Contamination of heterogeneous lower crust in Hannuoba tholeiite: evidence from in situ trace elements and strontium isotopes of plagioclase

Yu-Tong Su1,2,3  Zong-Feng Yang1,2,4  Shuang-Yan Guo1  Pei-Pei Li1,2,4

1 School of Earth Sciences and Resources, China University of Geosciences, Beijing, 100083, China

2 State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Beijing, 100083, China

3 Now at School of Earth and Space Sciences, Peking University, Beijing, 100871, China

4 Research Center of Genetic Mineralogy, China University of Geosciences, Beijing, 100083, China

Abstract

The Hannuoba basalt, located in the northern margin of the North China Craton, is a typical intracontinental basalt with ocean island basalt-like geochemical features and has been extensively studied. However, its origin and deep processes, such as magma mixing and crystallization conditions, are still unclear. To further understand the mechanisms leading to the compositional heterogeneity and magmatic processes of Hannuoba basalt at crustal and/or mantle depth, in-situ major element, trace element, and \(^{87}\text{Sr}/^{86}\text{Sr}\) compositional heterogeneity of four representative plagioclase crystals in three Hannuoba tholeiite samples, as well as whole-rock major and trace elements data, are reported. According to the petrographic characteristics, the basalts
are divided into fine-grained and coarse-grained groups. The anorthite content in plagioclase of samples varies in a small range (56-64%), but the content of trace elements in plagioclase from the coarse-grained samples is generally higher than that of the fine-grained samples. Clinopyroxene-melt equilibrium thermobarometer and plagioclase-clinopyroxene magnesium and rare earth element exchange thermometer show that the magma for the two types of basalt was stored and crystallized at a similar depth, and crystallized within a 20 °C (fine-grained basalt) and 50°C (coarse-grained basalt) temperature window, which may be a reason for the grain size differences between the two types of basalts. We found that $^{87}\text{Sr}/^{86}\text{Sr}$ of all the studied plagioclase crystals varied from 0.70333 ± 0.00018 (2SE) to 0.70556 ± 0.00031 (2SE), a much large range than the whole rock of Hannuoba basalts reported previously and consistent with that of Cenozoic basalts in North China. Therefore, at least two kinds of melts with significant differences in isotope and minor heterogeneity in major and trace elements are injected into each magma plumbing system. The content of trace elements in the Hanuoba tholeiite is between the Hanuoba alkaline basalt and the lower crust, which can be explained by the mixing of the alkaline basalt and the lower crust, but the low $^{87}\text{Sr}/^{86}\text{Sr}$ (<0.704) characteristics of plagioclase cannot come from alkaline basalt, because trace element in the plagioclase is not in equilibrium with the alkaline basalt. Therefore, we believe that the compositional heterogeneity of Hannuoba tholeiitic basalt is mainly caused by the mixing of heterogeneous lower crust rather than different mantle-derived melts, which indicates the contribution of the continental lower crust to the continental basalt is more complicated than
previously recognized.

**Keywords**: Basalt, plagioclase, strontium isotope, magmatic process, lower continental crust, Hannuoba

---

**Introduction**

A large number of studies show that the lower continental crust plays an important role in the geochemical diversity of continental basalts (Glazner et al., 1991; Jiang and Zhi, 2010; Liu et al., 2008b; Lustrino, 2005; Xu et al., 2017; Zeng et al., 2011). Many studies suggest that the signals of the lower continental crust imply that it is a source of material for basalt through the recycling of crustal materials. (Liu et al., 2008b; Xu et al., 2017; Zeng et al., 2011). Others, however have suggested that the contamination of the lower continental crust during the ascent of basaltic magma may be an important reason for the compositional diversity of continental basalts, but this contamination is usually very difficult to identify (Glazner and Farmer, 1992; Glazner et al., 1991; Jiang and Zhi, 2010) because the lower continental crust is mainly composed of mafic rocks with heterogeneous compositions (Rudnick and Fountain, 1995). Moreover, the heterogeneity becomes more significant through partial melting of the lower crust, crystallization differentiation, and mixing various mantle-derived magmas.
Hannuoba basalt is a typical continental ocean island type basalt in that its rock types, petrography, and geochemistry have significant diversity. Although there is a long history of research, there is still controversy about how the lower continental crust affects the diversity of Hannuoba basalts (Basu et al., 1991; Guo et al., 2016; Jiang and Zhi, 2010; Liu et al., 1994; Qian et al., 2015; Song et al., 1990; Xu et al., 2017; Yang et al., 2016; Zhi et al., 1990). The systematic whole rock data of major and trace elements, as well as Sr, Nd, and Pb isotopes, seem to indicate that the ancient lithospheric mantle (Basu et al., 1991; Liu et al., 1994; Song et al., 1990) or recycled ancient oceanic crust and sediments (Qian et al., 2015; Xu et al., 2017) may be the source of Enrich Mantle I (EMI) end components in Hannuoba tholeiite. However, recent Os isotopic data show that the very high Os isotopic ratios, especially tholeiites, can only be explained by significant crustal contamination (Jiang and Zhi, 2010) rather than recycled products of the lower continental crust (Liu et al., 2008b). However, the details of crustal contamination are still unclear. One of the critical reasons may be that previous studies usually focus on the geochemical characteristics of the whole rock scale. The complex processes of crustal contamination and magmatic mixing are more commonly recorded in mineral growth zoning, but whole-rock compositions that average the signals of various minerals and glasses will weaken or eliminate the information recorded in minerals. Recent studies on melt inclusions in olivine have shown that melt inclusions with very heterogeneous isotopes but relatively homogeneous major and trace elements contribute to Hannuoba tholeiite (Qian et al., 2015). However, these melt inclusions probably only record a
particular crystallization stage in the magma evolutionary history, and it may be
homogenized during the crystallization process. This suggests that more diverse
materials may be involved in the Hannuoba basalt magmatic system.

Plagioclase is an ideal material for strontium isotope analysis because of its high
strontium content and low rubidium content, and it is a widely existing rock-forming
mineral in igneous rocks. In the past few decades, with the development of analytical
techniques, a large number of studies have begun to use in-situ Sr isotopes of
plagioclase to reveal the complex evolutionary history of the magmatic system
(Davidson et al., 2001; Davidson and Tepley, 1997; Ramos et al., 2004; Ramos et al.,
2005; Tepley et al., 2000; Yan et al., 2020). Many researchers have found that the
strontium isotope heterogeneity of plagioclase is far more significant than that of
whole-rock scale (Edwards et al., 2019; Lange et al., 2013), and there is a significant
strontium isotopic disequilibria between phenocrysts and matrix, as well as within a
single grain, which is considered to be significant evidence of magma mixing,
contamination and contribution of multiple source materials (Davidson et al., 2001).

When the isotopic, minor, and trace elements data from the core to the rim of
plagioclase are combined with the geochemical characteristics of the whole rock, the
magma evolution history from crystal nucleation to eruption can be understood, and
the crustal contamination and mixing of different mantle-derived magmas can be
effectively distinguished, although some of the information might be lost due to the
dissolution of plagioclase (Ginibre and Davidson, 2014; Hagen-Peter et al., 2019;
Ramos and Reid, 2005).
In this study, the in-situ strontium isotope, major and trace elements of plagioclase, combined with the major and trace elements of the whole rock, are used to clarify or explain the contribution of the lower continental crust during the formation of Hannuoba tholeiite. We find that the range of strontium isotope recorded by plagioclase is much more extensive than that recorded by Hannuoba alkaline and tholeiitic whole-rock compositions, but it is consistent with the observed range Cenozoic basalts in the North China Craton. Although the mixing of the alkaline basalt and the lower crust can explain that the content of trace elements in the Hannuoba tholeiite is between the Hannuoba alkaline basalt and the lower crust, the low 87Sr/86Sr (<0.704) characteristics of plagioclase cannot come from alkaline basalt, because trace element in the plagioclase is not in equilibrium with alkaline basalt. Therefore, we believe that the compositional heterogeneity of Hannuoba tholeiitic basalt is caused by mixing heterogeneous lower crust rather than the mixing of different mantle-derived melts, which indicates the contribution of continental lower crust to continental basalt is more complicated than previously recognized.

Geological setting and samples

The North China Craton is one of the three largest cratons in China (Fig.1A), which has attracted international attention due to its relatively complete record of geological events from Archean to Cenozoic (Zhao et al., 2001). Cenozoic continental intraplate basalts with geochemical characteristics of oceanic island basalts are widely distributed in the North China Craton (Chu et al., 2017; Fan and Hooper, 1991; Yang...
The Hannuoba basaltic area, located 200 Km northwest of Beijing (Fig.1A), is an important occurrence because of its large area (> 1700 Km$^2$), compositional diversity in intercalated tholeiitic and alkaline lavas, and abundant mantle xenoliths in the alkaline basalts (Zhi et al., 1990). Previous studies suggest that Hannuoba volcanism was controlled by deep fractures and ranges in age from Miocene in the east to Pliocene in the west (Fig.1B) (Zhi et al., 1990). Geochemical analysis of whole-rock and olivine hosted melt inclusions has indicated that Hannuoba tholeiitic basalts have relatively homogeneous characteristics of major and trace elements but vary significantly in radiogenic isotopes compared with the alkaline basalt (Jiang and Zhi, 2010; Qian et al., 2015; Song et al., 1990). Source heterogeneity, magma mixing, high-pressure fractionation, and crustal contamination have been suggested to account for compositional diversity in Hannuoba basalts (Jiang and Zhi, 2010; Qian et al., 2015; Song et al., 1990; Yang et al., 2016; Zhi et al., 1990). Three tholeiitic basalts samples studied in this paper were collected from the eastern part because they are well exposed, and the stratigraphy is clear (Fig.1B). Their spatial relationship is shown in Fig. 1C. Samples SQB03 and JSB04 are collected from the lavas erupted before the eruption of alkaline basalt, and JSB12 is collected from relatively late lavas after the eruption of alkaline basalt. (Fig. 1C).
Analytical methods

Petrography and mineral major element analysis

Thin sections (30 µm thickness) were prepared from representative billets cut from the three samples, and optical and electrical microscopy was carried out on all thin sections to document petrographical features. High-resolution backscattered electron images were obtained at the Research Center of Genetic Mineralogy, China University of Geosciences (Beijing), using a field emission MIRA3 XMU scanning electron microscope. Electron-probe micro-analysis (EPMA) of individual plagioclase and clinopyroxene phenocrysts was carried out at Wuhan Sample Solution Analytical Technology Co., Ltd. using a JXA-8230 electron probe micro-analyzer (EPMA) under operating conditions of 20 nA, an accelerating voltage of 15 keV, and beam size of 1 µm in diameter for clinopyroxene and 3 µm for plagioclase. Peak and background counting times were 10 and 5 s for Si, Ca, Na, Al, Fe, and Mg, 20 and 10 s for Ti, Mn, Cr, K, Ni, and P. Analytical results were corrected using the ZAF correction routines. The standards used were SPI standard mineral and were analyzed as internal standards to monitor data quality. Analyses are accurate to 1–2% for major elements (>10 wt%) and 2–10% relative for minor elements (0.5–10% wt%). (Supplementary Tables 1, 2 and 3)

In-situ mineral trace element analysis

In situ trace element analyses of plagioclase and clinopyroxene were carried out using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) in the mineral laser microprobe analysis laboratory (Milma laboratory) of China.
University of Geosciences (Beijing). The Agilent 7900 ICP-MS instrument was coupled to a resonetic 193 nm excimer laser ablation system. Single spot ablation was adopted with a laser beam of 50 μm, and ablation frequency was 8 Hz. Helium gas was used as a carrier gas. The detailed parameter settings of the instrument and experimental process can be found in (Zhang et al., 2019). NIST610 was used as an external standard, while $^{43}$Ca was selected as the internal standard to correct the element composition. The Ca content in the samples is from the data obtained by EPMA. The precise value of Ca content in NIST 610 can be seen in (Jochum et al., 2011). The trace elements data were processed using the Iolite software based on the Igor platform (Paton et al., 2011). We analyzed the USGS reference glass BCR-2G as an unknown sample, and the results were within the error range of the recommended values (Supplementary Tables 4 and 5) which may be referred to (Jochum et al., 2005). The analytical uncertainty is better than 10% (relative).

**In-situ Sr isotope analysis**

In-situ Sr isotope measurements were performed on a Neptune Plus MC-ICP-MS (Thermo Fisher Scientific, Germany) in combination with a J-200 343 nm femtosecond laser ablation system (Applied Spectra, USA) housed at the National Research Center for Geoanalysis, Chinese Academy of Geological Sciences (CAGS), Beijing, China. The JET sample and X skimmer cones were used along with the guard electrode (GE), and all measurements were conducted under the low resolution and static mode. At the beginning of every analytical session, the fs-LA-ICP-MS system was optimized using NIST 612 to achieve maximum signal intensity and low oxide...
rates. Samples were ablated inline mode with a spot size of 30 μm, line length of 20 μm, stage movement speed of 0.65 μm/s, laser repetition rate of 8 Hz, and beam energy density of 1.5 J/cm². The instrumental mass bias for Sr isotopes was corrected using an exponential law function based on $^{86}\text{Sr}/^{88}\text{Sr}$ value of 0.1194. Correction of interferences of Kr isotopes on mass 84 and 86 was accomplished by background subtraction. The interferences of doubly charged ions of $^{168}\text{Er}^{2+}$ on $^{84}\text{Sr}$, $^{170}\text{Er}^{2+}$ and $^{170}\text{Yb}^{2+}$ on $^{85}\text{Rb}$, $^{172}\text{Yb}^{2+}$ on $^{86}\text{Sr}$, and $^{174}\text{Yb}^{2+}$ on $^{87}\text{Sr}$ were corrected based on the measured signal intensities of $^{167}\text{Er}^{2+}$ (m/z 83.5) and $^{173}\text{Yb}^{2+}$ (m/z 86.5) and the natural isotopic composition of Rb, Er and Yb (Li et al., 2018). The determined $^{87}\text{Sr}/^{86}\text{Sr}$ of Durango standard was 0.70675 ± 0.00012 (2SD, n = 9) (Supplementary Table 6), which is slightly higher than the results determined by previous studies with $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.70629 ± 0.00002 to 0.70638 ± 0.00013 (2SD, n = 8) (Yang et al., 2014) and references therein; however, $^{87}\text{Sr}/^{86}\text{Sr}$ for every single point ranges from 0.70670 ± 0.00027 to 0.70689 ± 0.00033 (2SE) which is consistent with the literature results within the error range. $^{84}\text{Sr}/^{86}\text{Sr}$ was also monitored during analyses, and the average values are 0.05596 ± 0.00034 (2SD, n = 9) for Durango standard and 0.05667 ± 0.0028 for all in-situ plagioclase points, which agree well with the “true” value of 0.0565 (2SD, n = 27). Further analysis of the reliability of the Sr isotope data will be presented in the discussion section.

**Whole-rock major and trace element analysis**

Quantitative analyses of major elements contents in whole rocks were conducted using X-ray Fluorescence Spectrometer (XRF) at the Ore Deposit Geochemistry
Microanalysis Laboratory, affiliated to the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences (Beijing). The laboratory is equipped with Shimadzu’s wavelength dispersive X-ray fluorescence spectrometer. The fused beads method was used in the preparation of test specimens. Mixed weighed amounts of sample and flux and placed the mixture in a clean platinum/gold crucible. A 0.7 g of sample (200 mesh) plus 7.0 g of mixed lithium borate fluxes were used in this study. The addition of a small amount (100 mg) of a halide, such as LiBr, acted as a release agent when using platinum/gold molds. The mixture was heated in a high-frequency fusion machine at a fixed temperature, usually from 950 °C to 1100 °C, until thoroughly melted. Then the fused beads were loaded into the XRF instrument for determination; the fusion time was about 30 min. The measurement procedure and data quality were monitored by repeat analysis of international basalt standards BCR-2 and BHVO-2. The analytical precision (RSD, relative standard deviation) and accuracy (RE, relative error between measured and recommended values) are better than 5% for major elements, with many elements agreeing to within 2% of the reference values (Supplementary Table 7).

All whole-rock trace element compositions were measured by ICP-MS (Agilent 7500a with a shielded torch) at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences (Wuhan). The detailed sample-digestion procedure for ICP-MS analyses has been described by (Liu et al., 2008a). The reproducibility is better than 5% (RSD) for all elements. The accuracy, determined relative to reference values of BHVO-2 and BCR-2, is better than 5% (RE)
Results

Petrography

Representative thin-section photographs of the samples are presented in Figure 2. The petrographic characteristics of the basalts may be divided into a fine-grained group (samples SQB03A, SQB03B, and JSB04) and a coarse-grained group (sample JSB12). For the fine-grained group, the most common phenocryst phase is plagioclase feldspar (~10-15 vol%), followed by clinopyroxene (~5-10 vol%) with trace amounts of olivine (<5 vol%). The plagioclase phenocrysts are euhedral and tabular, with sizes (length) ranging from ~400 µm to ~3 mm, and crystals of all sizes exhibit concentric zoning. Clinopyroxene phenocrysts are euhedral to rounded and commonly form glomerocrysts with plagioclase and olivine (Figure 2). Simple twinning of clinopyroxene is common, and phenocrysts range up to ~1 mm in size. Equant olivine phenocrysts (0.2–2 mm) are present. All phenocrysts are set in fine-grained plagioclase, clinopyroxene, olivine, and Fe-Ti oxide matrix. Although the overall grain size of the coarse-grained group is larger than that of the fine-grained group, its phenocrysts and matrix minerals are not easy to distinguish (sample JSB12 in Fig. 2). For the coarse-grained group, the major rock-forming minerals are plagioclase (~45 vol%) and clinopyroxene (~25 vol%), followed by olivine (~15 vol%) and K-feldspar (~10 vol%) with small amounts of Fe-Ti oxide (~5 vol%). Plagioclase phenocrysts are typically tabular-shaped in all the samples. The most significant difference between
the fine-grained and coarse-grained samples is that the former has an overall smaller
grain size but has some larger plagioclase phenocrysts (Fig. 2).

Whole-rock major and trace element

Whole-rock major and trace element data are presented in Supplementary Table 7.

All the samples are classified as basalt (Supplementary Fig. 1) and plot within the
range of Hannuoba tholeiitic basalt samples collected previously (Zhi et al., 1990).

The visible freshness of the lavas chosen for this study is confirmed by low loss on
ignition (LOI) values that range from 0.15 to 3.01 wt%, and the minerals in the
samples are fresh and have not undergone alteration. Compared with the fine-grained
samples, the coarse-grained samples have higher TiO$_2$, FeO, K$_2$O, and P$_2$O$_5$ content.

Other oxides contents are very similar in the two types of samples.

All the samples have a smooth chondrite-normalized rare earth element (REE)
pattern with a slight positive Eu anomaly (Supplementary Fig. 2,3). LREE and MREE
contents in the coarse-grained samples are higher than those in the fine-grained
samples, but their HREE contents are similar. Abundances of trace elements,
normalized to values for the primitive mantle (McDonough and Sun, 1995), show
typical continental oceanic island basalt-like pattern with marked depletion in Pb, Th,
and U, and enrichments in Ba, Nb, Ta, and Sr (Fig. 3), which is consistent with data
reported previously (Qian et al., 2015; Zhi et al., 1990). All the incompatible element
contents and Ce/Pb, Nb/U, and Nb/La ratios in the coarse-grained samples are higher
than those in the fine-grained samples (Supplementary Table 7).
Mineral major and trace element

The major and trace element data of all minerals are provided in Supplementary Tables 1-5. From the backscattered electron (BSE) images, it can be observed from Fig.4 that compositional zoning in plagioclase within a given sample generally consists of only oscillatory zoning type, and zoning is consistent between crystals. Representative backscattered electron images of four individual plagioclase crystals from the three samples and variation trends diagrams for An, Mg, Ti, and Sr from the interior to the rim are shown in Fig. 4. Given that the spot size for in-situ trace element measurement is ~50μm, which is significantly wider than the width for a single zoning, detailed EPMA data with data point distance ranging from 5μm to 40μm are shown in Fig. 5 and Supplementary Table 2.

Plagioclase phenocrysts in the fine-grained samples (SQB03A, SQB03B, and JSB04) are oscillatory zoned, with occasional dissolution surfaces. The An content fluctuates between 57 and 64 when the distance from the rim is more than 100μm (Figs 4 and 5) and decreases significantly to 32~56 in the rim as displayed by EMPA profiles (Fig. 5). Mg and Sr are positively correlated with An content, while other trace elements are scattered at a given An content (Fig. 6). Partially resorbed zones are richer in Ca (An=62~64), Sr (800~900 ppm) and Mg (>1000 ppm) than other zones (Fig. 4), which is interpreted as reflecting a more mafic recharge event by a Ca and Sr richer magma.

Plagioclase phenocrysts in the coarse-grained sample JSB12 are also oscillatory zoned but generally more sodic than those in the fine-grained samples. Two different
Oscillatory zones may be identified, inner calcic zones with An fluctuate between 54 and 62 and outer sodic zones with An fluctuate between 48 and 57 (Fig. 5). The zone with dissolution surface mainly occurs in the inner zones and has a thickness ranging from 5 to 20 μm. Partially resorbed zones with the embayed surface are richer in Ca (An=60–62) and Sr (1150–1300 ppm) than other zones (Fig. 4). Sr is positively correlated with An content, while other trace elements are scattered at a given An content, and Ti, Sr, Ba, La, and Eu contents are generally higher than those in the fine-grained samples (Fig. 6).

The chondrite-normalized diagram (supplementary Fig. 3) drawn according to the in-situ trace element data of plagioclase indicates that plagioclase phenocrysts from all the studied samples show enrichment in light rare earth elements and strong Eu positive anomalies. Variation of Eu anomalies ranges from 1.52 to 9.94. Except for a few individual data, the abundance of rare earth elements in plagioclase phenocrysts from the coarse-grained sample (JSB12) is higher than that in the other three fine-grained samples. The clinopyroxene phenocrysts in the two groups have comparable major element characteristics and range from En_{43} Fs_{12} Wo_{44} to En_{46} Fs_{12} Wo_{41} (Supplementary Table 3). All the clinopyroxene REE data show a similar pattern with enriched MREE compared with LREE and HREE (Figure 7), and the coarse-grained sample has overall higher LREE and lower HREE concentrations than those in the fine-grained samples.
Sr isotope in plagioclase

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of plagioclase phenocrysts are presented in Supplementary Table 6. All four plagioclase phenocrysts show large variation (>0.001) in $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, with the lowest ratio of 0.70333 ± 0.00018 (2SE) in sample JSB12 and the highest ratio of 0.70556 ± 0.00031 (2SE) in sample SQB03A (Figure 8). The average $^{87}\text{Sr}/^{86}\text{Sr}$ of the fine-grained samples are 0.70434 ± 0.00112 (2SD) (SQB03A), 0.70471 ± 0.00102 (2SD) (SQB03B) and 0.70455 ± 0.00074 (2SD) (JSB04), which all higher than the coarse-grained sample JSB12-1 of 0.70425 ± 0.00109 (2SD). The variation of strontium isotope recorded by plagioclase is much larger than that recorded by Hannuoba alkaline and tholeiitic whole rocks (Song et al., 1990), but it is consistent with the variation range of Cenozoic basalts in North China Craton (Fig. 9).

Partially resorbed zones with higher An contents may have either higher or lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than other zones in the fine-grained samples, the variation of Sr isotope value may be characteristic of the dissolution zone or may be caused by the adjacent bands (Fig. 9). Sample SQB03A show similar correlation trends between An and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with sample SQB03B, except the two rim points (Fig. 9), suggesting a similar crystallization process occurred for different individual crystals, which is consistent with their comparable zoning pattern as displayed by BSE images (Figure 8). For sample JSB04, rim and core have a higher $^{87}\text{Sr}/^{86}\text{Sr}$ Sr ratio than other zones. In contrast, partially resorbed zones in sample JSB12 are accompanied by a significant decrease in the $^{87}\text{Sr}/^{86}\text{Sr}$ Sr ratio and an abrupt increase in the rim zones.
Thermobarometers

The REE in plagioclase-clinopyroxene geothermometer (Sun and Liang, 2017) gives crystallization temperatures of 1088–1156°C for the fine-grained samples and 1113–1129°C for the coarse-grained sample (Supplementary Table 8.). Temperatures calculated from the Mg-Ca coupled exchange thermometer of plagioclase and clinopyroxene (Sun and Lissenberg, 2018) are 1078–1134°C for the fine-grained samples and 1076–1079°C for the coarse-grained samples (Supplementary Table 8.). Given that the two different thermometers were applied to the same samples, the systematic differences between $T_{\text{Mg}}$ and $T_{\text{REE}}$ (Figure 10) are most likely due to the differential diffusive responses of Mg and REE to changes in temperature after crystallization of the cumulus minerals. The average difference between $T_{\text{Mg}}$ and $T_{\text{REE}}$ (Figure 10) indicates that crystallization occurs within the range of 20°C (fine-grained basalt) and 50°C (coarse-grained basalt). The crystallization of these samples are complete within 20 to 50°C before eruption, which may be a reason for the textural differences between the two types of basalts. The inverted initial temperatures (1120-1140 °C) by Mg-REE coupled geothermometer are very close to $T_{\text{REE}}$ (1088-1156 °C), indicating a small diffusive redistribution of REE in Hannuoba basalt. Cooling rates calculated by Mg-REE coupled geospeedometer (Sun and Lissenberg, 2018) suggest that the coarse-grained sample generally (0.004 °C/yr) cooled slower than the fine-grained samples (0.0004–0.05 °C/yr), although a small number of results, possibly due to the large error, are abnormal. (Supplementary Table 8.).

Clinopyroxene-melt equilibrium thermometer Eq.33 of (Putirka, 2008) and
barometer of (Neave and Putirka, 2017) have been suggested as the most accurate and precise thermobarometer. Crystallization temperatures and pressures calculated from the thermobarometer are 1129~1189 °C and 0.7 ~4.4 Kbar for the fine-grained samples, and 1149~1159°C and 3.9 ~4.3 Kbar for the coarse-grained samples. The temperatures are slightly higher than T_{REE} but agree within error (Supplementary Table 8.). The temperature obtained by the rare earth element thermometers may be regarded as the crystallization temperature of the phenocrysts because 1) the error on the rare earth element exchange thermometers of plagioclase and pyroxene is smaller than that of the pyroxene thermometers and 2) the rare earth element thermometers are less affected by pressure and water concentrations (Sun and Liang, 2017).

Because the plagioclase mineral-melt equilibrium thermobarometer is significantly affected by the water content in the melt (Putirka, 2008) and the initial water content in Hannuoba tholeiitic basalt is unknown, this thermobarometer was not considered in this study.

Discussion

Reliability of in situ Sr isotope data

Possible interference with in situ Sr isotope analysis includes Kr and Rb and other elements (see Analytical methods section and Li et al. (2018)). Trace amounts of Kr may exist as impurities in trace amounts of argon, which may affect the accuracy of the data, because $^{84}$Kr and $^{86}$Kr interfere with $^{84}$Sr and $^{86}$Sr signals, respectively. This interference was corrected by measuring the Kr blank of the gas, and based on the
measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratio at the known apatite standard, the effect proved to be valid.

$^{87}\text{Rb}$ is a significant interference for Sr isotopic analysis. Generally, an analysis of $^{85}\text{Rb}$ is needed for corrections. The content of Rb in the plagioclase samples from Hannuoba basalts is relatively low (<1ppm), which indicates that $^{87}\text{Rb}$ has a minimal interference to the Sr isotope (<0.00001).

All the LA-ICPMS Sr isotope data in this study have more significant analytical error (0.00024 of average 2σ error) than micro-drilling data (Davidson et al., 2001; Ginibre and Davidson, 2014) mainly due to the spot size of 30μm. The accuracy of the data may be ensured because the data for the Durango standard analyzed in this study agree well with the recommended values and within the analytical error. On the other hand, the Sr isotope data for the compositional zones of plagioclase with a thickness less than 50μm are very close or nearly indistinguishable (Figure 9), suggesting that the precision of the Sr isotope is high enough to capture the isotopic heterogeneities within individual plagioclase crystal.

Magma mixing recorded in compositional and isotopic zoning

There are at least three mechanisms to explain the variation in the An content of the plagioclase: a hotter magma underplating increased the temperature of the magma, leading to an increase in An content of plagioclase; reductions in the water content of the melt through degassing or removing volatile fluids; changes in the composition of the melt caused by magma recharge. We may distinguish these processes using abundances and patterns of slow diffusing trace elements in plagioclase phenocrysts because each process should result in different trace element responses and patterns.
The An values of Hannuoba samples varied between 56 and 64. We assume that
the melt's composition (not including volatiles) remains the same, and the changes of
the An values may be caused by a modest increase in temperature or by the reduction
of H$_2$O content in the melt. Although temperature does affect the distribution of Sr
between plagioclase and siliceous melt, this effect does not affect the relationship
between An value and Sr (Bindeman et al., 1998). Using the partition coefficient of
Bindeman et al. (1998), to change the temperature by 100°C as suggested by the
plagioclase REE thermometer would only change the concentration of Sr in
plagioclase 10-15ppm. Moreover, at a given temperature, when the An content varies
from 56 to 64, the Sr partition coefficient could only change 20%. However, the Sr
variation in the plagioclase phenocrysts in Hannuoba basalts is far beyond this range
(Figure 6). Therefore, changes in the concentration of trace elements and An in
plagioclase are not caused by changes in temperature alone. Blundy and Wood (1991)
found that there is almost no difference in the distribution coefficient of Sr between
hydrothermal and silicate melts, which means that H$_2$O has only a weak effect on the
distribution coefficient of Sr. Therefore, zoning patterns in plagioclase is most likely
attributable to changes in melt composition, and changes in melt chemistry that may
accompany changes in melt temperature and H$_2$O content.

The dissolution surface and the oscillatory changes in An content (Fig. 5) suggest
compositionally distinct pulses of melt. Also, the intracrystalline Sr isotope data suggest
some episodes of magma recharge are occurring.

Thus, magma mixing could be responsible for the compositional and isotopic
diversity in the plagioclase phenocrysts. The relatively large size of the LC-ICPMS laser spot compared to the width of the individual oscillatory zones results in the simultaneous analysis of multiple zones, providing an averaged composition, so the observed variation should be considered a minimum. Even with the limited spatial resolution of the laser-ablation system, our data demonstrate that some plagioclase phenocrysts in Hannuoba basalts preserve significant isotopic variation and that the Sr isotope compositions of these crystals are commonly higher or lower than bulk-rock \(^{87}\text{Sr}/^{86}\text{Sr}\) in Hannuoba basalts (Figure 9). To preserve intracrystalline Sr isotopic disequilibria on the scale of 30 μm or less, plagioclase phenocrysts cannot have been kept at magmatic temperatures (~1000°C) for significant periods (100 years) because this would result in diffusive re-equilibration (Davidson et al., 2001; Ramos and Reid, 2005). This is consistent with the fast cooling rate obtained from plagioclase-clinopyroxene Mg-REE coupled geospeedometer (Sun and Lissenberg, 2018) and a small diffusive redistribution of REE in Hannuoba basalt. The intracrystalline disequilibria were most likely generated during episodic crystal growth through interaction with isotopically distinct melts at crustal pressures, possibly within the middle-crust magma chamber or plumbing system as recorded by crystallization pressures from the barometer of clinopyroxene.

**Contamination of heterogeneous continental lower crust**

Two hypotheses have been proposed to account for compositional and isotope variations in Hannuoba basalts. The first attributes them to the mixing of basaltic melts generated from compositionally and isotopically distinct mantle sources with
negligible crustal contamination based on trace elements and Sr-Nd-Pb isotopic characteristics (Qian et al., 2015; Song et al., 1990; Zhi et al., 1990). The second suggests that the compositional characteristics result from mantle melts assimilating crustal components (Jiang and Zhi, 2010) based on very high $^{187}\text{Os}/^{188}\text{Os}$. Although the Nb/U ratio in Hannuoba alkaline and tholeiitic basalts are significantly higher than average continental crust (Qian et al., 2015), lower crust contamination cannot be excluded because the Nb/U ratio in the lower continental crust has been suggested to be very heterogeneous (Gao et al., 1998; Huang et al., 2004; Rudnick and Fountain, 1995), and mafic lower crustal materials can have Nb/U up to 50 (Rudnick and Fountain, 1995), which is very close to the values documented in the Hannuoba tholeiitic basalts (Nb/U=46~51). In addition, the $^{187}\text{Os}/^{188}\text{Os}$ of the Hannuoba tholeiites (0.15882 - 0.61607) are mostly higher than those of the transitional basalts (0.23425-0.35779) and alkaline basalts (0.14869- 0.29528) (Jiang and Zhi, 2010), and they are significantly higher than those of the lithospheric mantle, suggesting that crustal contamination is widespread in the Hannuoba basalts. Therefore, the best explanation for the EMI characteristics of the enriched radiogenic strontium isotopes of the Hannuoba tholeiites seems to be contamination by the lower continental crust.

The significant change of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is likely due to assimilation of Hannuoba alkaline basalts by lower continental crust because the former has significantly lower $^{87}\text{Sr}/^{86}\text{Sr}$. However, trace element contents in the melt that are in equilibrium with the plagioclase, calculated using the Bindeman et al. (1998) model, show minimal variation (Figure 11, Supplementary Table 9), and Sr and Ba contents similar to that in
tholeiitic basalts, but significantly lower than those in alkaline basalts, suggesting that, at least, Hannuoba alkaline basaltic melts were not directly contributing to the intracrystalline Sr isotopic disequilibria. Other trace elements such as La and Eu are either lower or higher than that in tholeiitic basalts (Figure 11), which is possibly due to model uncertainty as shown by many other experimental and theoretical studies (Bedard, 2006; Bindeman et al., 1998). Given that trace element content in Hannuoba tholeiite is between Hannuoba alkaline basalts and lower continental crust (Figure 3), mixing of Hannuoba alkaline basalts and the lower continental crust can explain the bulk rock compositional characteristic of Hannuoba tholeiite, which is also consistent with intercalated tholeiitic and alkaline lavas. However, in this case, the low $^{87}\text{Sr}^{86}\text{Sr}$ (<0.704) signature in plagioclase cannot be from alkaline basaltic melts. It is likely that the alkali basalt interacted with the lower continental crust and formed a mixed magma. The trace element abundances and ratios in this magma are similar to the Hannuoba tholeiite and relatively homogeneous, but the isotopes are heterogeneous. The crystalline plagioclase will inherit the decoupled isotopic and trace element characteristics when the magma rises and injects into the magma chamber. The Hannuoba tholeiite crystallized within a 20 °C (fine-grained basalt) and 50°C (coarse-grained basalt) temperature window also suggest that compositionally (major and trace element) similar magmas were mixed with each other before the eruption. This understanding is similar to that obtained from the study of melt inclusions: the Pb isotope variation range of melt inclusions entrapped in olivine in a Hannuoba tholeiite vary significantly and extend toward an EM1-type isotopic
composition, similar to that of all tholeiites, but the variation range of major and minor elements is relatively tiny (Qian et al., 2015).

The potential problem is that the major and trace elements and isotopes in the lower crust are quite heterogeneous. If significant isotope heterogeneity is recorded in plagioclases in the two types of tholeiitic basalts in Hannuoba, then it would be expected that the strontium isotope ratios would be lower than those for the average lower continental crust. This may be related to the highly compositional heterogeneity and multi-stage evolution of the lower crust in the North China Craton (Jiang et al., 2013; Liu et al., 2004). Previous studies have shown that strontium isotopes in the lower crust of the North China Craton vary from 0.704 to 0.746, and strontium contents vary from $< 100$ ppm to $> 1500$ ppm (Jiang et al., 2013; Liu et al., 2004). The major and trace elements in the lower crust (probably local) may be relatively homogeneous due to the long-term and multi-stage magmatic underplating, but the isotopic heterogeneity is still significant. In addition, it should be noted that the contents of trace elements in the whole rock and plagioclase of the two types of Hannuoba basalts are different, which indicates that there are differences in the parent magma itself. This difference may be caused by the heterogeneity of local lower crust materials, or it may be the product of magma evolution by crystallization and differentiation after mixing alkaline basaltic rocks and different proportions of the lower crust. Our current research does not distinguish between these possibilities. In general, the contribution of lower crustal contamination to the formation of Hannuoba tholeiite is more complex than previously thought. Identifying the existence of lower
crust contamination on the basis of whole-rock geochemical characteristics and the average composition of the lower crust is challenging. However, in-situ trace elements and isotopes of plagioclase may help solve these problems.

**Implication**

Although the plagioclase phenocryst zoning in Hannuoba tholeiite is oscillatory and normal, and the content of anorthite and trace elements in each plagioclase grain does not vary significantly, which is similar to the oscillatory zoning formed by a closed system, the strontium isotope in the plagioclase micro area shows significant isotope disequilibrium. Moreover, the range of strontium isotope ratios is far more than that of all Hannuoba basalts, which has not been found in previous studies. Although the error on strontium isotope ratios is significant, we have detected greater than expected isotopic variation. If the beam spot increases, the error will decrease, but the observed isotope heterogeneity will be reduced or eliminated.

Because the isotopic heterogeneity of plagioclase zoning occurs in the crystallization process at the depths of the middle crust, both the lower crust and the upper mantle of the continent may contribute to the heterogeneity of magma, and the contamination and magma mixing may mainly occur in the lower crust and/or the upper mantle. Our study suggests that the contamination by the lower continental crust is more critical because the addition of material from the lower continental crust can explain the very high osmium isotope, the typical EMI type Sr-Nd-Pb isotope, and the lower incompatible element content of tholeiitic basalts compared with alkaline basalts. This phenomenon may be shared in Cenozoic basalts in eastern
China; However, previous studies have attributed the compositional characteristics of EMI endmembers to the continental lithosphere, recycled continental or oceanic crust materials. An important reason for this phenomenon is that previous studies usually exclude contamination of the lower crust by comparing the whole rock composition characteristics with the global average continental lower crust composition, but this practice has a substantial uncertainty because the continental lower crust has significant compositional heterogeneity (Jiang et al., 2013; Liu et al., 2004; Rudnick and Fountain, 1995). The mafic lower crust may have a high degree of partial melting, mixing, and evolution, and then injected into the magma chamber of the shallow crust, resulting in heterogeneous geochemical characteristics and even leading to the decoupling of isotopes and trace elements, similar to those recorded in the plagioclase micro zonation in this study.

Another important finding of this study is that there are significant differences in petrography and trace element contents in mineral micro areas between the two types of tholeiites with different whole-rock compositions, which indicates that the magma with different initial compositions has undergone different crystallization history. The crystallization process of the two tholeiites might occur in an independent magma chamber or plumbing system. The in-situ study of mineral composition and isotope at the micro-regional scale, and the selection of basalts with significant differences in petrography, will help to reveal the complex evolutionary process of the magmatic system and is also of great significance for a comprehensive understanding of the origin and genesis of continental basaltic magma.
Acknowledgments

Thanks to Zhang Liangliang and others from the Milia Laboratory of China University of Geosciences (Beijing) for their help in the in-situ trace element experiment, and Li Chao from the national testing and experimental center of the Chinese Academy of Geological Sciences for help in the in situ strontium isotope experiment. We thank an anonymous reviewer and Jenna Adams for their constructive and thorough reviews. In addition, thanks to the comments and editorial work from Professor Callum Hetherington. This work is supported by the Fundamental Research Funds for the Central Universities (2652019049), the national college students' innovation and entrepreneurship training program (202011415009), and the 111 project (B18048). This is CUGB petro-geochemical contribution No. PGC-2015##.

References


Bindeman, I.N., Davis, A.M., Drake, M.J., 1998. Ion microprobe study of plagioclase-basalt partition experiments at natural concentration levels of trace


Gao, S. et al., 1998. How mafic is the lower continental crust? Earth and Planetary


Li, C. et al., 2018. In-situ Sr isotopic measurement of scheelite using


Neave, D.A., Putirka, K.D., 2017. A new clinopyroxene-liquid barometer, and


inter-grain variation of Sr isotope of plagioclase. Journal of Asian Earth Sciences, 201.


Figures

Figure 1. (a). Sketch map of the North China Craton (modified according to (Liu et al., 2019; Xu et al., 2005) (b). Geological map of Hannuoba (modified according to (Zhi et al., 1990) (c). Spatial distribution of basalt in the sampling area.
Figure 2. Representative micro-textural characteristics of the Hannuoba tholeiite under crossed polars

Figure 3. Primitive mantle (McDonough and Sun, 1995) normalized trace
element pattern for Hannuoba basalts and the average lower continental crust.

**Figure 4**

The relationship between An value and Mg, Ti, Sr element. (The circles in yellow represent the in-situ trace element analyses, and the circles in red represent the in-situ strontium isotope analyses. Error bars are 2σ SE)
Figure 5. Variation diagram of Sr isotope, An, and distance in plagioclase.

The arrow indicates dissolution surfaces and major Sr isotope variation trends.

Error bars are 2σ SE.
Figure 6. Relationship between trace element concentration and An content in plagioclase. The circle data measured isotopes simultaneously, and the diamond data are other plagioclase crystals randomly selected from each sample. Colored circles from large to small represent from rim to core.
**Figure 7.** Chondrite-normalized (McDonough and Sun, 1995) REE concentration patterns for clinopyroxenes from Hannuoba tholeiite.

**Figure 8.** BSE image of the plagioclase sample with strontium isotope indicated.
Figure 9. In situ $^{87}\text{Sr}/^{86}\text{Sr}$ variations of plagioclase samples from Hannuoba basalts. Sr isotope data of whole-rock Hannuoba alkaline, transitional and tholeiitic basalts are from (Song et al., 1990); Cenozoic basalts from North China Craton after (Liu et al., 2008b). The error bar indicates 2σ SE.
Figure 10. Relationship between crystallization temperature and pressure of tholeiite in Hannuoba. (a) Crystallization pressure and temperature of clinopyroxene–melt. (b) Closure temperature obtained by pyroxene-plagioclase magnesium thermometer. (c) Closure the temperature obtained by pyroxene-plagioclase trace element thermometer. (d) The temperature difference between $T_{\text{Mg}}$ and $T_{\text{REE}}$. The error bar indicates $2\sigma$ SE.
Figure 11. Sr isotope versus trace element content for Hannuoba basalts and the calculated melts in equilibrium with plagioclase. Hannuoba basalts from Zhi et al., 1990; Song et al., 1990. Error bars smaller than the symbol are not shown.