | 0.04   | 0.06   |
| **Total** | 100.56           | 98.7        | 99.47  | 99.39  | 99.82  |
| **Si** | 1.49            | 1.5         | 1.5    | 1.51   | 1.01   |
| **Al** | 0              | 0           | 0      | 0      | 0      |
| **Ti** | 0              | 0           | 0      | 0      | 0      |
| **Cr** | 0.06            | 0           | 0      | 0      | 0      |
| **Fe** | 0.28            | 0.28        | 0.77   | 0.27   | 0.52   |
| **Mn** | 0.01            | 0           | 0.01   | 0      | 0.01   |
| **Ni** | 0.01            | 0.01        | 0      | 0      | 0.01   |
| **Mg** | 2.71            | 2.69        | 3.19   | 3.26   | 1.43   |
| **Ca** | 0              | 0           | 0      | 0      | 0.01   |
| **Na** | 0.01            | 0.02        | 0      | 0      | 0.01   |
| **K** | 0              | 0           | 0      | 0      | 0.01   |
| **Zn** | 0              | 0           | 0      | 0      | 0      |
| **Total** | 4.51           | 4.5         | 4.52   | 4.49   | 2.99   |
| **Fo** | 90.59           | 90.42       | 74.01  | 90.88  | 73.44  |
Figure 5. Whole-rock Mg# vs. Fo value of olivine. Mg# = 100*Mg/(Mg+Fe^{2+}), calculated assuming Fe^{2+}/Fe^{total} = 0.9 for whole-rock and total Fe as Fe^{2+} in olivine.

5. Discussion

5.1. Possible Crustal Contamination

The composition may be modified by crustal contamination during the ascent and migration of primary mantle magmas. The effects of crustal contamination can be evaluated by trace elements [42–43]. The Leiqiong basaltic rocks have a relatively variable Ce/Pb ratios (6.71–16.33, with an average of 9.52) and Nb/U ratios (26.30–65.58, with an average of 36.43), which is substantially higher than those of continental crust (Ce/Pb=3.91 and Nb/U=6.15; [42–43]) (Figures 6a, 6b). Most of samples are correlated with previous reported samples from the continental margin of northern SCS [44]. Some authors have reported crustal contamination for Vietnamese basalts [13, 16]. However, the Ce/Pb ratios and Nb/U ratios of our samples, with yield values range from 13.94–29.80 (average 22.63) and 33.72–50.67 (average 42.26), are obviously higher than those of primitive mantle (Ce/Pb=9 and Nb/U=30; [45]) and generally within the range of oceanic basalts (47±10; [45–46]) (Figures 6a, 6b), suggesting limited crustal contamination. In addition, the lack of strong negative Nb or Ta anomalies in trace element spider diagram (Figure 3a) support the evidence of negligible continental crustal contamination [20–21, 47]. In conclusion, the characteristics of trace element suggest that crustal contamination of our basaltic rocks from two areas are negligible, and these rocks were therefore likely derived from mantle sources.
Figure 6. Plots of Ce/Pb vs. Ce (a) and Nb/U vs. Nb (b) for the basaltic rocks from the Leiqiong and Kontum Areas. Data for primitive mantle and oceanic island basalt (OIB) are from [45], and data for continental crust (CC) is from [42]. Data for the Northern margin of SCS and the Indochina Block are from [44]. Values in Y-axis is logarithmic scale.

Figure 7. Variation diagram of Mg# versus selected Major, trace element, and element ratios for basaltic rocks from Leiqiong and Kontum Areas.

5.2. Fractional Crystallization

Fractional crystallization is an important process of magma evolution. In order to better observe the fractional crystallization processes, we combined our samples with previous reported samples in the Mg# correlation diagrams (Figure 7). For our basaltic rocks, both from the Leiqiong and Kontum Areas, with the decreasing of Mg# values, SiO₂, Al₂O₃ and Sc are increased (Figures 7a, 7b, 7c), whereas Ni is decreased (Figure 7d), no systematic variations occurred in CaO, CaO/Al₂O₃ (Figures 7e, 7f). The olivine fractionation increases contents of SiO₂, Al₂O₃ and strongly incompatible elements, the olivine+clinopyroxene fractionation decrease the contents of CaO and Ni, the
The pattern of SiO$_2$, Al$_2$O$_3$, and Ni indicates some fractional crystallization of olivine or olivine+clinopyroxene. Ca is compatible in clinopyroxene, of which fractionation decreases CaO contents. The nearly constant of CaO and CaO/Al$_2$O$_3$ suggest clinopyroxene may not be the main fractional phase. The Leiqiong basaltic rocks show slightly Eu anomalies, indicating that the crystallization of plagioclase. However, the Kontum basaltic rocks shown no Eu anomalies, indicating the insignificance of plagioclase fractional crystallization. In summary, samples from the Leiqiong and Kontum Areas have mainly undergone the fractional crystallization of olivine, accompanied by the relatively weak fractional crystallization of clinopyroxene and very limited plagioclase fractionation. In addition, samples with highest Mg#' values can be regarded as relatively primitive magmas which is closed to primary melts.

5.3. Estimation of Mantle Potential Temperature

The basaltic rocks produced by mantle plume usually shown some OIB-like features, while the primary melt composition is different from MORB. However, OIB-like characteristics are not always produced by mantle plume [48]. In order to constrain the mantle plume, the excess temperature ($T_p$) was proposed to identify the thermal anomalies in the mantle. Meanwhile, $T_p$ in regimes affected by mantle plume are 160–300°C demonstrated in different calculations [49–51]. In this section, the estimates of the $T_p$ and $T_{ex}$ in the Leiqiong and Kontum Areas were made in this study.

### 5.3.1. Primary Melt Composition

The basaltic rocks from both the Leiqiong and Kontum Areas had experienced olivine and clinopyroxene fractional crystallization. In order to calculate the primary melt compositions, we selected samples with high Mg#' (high MgO), as basaltic rocks with lower values are more likely to experienced clinopyroxene and plagioclase fractionation which are unsuitable for the calculation.

For the Leiqiong basaltic rocks, effect of clinopyroxene fractionation on samples with Mg#'>61 (MgO=8.5%) is negligible [15], allowing us to use MM028-1 (from the Leizhou Peninsula) and HK005-7 (from the Northern Hainan) as the starting composition. For the Kontum basaltic rocks, samples with MgO>9% were chosen for the starting materials [20].

The compositions of primary magmas can be reconstructed by stepwise additions of olivine to computed melts (olivine mass fractions=0.01), with the compositions of added olivine being calculated based on the Fe-Mg exchange coefficient between olivine and silicate melt (KD = 0.3; [28]). Repeated addition of olivine was continued until the calculated melt had the composition in equilibrium with olivine as well as reaching the highest Fo values measured for olivine phenocrysts: 90.88 for the Leiqiong basaltic rocks and 89.27 for the Kontum basaltic rocks (Table 2).

The primary melt compositions were calculated by PRIMELT 3 MEGA software [52]. H$_2$O content concentrations in the magmas were estimated by the primary Ce contents, assuming that the same H$_2$O/Ce ratios of ~200 as oceanic basalts [29]. The results of primary melt composition are listed in Table 3.

| Location       | Leizhou Peninsula | Northern Hainan | Kontum Area |
|----------------|-------------------|-----------------|-------------|
| Starting sample | MM28-1            | HK05-7          | VN23-1      | VN23-2 | VN25-1 | VN25-2 | VN25-3 |
| % Ol addition  | 18.00             | 19.00           | 14.00       | 15.00   | 16.00   | 15.00   | 16.00   |
| SiO$_2$        | 49.44             | 48.37           | 45.20       | 45.93   | 45.56   | 45.50   | 45.62   |
| TiO$_2$        | 1.50              | 1.77            | 2.72        | 2.62    | 2.60    | 2.58    | 2.61    |
| Al$_2$O$_3$    | 12.56             | 10.58           | 11.19       | 11.31   | 10.91   | 11.00   | 11.02   |
| Cr$_2$O$_3$    | 0.00              | 0.00            | 0.00        | 0.00    | 0.00    | 0.00    | 0.00    |
| FeO$_2$        | 0.87              | 1.02            | 1.17        | 1.13    | 1.17    | 1.18    | 1.16    |
| FeO            | 8.82              | 10.13           | 11.08       | 10.82   | 11.23   | 11.20   | 11.19   |
| MnO            | 0.15              | 0.17            | 0.17        | 0.18    | 0.18    | 0.18    | 0.18    |
| MgO            | 14.91             | 17.13           | 14.94       | 15.07   | 15.62   | 15.49   | 15.52   |
| CaO            | 7.00              | 5.60            | 7.70        | 7.29    | 7.46    | 7.60    | 7.42    |
| Na$_2$O        | 2.94              | 2.57            | 2.47        | 2.16    | 2.31    | 2.35    | 2.30    |
| K$_2$O         | 1.46              | 1.96            | 2.51        | 2.64    | 2.14    | 2.09    | 2.15    |
| NiO            | 0.00              | 0.00            | 0.00        | 0.00    | 0.00    | 0.00    | 0.00    |
| P$_2$O$_5$     | 0.37              | 0.70            | 0.85        | 0.83    | 0.81    | 0.84    | 0.82    |
| H$_2$O         | 0.77              | 1.69            | 2.06        | 1.99    | 1.68    | 2.11    | 1.70    |
| $F$ (%)        | 14.47             | 16.75           | 0.08        | 2.83    | 3.00    | 2.53    | 2.90    |
| $P_a$ ($\%$)   | 14.94             | 19.73           | 27.01       | 24.60   | 26.80   | 26.82   | 24.64   |
| $P_e$ ($\%$)   | 15.57             | 20.24           | 34.14       | 30.95   | 32.56   | 32.84   | 32.33   |
| $P_{aq}$       | 18.96             | 23.52           | 24.05       | 22.92   | 24.05   | 23.69   | 23.78   |
| $P_{aq}$       | 16.49             | 21.16           | 25.40       | 26.15   | 27.80   | 27.78   | 27.52   |
| $T_{po}$       | 1432.35           | 1492.00         | 1465.73     | 1463.19 | 1479.62 | 1476.96 | 1476.84 |
| $T_{po}$       | 1427.71           | 1491.61         | 1440.69     | 1440.82 | 1456.49 | 1448.58 | 1453.25 |
| $T_{po}$       | 1430.03           | 1491.81         | 1453.21     | 1452.01 | 1468.05 | 1462.77 | 1465.04 |
| $T_{po}$       | 1453.43           | 1507.60         | 1454.18     | 1457.74 | 1471.61 | 1468.34 | 1469.22 |
| $T_{po}$       | 1445.00           | 1554.03         | 1644.86     | 1619.73 | 1658.33 | 1656.24 | 1654.18 |
The added olivine for the basaltic rocks from the Leizhou Peninsula, the Northern Hainan, and the Kontum Area are 18%, 19% and 14–16%, respectively. The degree of partial melting (F) of basaltic rocks in Leizhou Peninsula (14.47%) and Northern Hainan (16.75%) are similar, within the ranges of previous reported Hainan basalt (11–19%; [15]). In the Kontum basaltic rocks from Central Vietnam, F ranges from 0.08–3% (Table 3), slightly lower than the basaltic rocks from the Southern Vietnam (4–7%; [20]).

5.3.2. Mantle Potential Temperature
The effective crystallization pressures in the Leiqiong Area (16.49–21.16 kbar) are slightly lower than that in the Kontum Area (26.15–28.40 kbar), where the melting temperatures are in a small range of 1430–1491°C (Table 3). Following empirical equations of [36], we used the MgO contents in the primary melts to estimate the mantle potential temperature (T_p). The results in the Leizhou Peninsula, the Northern Hainan and the Kontum Area are 1453°C, 1507°C and 1454–1472°C, respectively. In order to be more confident for the calculated results, we further estimated T_p from olivine-liquid equilibration thermometer for comparison [51]. The estimated T_p in the Leizhou Peninsula, the Northern Hainan, and the Kontum Area are 1524°C, 1603°C and 1441–1476°C, respectively. Comparing the two methods, the average T_p is defined as the results, of which value beneath the Leizhou Peninsula, the Northern Hainan and the Kontum Area are 1489°C, 1555°C and 1458±2.6°C (weighted average).

The T_p estimated from SCS MORB is around 1380°C [9], which is comparable with global MORs (1280–1450°C, [28]). Using T_p of SCS MORB as the background of upper mantle temperature under the SCS region, we obtained the T_p beneath the studied areas, which shows in a range of ~78–175°C. Compared in typical plume affected areas, the T_p of Hawaii (Mauna Kea) and Iceland are ~220°C and ~170°C, respectively [51]; Moreover, the T_p estimated from basaltic rocks in regions of Tristan Plume and Circe Plume are ~160°C and ~80°C [50]. Although T_p values varies in different plume, the generally range of ~160–~300°C were considered affected by mantle plume. Therefore, the highest T_p (~175°C) indicate that the studied area was affected by mantle plume.

5.3.3. Thermal Structure of the Hainan Plume
The result of calculated T_p in the Northern Hainan (1555°C) is consistent with previous reported T_p from Northern Hainan (1521±24°C, [15]), which increases our confidence of the calculation. T_p is beneath the Northern Hainan is ~65°C higher than that of the Leizhou Peninsula (1489°C), possibly due to the deeper source of the Northern Hainan basaltic rocks. The estimated T_p from the Kontum basaltic rocks range from 1448–1474°C, while the reported T_p from the Southern Vietnam was in a range of 1470–1480°C [20]. The similar results indicate the similar source depth of basaltic rocks from the Central and Southern Vietnam. However, these temperatures are ~90°C lower than that in the Northern Hainan. The plume theory suggested that the temperature variability attributed to the thermal structure of the mantle plume. The temperature of a plume head is predicted to be appreciably higher at the center of the head than at its margins [56–57]. Therefore, the higher T_p beneath Northern Hainan may be caused by its position that closer to the center of plume head, whereas T_p under the Leizhou Peninsula, the Central Vietnam and the Southern Vietnam might derive from peripheral regions far from the plume center.

The geophysical investigations reveal the head of Hainan Plume is beneath the northern part of Hainan Island [23–24], which is consistent with higher T_p under the Northern Hainan. The tomographic images in South China reveal that the Hainan Plume raises sub-vertically from lower mantle and accumulated in the mantle transition zone, then diffuses laterally, and divides into multiple branches [26]. The low velocity also extends to the Southern Vietnam [25]. The collision of India with Eurasia might induce the lateral diffuses of lithosphere and reactive Cenozoic fault systems in the Indochina Peninsula [58], revealing the fact that these fault systems maybe promote the magma upwelling branching of from Hainan Plume.

5.4. Tectonic Signification
The upwelling of Hainan Plume suggested the acceleration of the development of western Pacific marginal sea basins [59], among which the SCS experienced a nearly complete Wilson cycle [60]. The continental rift stage of the SCS was featured by volcanic basins in South China. The Sanshui Basin is one of a representation, where the volcanism can be divided into earlier phase dominated by trachyte and, the later phase dominated by intraplate basaltic rocks [61]. The intraplate basaltic rocks shown OIB-like characteristics, indicating a mixture of DMM and EM2 mantle source [21], which is similar to the post-spreading basaltic rocks we analyzed. The magmatism in the Sanshui Basin is widely considered to be the consequence of regional asthenosphere upwelling [62–63].
The comparison of lithological combination between the Sanshui Basin and the Red Sea Area suggest that the development of the Sanshui Basin is very similar to the Red Sea model, as magmatism in the Sanshui Basin representing the infancy of the SCS [61].

However, in the syn-spreading stage of SCS basin, only limited magmatism reported in the surrounding region of the SCS. The extraction of Indochina Block was induced by the India-Asian collision [64]. This lateral movement of tectonic layers might suspend the magmatic supply and ended the break of continental rift. In this case, only basic magmas sourced from the decompression melting of lithospheric upper mantle upwelling, which formed the oceanic crust of the SCS [65].

The northwards movement of the Philippine Plate was considered to be one of the reasons for the cease of SCS basin spreading [66]. The Philippine Plate counteracted the effect of extraction of Indochina block, which resuscitated the upwelling of deep mantle. The Hainan Plume formed a subvertical column, with plume center beneath Northern Hainan and small conduits branched along fault systems to Indochina Peninsula and South China, producing large scale Late Cenozoic magmatism in the SCS and its surrounding regions.

The magmatism in the pre- and post-spreading stages of the SCS reflect similar mantle source. However, the scale of pre-spreading stage is smaller than post-spreading stage. We hypothesize that the small scaly magmatism in pre-spreading stage of the SCS has reflect on the infancy of mantle upwelling, which is constrained by plate tectonic activities in syn-spreading stage. In the post-spreading stage, with the revoking of tectonic constrains, the ascent of plume-affected deep mantle materials formed large scale magmatism in the SCS and its surroundings, which probably suggest the arising of a new continental rift environment.

6. Conclusions

This paper studies the geochemical characteristics of the Late Cenozoic basaltic rocks from Leiqiong Area and Kontum Area in the continental margins of the northern and western SCS, and reaches to the following conclusions:

1. The geochemical characteristics of basaltic rocks from the Leiqiong and Kontum Areas were consistent, featured with OIB-like trace element distribution and REE pattern.
2. The $T_p$ values beneath the Leizhou Peninsula, the Northern Hainan and the Kontum Area are 1489°C, 1555°C and 1458±2.6°C, respectively. The $T_p$ in studied areas range from ~78–175°C, suggest the influence by mantle plume.

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