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Journal of Asian Earth Sciences

journal homepage: www.elsevier.com/locate/jseaes

Hydrothermal He and $CO₂$ at Wudalianchi intra-plate volcano, NE China

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article info

Article history: Received 9 April 2012 Received in revised form 26 October 2012 Accepted 1 November 2012 Available online 15 November 2012

Keywords: Hydrothermal gas He–C isotopes $\rm CO_2/^{3}He$ Sub-continental lithospheric mantle Wudalianchi NE China

ABSTRACT

Chemical and isotopic compositions have been measured for $CO₂$ -rich bubbling gases discharging from cold springs in Wudalianchi intra-plate volcanic area, NE China. Observed ³He/⁴He ratios (2–3 R_A) and δ^{13} C values of CO₂ (-5‰ to -3‰) indicate the occurrence of a mantle component released and transferred to the surface by the Cenozoic extension-related magmatic activities. The $CO_2/{}^{3}$ He ratios are in wide range of (0.4–97 \times 10⁹). Based on the apparent mixing trend in a ³He/⁴He and δ ¹³C of CO₂ diagram from all published data, the extracted magmatic end-member in the Wudalianchi Volcano has 3 He/ 4 He, δ^{13} C and CO₂/³He value of ~3.2 R_A, ~–4.6‰ and ~6 × 10¹⁰, respectively. These values suggest that the volatiles originate from the sub-continental lithospheric mantle (SCLM) in NE China and represent ancient fluids captured by prior metasomatic events, as revealed by geothermal He and $CO₂$ from the adjacent Changbaishan volcanic area.

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1. Introduction

The sub-continental lithospheric mantle (SCLM) is an important interface between the chemically-heterogeneous continental crust and the convecting, asthenospheric mantle. Information on its geochemical nature relies mainly on intra-plate volcanic products such as alkali basalts and/or ultramafic xenoliths. Along the southeast segment of the Eurasian Plate (Siberia, NE China and the Korean Peninsula), there is widespread late Cenozoic intra-plate volcanism ([Zhou et al., 1988](#page-4-0)). Geochemical studies (major/trace elements, Sr–Nd–Pb isotopes and noble gas data) on xenoliths and host lavas indicate that the SCLM in this region has been enriched by metasomatic fluids derived from ancient subduction at a continental margin ([Wang et al., 1988; Hsu and Chen, 1998;](#page-4-0) [Yamamoto et al., 2004; Kim et al., 2005](#page-4-0)). However, although $CO₂$ is the major gaseous component in the analyzed xenolith and phenocryst phases ([Xia, 1990\)](#page-4-0) and has a close association with noble gases, there are still difficulties to make chemically and isotopically measurements on extremely small quantities of volatiles trapped in ultramafic crystals. As a result, no information is currently available on the CO₂ itself, either δ^{13} C or CO₂/³He that are two indicators that could identify provenance on the subducted slab and confirm its role as the metasomatic agent. Instead, using

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geothermal He and $CO₂$ from Changbaishan Volcano on the border of China and North Korea (CSB in [Fig. 1\)](#page-1-0), [Hahm et al. \(2008\)](#page-4-0) proposed that modern-day geothermal fluids may present a valuable addition to xenolith and phenocryst studies aimed at characterizing fluid origins and processes associated with past mantle metasomatic events. They concluded that these volatiles originate from the SCLM in NE China and represent ancient fluids captured by prior metasomatic events.

Like Changbaishan, Wudalianchi is another Cenozoic intra-plate volcanic site in NE China [\(Fig. 1](#page-1-0)) and should also be a prime locality to assess the possible influence of subduction-related $CO₂$ -components on its magma source as basement lithologies are Archean and Mesozoic granites and not limestone [\(Wang et al., 2003](#page-4-0)). The Wudalianchi volcanic group consists of 14 volcanoes and lava platforms covering an area of 800 $km²$. Lava flows blocked the Bailonghe River and forms five interconnected lakes (Wudalianchi). [Mao](#page-4-0) [et al. \(2010\)](#page-4-0) pointed out the initial eruptions of the Wudalianchi Volcano in Pliocene (\sim 2 Ma) and the major eruptions in Pleistocene (0.27–0.56 Ma and 0.7–0.9 Ma). The latest eruption was recorded in A.D. 1719–1721 at Mts. Laohei and Huoshao. The composition of the volcanic rocks varies from tholeiites to alkali basalts ([Hsu and Chen, 1998\)](#page-4-0). Petrological and geochemical studies (major-, trace- and REE-elements, Sr–Nd–Pb isotopes) suggested the various alkali basalts from Wudalianchi were derived from a mantle source which had been metasomatized ([Wang et al.,](#page-4-0) [1988; Hsu and Chen, 1998; Fan et al., 2001\)](#page-4-0).

Accompanying the recent volcanic activities, a number of cold springs are distributed around the volcanoes. Previous works on

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Fig. 1. Geological map showing tectonic locations and sampling sites (modified from [Du et al. \(1999\)](#page-4-0)).

He and C isotopes in spring gases from Wudalianchi have found ³He/⁴He ratios and δ^{13} C of CO₂ ranging 1–3.3 R_A and -10% to -4‰, respectively ([Dai et al., 1992; Du et al., 1999; Shangguan](#page-4-0) [et al., 2006\)](#page-4-0). However, these analytical results (³He/⁴He and $\delta^{13}C$) were simply interpreted as general binary mixing of MORB-type mantle-derived and crustal components. Combining these published data and new data in this study, we re-investigate the origin of He and CO₂ in more details by focusing $CO₂/³$ He in addition to 3 He/ 4 He and δ^{13} C, and consequently discuss the nature of SCLM beneath Wudalianchi in comparison with the adjacent Changbaishan volcanic area.

2. Materials and analytical methods

Gas samples were collected from three sites on and around the Wudalianchi Volcanoes in 1993 (Fig. 1). The samples include free gas phase of mineral water located on the outer flanks of Mt. Yaoquan Volcano and on the lava of Mt. Huoshao. Standard sampling techniques (e.g., using a plastic funnel for collection of gases, and prolonged flushing of connecting tubes, etc.) were adopted to minimize air contamination. The samples were transferred back to the laboratory in lead–glass bottles.

All measurements were carried out in University of Tokuyo in 1993-94. The abundance and isotopic composition of He and Ne in gas were measured using a VG5400 noble gas mass spectrometer. Repeat He and Ne measurements of air standard indicated precision of less than 10%. The abundance and isotopic composition of $CO₂$ in gas were measured using Delta E stable isotope mass spectrometer. Routine precisions are 5% and 0.2‰ for abundance and isotopic composition, respectively [\(Xu et al., 1997](#page-4-0)).

3. Results

He and $CO₂$ results of gases from cold springs in Wudalianchi are listed in [Table 1.](#page-2-0) Observed ³He/⁴He ratios are air-corrected assuming atmospheric origin for Ne. Our results $(^{3}$ He/ 4 He and δ^{13} C) are in excellent agreement with prior work on mineral fluids at Wudalianchi ([Dai et al., 1992; Du et al., 1999; Shangguan et al.,](#page-4-0) [2006](#page-4-0)). The highest ³He/⁴He value (3.3 R_A, where R_A is atmospheric $\frac{3}{4}He/4He$ value of 1.4×10^{-6}) is significantly lower than the capon. He/⁴He value of 1.4 \times 10⁻⁶) is significantly lower than the canonical range associated with the uppermost mantle (8 ± 1) R_A , [Graham, 2002](#page-4-0)). However, they overlap with typical of arc-related volcanism (5.37 \pm 1.87 R_A, [Hilton et al., 2002](#page-4-0)), including the NE Japanese arc $(2-7 R_A, Hilton et al., 2002; Sano and Nakamura,$ $(2-7 R_A, Hilton et al., 2002; Sano and Nakamura,$ [2008](#page-4-0)). Therefore, our data in this study fully support the conclusion made by other authors [\(Dai et al., 1992; Du et al., 1999;](#page-4-0) [Shangguan and Wu, 2008\)](#page-4-0) that ³He/⁴He indicates a dominant input of mantle-derived volatiles at Wudalianchi Volcano.

The isotopic composition of $CO₂$ (δ^{13} C) of the gas samples falls in a narrow range between -5% and -3% . This relatively narrow range of δ^{13} C values spans that found at mid-ocean ridges ([Marty](#page-4-0) [and Jambon, 1987\)](#page-4-0) and subduction zones ([Sano and Marty, 1995;](#page-4-0) [Hilton et al., 2002\)](#page-4-0). In the former case, a mantle origin for the $CO₂$ is assumed whereas, in the latter, the $CO₂$ is dominated by input from the suducted slab.

In contrast to narrow range of ³He/⁴He and δ^{13} C, the relative abundance of He and $CO₂$ is highly variable $(CO₂)³$ He = 0.4– 97×10^9) at Wudalianchi, overlapping the arc-like values (7.7– 118×10^9 with an average $\sim 12 \times 10^9$; [Sano and Marty, 1995\)](#page-4-0) and values of \sim 2 \times 10⁹ which characterizes the asthenospheric mantle at spreading ridges [\(Marty and Jambon, 1987](#page-4-0)). Such a large

^a Air-corrected ³He/⁴He ratio. (³He/⁴He)_{cORR} = {(³He/⁴He)_{sample} - *r*}/{1 - *r*}, where *r* = (⁴He/²⁰Ne)_{air}/(⁴He/²⁰Ne)_{sample}.

range of CO $_2$ / 3 He values suggests mixture of different source ([O'Nions and Oxburgh, 1988](#page-4-0)) and/or physical–chemical fractionation between He and $CO₂$ during fluids migration ([Marty and](#page-4-0) [Jambon, 1987\)](#page-4-0).

4. Discussion

4.1. Chemical and isotopic features of magmatic component at Wudalianchi

Apparently, variation of air-corrected 3 He/ 4 He ratios (1–3.3 R_A) and δ^{13} C values of CO₂ (–9.6‰ to –3.1‰) from all published data in Wudalianchi can be simply interpreted as binary mixing between crustal and MORB-type mantle components. The former has typical 3 He/ 4 He of 0.02 R_A and δ^{13} C of ${\sim}0$ ‰ for carbonates or $<$ –20 $\%$ for organic sediments, whereas the latter is characterized by the MORB-type mantle of 8 ± 1 $\rm R_A$ and -6.5 ‰. However, among all published data, 9 of 14 samples have narrow variations of ³He/⁴He and δ^{13} C with average 3.2 ± 0.1 R_A and -4.6 ± 0.8‰, respectively. Hence, the high and consistent ³He/⁴He ratios most likely reflect a local magmatic component. Such a consideration is supported by the 3 He/ 4 He and δ^{13} C relationship.

There is a positive correlation between the $\rm{^3He/^4He}$ ratio and observed δ^{13} C value with a correlation coefficient of 0.84 (Fig. 2). Least-squares fitting yielded a straight line described by:

$$
{}^{3}\text{He}/{}^{4}\text{He} = 4.55 + 0.33 \times \delta^{13}\text{C}
$$
 (1)

Fig. 2. 3 He/ 4 He versus δ^{13} C of CO₂ plot in gas samples from Wudalianchi Volcano. The solid circles represent samples in this study whereas the open circles from the previous studies ([Dai et al., 1992; Du et al., 1999; Shangguan et al., 2006\)](#page-4-0).

where ³He/⁴He ratio and δ^{13} C value are given in the units of R_A and ‰, respectively. Apparently, this positive correlation suggests mixing of two components: low- $3\text{He}/4\text{He}-\delta^{13}\text{C}$ and high- $3\text{He}/4\text{He}-\delta^{13}\text{C}$ end-members. If the above He–C isotope relationship is extrapolated to the region of crustal He with the 3 He/ 4 He ratio of 0.02 R_A, the δ^{13} C value of crustal CO₂ can be obtained. The estimated crustal δ^{13} C value of -15% agrees well with the δ^{13} C range of biogenic CO₂ in terrestrial freshwater environments ([Schoell, 1980\)](#page-4-0). On the other hand, taking a mantle ³He/⁴He ratio of 8 R_A, we can estimate a δ^{13} C value for the mantle $CO₂$ of 10.5‰. Obviously, this value cannot reflect the average MORB-type mantle C compositions of -6.5% ([Marty and Jambon, 1987\)](#page-4-0). Alternatively the end-member of high- 3 He/ 4 He- δ ¹³C may reflect a local magmatic component with ³He/⁴He ~3.2 R_A and $\delta^{13}C$ ~-4.2‰, which are consistent with the averaged values by above nine of fourteen gas samples.

In ³He/⁴He versus δ^{13} C plot, any linear correlation would require a ratio of $(CO_2)^4$ He)_{magmatic}/ $(CO_2)^4$ He)_{crustal} = 1 ([Langmuir](#page-4-0) [et al., 1978\)](#page-4-0). Taking the crustal ³He/⁴He and CO_2 /³He of 0.02 R_A and 10^{13} respectively, we can estimate a $CO₂/³$ He value for the magmatic end-member of $\sim 6 \times 10^{10}$ if applying the magmatic end-member 3 He/ 4 He of 3.2 R_A. This value is higher than that observed in typical MORB-type mantle and lower than those for typical crustal components (organic or limestone, i.e., [Marty and](#page-4-0) [Jambon, 1987\)](#page-4-0). However, it overlaps the values observed in present-day subduction zones and is comparable with the highest value of the observed CO₂/³He in Wudalianchi (2.7 \times 10¹⁰, [Du et al.,](#page-4-0) [1999\)](#page-4-0).

If the two component mixing inferred by the 3 He/ 4 He- δ^{13} C plot diagram (Fig. 2) is valid, there should be a negative correlation between 3 He/ 4 He and CO₂/ 3 He ratios in the region. [Poreda et al.](#page-4-0) [\(1988\)](#page-4-0) argued that mixing of two components, low^{-3} He/ $/4$ Hehigh-CO₂/³He gases and high- 3 He/⁴He-low-CO₂/³He gases could account for $CO₂$ and He in volcanic and hydrothermal gases from subduction zones. The former component may result from decarbonation reactions in the crust, while the latter component may be due to a mantle CO_2 contribution with a $CO_2/{}^{3}$ He ratio of $2.0 \pm 0.5 \times 10^9$ [\(Marty and Jambon, 1987\)](#page-4-0). However, we cannot find any such correlation in Wudalianchi gases, suggesting that the factor controlling the $CO_2/{}^{3}$ He ratio is not simple two component mixing between magmatic and crustal gases [\(O'Nions and](#page-4-0) [Oxburgh, 1988](#page-4-0)).

In [Fig. 3](#page-3-0), we plot all published data with high $3He/4He$ ratios (\sim 3 R_A) on a CO₂ $-$ ³He–⁴He ternary plot. The most striking relationship is that they all fall on a linear trajectory, extending from the $CO₂$ apex (i.e., high $CO₂/³$ He) to the pure helium axis (i.e., low $CO₂/³He$) with a ³He/⁴He ratio of \sim 3.2 R_A (the mean value of all gas samples). Such a distribution pattern in Wudalianchi is quite similar to that observed in the Changbaishan Volcano. The later has been explained by physical and chemical controls on the $CO₂/³$ He ratios ([Hahm et al., 2008](#page-4-0)). Hence, two possibilities (one magmatic- and one hydrothermal-related) can be considered for explaining variations in $CO_2/{}^{3}$ He of the gas samples in Wudalianchi.

Fig. 3. Ternary plot of CO₂, ³He and ⁴He in gas samples from Wudalianchi Volcano. The solid star represents the Wudalianchi magmatic component with CO $_2$ / 3 He ratio extracted by linear correlation between 3 He/ 4 He and $\delta {}^{13}$ C. CBS denotes the Changbaishan magmatic component from [Hahm et al. \(2008\).](#page-4-0) Gray area indicates 3 He/ 4 He range of arc-related volcanism (5.37 \pm 1.87 R_A, [Hilton et al., 2002\)](#page-4-0).

It is difficult to assess the elemental fractionation of the CO₂/³He ratio. However, the CO₂/³He ratio is expected to remain constant as gas phase separates from molten basalt [\(Marty and](#page-4-0) [Jambon, 1987](#page-4-0)). As solubility of $CO₂$ is greater than He in alkali melt ([Dixon, 1997\)](#page-4-0), volatiles exsolved from degassed magma would be expected to evolve to CO $_2$ / 3 He values higher than initial magmatic values. The Wudalianchi region is mainly characterized by alkali basalts so that it is impossible to account for the observed $\rm{CO_2}/^3$ He values $\times 10^9$ at Wudalianchi by this process as there are no plausible initial values of magmatic sources with values even lower than those observed. These are also a difference of solubility between $CO₂$ and He in water, and a selective removal of $CO₂$ by precipitation as carbonate. Bunsen solubility coefficient of $CO₂$ and He in water were well documented by [Weiss \(1971, 1974\)](#page-4-0). For instance, the ratio of solubility coefficients, K_{CO2}/K_{He} decreases from 4.48 at 20 °C to 1.13 at 90 °C. This tendency is not significantly affected by the salinity of the solution. Thus $CO₂$ relative to He would be exsolved about four times more effectively at 90 \degree C than at 20 \degree C in the equilibrium condition. Such a process is highly likely at Wudalianchi given the discrepancy between observed temperatures at the site of sample collection and estimates of equilibration temperatures at depth in the geothermal system (\sim 160 °C, [Shangguan](#page-4-0) [et al., 2006](#page-4-0)). Furthermore, both gas loss and temperature decrease lowered the partial pressure of $CO₂$ in solution, resulting in precipitation of carbonate. Consequently, it can be concluded that the $\rm CO_2/^{3}$ He ratios of gas samples at Wudalianchi can only be lower than (initial) magmatic values (i.e., they follow the $CO₂$ loss trajectory in Fig. 3), so that the sample with the highest $\rm{CO_2}/^3$ He ratio of 2.7 \times 10¹⁰ represents the minimal CO₂/³He value of the source region. Consequently, the CO $_2$ / 3 He value of ${\sim}6 \times 10^{10}$ extracted by linear correlation between 3 He/ 4 He and $\delta {}^{13}$ C ([Fig. 2](#page-2-0)) most likely gives the best estimate of the Wudalianchi magmatic source.

Calcite precipitation can also cause carbon isotopic fractionation in gas phase, which is highly dependent on temperature. Such a fractionation effect is likely minimal at Wudalianchi as estimated geothermal reservoir temperatures at Wudalianchi (\sim 160 °C) are close to temperature (\sim 190 °C) where there is no fractionation in the $CO₂(g)$ -calcite system [\(Bottinga, 1969](#page-4-0)). Consequently, magmatic values ($\delta^{13}C_{\rm CO2}$ = \sim –4.2‰) are preserved in gas phase samples whereas slight variations of δ^{13} C likely reflect modifications due to phase change and/or calcite equilibration at lower temperatures.

Hence, chemical and isotopic features of magmatic components at Wudalianchi can be summarized as 3 He/ 4 He \sim 3.2 R_A, δ^{13} C \sim -4.2‰ and CO₂/³He \sim 6 \times 10¹⁰. We can then estimate the relative contributions of upper mantle (M), slab-derived limestone (L) and organic sediment (S) to the total $CO₂$ inventory by utilizing the ternary mixing model of [Sano and Marty \(1995\).](#page-4-0) Using magmatic δ^{13} C = -4.6% and CO₂/³He = 6 \times 10¹⁰, the relative proportions of M:L:S for Wudalianchi are 3:15:82 assuming the following end-member values: $\delta^{13}C_M = -6.5\%$, $\delta^{13}C_L = 0\%$ $\delta^{13}C_s = -20\%$, $(CO_2)^3$ He)_M = 2 × 10⁹, $(CO_2)^3$ He)_L = 1 × 10¹³ and $(CO_2)^3$ He)_S = 1 \times 10¹³. This estimate shows that \sim 97% of the CO₂ in Wudalianchi volcanic regions is slab-derived. It should be pointed out that choice of end-member values may not largely change the relative proportions ([Sano and Marty, 1995](#page-4-0)). For example, the significant change in relative proportion of upper mantle would be a factor of \sim 2 if varying $\left({\rm CO_2}/^3{\rm He} \right)_{\rm M}$ from 2×10^9 to 1×10^9 . As a result, the estimated relative proportion of slab-derived CO₂ in Wudalianchi (\sim 97%) is comparable with 88 ± 6% in modern circum-Pacific volcanic regions ([Sano and Williams, 1996\)](#page-4-0).

4.2. Heterogeneity of the SCLM beneath the NE China

The proposed subduction zone origin of $CO₂$ at Wudalianchi is in agreement with other geological, mineralogical and geochemical evidences that also identified subduction-related fluids as the enrichment agent of the SCLM in the region [\(Wang et al., 1988;](#page-4-0) [Hsu and Chen, 1998\)](#page-4-0). Although new tomographic studies of the mantle beneath NE China have revealed convincing imaging of the subducted Pacific Plate ([Lei and Zhao, 2005](#page-4-0)), there is no evidence to suggest that it can supply volatiles to Wudalianchi from depths of 500–600 km. Accordingly, we conclude that the Wudalianchi SCLM must have acquired and stored its slab-derived $CO₂$ since the Mesozoic (\sim 100 Ma), when the Izanagi oceanic plate was subducting under the Eurasian continental margin ([Maruyama](#page-4-0) [et al., 1989\)](#page-4-0).

It is unlikely that ³He/⁴He ratios would have changed significantly over this period. Evolution of 3 He/ 4 He ratio with time in lithospheric mantle has been discussed by several authors (e.g., [Reid and Graham, 1996; Gautheron and Moreira, 2002\)](#page-4-0). They calculated a contribution of radiogenic ⁴He from U and Th to the 3 He/ 4 He ratio assuming closed or open system. In the models, metasomatism causes U and Th enrichments in the subcontinental lithospheric mantle. In open system modeling, [Gautheron and](#page-4-0) [Moreira \(2002\)](#page-4-0) indicated that 3 He/ 4 He ratios would remain constant with time. In closed system, the ³He/⁴He ratio of SCLM beneath Wudalianchi could have decreased along with time.

We have estimated the enrichments of U relative to ³He for Wudalianchi, following principally the same method discussed by [Kim et al. \(2005\).](#page-4-0) [Fig. 4](#page-4-0) shows the time dependent variation of 3 He/ 4 He ratios starting from the upper mantle values for Wudalianchi and other Cenozoic intra-plate volcanic sites in NE China and Korean peninsula. Based on the U/ 3 He value in present-day mantle, 3 He/ 4 He ratio at 100 Ma ago is calculated to be 8.09 R_A. The calculation indicates that the U enrichment factors defined as $r = (U)^3$ He)_{SCLM}/(U/³He)_{UPPER-MANTLE} are 130 for Wudalianchi and vary from 4 up to 3400 in other areas. The enrichment factor can be enhanced by a He loss from the lithospheric reservoir as well as the low concentration of initially trapped He. [Kim et al. \(2005\)](#page-4-0) proposed that the large variation of enrichment factors obtained for the mantle-derived xenoliths in the Korean peninsula represent heterogeneously metasomatized lithospheric mantle beneath the Eurasian continental margin. This conclusion is supported by results of hydrothermal fluids in Wudalianchi (low-³He/⁴He-high- $CO₂/³He$) and Changbaishan (high- $³He/⁴He$ -low-CO₂/³He). In</sup>

Fig. 4. Growth curve of 3 He/ 4 He ratio in the SCLM after the metasomatic event at 100 Ma. The ³He/⁴He ratio (R/R_A) observed at present is shown for each locality. Enrichment factors defined as $r = (U/^{3}He)_{\rm SCLM}/(U/^{3}He)_{\rm UPPER-MANTLE}$ are 130, 41 and 4–3400 for Wudalianchi, Changbaishan and other sites in NE China and Korean peninsula (Kim et al., 2005), respectively. The U/³He ratio for present-day upper mantle adopted here was 5 \times 10⁷ ppm/(cm³ STP g⁻¹).

addition, geochemical studies on trace elements and isotopes of volcanic rocks have confirmed SCLM heterogeneity within a scale of \sim 40 km beneath the Changbaishan volcanic province (Sui et al., 2007).

5. Conclusions

The isotopic and relative abundance systematics of hydrothermal He and $CO₂$ display a strong slab-derived influence in Wudalianchi volcanic area. Although the slab contribution to the total $CO₂$ inventory at Wudalianchi is approximately the same as observed at modern-day circum-Pacific volcanoes, He and $CO₂$ likely represent ancient subduction zone fluids trapped in the SCLM since the Mesozoic. The large variations of mantle enrichment represent heterogeneity of the SCLM beneath the NE China.

Acknowledgments

This work was partially supported by the National Natural Science Foundation of China (No. 41020124002). We are grateful to two reviewers and Professor B.-M. Jahn for their constructive comments that greatly improved the quality of paper.

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