In Situ LA-ICP-MS Analysis of Minerals Hosted by Late Cenozoic Basaltic Rocks from Thailand

Long Yuan 1, Quanshu Yan 1,2,3,*, Xuefa Shi 1,2, Haitao Zhang 1,2 and Xijun Liu 4

1 Key Laboratory of Marine Sedimentology and Environmental Geology, First Institute of Oceanography, Ministry of Natural Resources, Qingdao 266061, China
2 Laboratory for Marine Geology, Qingdao National Laboratory for Marine Science and Technology, Qingdao 266061, China
3 College of Earth Science and Engineering, Shandong University of Science and Technology, Qingdao 266590, China
4 Guangxi Key Laboratory of Hidden Metallic Ore Deposits Exploration, Guilin University of Technology, Guilin 541004, China
* Correspondence: yanquanshu@163.com or qsyuan@fio.org.cn

Received: 19 June 2019; Accepted: 17 July 2019; Published: 19 July 2019

Abstract: Shortly after the cessation of seafloor spreading, intraplate magmatism affected large areas in the South China Sea (SCS) region. The origin and geodynamic setting of the post-spreading volcanism is still in debate, for many previous studies have focused on petrogenesis and mantle source of the late Cenozoic basalts from the SCS region. In this study, we obtained in situ major element compositions (by using Electron microprobe analysis—EMPA) and trace element compositions (by using laser ablation inductively coupled plasma mass spectrometry—LA-ICP-MS) for minerals (clinopyroxenes (Cpx), plagioclases (Pl), and olivines (Ol)) hosted by late Cenozoic basaltic rocks from Thailand. The results showed that the olivines had forsterite contents between 60.12% and 84.74%. Clinopyroxene were diopside and augite, and they were enriched in light rare earth elements (LREEs) (LaN/YbN = 1.93–4.27) and depleted in large-ion lithophile elements (LILEs). Mineral compositions (mainly based on clinopyroxene) confirmed that these late Cenozoic basaltic rocks were of an intraplate affinity and were similar to contemporaneous basaltic fields in the SCS region (Southern Vietnam, Northern Hainan, and SCS seamounts). Plagioclases were predominantly labradorite, with a few andesine and bytownite, and they were enriched in LREEs and Ba, Sr, and Pb, and most of them exhibited strong positive Eu anomalies. The source lithology of Thailand basaltic rocks could be garnet pyroxenite. The mantle potential temperature beneath Thailand is in the range of 1448–1467 °C, which can be comparable to those beneath Southern Vietnam and Northern Hainan, indicating the Thailand basaltic rocks could be produced by the Hainan mantle plume. In addition, the crystallization temperature of clinopyroxenes (1145–1214 °C) and plagioclase (1067–1133 °C) and their composition characteristics indicate that the magmatic processes have a conspicuous characteristic of fast rate of magma upwelling. Thus, we proposed that the deep geodynamic setting of Thailand late Cenozoic basaltic rocks is similar to those of the whole SCS region, and Hainan mantle plume plays a significant role in the petrogenesis of these basaltic rocks.

Keywords: mineral chemistry; source lithology; magmatic processes; late Cenozoic basalts; Thailand; Hainan plume

1. Introduction

The South China Sea (SCS) region, including Leiqiong Peninsula, the Indochina Block, and the SCS basin itself, lies at the intersection of the Indo–Australian plate, Philippine sea plate (or Pacific
plate), and Eurasian plate (Figure 1). Recent studies have shown that Cenozoic igneous activities in the SCS region are as follows: In the earlier time of Cenozoic (60–43 Ma), bimodal volcanism occurred in the strike-slip rifting basin of the SCS northern continental margin [1–4]. During the Cenozoic seafloor spreading (32–16 Ma) in the SCS, basaltic volcanism occurred in the Pearl River Mouth basin and spreading axis [1]. Shortly after the cessation of seafloor spreading, widespread intraplate volcanism occurred in the SCS region, and the magmatic series of these volcanic activities gradually evolved from tholeiitic to alkalic [5,6]. The post-spreading volcanism has not only affected the SCS basin itself, but also Leiqiong Peninsula and Indochina Peninsula [6–26]. Although many previous studies have focused on petrogenesis and mantle source of the late Cenozoic basalts from the SCS region [6–26], the origin and geodynamic setting of the post-spreading volcanism is still in debate, with present models including: (1) A petrogenetic association with Hainan mantle plume [18,25,26]; (2) origin from the melting of a mixed peridotite/pyroxenite source [25]; (3) interaction of a mid-ocean ridge basalt (MORB) source with subcontinental lithosphere [8,27]. Understanding the issue of tectonic evolution of the SCS region needs more direct geologic evidence, such as petrologic and geochemical constraints from post-spreading volcanic rocks.

The available geochronological and geochemical data of the SCS region suggest that the younger basalts (8–0.5 Ma) of the SCS seamounts and Indochina block belong to the alkalic series, and the Cenozoic basalts of northern Hainan predominantly belong to the tholeiitic series [10,18,19]. Furthermore, all of the SCS seamounts, Indochina block, and northern Hainan basalts generally display light rare earth element (LREE)-enriched REE patterns and ocean island basalt (OIB)-like trace element compositions [10,18,19,23,25–27]. Isotopic studies on these post-spreading basalts from the SCS region suggested that their mantle source can be explained by a mixing model involving two mantle end members: A moderately depleted Indian MORB-like mantle and an enriched mantle of type 2 (EM2) [6,8,10,13,18,19,22,25–29]. However, although there are a number of studies focusing on whole rock geochemistry for late Cenozoic basaltic rocks from Thailand, in situ major and trace element compositions for these rocks are still lacking, which hinder the ability to understand their petrogenesis and magmatic processes.

In this study, we obtained in situ trace element (by using laser ablation inductively coupled plasma mass spectrometry—LA-ICP-MS) and major element compositions (by using electron microprobe analysis—EMPA) for clinopyroxenes, plagioclases, and olivines in basalts. These data, combined with bulk rock major and trace elements [26], have been used to reveal the source lithology, mantle potential temperature, and primary melt compositions and magmatic processes of late Cenozoic basalts from Thailand. This study provides strong evidence for the Hainan plume affecting post-spreading volcanic activities in Thailand (Indochina block).

2. Geological Setting and Sample Description

Thailand, and its adjacent regions, can be divided into three tectonostratigraphic units: The West Sibumasu Block (Sino–Burma–Malaya–Sumatra), the middle Sukhothai Arc terrane, and the East Indochina Block, which are separated by two sutures [30,31] (Figure 1). One of sutures is the Chiangmai–Chanthaburi Suture, which consists of Middle Devonian to Middle Triassic radiolarian cherts and deep oceanic sediments [26], and the other one is the back-arc Nan-Uttaradit Sra Kaeo Suture, which is composed of a thin block of disaggregated ophiolites and melanges [26,27]. The Sibumasu Block, Indochina Block, and the SCS region were influenced by the Tethys tectonic regime during the late Paleozoic to early Mesozoic, and then by the Pacific Ocean tectonic regime during the late Mesozoic [26,30–32]. During the Cenozoic era (especially for the post SCS spreading period), widespread intraplate volcanism in the SCS also affected Thailand and its adjacent regions (Figure 1). Furthermore, two Cenozoic strike-slip faults (Mae Ping fault and Three Pagodas fault) pass through the Western part of Thailand [26] (Figure 1).
Late Cenozoic (0.4–11 Ma) basaltic rocks of Thailand are mainly distributed in the Khorat Plateau and the Northern part of the Sukhothai Arc terrane [23,25,26,32]. We collected 14 samples from the 11 basaltic flows of Cenozoic lavas in the Khorat Plateau and the Northern part of the Sukhothai Arc terrane (Figure 1). All basaltic rock samples showed porphyritic textures and contained olivine, clinopyroxene, plagioclase phenocrysts, and some microlites (olivines, clinopyroxenes, and plagioclases) in the groundmass, and these microlites were less than 0.2 mm in size. The phenocryst content was 5–20%, and the olivine content was 30–70% from total phenocrysts. The grain size of olivine phenocrysts mostly varied from 0.4 to 1.2 mm, even to 2 mm (sample SP-2), the shape of which was idiomorphic and hypidiomorphic, and some of which were transformed to iddingsite. The grain size of plagioclase phenocrysts ranged from 0.02 × 0.20 mm^2 to 1.30 mm^2, and most were present as polysynthetic twins. Clinopyroxene phenocrysts had grain sizes of 0.5–1.1 mm, and clinopyroxene phenocrysts of sample CHC-1 had a ring structure.

3. Methods and Results

3.1. Methods

The major elements were analyzed by the JXA-8230 Electron Microprobe Analyzer (EMPA) in Key Laboratory of Marine Sedimentology and Environmental Geology, First Institute of Oceanography, SOA (Qingdao, China). The working conditions of the instrument were as follows: The acceleration voltage was 15 kV, the electron beam current was about 2 × 10^{-8} A, the electron beam spot was 1 μm, and the quantitative detection limit was about 100 ppm. The standards used in these analyses were albite for Na and Si; orthoclase for K; diopside for Ca; olivine for Mg; haematite for Fe; garnet for Al; chromium oxide for Cr; rutile for Ti; rhodonite for Mn; and nickel silicide for Ni. The analytical results were corrected by the ZAF method (Z, A, and F represent atomic number, atomic weight, and electron density of elements, respectively). The accuracy of the analysis was ±1%.
results were corrected by the ZAF method (Z, A, and F represent atomic number, absorption, and fluorescence, respectively). The precision of major element (SiO$_2$, Al$_2$O$_3$, and CaO) analyses was better than 1%, and that of the minor element (Na$_2$O, K$_2$O, TiO$_2$, P$_2$O$_5$, MnO, Cr$_2$O$_3$, and MgO) analyses was better than 5%. During performing the EMPA analysis, backscattering electron (BSE) images for typical minerals were also obtained (Figure 2). The data were processed with the geochemical software tool “Geokit” [34].

In situ analysis of trace elements of minerals hosted by late Cenozoic basaltic rocks from Thailand were conducted at Beijing Createch Testing International Co. Ltd (Beijing, China). Laser sampling was performed using an ESI NWR 193 nm excimer laser ablation system. An Analytik Jena Plasma Quant MS instrument was used to acquire ion-signal intensities. The spot diameter of laser beam was 35 µm and the ablation frequency was 10 Hz. Helium was applied as a carrier gas. Each spot analysis incorporated an approximately 20 s background acquisition from the sample. Element contents were calibrated against multiple reference materials (NIST SRM612 and NIST SRM610). Data calibration using suitable internal standard depended on different samples by Glitter (Si was the internal standard for this experiment). The analysis of most of the elements had an accuracy of less than 5% and a precision greater than 10%.

Figure 2. The typical backscattered electron (BSE) images of olivine, clinopyroxene, and plagioclase phenocrysts. (a) Olivine phenocryst of sample KHK-1; (b) plagioclase phenocryst of sample PF-1; (c) olivine phenocryst of sample WCB-1; and (d) clinopyroxene phenocryst of sample CHC-1. The yellow circles are the analysis points of sample CHC-1.
3.2. Results

3.2.1. Olivine

The analytical results of olivines in late Cenozoic basaltic rocks from Thailand are reported in Supplementary Table S1. The olivines had forsterite contents between 60.12% and 84.74%. In the sample of SP-2 from Sukhothai Arc terrane, the Fo content of olivines ranged from 80.87 to 84.60 wt. % (Supplementary Table S1), exhibiting no obvious variations from core to rim of the phenocrysts. In the Khorat Plateau, the Fo contents of olivine phenocrysts and microlites ranged from 60.12% to 84.74% and 66.71% to 73.02%, respectively (Supplementary Table S1). In general, the FeO, MnO, and CaO increased, and NiO decreased, with decreasing Fo content. In some basaltic rock samples (WCB-1, SP-2, and PHN-1), the Fo content of olivine microlites was significantly lower than that of the phenocrysts rim, while that of the other samples was similar to that of the phenocrysts edge. Except for sample MATA-1, some oxides (such as TiO$_2$, FeO, MnO, and CaO) of olivine phenocrysts in other samples in this study showed no obvious variations from core to rim of the phenocrysts (Supplementary Table S1), suggesting that the chemical compositions of the olivine phenocrysts are relatively uniform.

The CaO contents in olivine ranged from 0.19 to 0.42 wt. %, which is within the range of basaltic phenocrysts (>0.1%) but much higher than mantle peridotite xenoliths (<0.1%) [35]. The grain size of olivines was relatively small and showed no reaction rims, or deformation structures common to olivine xenocrysts, indicating that the olivine phenocrysts of this study were magmatic in origin [36]. In addition, NiO decreased with the decreasing Fo content, which differed from the mantle olivine array [35,37,38] (Figure 3). However, the olivines of one phenocryst from sample WCB-3 (analytical No. WCB-3-4-1 to WCB-3-4-3) had a low CaO content (<0.1%) and relative high Fo content (88.97–90.90), and a large grain size (1.0–1.6 mm), which suggests that they were probably derived from disaggregated xenoliths [39] (Figure 3, Supplementary Table S1).

![Figure 3](image_url)

**Figure 3.** (a,b) Variations in the composition of olivine phenocrysts. WCB-3# represent the xenocrystic olivine in sample WCB-3. The dashed line that separates magmatic and xenocrystic olivines on the basis of CaO in (a) is from Thompson and Gibson [35]. The field “common olivines” outlines the compositional range of olivines from peridotite xenoliths, orogenic massifs and ophiolites, oceanic abyssal basalt, and mid-ocean ridge basalt (MORB) [37]. In contrast, “Hawaiian tholeiite olivines” denotes the range of olivines from Hawaiian tholeiite basalts [37]. The fractional crystallization is from Sato [38]. “Hainan basalt olivines” is based on Wang et al. [18] and “Vietnam basalt olivines” is based on An et al. [25].

In sample MATA-1, the Fo content of olivine microlite was significantly lower than that of the phenocryst rim. The oxides (such as TiO$_2$, FeO, MnO, and CaO) of olivine phenocryst in sample MATA-1 showed obvious variations from core to rim of the phenocryst. The olivine of sample MATA-1 had relative high Mg# (core: 90.79–92.15, rim: 83.41), CaO content (core: 0.08, rim: 0.32), and NiO content (core: 0.31–0.34, rim: 0.11), indicating the core of olivine was xenocryst from the mantle rock...
and the rim of olivine could simply form over a few years prior to eruption due to magma chamber process (Figure 3).

3.2.2. Clinopyroxene

Major Element Composition

The analytical results of pyroxenes are reported in Supplementary Table S2. Pyroxenes are augite and diopside [40] (Figure 4a). The content of SiO$_2$ in clinopyroxene changed considerably, ranging from 44.83 to 51.55 wt. %. Some chemical differences between phenocrysts and microlites were identified in this study. For example, in general, the SiO$_2$ and MgO contents of the clinopyroxene microlites in the groundmass were lower than those of the phenocryst, whereas the TiO$_2$, FeO, and Na$_2$O contents of the former were higher than those of the latter, indicating that the evolution of magma enriched Fe and Ti. The Al$_2$O$_3$ contents (ranging from 1.43 to 7.03, with an average of 3.90) of clinopyroxene were low in all of the samples, suggesting that these clinopyroxenes were the result of low-pressure crystallization [9].

![Figure 4. (a) Wo-En-Fs diagram of pyroxenes [40], (b) The variation in the composition of clinopyroxene with concentric zoning of sample CHC-1. * refers to clinopyroxenes microlites. The five analysis points (yellow circle) are listed in Figure 2c.](image)

Clinopyroxene phenocrysts of sample CHC-1 (analytical No. CHC-1-1 to CHC-1-5) had an obvious concentric zoning. From Supplementary Table S2 and Figure 4b, we can see that MgO and Cr$_2$O$_3$ content increased, and FeO, TiO$_2$, Na$_2$O, and Al$_2$O$_3$ decreased, from core to rim, indicating that the core crystallized in relatively fractionated melts and the rim crystallized in response to introduction of more primitive (Mg and Cr rich) magma into the crystallization environment.

Yan et al. [26] presented the plots of Mg# versus other oxides, CaO/Al$_2$O$_3$ and trace elements (Sc, Cr), for basaltic rocks (host rock of these clinopyroxene), and suggested that parent magma derived from mantle source may undergo fractional crystallization of mafic minerals (e.g., olivine and clinopyroxens, etc.) en route to the surface. Figure 5 provides the compositional spectrum of clinopyroxenes. The clinopyroxenes were characterized by low Al$_2$O$_3$ contents (inferior to 7.03%). Na$_2$O, MnO, and TiO$_2$ did not systematically correlate with Mg#. Cr$_2$O$_3$ and Al$_2$O$_3$ contents correlated positively with Mg#. FeO contents correlated negatively with Mg#. The inverse FeO-Mg#Cpx trend, though self-correlated because of Mg# = 100 × Mg$^{2+}$/(Mg$^{2+}$ + Fe$^{2+}$), was purposely plotted to show data coherence [41]. The Cr$_2$O$_3$ contents of clinopyroxenes decreased with decreasing Mg#Cpx. Cr was highly compatible in clinopyroxene [41,42]. The decrease of CaO is owing to the fractionation of clinopyroxene, because clinopyroxene fractionation can reduce the CaO content in the residual
melt [18]. The Al₂O₃ and CaO contents decreased with decreasing Mg#Cpx at Mg#Cpx < 80, suggesting that plagioclase fractionation may began at Mg#Cpx = 80, because the crystallization of plagioclase would lower the Al₂O₃ and CaO contents of the melt dramatically [18]. Thus, this study, combined with previous studies [26,43], showed that the order of mineral crystallization of the late Cenozoic basalts of Thailand is as follows, olivine, clinopyroxene, plagioclase.

Figure 5. Chemical variations of clinopyroxenes phenocrysts. Data for northern Hainan basalts are from Wang et al. [18], and data for Vietnam are from Hoang et al. [43]. c-core; m-mantle; r- rim. The analyses of core–mantle–rim in a single phenocryst is linked by broken line. (a) Cr₂O₃ vs. Mg#; (b) Na₂O vs. Mg#; (c) TiO₂ vs. Mg#; (d) MnO vs. Mg#; (e) Al₂O₃ vs. Mg#; (f) CaO vs. Mg#; (g) SiO₂ vs. Mg#; (h) FeO vs. Mg#.
Trace Element Composition

Trace element concentrations of clinopyroxenes from late Cenozoic basalts from Thailand are listed in Supplementary Table S3. The total concentrations of rare earth elements (ΣREE) of clinopyroxenes ranged from 52 to 214 ppm, with an average of 84 ppm, which was slightly higher than that of clinopyroxenes from the contemporaneous lavas of other areas in the South China Sea region (with an average of 62 ppm) [6]. Except for one phenocryst from sample WCB-3 (analytical no. WCB-3-4-1 to WCB-3-4-6) (Supplementary Table S3), compared to clinopyroxenes from other areas in the SCS region [9,14], other clinopyroxenes (both phenocrysts and microlites) exhibited light rare earth element enrichment (LREE) with relatively high ratio of LREE/HREE (ranging from 2.51 to 4.73, with an average value of 3.28), LaN/YbN (ranging from 1.93 to 4.27, with an average value of 2.89), CeN/YbN (ranging from 2.43 to 5.04, with an average value of 3.88), and SmN/YbN (ranging from 2.81 to 7.38, with an average value of 5.27) (Figure 6, Supplementary Table S3). Furthermore, these clinopyroxenes had a relatively low ratio of LaN/NdN (ranging from 0.44–0.88, with an average value of 0.58) and LaN/SmN (ranging from 0.39–1.22, with an average value of 0.61). These clinopyroxenes from the sample of PHN-1 and PF-1 showed slightly negative Eu anomalies (Eu/Eu* = 0.81–0.88, with an average of 0.85) and no obvious Ce anomalies (Figure 6, Supplementary Table S3), indicating slight fractionation of plagioclase during the magma process. Note that one clinopyroxene phenocryst from sample WCB-3 (analytical no. WCB-3-4-1 to WCB-3-4-6) showed a relative flattened chondrite-normalized REE pattern (Figure 5a) and no obvious Eu and Ce anomalies, with constant ratio of LREE/HREE (ranging from 2.27 to 2.36, with an average value of 2.32) and LaN/YbN (ranging from 1.20 to 1.34, with an average value of 1.25), indicating the clinopyroxenes of WCB-3 may be not phenocrysts, but xenocrysts, which is consistent with the occurrence of olivine xenocrysts in the same sample, suggesting that mantle xenocrysts are entrained by sample WCB-3 during its ascent to the surface.

![Figure 6](image_url). (a) Chondrite-normalized rare earth element (REE) patterns for the clinopyroxenes from the late Cenozoic basaltic rocks of Thailand, (b) primitive mantle-normalized trace element diagram for clinopyroxenes from the late Cenozoic basaltic rocks of Thailand. Data for chondrite and primitive mantle are from Sun and McDonough [44]. * refers to clinopyroxenes microlites.
In primitive mantle-normalized trace element spider diagrams (Figure 6b), most samples were generally depleted in large-ion lithophile elements (LILEs) (such as Ba and Sr), indicating the fractionation of plagioclase during the magma process, because the Ba and Sr were mainly entered into K-rich and Ca-rich minerals in the form of isomorphism.

3.2.3. Plagioclase

Major Element Composition

The analytical results of plagioclases are reported in Supplementary Table S4. The plagioclase in this study were predominantly labradorite, with a few andesine and bytownite (Figure 7). The An value of plagioclase microlites from the Sukhothai Arc terrane ranged from 58.84 to 63.76 (Supplementary Table S4). In contrast, the An value of plagioclase phenocrysts from the Khorat Plateau ranged from 44.48 to 70.71, and the An value of plagioclase microlites in these lavas ranged from 40.27 to 60.56 (Supplementary Table S4). In addition, plagioclase phenocrysts in sample PHN-1 basalt had a typical concentric zoning, possibly representing the rapid cooling stage when magma erupts. In general, the high An value of the plagioclase in this study indicate that the plagioclase was formed in a rapidly upwelling magma environment [10].

Figure 7. Classification of plagioclase in terms of its composition. * refers to plagioclases microlites.

Trace Element Composition

Trace element concentrations of plagioclases are reported in Supplementary Table S5. In primitive mantle-normalized trace element spider diagrams and chondrite-normalized REE patterns (Figure 8a,b), all of the plagioclases were enriched in LREEs. Except for MATA-1, most of the plagioclase samples exhibited strong positive Eu anomalies (Figure 8a) and enrichment of Ba, Sr, and Pb (Figure 8b). However, the plagioclases of MATA-1 showed negative Eu anomalies and depletion of Ba and Sr. The plagioclase with negative Eu anomalies can form during the late stage of granitic magma [45], indicating the clinopyroxenes of MATA-1 may be not phenocrysts, but xenocrysts, which could have been trapped by sample MATA-1 during its ascent to the surface.
These basaltic rocks had low CaO contents, which are plotted within the pyroxenite-derived melt field in the CaO-MgO diagram (Figure 9a), which is similar to the case for contemporaneous basaltic rocks from Southern Vietnam [25,43]. Based on these experimental parameters [43,46–48], we used the whole-rock major element compositions [26] to deduce the nature of the source lithology of the Thailand late Cenozoic basaltic rocks (Table 1). The results are as follows. (1) These basaltic rocks had high Fe/Mn ratios (>60) that fall within the pyroxenite-derived melt field (Figure 9a), which is similar to the case for contemporaneous basaltic rocks from Southern Vietnam [25,43]. (2) The majority of these basaltic rocks had high FC3MS values (>0.5), which are plotted within the pyroxenite-derived melt field in the FC3MS-MgO diagram (Figure 9b), which is consistent with those contemporaneous basaltic rocks from Southern Vietnam and Hawaiian basalts [37,43]. (3) These basaltic rocks had low CaO contents, which are plotted within the pyroxenite-derived melt field in the CaO-MgO diagram (Figure 9c), which is similar to contemporaneous basaltic rocks from Southern Vietnam [43], and the olivine phenocrysts inherited this low-CaO signature. According to the above results, we assessed the presence of pyroxenite in these contemporaneous basaltic rocks from Southern Vietnam and Hawaiian basalts [37,43]. (3) Within the pyroxenite-derived melt field in the FC3MS-MgO diagram (Figure 9b), which is consistent with the case for contemporaneous basaltic rocks from Southern Vietnam [43].

4. Discussion

4.1. Nature of the Source Lithology

Traditional radiogenic isotopic studies (e.g., Sr-Nd-Pb-Hf) have shown that the mantle source of late Cenozoic basalt from the Indochina Block can be explained by a binary mixing model, one is an Indian MORB-like mantle, and the other is EM2, which may have originated from Hainan plume [6,22,25–27,29]. Previous authors have investigated the geochemical characteristics and petrogenesis of these basaltic rocks in past decades [23–27]. However, there is still in debate on the nature of the source lithology. Previous studies have proposed different rock types as pre-melting mantle source rocks, e.g., garnet pyroxenite, garnet peridotite, and recycled upper oceanic crust-derived eclogite/pyroxenite [18,25,26,43,46,47]. In recent decades, researchers have successfully used the Fe/Mn ratio, FC3MS parameter (FeO/CaO – 3 × MgO/SiO2), CaO content, Dy/Yb ratio, and Yb content to indicate the nature of the source lithology [18,25,26,43,46–48]. Based on these experimental parameters [43,46,47], we used the whole-rock major element compositions [26] to deduce the nature of the source lithology of the Thailand late Cenozoic basaltic rocks (Table 1). Data for chondrite and primitive mantle are from Sun and McDonough [44].

![Figure 8](https://example.com/image8.png)

Figure 8. (a) Chondrite-normalized REE patterns for the plagioclases from the late Cenozoic basaltic rocks of Thailand, (b) Primitive mantle-normalized trace element spider diagram for plagioclases from the late Cenozoic basaltic rocks of Thailand. Data for chondrite and primitive mantle are from Sun and McDonough [44].
results, we assessed the presence of pyroxenite in the mantle source of Thailand basalts. The basaltic rocks of this study had high Dy/Yb ratio and relatively low Yb content [26], indicating that the basalts were derived from a garnet-bearing mantle source. In addition, the effective melting pressure and melting temperature based on the primary melts were $P_f = 22.3–27.4$ kbar and $T = 1425–1442$ °C (Table 1), which is in accordance with the transition of source lithology from spinel to garnet lherzolite [49]. This suggests that the basaltic rocks in this study were derived from a garnet-bearing mantle source.

Figure 9. (a) MnO vs. Fe/Mn, (b) MgO vs. FeO$_T$/CaO - 3 × MgO/SiO$_2$, (c) MgO vs. CaO values for Thailand late Cenozoic basaltic rocks (MgO content > 6 wt. %). The fields showing experimental melts in (a) are modified from Liu et al. [46]. Data for Northern Hainan basalts are from Wang et al. [18], and data for Vietnam are from Hoang et al. [43]. The fields showing experimental melts in (b) are modified from Liu et al. [46]. Data for Vietnam are from Hoang et al. [43]. The thick green line in (c) separates peridotite- and pyroxenite-sourced primary melts [48]. The dashed orange arrow in (c) indicates the typical liquid line of descent (LLD) for primary magmas that crystallize gabbro in the crust [48]. Data for this study region are from Yan et al. [26].
Bulk rock trace element concentrations of host rocks can also provide some invaluable information on the source lithology. Experimental petrology shows that the concentration of a trace element in melt $C_L$ is related to its concentration in the source mantle $C_0$ by the expression. $C_L/C_0 = 1/[F + D_{RS}(1 - F)]$, where $F$ is the degree of melting and $D_{RS}$ is the bulk distribution coefficient of the residual solids [50,51]. Here, we assumed that the source is similar to the primitive mantle as defined by Sun and McDonough [43]. Thus, $La_N$, $Sm_N$, $Yb_N$ represent $C_L/C_0$ of La, Sm, Yb, respectively. The expression can be changed into $(La/Sm)_N = [F + D_{Sm}(1-F)]/[F + D_{La}(1-F)]$ and $(La/Yb)_N = [F + D_{Yb}(1-F)]/[F + D_{La}(1-F)]$ [50,51]. Where $D_{La}$, $D_{Sm}$, $D_{Yb}$ are bulk distribution coefficients of the residual solids of La, Sm, Yb. Trace element mineral/melt partition coefficients are from Kelemen et al. [52].

The calculated results are shown in Supplementary Table S6. The $(La/Yb)_N$ in basaltic rocks of this study range from 9.05 to 25.35 [26], indicating the basalts were derived from a garnet-bearing mantle source. The $(La/Sm)_N$ in basaltic rocks of this study range from 1.85 to 3.79, suggesting the basalts may have been produced by the degree of melting ranging from 5%–20% of garnet pyroxenite, which is similar to the results of Vietnam and Hainan [18,25]. Thus, bulk rock major- and trace element compositions give a consistent result for the source lithology of late Cenozoic basaltic rocks from Thailand, garnet pyroxenite.

### 4.2. Primary Melt Compositions and the Mantle Potential Temperature

Primary melt compositions have been widely used to estimate the thermal state of mantle sources [25,53–58]. The major element data of the late Cenozoic basalts from Thailand have been provided in Yan et al. [26]. The correlation of MgO and CaO contents suggests that the effect of clinopyroxene fractionation in the Thailand basalts likely took place at MgO contents <8 wt. %.

Therefore, to minimize the influence of clinopyroxene fractionation, only samples with MgO contents >8 wt. % were chosen as the starting composition. The primary melt compositions for the Thailand basalts were estimated (Table 1) by adding small (0.1%) increments of olivine ($Fo = 90.1$) to samples with MgO contents <8 wt. %, supposing the olivine-melt distribution coefficient $K_{Oliq}$ ($Fe/Mg)Oliq = 0.31$, $Fe^{2+}/(Fe^{2+} + Fe^{3+}) = 0.9$ in the melt (Roder and Emslie, 1970). Melting conditions and mantle potential temperatures ($T_p$; Table 1) were estimated based on primary melt compositions [18,25,55–61].

The effective melting pressure ($P_f$) and melting temperature ($T$) based on the primary melts were $P_f = 22.3–27.4$ kbar (average value = 23.9 kbar) and $T = 1425–1442$ °C (average value = 1430 °C), which are similar to ranges characteristic of Southern Vietnam ($P_f = 29.6–32.8$ kbar, $T = 1470–1480$ °C) and Northern Hainan basalts ($P_f = 18–32$ kbar, $T = 1420–1530$ °C) (Table 1) [18,25]. The mantle potential temperature beneath Thailand varies from 1448 to 1467 °C, which is slightly lower than Southern Vietnam (1468–1490 °C) and north of Hainan Island (1500–1580 °C) (Table 1), indicating that the mantle source of Thailand basaltic rocks, similar to those of Southern Vietnam and Northern Hainan, is related to the Hainan mantle plume [18,25]. The slightly lower $T_p$ of late Cenozoic basaltic rocks from Thailand than those from northern Hainan Island and southern Vietnam may reflect that some energy is consumed when the mantle plume material flows along the lithosphere rheology boundary layer westward to farther Thailand region (relative to Vietnam and Hainan). Specifically, the $T_p$ of northern Hainan Island, near the center of mantle plume, was higher than that of the Indochina Peninsula, which is more distant from the center of the mantle plume.
Table 1. Estimated primary melt compositions, mantle potential temperatures and melting conditions for representative samples of late Cenozoic basaltic rocks from Thailand. H₂O content in primary melt was estimated by fractionation correction of Ce. F (degree of melting) was estimated by Equation (A2) of Putirka et al. [56]. P₁ to P₃ are effective melting pressures in kbar. P₂ is defined by Haase [54]; P₃ is the average of P₁ to P₂. T₁ to T₃ are the melting temperatures (°C) of the melt segregation. T₁ is according to Herzberg et al. [57]; T₂ is according to Putirka [59]; T₃ is the average of T₁ to T₂. T₁ to T₄ are the mantle potential temperature in °C. T₁ to T₄ were estimated using the MgO contents in the primary melts following Herzberg et al. [57]; T₂ to T₄ were estimated following Herzberg et al. [60]; T₅ was estimated following Putirka [61]; T₆ is the average of T₅ to T₆. SD, standard deviation. Data for Northern Hainan basalts are from Wang et al. [18], and data for Vietnam are from An et al. [25].

<table>
<thead>
<tr>
<th>Starting Sample</th>
<th>WCB-1</th>
<th>WCB-2</th>
<th>WCB-3</th>
<th>MATA-2</th>
<th>Southern Vietnam</th>
<th>Northern Hainan</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rock type</td>
<td>Trachybasalt</td>
<td>Trachybasalt</td>
<td>Trachybasalt</td>
<td>Basanite</td>
<td>Basanite</td>
<td></td>
</tr>
<tr>
<td>Olivine add (%)</td>
<td>15</td>
<td>15</td>
<td>17</td>
<td>16</td>
<td>13–15</td>
<td>18–25</td>
</tr>
<tr>
<td>SiO₂</td>
<td>47.3</td>
<td>47.1</td>
<td>47.3</td>
<td>45.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.7</td>
<td>1.7</td>
<td>1.7</td>
<td>1.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>13.2</td>
<td>13.8</td>
<td>13.3</td>
<td>12.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.8</td>
<td>0.9</td>
<td>0.8</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeO</td>
<td>8.8</td>
<td>8.7</td>
<td>8.6</td>
<td>9.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>15.5</td>
<td>15.2</td>
<td>15.9</td>
<td>15.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>7.5</td>
<td>7.3</td>
<td>7.4</td>
<td>7.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂O</td>
<td>2.8</td>
<td>2.9</td>
<td>2.5</td>
<td>3.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>1.9</td>
<td>2.0</td>
<td>1.9</td>
<td>2.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiO</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.4</td>
<td>1.0</td>
<td>1.0</td>
<td>1.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F (%)</td>
<td>13.0</td>
<td>12.4</td>
<td>15.5</td>
<td>7.1</td>
<td>4–7</td>
<td>14–19</td>
</tr>
<tr>
<td>P₁</td>
<td>24.8</td>
<td>25.9</td>
<td>25.0</td>
<td>30.9</td>
<td>33.6–36.6</td>
<td>17.2–33.7</td>
</tr>
<tr>
<td>P₂</td>
<td>19.8</td>
<td>20.5</td>
<td>20.7</td>
<td>23.9</td>
<td>27.5–30.4</td>
<td>15.6–30.2</td>
</tr>
<tr>
<td>P₃</td>
<td>22.3</td>
<td>23.2</td>
<td>22.9</td>
<td>27.4</td>
<td>29.7–32.8</td>
<td>17.8–31.6</td>
</tr>
<tr>
<td>SD</td>
<td>2.5</td>
<td>2.7</td>
<td>2.1</td>
<td>3.5</td>
<td>3–4</td>
<td>1.5–3.6</td>
</tr>
<tr>
<td>T₁</td>
<td>1457</td>
<td>1457</td>
<td>1471</td>
<td>1464</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T₂</td>
<td>1396</td>
<td>1394</td>
<td>1412</td>
<td>1391</td>
<td>1444–1459</td>
<td>1429–1514</td>
</tr>
<tr>
<td>T₃</td>
<td>1426</td>
<td>1425</td>
<td>1442</td>
<td>1427</td>
<td>1463–1480</td>
<td>1420–1529</td>
</tr>
<tr>
<td>SD</td>
<td>30</td>
<td>31</td>
<td>30</td>
<td>36</td>
<td>16–22</td>
<td>3–34</td>
</tr>
<tr>
<td>T₁</td>
<td>1466</td>
<td>1464</td>
<td>1481</td>
<td>1461</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T₂</td>
<td>1442</td>
<td>1440</td>
<td>1458</td>
<td>1437</td>
<td>1469–1482</td>
<td>1454–1536</td>
</tr>
<tr>
<td>T₃</td>
<td>1447</td>
<td>1443</td>
<td>1462</td>
<td>1445</td>
<td>1458–1496</td>
<td>1413–1611</td>
</tr>
<tr>
<td>T₄</td>
<td>1452</td>
<td>1449</td>
<td>1467</td>
<td>1448</td>
<td>1468–1490</td>
<td>1468–1561</td>
</tr>
<tr>
<td>SD</td>
<td>10</td>
<td>11</td>
<td>10</td>
<td>10</td>
<td>1–9</td>
<td>25–55</td>
</tr>
</tbody>
</table>

4.3. Physical Conditions of Crystallization

4.3.1. Crystallization Pressure and Temperature of Clinopyroxenes

In recent decades, many researchers have proposed various thermobarometers for calculating crystallization pressures and temperatures of clinopyroxene formation [59,62–64]. Putirka et al. [62] established a series of thermodynamic equations based on experimental work that relates temperature and pressure to equilibrium constants and allows for the construction of clinopyroxene-liquid thermobarometers. However, the thermobarometers were only applied to the basaltic magma temperature and pressure calculation, with an application range of 1110–1475 °C and 0.4–0.9 GPa. Putirka et al. [59] experimentally re-calibrated the thermobarometers and established a new equilibrium temperature and pressure formula that can be applied to mafic magma and intermediate-acid magma. In this study we used the Putirka [59] equation to calculate the crystallization pressures and temperatures of clinopyroxenes (Table 2) [59]. The calculated results showed that temperature and pressure ranges were 1145–1214 °C (average value = 1190 °C) and 0.4–0.9 GPa (average value = 0.7 GPa), respectively, which is similar to the SCS basin (1095–1261 °C, 0.4–1.5 GPa) and Northern Hainan Island (1100–1250 °C, 0.7–1.5 GPa) (Table 2) [9,18]. Based on the calculated pressures, the depth of magma chambers of late
Cenozoic basaltic rocks (including basanite, basalt, trachybasalt, and basaltic trachyandesite) calculated from equilibrium temperatures and pressures between clinopyroxene and melt can be inferred to 11 to 26 km, which is in the middle and upper part of the continental crust.

4.3.2. Crystallization Pressure and Temperature of Plagioclase

Kudo and Weill [65] proposed the first plagioclase-liquid geothermometer. Subsequently, many workers proposed various thermobarometers for calculating crystallization pressures and temperatures of plagioclase formation. In this study, we used the methods from Kudo and Weill and Putirka [59,65] to calculate the crystallization pressures and temperatures of plagioclase (Table 2). It was found that the crystallization temperature based on the Kudo and Weill [65] geothermometer was similar to the temperature determined based on the Putirka [59] thermobarometer. However, since the geothermometer of Kudo and Weill [62] does not consider whether the melt and plagioclase reached equilibrium and the effect of water on the plagioclase crystallization, we adopted the pressure and temperature calculations based on Putirka [59].

Table 2. Crystallization temperatures and pressures of the clinopyroxenes and plagioclases in late Cenozoic basaltic rocks from Thailand and surrounding regions. The crystallization temperature and pressure of the clinopyroxenes and plagioclases were estimated following Putirka [59].

<table>
<thead>
<tr>
<th>Regions</th>
<th>Clinopyroxene</th>
<th>Plagioclase</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T (°C)</td>
<td>P (Gpa)</td>
<td>T (°C)</td>
</tr>
<tr>
<td>Thailand</td>
<td>1145–1214</td>
<td>0.4–0.9</td>
<td>1067–1133</td>
</tr>
<tr>
<td>Hainan Island</td>
<td>1100–1250</td>
<td>0.7–1.5</td>
<td>-</td>
</tr>
<tr>
<td>South China Sea basin</td>
<td>1095–1261</td>
<td>0.4–1.5</td>
<td>927–1179</td>
</tr>
<tr>
<td>Okinawa trough</td>
<td>-</td>
<td>-</td>
<td>1012–1280</td>
</tr>
</tbody>
</table>

The crystallization pressures and temperatures of plagioclase from the Thailand basalts were 0.3–0.9 GPa (average value = 0.6 GPa) and 1067–1133 °C (average value = 1095 °C) (Table 2), which can be comparable to those for the SCS regions (927–1179 °C), and the Okinawa trough (1012–1280 °C) (Table 2) [10,66].

4.4. Tectonic Implications

The tectonic setting for late Cenozoic basaltic rocks in the Indochina block is still not clear, and they may be related to plate tectonics processes [22,23], or to the mantle plume [25,26]. Major- and trace element compositions of clinopyroxene can provide some information for tectonic setting of host rock. Base on clinopyroxene compositions [67–69], Aparicio [67] developed Na-Fe-Mn triangular diagram to distinguish the tectonic setting of the host rock, and Nisbet and Pearce [70] developed TiO₂-Na₂O-MnO triangular diagram to determine the tectonic setting of the host rock. In Figure 10a, all samples are plotted in the within-plate volcanism field, indicating that these basaltic rocks in this study were formed in an intraplate tectonic setting. In addition, there were obvious distinctions between the clinopyroxene samples with high Mg# and low Mg#, and this may have been caused by fractionation or the contamination process. In the TiO₂-Na₂O-MnO triangular diagram, all clinopyroxenes are also plotted in the field of WPA (Figure 10b), suggesting that the host rock of these clinopyroxenes could be within-plate basalts. In addition, the clinopyroxenes in this study belong to Ca-Mg-Fe series, which are beneficial to the isomorphism of REE, owing to REE existing mainly in the form of isomorphism in clinopyroxene [71]. We used the clinopyroxene/melt partition coefficient [49] and REE contents (measured in this study) of clinopyroxenes in late Cenozoic basaltic rocks in Thailand to calculate the hypothetical parental melt (shown on Figure 11), which were similar to the host rock of the clinopyroxenes [26] (Figure 11), with typical feature of intraplate OIB [52].
Recent geophysical and geochemical studies have shown that there is a mantle plume beneath Hainan Island [6,9,72,73]. Seismic tomographic studies have also shown that there is a sub-vertical low-velocity column, extending from shallow depths to the 660 km discontinuity, and even reaching 1300 km depth beneath Hainan Island and the SCS [72,74,75]. Due to the existence of the Hainan mantle plume, the alkaline volcanic rocks of the Indochina Peninsula and the SCS exhibit OIB-like characteristics, with high potential mantle temperature [6,18,25]. In this study, the volcanic rocks were composed of basanite, basalt, trachybasalt, and basaltic trachyandesite, and trace element patterns of these rocks showed typical OIB-like characteristics [26]. These, together with high $T_p$ and the nature of the source lithology (garnet pyroxenite), indicate that the mantle beneath Thailand has been affected by the mantle plume.
5. Conclusions

(1) The order of mineral crystallization of the late Cenozoic basalts of Thailand was olivine, clinopyroxene, plagioclase, which is consistent with that of typical OIB. The source lithology of the Thailand basaltic rocks could be garnet pyroxenite.

(2) The clinopyroxene discrimination diagrams exhibited that the parental-magma formed in an intraplate tectonic setting environment.

(3) The crystallization pressure and temperature of clinopyroxenes in late Cenozoic basalts in Thailand ranged from 0.4–0.9 GPa and 1145–1214 °C, similar to those of the SCS basin and northern Hainan Island. The crystallization pressure and temperatures of plagioclase ranged from 0.3–0.9 Gpa and 1067 °C to 1133 °C, which is similar to those for the SCS. The above characteristics showed that parental magmas of late Cenozoic basaltic rocks from Thailand had experienced multiphase crystallization and fractionation during its ascent to the surface. Moreover, the plagioclase had a high An content, suggesting that it was produced during the rapid upwelling of magma.

(4) The effective melting pressure and melting temperature based on the primary melts were 22.3–27.4 kbar and 1425–1442 °C, respectively, which was similar to the northern Hainan Island and the Southern Vietnam. The mantle potential temperature beneath Thailand is in the range 1448–1467 °C, slightly lower than north of Hainan Island and Southern Vietnam.

(5) This study provides some additional important evidence (e.g., magmatic processes, mantle potential temperatures) for the Hainan mantle plume affecting Thailand and other areas in the Indochina block (e.g., Vietnam).

Supplementary Materials: The following are available online at http://www.mdpi.com/2075-163X/9/7/446/s1, Table S1 Electron probe analyses (wt. %) of olivines in basalt from the Thailand. Table S2 Electron probe analyses (wt. %) of clinopyroxene in basalt from the Thailand. Table S3 LA-ICP-MS analysis (ppm) of clinopyroxene in basalt from the Thailand. Table S4 Electron probe analyses (wt. %) of plagioclase in basalt from the Thailand. Table S5 LA-ICP-MS analysis (ppm) of plagioclase in basalt from the Thailand. Table S6 Estimated (La/Sm)N and (La/Yb)N through partial melting of primitive mantle.

Author Contributions: L.Y., Q.Y., and X.S. conceived the experiments; L.Y., Q.Y., H.Z., and X.L., conducted experiments; L.Y., Q.Y., and X.S., wrote the manuscript. All authors analyzed data, contributed to interpretive aspects and reviewed the manuscript.

Funding: This research was funded by the National Programme on Global Change and Air-Sea Interaction (No. GASI-GEOGE-02), Basic Scientific Fund for National Public Research Institutes of China (2016S01), the Scientific and Technological Innovation Project Financially Supported by Qingdao National Laboratory for Marine Science and Technology (No. 2016ASKJ05), the National Natural Science Foundations of China (grants Nos. 41776070, U1606401, 41230960, 41322036), AoShan Talents Program Supported by Qingdao National Laboratory for Marine Science and Technology (No. 2015ASTP-ES16) and Taishan Scholarship from Shandong Province.

Acknowledgments: We thank Igor Ashchepkov and two anonymous reviewers for their constructive comments and suggestions. We thank LetPub (www.letpub.com) for its linguistic assistance during the preparation of this manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

References


38. Sato, H. Nickel content of basaltic magmas: Identification of primary magmas and a measure of the degree of olivine fractionation. *Lithos* 1977, 10, 113–120. [CrossRef]


64. Ashchepkov, I.; Ntaflos, T.; Logvinova, A.; Spetsius, Z.; Downes, H.; Vladykin, N.; Ashchepkov, I. Monomineral universal clinopyroxene and garnet barometers for peridotitic, eclogitic and basaltic systems. Geosci. Front. 2017, 8, 775–795. [CrossRef]


© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).