Liu Haiyang (Orcid ID: 0000-0002-7055-3482)
Xiao Yilin (Orcid ID: 0000-0002-5309-0711)
Heuser Alexander (Orcid ID: 0000-0003-3772-5534)
Churikova Tatyana (Orcid ID: 0000-0002-9929-9764)
Wörner Gerhard (Orcid ID: 0000-0003-1110-8976)

Trace elements and Li isotope compositions across the Kamchatka arc: Constraints on slab-derived fluid sources

Haiyang Liu^{1,2,4,5}, Yilin Xiao^{1,3*}, He Sun^{1,6}, Fengtai Tong¹, Alexander Heuser^{7,9},
Tatiana Churikova⁸, Gerhard Wörner⁹

¹ *CAS Key Laboratory of Crust-Mantle and Environments, School of Earth and Space
Sciences, University of Science and Technology of China, Hefei 230026, P. R. China*

² *Laboratory for Marine Mineral Resources, Pilot National Laboratory for Marine Science
and Technology (Qingdao), Qingdao 266237, P. R. China*

³ *CAS Center for Excellence in Comparative Planetology, Hefei, 230026, P. R. China*

⁴ *Center of Deep Sea Research, Institute of Oceanology, Chinese Academy of Sciences,
Qingdao 266071, P. R. China*

⁵ *Center for Ocean Mega-Science, Chinese Academy of Sciences, Qingdao 266071, P. R. China*

⁶ *School of resources and environmental engineering, Hefei University of Technology,
Hefei 230009, P. R. China*

⁷ *Helmholtz Centre for Ocean Research Kiel, Division of Marine Geosystems Kiel,
Kiel 24148, Germany*

⁸ *Institute of Volcanology and Seismology, Far East Branch, Russian Academy of Sciences,*

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1029/2019JB019237

Petropavlovsk-Kamchatsky, 683006, Russia

⁹ Geowissenschaftliches Zentrum der Universität Göttingen, Göttingen 37077, Germany

**Correspondence: ylxiao@ustc.edu.cn*

Key Points:

- The Kamchatka arc lavas show across-arc variations in chalcophile elements, suggesting that the amount of fluid decreases with depth
- Slab-derived fluids have a negligible contribution to the Li budget of the Kamchatka arc lavas
- CKD lavas have high U/Th, Li/Y, La/Sm and B/Nb ratios, indicating that lawsonite breakdown reaction dominates the water release

Abstract

Chalcophile elements and lithium (Li) isotopes were measured on lavas from a 220 km transect across the Kamchatka arc in order to investigate the fluid variations below arc volcanoes and to trace the geochemical behaviour of Li in convergent plate margins. From the Eastern Volcanic Front (EVF), through the Central Kamchatka Depression (CKD), into the Sredinny Range (SR) volcanic zones, chalcophile element ratios (e.g., As/Ce and Sb/Ce) show clear across-arc variations, decreasing (e.g., As/Ce: 0.20 to 0.03 and Sb/Ce: 0.013 to 0.002) with increasing depth above the slab (110 to 400 km). This clearly indicates a gradually decreasing influx of slab-derived fluids added to the mantle wedge as the slab subducts below Kamchatka. In addition, the anomalously high U/Th, La/Sm and B/Nb ratios in the CKD lavas suggest lawsonite breakdown reaction dominates the fluid release in this area. However, Li/Y (0.07 to 1.78) and $\delta^7\text{Li}$ (+1.8 to +5.4‰, with an exception of +8.6‰ in CKD) show limited variations and values similar to the MORB mantle. A dehydration model suggests that slab-derived fluids, which are characterized by high Li concentration and high $\delta^7\text{Li}$, do not control the Li budget in Kamchatka arc lavas. Therefore, the isotopic heavy Li from slab-derived fluids likely equilibrates in the sub-arc mantle, which acts as a buffer for Li systematics. In addition, based on the Li isotopic signatures of Klyuchevskoy volcano, our study demonstrates insignificant Li isotopic fractionation during mantle melting and subsequent differentiation.

Keywords

Li isotopes; chalcophile element; Kamchatka; hydrous mineral; serpentinite; lawsonite

1. Introduction

The mantle wedge above the subducted slab is the main source of arc magmatism, which is triggered by lowering the solidus of the mantle wedge through a contribution of the fluid and/or melt from a variety of sources. The nature of the slab fluid and/or melt can be traced by certain major and trace element abundances and isotope ratios (e.g., Auer et al., 2009; Churikova et al., 2001; Moriguti et al., 2004; Tang et al., 2014). Trace element and isotopic signatures also allow to distinguish fluids or melts derived mainly from subducted sediments, altered oceanic crust (AOC), serpentinites, or the basaltic subducted slab itself (Agostini et al., 2008; Bebout & Nakamura, 2003; Ishikawa & Tera, 1999; Ishikawa & Nakamura, 1994; Tang et al., 2014).

During subduction, due to varying proportions of variably hydrous minerals, hydrous fluids are expelled from the subducted slab and should change in composition and volume with increasing slab depth (Agostini et al., 2008; Schmidt & Poli, 1998; Walker et al., 2009). Glaucofane changes to barroisitic amphibole with increasing temperature, therefore, amphibole might be the dominant hydrous mineral below the volcanic front (Schmidt & Poli, 1998). With increasing temperature and pressure, amphibole decomposes at pressures higher than 2.2-2.4 GPa forming chloritoid while the residual mineralogy transforms to lawsonite eclogites (Schmidt & Poli, 1998). As the temperature and pressure continue to increase, lawsonite and phengite (if potassium is present) become the dominant hydrous minerals (Schmidt & Poli, 1998). Consequently, the fluids added to the arc mantle sources behind the volcanic front should be derived mainly from lawsonite and phengite breakdown reactions (Moriguti et al., 2004; Schmidt & Poli, 1998). Thus, the compositions of slab-derived fluids should vary during the subduction process (Du et al., 2018; 2019; Moriguti et al., 2004; Walker et al., 2009). However, studies that can reliably trace such changing fluid compositions at different subduction depth through across-arc geochemical traverses are limited by commonly overlapping geochemical signatures from slab contributions (serpentinite, AOC, sediments and

melts thereof) (Agostini et al., 2008; Churikova et al., 2001; Huang et al., 2018; Leeman et al., 2017; Leeman et al., 2004; Moriguti et al., 2004; Walker et al., 2009). In addition, very few arc systems exist where active mafic volcanism occurs over a large across-arc distance, such as the 220 km from Kronotsky and Gamchen volcanoes at the arc front in Kamchatka to Itchinsky in the back arc (Churikova et al., 2001; Münker et al., 2004).

Chemical elements such as As, Sb, Pb, W, Mo, Sn, are moderately chalcophile and siderophile as well as being moderately incompatible during magmatic processes, which cause them to be partitioned into metal/sulfide as well as into silicate liquids (Jochum & Hofmann, 1997; Jochum et al., 1993; Noll et al., 1996; Yi et al., 1995). In addition, several of these elements are also mobilized in aqueous fluids, which make them powerful tracers of subduction zone processes (Hofmann et al., 1986; Jochum & Hofmann, 1997; Noll et al., 1996; Pitcairn et al., 2006; Ryan et al., 1995). The fluid mobility of As, Sb and Pb is similar to that of B in subduction environment (Jochum & Hofmann, 1997; Noll et al., 1996; Ryan et al., 1995). In contrast, W, Mo and Sn are not seriously affected by water-rock interaction (Jochum & Verma, 1996; Newsom & Palme, 1984; Newsom et al., 1996; Noll et al., 1996; Yi et al., 1995) and W is often classified as an immobile high field strength elements (HFSE) like U, Th, Nb and Ta (Newsom & Palme, 1984; Newsom et al., 1996; Noll et al., 1996). Several across-arc traverses were employed to identify systematic changes in these element concentrations and/or ratios (Leeman, 1996; Noll et al., 1996; Ryan et al., 1995). However, the link between metamorphic dehydration and the mobility of these elements in subduction zone on one hand, and the behavior of these element in global elements cycling on the other hand, is not yet fully understood.

Lithium isotopes may be useful tracers for unrevealing the fluid sources of arc lavas because they have unique characteristics: (1) The two stable isotopes, ^6Li and ^7Li , show large relative mass difference. Consequently, the potential of mass-dependent isotopic fractionation is large (Penniston-Dorland et al., 2017; Sun et al., 2016; Tang Yanjie, 2009; Tomascak et al., 2016).

(2) the heavy isotope, ^7Li , preferentially partitions into hydrous fluids during fluid-rock interaction (Liu et al., 2019a; Marschall et al., 2007a; Moriguti & Nakamura, 1998; Penniston-Dorland et al., 2012; Penniston-Dorland et al., 2010; Tian et al., 2019; Xiao et al., 2011; Zhou et al., 2018). (3) Li can trace distinct slab fluids because it is relatively enriched in, and easily mobilized from, AOC and/or marine sediments, yet is depleted in the oceanic upper mantle (Marschall et al., 2017; Penniston-Dorland et al., 2017; Tomascak et al., 2016). (4) Li isotopic fractionation during high temperature partial melting is negligible (Halama et al., 2007; Halama et al., 2009; Tomascak et al., 1999) and therefore Li isotopes should be controlled by the sources rather than processes of melting. For these reasons, arc magmas are thought to reflect the Li isotopic compositions of slab contributions in subduction-related magmatism.

Lithium isotopes have been studied in arc lavas, and it has been suggested that Li isotopic characteristics of arc lavas could reflect the fluid signatures derived from the dehydration of the subducted slab (Agostini et al., 2008; Chan et al., 2002; Elliott et al., 2004; Elliott et al., 1997; Leeman et al., 2004; Magna et al., 2006; Moriguti & Nakamura, 1998; Moriguti et al., 2004; Tang et al., 2014). However, some arc lavas (e.g., Kurile arc, Eastern Russia, Sunda arc, Indonesia, Aleutian arc, Western Alaska, Tomascak et al., 2002) display relatively restricted Li isotopic compositions ($\delta^7\text{Li} = +2.1$ to $+5.1\%$), which overlap the values of unaltered N-MORB. Tomascak et al. (2002) suggested that the heavy Li released by the slab is sequestered in the subarc mantle prior to reaching the region of melt generation. To further test this hypothesis, we studied Li isotopic systematics across the Kamchatka arc based on a set of samples that has been characterized previously for major and trace elements, as well as radiogenic Sr, Nd, Pb and stable O, Zn, and Cu isotope compositions (Churikova et al., 2001; 2007; Dorendorf et al., 2000; Huang et al., 2018; Liu et al., 2015).

Our $\delta^7\text{Li}$ isotope and chalcophile trace element analyses for samples from a transect across the Kamchatka arc have been carried out on selected, fresh Holocene and historic mafic arc lavas

from the Churikova et al (2001) sample collection, which are particularly suited because earlier studies have demonstrated – based on a lack of correlation between Pb-isotopes and slab-signatures – that fluids or melts from subducted sediments are absent in their magma source (Churikova et al., 2001; Kersting & Arculus, 1995). Effects of alteration are excluded and therefore compositions should reflect Li-isotopic characteristics of the arc magma sources. These data are used to constrain the distinct fluid compositions as the slab descends below the arc and trace the geochemical behaviour of Li and its isotopes at convergent plate margins.

2. Geological background

The Kamchatka in the northwestern part of the Pacific ‘Ring of Fire’ is an area of high seismic activity and abundant volcanism, along the northern part of the Kurile-Kamchatka volcanic arc (Figure 1a, Kepezhinskias et al., 1997; Portnyagin et al., 2007). Volcanic activity on Kamchatka dates back to the Cretaceous. The current plate-tectonic configuration formed in the Late Miocene to Early Pliocene (Churikova et al., 2001; Dorendorf et al., 2000; Volynets et al., 2010). Today, the 87-104 Ma old Pacific plate is subducting at an angle of $\sim 55^\circ$ below southern and central Kamchatka at a rate of ~ 9 cm/a (Figure 1a, Geist & Scholl, 1994; Renkin & Sclater, 1988). The plate angle shallows to $\sim 30^\circ$ near the Kamchatka-Aleutian junction where subduction terminates at a series of transform faults separating the Pacific from the Komandorsky plate (Volynets et al., 2010).

Kamchatka has more than 240 volcanic centers, with 34 currently active (Kepezhinskias et al., 1997). From east to west, volcanic centres on Kamchatka are concentrated in three zones parallel to the trench (Figure 1b): (1) the Eastern Volcanic Front (EVF); (2) the Central Kamchatka Depression (CKD) a rift-like structure with the large Klyuchevskaya Group and three more northern volcanoes (NCKD). This volcano zone produces $\sim 50\%$ of all the volume erupted from active volcanoes of the Kurile-Kamchatka arc (Ishikawa et al., 2001); Finally (3) the Sredinny Ridge (SR) represents the back arc. The slab depth varies from 100-140 km below

the EVF to 100-200 km below the CKD and 300-400 km below the SR (Gorbatov et al., 1997). Crustal thickness increases from 20 km in the south to 42 km in the north (Balesta, 1991; Gorbatov et al., 1997).

Kamchatka magmas display typical arc signatures with enrichment in fluid-mobile elements (LILE, Sr, Pb) and variable depletion in HFSE (e.g. Churikova et al, 2001, 2007, Figure S1). A narrow range of Pb isotope values ($^{206}\text{Pb}/^{204}\text{Pb}=18.15$ to 18.30 , $^{207}\text{Pb}/^{204}\text{Pb}=15.45$ to 15.48 , $^{208}\text{Pb}/^{204}\text{Pb}=37.74$ to 37.95) for samples with large variations in fluid-mobile elements and similar Sr-isotope compositions and the absence of elevated ^{10}Be concentrations ($<1.2 \times 10^6$ at/g) was interpreted to imply that pelagic sediments were not involved in the genesis of Kamchatka lavas at this latitude and that the slab signature was dominated by fluids from the subducted slab and associated serpentinites (Churikova et al., 2001; 2007; Dorendorf et al., 2000; Ishikawa et al., 2001; Kersting & Arculus, 1995; Koulakov et al., 2016; Leeman et al., 2001; Tsvetkov et al., 1989). In detail, the investigation of melt inclusions in olivine suggests successive changes and three compositionally distinct fluids are identified for the EVF, CKD and SR below the Kamchatka arc (Churikova et al., 2007).

The arc-front magma source is most enriched in fluid-mobile elements, e.g., high B/La, only moderately enriched in Li and shows mantle-like O-isotopes (Churikova et al., 2007). Fluids that dominate lavas from the most productive intra-arc rift zone, the Central Kamchatka depression, are distinct in being strongly enriched in ^{18}O (up to $\delta^{18}\text{O}=7.5$ ‰ for olivine Fo_{87-92} , Dorendorf et al., 2000), relatively poor in B but with high U/Th. Ba/La ratios and Li are mildly enriched and $^{87}\text{Sr}/^{86}\text{Sr}$ is slightly higher compared to arc front lavas (Churikova et al., 2001; Churikova et al., 2007; Dorendorf et al., 2000). At the same time, ratios of fluid-immobile elements such as Nb/Zr increase by an order of magnitude from the Eastern Volcanic Front (EVF) to the Sredinny Ridge (SR), indicating that the mantle wedge was highly depleted at the arc front and enriched below the back arc (Churikova et al., 2001). This documents variation

in the signatures of fluid-mobile elements overprinting a variably depleted/enriched mantle source.

We selected 31 samples from a traverse of ~210 km, covering 9 Holocene volcanoes (Figure 1). The transect starts from the EVF (Gamchen: GAM, Shmidt: SHM, Komarov: KOM, Kizimen: KIZ) through the CKD (Klyuchevskoy: KLU, Tolbachik: TOL) and NCKD (Shiveluch: SHIV) into the back-arc (Ichinsky: ICH, Esso: ESO). Detailed sample description and analytical data are given in (Churikova et al., 2001).

3. Analytical Methods

3.1. Major and trace elements

Most of the selected samples were previously determined by X-ray fluorescence (XRF) for major and some trace elements (Sc, V, Cr, Co, Ni, Zn, Ga, Sr, Zr, Ba) and for other trace elements by ICP MS at Göttingen University, see details in Churikova et al. (2001). Three additional samples (SHIV-01-01, 05, 12) from Shiveluch eruption 2001 (NCKD) were analyzed by XRF with the same method in this study. Trace elements for these samples were determined by ICPMS at the CAS Key Laboratory of Crust-Mantle Materials and Environments, University of Science and Technology of China (USTC). Single-element Rh was used as the internal standard. The accuracy of analysis is better than 5% for most trace elements (Hou and Wang, 2007).

Chalcophile elements (e.g., As, Mo, Sn, W and Sb) were determined separately from sample splits. About 100 mg of powdered rock were digested in two multi-acids solutions: a combination of ultra-pure HF/HClO₄ and, for reasons given below, of ultra-pure HF/HNO₃. Three mL of each acid were used to dissolve the powdered rocks. Two Japanese geostandards (JA-2 and JB-3) were handled in the same way as the samples. The samples have been digested for 12 hours at 200°C in closed teflon beakers (Picotrace®). After digestion the solutions have been evaporated to dryness for 2 hours by 150° C. The precipitates were dissolved in 2 mL

ultra-pure HNO₃ and 200 µL of a 10 µg/g solution of In and Re as internal standard have been added. These solutions then were diluted up to 100 mL with ultra-pure H₂O. In some solutions a white flaky precipitate was observed. Therefore, all solutions were treated for 20 minutes in an ultrasonic bath until the precipitates dissolved. These solutions remained stable for at least 48 hours.

Two different calibration solutions with four different concentrations of the elements were applied during the analytical procedures. This was a necessity because the mass resolution of the current ICP-MS is insufficient to separate the peaks of Arsenic (75 µ) from ⁴⁰Ar³⁵Cl⁺, hence introducing severe interferences. A correction strategy for this interference was via mass 77 (⁴⁰Ar³⁷Cl⁺), however, failed because the count rates on mass 77 were not sufficiently high above background. As a consequence, the only way to precisely analyse As is to minimize Cl in the final solutions. Sample digestions therefore were repeated using only ultra-pure HF/HNO₃ without the use of HCl or perchloric acid to avoid Cl-interferences. However, without energy filtration or similar technology, As-Cl interference is unavoidable. The As concentrations of the reference materials (JA-2 and JB-3) measured in this paper are a factor of 1.4 to 1.8 higher than the recommended values. Even though, compared to the observed large differences in Kamchatka lavas these deviations may be considered negligible.

The concentrations of chalcophile elements As, Sb, Bi, Cd, Pb, Sn and Mo were thus determined separately from the other trace elements by a VG PQ2+ ICPMS with instrument settings specifically optimised to measure chalcophile elements. Measurements were done using a V-Groove and a Meinhard nebulizer. The incident power of the ICP generator was 1350W, only one determination of As was done with a power of 1250 W.

Isotopes analysed include: ⁷⁵As, ⁹⁵Mo, ⁹⁸Mo, ¹¹¹Cd, ¹¹²Cd, ¹¹⁴Cd, ¹¹⁷Sn, ¹¹⁸Sn, ¹²⁰Sn, ¹²¹Sb, ¹²³Sb, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb. For the calculation of the results the averages of the different isotopes were used. When interferences were detected that could affect the analysis, the measurements were

rejected. Dissolved sample splits from different dissolution procedures were done and measured several times to secure external and internal reproducibility. For each measurement and for the calculated mean of all measurements the limit of detection (LOD), the lower limit of determination (LLD) and limit of quantification (LOQ) were calculated and considered in the data evaluation.

The accuracy of these measurements is difficult to assess, the reason being that reference materials generally do not have reliable recommended values for some of these elements. Therefore, we focused on the reproducibility based on our repeat measurements (Table S5).

3.2. Lithium isotopes

Lithium isotopic compositions ($\delta^7\text{Li}$) of the selected lavas were determined at the CAS Key Laboratory of Crust-Mantle Materials and Environments, University of Science and Technology of China (USTC). Sample dissolution procedures, column chemistry and instrumental parameter are reported in Sun et al. (2016) and Liu et al. (2019). Whole rock powders (~50mg) were weighed and dissolved in a teflon PFA beaker with a combination of ultra-pure HF-HNO₃-HCl. Li was purified on a cation exchange resin (Bio-RAD AG50W-X12) by an organic solvent-free two-step chromatography. Lithium isotopic compositions were measured on a Neptune Plus MC-ICPMS using a standard-sample-bracketing method, using L-SVEC as calibration standard. The external precision is better than 0.5‰, based on repeat measurements of in-house ($Q_{\text{USTC}} = + 8.8 \pm 0.2\text{‰}$, 2SD, $n = 261$) and international rock standards (BHVO-2 = $+ 4.2 \pm 0.5\text{‰}$, 2SD, $n = 5$, GSP-2 = $- 0.8 \pm 0.3\text{‰}$, 2SD, $n = 9$, and AGV-1 = $+ 5.9 \pm 0.5\text{‰}$, 2SD, $n = 5$), during the course of this study.

4. Results

Previously published whole rock major and trace elements and Sr-Nd-Pb-O isotope compositions (Churikova et al., 2001; Dorendorf et al., 2000) are combined in Appendix Table S1, S2 and Table 1 with new Li isotope compositions and chalcophile element data from this

study. The compiled data set also includes new XRF and ICPMS data for three additional NCKD samples.

4.1. Chalcophile element contents

Fluid-mobile chalcophile trace element concentrations (Table S5) are normalized to immobile elements of similar incompatibility to avoid effects of fractional crystallization on absolute concentrations and to highlight the relative behaviour of fluid-mobile elements (Figures. 2 and 3). Crystal-melt partition coefficients $D_{As, Sb, Pb, Mo} \approx D_{Ce}$, $D_W \approx D_{Th}$, $D_{Sn} \approx D_{Sm}$ are similar for typical silicate minerals in mafic magmatic rocks (e.g., Jochum & Verma, 1996; Newsom & Palme, 1984; Newsom et al., 1996; Noll et al., 1996; Yi et al., 1995). Therefore, the ratios of As/Ce, Sb/Ce, Pb/Ce, W/Th, Mo/Ce and Sn/Sm should be independent of melting and crystallization processes and are used here to monitor enrichments/depletions during magma genesis (Jochum & Verma, 1996; Newsom & Palme, 1984; Newsom et al., 1996; Noll et al., 1996; Yi et al., 1995). The As/Ce (from 0.20 to 0.03), Sb/Ce (from 0.013 to 0.002) and Pb/Ce (from 0.34 to 0.05) ratios are highest in arc magmas from the volcanic front declining towards the Kamchatka Depression lavas and towards depleted mantle values for Sredinny Ridge back arc lavas (Figure. 2). In addition, As/Ce, Sb/Ce and Pb/Ce ratios of the Kamchatka samples show positive correlations with B/La and B/Zr (Figure. 3). The Mo/Ce ratios also decrease slightly whereas the W/Th and Sn/Sm ratios are generally constant from volcanic front to back arc (Figure. 2). The CKD samples, however, display slightly decreasing W/Th ratios with distance from the volcanic front (Figure. 2d). Despite the fact that SR samples have lower ratios than EVF and CKD, they still show enrichment in some chalcophile element ratios (e.g., Sb/Ce, Pb/Ce and Mo/Ce).

4.2. Li contents and Li isotopic compositions

The 24 out of 31 Kamchatka samples contain higher Li concentrations (average 8.78 ± 8.95 $\mu\text{g/g}$, Figure 4) than fresh MORB (~ 4 $\mu\text{g/g}$, e.g., Tomascak et al., 2008; Marschall et al., 2017).

EVF samples range considerably in Li concentrations from 1.45 $\mu\text{g/g}$ to 16.7 $\mu\text{g/g}$, whereas almost all CKD and SR rocks show higher Li concentrations than the N-MORB (7.50 to 15.8 $\mu\text{g/g}$, 3.13 to 11.5 $\mu\text{g/g}$, respectively).

The $\delta^7\text{Li}$ of most Kamchatka samples (+1.8 to +8.6‰, average 4.2 ± 2.4 ‰, Figure 4, Table 1) overlap the range of fresh N-MORB ($+3.5 \pm 1.0$ ‰, Tomascak et al., 2008; Marschall et al., 2017). However, CKD (+3.6 to +8.6‰, average +5.1‰) show generally higher $\delta^7\text{Li}$ values than EVF (+1.8 to +5.4‰, average +3.9‰), NCKD (+2.7 to +4.3‰, average +3.4‰) and SR (+3.5 to +4.1‰, average +3.8‰). Whereas, the Li isotopic compositions of EVF are comparable to the published $\delta^7\text{Li}$ values of mantle xenoliths from Kamchatka (-0.3 to +4.6‰, average +2.5‰, Ionov & Seitz, 2008; +3.0 to +5.6‰, average 4.4‰, Halama et al., 2009, Figure 4). The $\delta^7\text{Li}$ values are not significantly correlated with Li concentrations or with any simple index of differentiation (Figures. 4 and 5) or fluid-mobile elements (FME) such as chalcophile elements and B.

For instance, at an MgO of 8 wt%, $\delta^7\text{Li}$ values vary over the total observed range (Figure 5a). In essence, our Kamchatka samples form a trend between N-MORB values and altered oceanic crust without reaching the high values of the latter (Figure 4).

5. Discussion

5.1. Secondary alteration and crustal contamination

Chan et al. (2009) demonstrated that the Li isotope compositions of basaltic rocks are susceptible to secondary alteration and crustal contamination. Therefore, extreme caution is necessary to evaluate the effects of assimilation, post-magmatic contamination and alteration. Our samples are completely fresh without any indication of weathering such as vesicles or cracks filled by secondary minerals, red oxidation, or elevated LOI. Inspection of thin sections also did not reveal any signs of alteration such as carbonates and other secondary minerals. In addition, there is no correlation between the $\delta^7\text{Li}$ values and LOI (0.21 to 1.87 wt%, Figure 5b)

for our samples. The sample with the highest $\delta^7\text{Li}$ value (KLU-96-06= $+8.6\pm0.1\text{‰}$) still has low LOI (0.31 wt %, Figure 5b). Crustal assimilation during magmatic processes at depth is also ruled out because the $\delta^7\text{Li}$ values of Kamchatka lavas show no correlation with SiO_2 or Sr-Nd isotope compositions (Figure S2). Even the sample with the highest SiO_2 (KOM-96-11/2= 61.0%) from the EVF has MORB-like $\delta^7\text{Li}$ ($+3.5\pm0.2\text{‰}$). Crustal contamination is also unlikely to have significantly affected Li-isotope systematics in Kamchatka lavas as shown by previous studies on trace elements and radiogenic isotopes (Churikova et al., 2001; 2007; Münker et al., 2004). Therefore, even though data on clean separated minerals and melt inclusions preserved in olivine may be more reliable indicators of original, magmatic $\delta^7\text{Li}$ values (Chan et al., 2009), we conclude that the influence on the Li isotope systematics by contamination and/or alteration on our samples is negligible, and that the Li isotopic compositions of whole rock data can be confidently used in the following discussion.

5.2. Insignificant Li isotope fractionation during magmatic differentiation: constraints from Klyuchevskoy volcano

Klyuchevskoy is only the most prominent one of the Klyuchevskaya Group of large stratovolcanoes located in the CKD intra-arc rift-like zone. Klyuchevskaya Group contains 13 volcanoes, including Bezymianny, Kamen, Ploskie Sopki, Tolbachick, all of which were active in the Holocene. This area is also characterized by the subduction of the Hawaiian-Emperor seamount chain below the CKD (Figure 1). Therefore, rifting and upwelling from a highly fluxed mantle wedge rich in slab-derived fluids has been proposed as the cause of high magmatic productivity of the region and the unusually heavy O-isotope composition of the magma source (Dorendorf et al., 2000).

Klyuchevskoy erupted dominantly basaltic and basaltic-andesitic lavas and rarely pyroclastic rocks. Previous studies (Khrenov et al., 1989; Kersting & Arculus, 1995) have distinguished “high-Mg basalts” (>7 wt% MgO) and “high-Al basalts” (<7 wt% MgO). Based on petrologic,

major and trace element data, Kersting and Arculus (1994) suggested that the variable compositions result from non-steady processes of recharge and crystal fractionating of parental high-MgO basaltic melts to produce high-Al₂O₃ basalts. However, neither $\delta^7\text{Li}$ values vs MgO (wt%) nor $\delta^7\text{Li}$ values vs K₂O (wt%) show clear correlations to link any of these magmatic processes to variable $\delta^7\text{Li}$ signatures (Figure S3). From this observation, we conclude that high temperature ($\sim 1200^\circ\text{C}$) magmatic processes did not cause resolvable Li isotopic fractionation, similar to previous conclusions (e.g., Tomascak et al., 1999). It is worth noting that there is one unusually high $\delta^7\text{Li}$ value (KLU-96-06, $+8.6 \pm 0.1\text{‰}$, repeatedly measured, $n=6$) in a Klyuchevskoy lava sample, which otherwise does not show any unusual compositions (e.g., SiO₂, MgO, K₂O, Li, and LOI, Figures. 4 and 5) or isotopic ratios (e.g., Sr, Nd, Pb, O, Figure S2). Weathering or alteration is unlikely, because these processes would cause lower, rather than higher $\delta^7\text{Li}$ values (Figure 4). Olivine from this sample has only slightly elevated $\delta^{18}\text{O}$, but fall within the range reported for Klyuchevskoy volcano (Figure S2, Dorendorf et al., 2000). Fluids derived from altered oceanic crust should be ^7Li -enriched, however, this should also apply to the other samples and therefore our data are too limited to explain the elevated $\delta^7\text{Li}$ value of this sample (Figure S2).

5.3. The Li isotopic signature of slab-derived melts

NCKD samples (Shiveluch volcano) will be discussed first and separately as they show distinct geochemical compositions (Churikova et al., 2001; Yogodzinski et al., 2001). HREE-depleted trace element signatures at Shiveluch volcano, located at the junction between the Kuril-Kamchatka and the Aleutians island-arc segments, have been associated with the partial melting at the edge of the Pacific plate subducting under Kamchatka where it is torn and exposed to hot asthenospheric mantle (Ferlito, 2011; Yogodzinski et al., 2001). Our samples from Shiveluch have an "adakitic" signature, e.g., higher SiO₂ at a given MgO, and higher Sr/Y and La/Yb (31 to 53 and 3.66 to 6.22, respectively, Table S1, Figure 6) than adjacent lavas in

CKD volcanoes. Melts derived from subducted oceanic slab are expected to be isotopically light due to a negative $\delta^7\text{Li}$ value of eclogite (global average $\delta^7\text{Li}$ value is -1.6 ± 2.0 , Marschall et al., 2007b). However, neither negative $\delta^7\text{Li}$ values nor correlations between $\delta^7\text{Li}$ values and Sr/Y ratios (Figure 6) were observed. The MORB-like $\delta^7\text{Li}$ of Shiveluch lavas are inconsistent with direct derivation from an isotopically light eclogite source. However, Li isotopic fractionation during metamorphic dehydration and melting of subducted basaltic crust remains a subject of debate. Variable parameters of modeling the composition of dehydrated slab residuals show a large range in $\delta^7\text{Li}$ values ($\delta^7\text{Li} = -1$ in Simons et al., 2010; $\delta^7\text{Li} = +8\text{‰}$ in Marschall et al., 2007b; $\delta^7\text{Li} = +4.5\text{‰}$ in Liu et al., 2019a). Significant $\delta^7\text{Li}$ fractionation also appears to be absent in published $\delta^7\text{Li}$ data for adakites (e.g., Panama adakites $+1.4$ to $+4.6\text{‰}$, Tomascak et al., 2000), which is consistent with our data for NCKD lavas. Two possible explanations for the MORB-like $\delta^7\text{Li}$ values in "adakitic" arc magmas can be considered: (1) the MORB-like Li isotopic compositions are preserved during slab dehydration (section 5.6 will discuss this in more details), which is supported by the limited Li isotope fractionation during prograde metamorphism (e.g., Marschall et al., 2007b; Qiu et al., 2009, 2011a, 2011b; Liu et al., 2019a; Simons et al., 2010; Teng et al., 2007); (2) Alternatively, slab dehydration did produce an anomalous "heavy" Li isotopic signature, but this has been obliterated by the dominance of mantle-Li in the mantle-wedge magmas source and mixing by vigorous mantle convection under the NCKD (Ferlito, 2011; G. Yogodzinski et al., 1995), as proposed by Tomascak et al. (2000). From this follows that subduction dehydration, slab melting and mixing with Li from the mantle wedge will only have minor effects on $\delta^7\text{Li}$ values and therefore arc magmas do not deviate significantly from MORB-type mantle.

5.4. Across-arc trends in chalcophile elements and B

Trace element ratios (e.g., B/Nb, Ba/Nb) and $\delta^{11}\text{B}$ values of the Kamchatka lavas show a systematic decrease with increasing slab depth, which was explained by the continuously

decreasing flux of slab-derived fluids in the mantle wedge (Ishikawa et al., 2001). This conclusion was supported by strong correlations between H₂O/Ce and B/Zr ratios observed in melt inclusions of olivine from volcanoes across Kamchatka (Churikova et al., 2007; Portnyagin et al., 2007). Therefore, the fluid mobile element B can be employed here to evaluate the behavior of the chalcophile elements. In the present study, we observe that from EVF through CKD into SR, As/Ce (from 0.20 to 0.03), Sb/Ce (from 0.013 to 0.002) and Pb/Ce (from 0.34 to 0.05) show strongly decreasing trends with increasing slab depth (Figures. 2, 3 and S4). This together with the strong positive correlations between these ratios (e.g., As/Ce, Sb/Ce and Pb/Ce,) and B/La and B/Zr ratios (Figure. 3) suggest that As, Sb and Pb were mobilized during metamorphic dehydration from subducted basalt and that slab-derived fluid influx into the mantle decreases across the arc (Noll et al., 1996; Ryan et al., 1995; Zack et al., 2002). In contrast, W/Th, Mo/Ce and Sn/Sm ratio diagrams show generally subhorizontal trends versus slab depth, with values similar to N-MORB (Figure. 2). This indicates that, on one hand, W, Mo and Sn have similar bulk partition coefficients relative to Th, Ce and Sm and, on the other hand, that these elements are not significantly mobilized by metamorphic dehydration during slab subduction (Noll et al., 1996).

Sulfide minerals (e.g., pyrite, sphalerite, chalcopyrite, cobaltite and pyrrhotite) and rutile (for W, Sb, Sn and Mo) are the main host of chalcophile elements (Chen et al., 2019; Pitcairn et al., 2006; Zack et al., 2002). Besides, clinopyroxene and garnet in eclogite can also store significant amounts of Sn and Mo (Zack et al., 2002). During prograde metamorphism, S is abundant in the dehydrated fluids and thus may be sufficient to transport these elements (Noll et al., 1996; Pitcairn et al., 2006). For instance, investigation of the trace element mobility found that mid- to high-grade (450°C and 0.8 to 1 GPa) metamorphosed schists are depleted in As, Sb, Mo, and W compared to unmetamorphosed protolith samples, which was explained by the decomposition of and liberation from pyrite, galena, sphalerite and cobaltite (Pitcairn et al.,

2006). In addition, the study of sulfide phases in peridotite mantle xenoliths also suggested that As and Sb can be transported by aqueous fluid phase from slabs to arc magma sources (Hattori et al., 2002). The studies of active serpentinite mud volcanoes from the Mariana forearc also found that serpentinitized peridotites are highly enriched in B, As and Sb, which demonstrates that these elements are highly fluid-mobile during shallow subduction at low temperatures (Savov et al., 2005). Such mobility is supported by the chemical composition characteristics of subducted sediments from the Catalina schist, which shows that As and Sb display decreases in mean concentration and in the range of concentrations with increasing grade (Bebout et al., 1999).

Molybdenum and Sn have similar compatibility to As, Sb and Pb, however, they are not quite as mobile in low-temperature fluids, as demonstrated by the high-temperature formation of most Sn and Mo deposits (Zhang et al., 2017; Zhang et al., 2019). Most of the Kamchatka samples have marginally higher Mo/Ce ratios than the N-MORB, which may indicate that Mo has a relatively low degree of fluid mobility during subduction (Noll et al., 1996). This is consistent with the recently observed Mo isotope fractionation during oxidized fluid activity in subduction zones (Chen et al., 2019). The W/Th and Sn/Sm ratios do not decrease noticeably with slab depth, which is similar to across-arc trends in Japan and Kurile arc (Noll et al., 1996). Collectively, we suggest that the behavior of As, Sb and Pb during subduction zone resembles the high fluid mobility of B, while Mo shows relatively weaker fluid mobility. In contrast, both W and Sn have very limited mobility and show restricted transport during metamorphic dehydration.

Based on the relative variations of chalcophile elements ratios, B, Li, U/Th, Ba/Th ratios as well as Sr, O and Li isotopes, we can clearly distinguish three fluids by taking the highest values (Figures. 3 and S4): (1) The *EVF fluid* is characterized by high B/La, As/Ce, Sb/Ce and Pb/Ce ratios, but low Li/B and Ba/Th (Figures. 3 and 7). (2) the *CKD fluid* has high Li/Y and

U/Th, as well as $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}$. Interestingly, the CKD lavas show even slightly higher $\delta^7\text{Li}$ values than the EVF and SR lavas, which together with the high Li/Y ratios, suggest a significant contribution from AOC-derived fluid below CKD (Figures. 3 and S4). (3) The back arc is dominated by the mantle wedge in many respects. The *back-arc fluid* signature is weak but can still be identified by having enrichments in Ba/Th, B/La, La/Nb, and Pb/Ce relative to MORB and depleted mantle wedge (Figures. 3 and S4). The *back-arc fluid* has, however, low B/Li (Figure S4) and high F/Cl ratios (Churikova et al., 2007).

5.5. Control of fluid compositions by mineral breakdown reactions in the slab

In the following chapter we propose explanations for the origin of distinct fluid compositions that we characterized above. Like B/Nb, Li/Y is expected to decrease with depth to the slab (Agostini et al., 2008; Moriguti & Nakamura, 1998). However, Li/Y ratios (Figure 7a) show variable and overlapping values from EVF (0.07 to 0.73, average 0.33) through CKD (0.51 to 0.63, average 0.56) to SR (0.17 to 0.53, average 0.33), which cannot be explained by a systematic decrease in the addition of Li from slab-derived fluids in the source regions of arc magma (Moriguti et al., 2004). During prograde metamorphism, Li shows more complex behavior than B, since Li is not strongly partitioned into a single mineral; chlorite, lawsonite, amphibole, clinopyroxene, and garnet can all incorporate significant amounts of Li (Bebout et al., 2007; Bebout et al., 2013; Halama et al., 2010). This may be the reason why no systematic across-arc variation in Li/Y ratios observed (Bouvier et al., 2010; Tomascak et al., 2002; Walker et al., 2009).

As/Ce, Sb/Ce, Pb/Ce and B/Nb ratios are highest in EVF lavas indicating that the early pulse of dehydration reactions in the slab liberated the largest amounts of fluid-mobile elements. These early dehydration reactions below the arc front probably involved chlorite, as argued above. CKD lavas, in addition, show particularly high U/Th (average: CKD=0.58, EVF=0.41, Figure 8a) and La/Sm ratios (average: CKD=2.01, EVF=1.64, Figure 8b) compare to the arc

front. It is unlikely that the high Li/Y, La/Sm and B/Nb ratios for the CKD lavas are produced only by different amounts of slab derived fluids, because these elements have similar geochemical behaviors during solid/fluid interaction (Churikova et al., 2001; 2007; Moriguti et al., 2004; Sun & McDonough, 1989). Therefore, we suggest that the high Li/Y, La/Sm and B/Nb ratios for the CKD lavas are likely caused by a specific fluid that resulted from and locally focused breakdown reactions of hydrous minerals in the subducting slab. In the case of U/Th and under oxidized conditions of slab fluids, U may be more mobile than Th and this should cause additional enrichment of U over Th.

Schmidt & Poli (1998) demonstrated that lawsonite or phengite may be the hydrous minerals in the subducting slab to about 6 GPa (equivalent to the source depth of CKD lavas). Lawsonite is the dominant host mineral for U and LREE in high-pressure metamorphic rocks (Usui et al., 2003). In addition, garnet may replace lawsonite during continuous lawsonite breakdown reactions (e.g., lawsonite + diopside + garnet 1 = garnet 2 + coesite + H₂O; Schmidt & Poli, 1998; Moriguti et al., 2004). As Y and middle to heavy REE are strongly partitioned into garnet (Liu et al., 2019b), consequently lawsonite breakdown could result in both high U/Th as well as high Li/Y and La/Sm ratios. The interpretation of lawsonite breakdown dominating the slab-derived fluid below CKD is consistent with the glass inclusion study in olivine from Kamchatka lavas (Churikova et al., 2007) and was also used to explain the convex-up across-arc profile of Li/Y, U/Nb, La/Sm ratios observed in the north-eastern Japan arc (Moriguti et al., 2004).

5.6. What controls Li isotopic compositions in arc magma sources?

As discussed above, chalcophile element ratios (e.g., As/Ce, Sb/Ce, Pb/Ce Figures. 2 and 3) and $\delta^{11}\text{B}$ values systematically decrease with increasing slab depth (from +5.6‰ to -2‰, Ishikawa et al., 2001). However, a systematic Li isotope variation with increasing slab depth is not observed (Figure 7). $\delta^7\text{Li}$ values of Kamchatka lavas are relatively restricted, and generally

overlap the values of unaltered N-MORB ($+3.5 \pm 1.0\%$, Marschall et al., 2017; Tomascak et al., 2008) and also those of other arc lavas (Agostini et al., 2008; Leeman et al., 2004; Magna et al., 2006; Moriguti & Nakamura, 1998; Moriguti et al., 2004; Tang et al., 2014; Tomascak et al., 2002; Walker et al., 2009). $\delta^7\text{Li}$ values show no clear correlations with fluid mobile/chalcophile element ratios (Figures. 4 and 9) and isotope data (e.g., O, Sr, Nd, Pb, Hf and Cu, Figure S2). Therefore, rather similar range in Li isotopes from arc front to back arc cannot be simply explained by the decreasing amount of slab-derived fluid added to the source region with increasing slab depth (Moriguti & Nakamura, 1998; Tomascak et al., 2002). Moreover, such a process also fails to take into account the isotopic fractionation expected during progressive dehydration of the subducted oceanic crust (Benton et al., 2004; Liu et al., 2019a; Marschall et al., 2007a; 2007b; Simons et al., 2010; Walker et al., 2009). Such a continuous decrease of $\delta^7\text{Li}$ values in slab fluids with increasing slab depth was demonstrated in the southern Cascades (Magna et al., 2006) and high-pressure metamorphic rocks (Halama et al., 2011; Liu et al., 2019a; Marschall et al., 2007; Simons et al., 2010).

To evaluate whether the Li isotope system of Kamchatka arc lavas has been affected by the slab-derived fluid, the effect of dehydration of altered oceanic crust and serpentinites has been modeled and compared to observed data (Figure 10). As endmembers we adopted values from the literature for altered oceanic crust and serpentinite. Sediment-derived fluid was not modeled due to the absence of sediments in the Kamchatka arc magma sources.

We used endmember values of altered oceanic crust (Li: 10 $\mu\text{g/g}$, $\delta^7\text{Li}$: $+6.0\%$, Liu et al., 2019a; Marschall et al., 2007a; Chan et al., 2002; Bouman et al., 2004) in the dehydration model (Figure 10). Sub-arc depth (100-400 km) corresponds to high temperature dehydration. Therefore, only a high temperature continuous dehydration processes was modeled according to the method of Marschall et al. (2007a), running in 24 steps with variable P, T, D (bulk partition coefficient) and α (fractionation factor, Marschall et al., 2007a). The Li isotopic

composition of a potential serpentinite fluid source in the model is deduced from serpentinite recovered from the Mariana forearc (Li: 6 $\mu\text{g/g}$, $\delta^7\text{Li}$: 4.5‰, Benton et al., 2004, Figure 10). Experimental data suggest that Li isotope fractionation between serpentinite and aqueous fluid (0.2-4.0 GPa, 200-500°C) is strongly influenced by the three serpentine varieties involved: in lizardite and antigorite Li has a six-fold coordination, whereas in chrysotile Li is incorporated in both octahedrally and as Li-bearing water clusters filling the nanotube cores (Wunder et al., 2010). Consequently, in the lizardite- and antigorite-fluid systems, ^7Li preferentially partitioned into the fluid and except for chrysotile-fluid system where ^7Li is weakly partitioned into chrysotile (Tian et al., 2019; Wunder et al., 2010). Antigorite, the high pressure serpentine polymorph, should be the dominant phase during sub-arc dehydration (Wunder et al., 2010). However, the dehydration model for serpentinites is limited by the lack of constraints on the dependence of temperature and pressure on relative parameters (e.g., D and α , Wunder et al., 2010). Therefore, it is assumed that the partition coefficient and the isotopic fractionation factor ($D=0.15$, $\alpha=1.0011$, $\Delta_{\text{fluid-serpentinite}}=+1.1\text{‰}$, based on antigorite, $P=4\text{GPa}$, $T=500^\circ\text{C}$, Wunder et al., 2010) between serpentinite and fluid are constant during dehydration (Figure 10).

The modeling results show that the AOC and serpentinite-derived fluids both should display higher Li concentration (20 to 307 $\mu\text{g/g}$) and $\delta^7\text{Li}$ values (+4.1 to +10.2‰) as compared to values for fresh MORB and our data on Kamchatka arc lavas (Figure 10). By contrast, the modeled residual dehydrated oceanic crust (Li: 5.8 to 10 $\mu\text{g/g}$, $\delta^7\text{Li}$: +4.1 to +6.0‰) and serpentinite (Li: 1.6 to 6 $\mu\text{g/g}$, $\delta^7\text{Li}$: +3.0 to +4.5‰) show Li isotopic characteristic similar to fresh MORB and comparable to Kamchatka arc lavas (Figure 10).

Collectively, the various slab-derived fluids all are characterized by high Li concentration and $\delta^7\text{Li}$ values (Figure 10). However, Kamchatka lavas show neither positive trend in Li- $\delta^7\text{Li}$ diagram, nor higher Li concentrations and $\delta^7\text{Li}$ values than that of the fresh MORB, which may suggest that the influence of slab-derived fluids is insignificant (Figure 10). In contrast, the

influx of Li from slab-derived fluids may be chromatographically retained in the subarc mantle (Figure 11) before it reaches the zone of melting as suggested by Tomascak et al. (2002). As discussed above, considering that neither the veined mantle xenoliths (olivine in harzburgites, +3.0 to +5.6‰; pyroxenite veins, +3.5 to +5.0‰) nor the arc lavas (+3.5 to +5.1‰) in Avachinsky volcano record abnormal $\delta^7\text{Li}$ signatures, Halama et al. (2009) suggested that diffusional Li isotope equilibrium is achieved over short time scales (10 to 10^5 year), which may explain the MORB-like Li isotopic compositions in Kamchatka arc lavas (Figure 11). Specifically, NCKD lavas were proposed to be affected by a contribution of partial melts from the devolatilized oceanic crust at the slab edge (Portnyagin et al., 2005; Yogodzinski et al., 2001). The most reasonable explanation for their MORB-like Li isotopic characteristic is that the potentially anomalous "heavy" Li isotopic signature of such melts (if any) has been obliterated by the dominance of mantle-Li in the mantle-wedge magma source. Any heterogeneities may further be homogenized by vigorous mantle convection under the NCKD (Portnyagin et al., 2005; Yogodzinski et al., 2001).

Subduction zones act as a filter that may strongly fractionate elements with different fluid mobility (Ryan & Chauvel, 2014). For instance, a large part of the fluid-immobile elements (e.g., REE and HFSE budget >80%) in subducted materials is carried into the deep mantle, while highly fluid-mobile elements (e.g., B, As, Sb and Cs <20%) are almost completely extracted from the descending plate beneath the sub-arc mantle and are not available to subduct to the deeper mantle (Ryan & Chauvel, 2014). As for Li, the ionic radius is similar to that of Mg, so Li may partition into most Mg-bearing minerals in mantle (Brenan et al., 1998a; 1998b; Marschall et al., 2007; Ryan & Chauvel, 2014; Wunder et al., 2006). As such, anomalous Li signatures caused by components from the subducted slab (fluids or melts) may be removed during equilibration with subarc mantle (Figure 11, Ryan & Chauvel, 2014; Tomascak et al., 2002). In addition, previous studies have shown that the diffusivity of Li is two or three orders

of magnitude faster than that of other elements in natural outcrops at contact zones (e.g., Mg, Fe, Ca. Penniston-Dorland et al., 2010; Richter et al., 2003; Tang et al., 2017). Therefore, the Li concentration gradients and any Li isotope anomalies produced by slab subduction components in the mantle wedge could be equilibrated by diffusion in short time (e.g., 10^{-10} to 10^{-5} year, Richter et al., 2003; Halama et al., 2009). Consequently, subduction may actually act as a buffer, erasing most of the isotopically anomalous Li signal over comparatively short time scales (Figure 11, Ryan & Chauvel, 2014; Tomascak et al., 2002).

6. Conclusions

Several general conclusions can be drawn from this study:

- (1) Neither $\delta^7\text{Li}$ vs MgO (wt%) nor $\delta^7\text{Li}$ vs K_2O (wt%) show clear correlation in Klyuchevskoy volcano, which clearly suggest that high temperature magmatic processes did not cause significant Li isotopic fractionation.
- (2) Arc basalts from NCKD samples (Shiveluch volcano) show no anomalous Li isotopic signatures, suggesting that melting of a devolatilized MORB slab should produce magmas with MORB-like $\delta^7\text{Li}$.
- (3) Across-arc chalcophile element variations (e.g., As, Sb and Pb) together with previously studied fluid-mobile elements suggest that the fluid added to the mantle source mainly derived from the dehydration of subducted oceanic crust and the amount of slab-derived fluid added to the source region decreases with depth to the slab. Below CKD area, the high U/Th, Li/Y, La/Sm and B/Nb ratios suggest that lawsonite breakdown reactions dominate the water release.
- (4) The dehydration model suggests that the slab-derived fluids (e.g., serpentinite, and AOC) show distinctly higher Li concentration and $\delta^7\text{Li}$ values than the arc lavas in Kamchatka. The MORB-like Li isotopic compositions in Kamchatka arc lavas therefore suggest that the isotopically heavy Li in fluids were equilibrated within and/or dominated by the sub-arc mantle (Ryan & Chauvel, 2014; Tomascak et al., 2002). Therefore, subduction zones in general should act as a

filter for Li and transfer of isotopically anomalous Li through subduction processes may not be unusual.

Acknowledgments

This work is supported by the Strategic Priority Research Program (B) of the Chinese Academy of Sciences (XDB18000000), the National Natural Science Foundation of China (41673031, 41729001, 41903006) and the China Postdoctoral Science Foundation to Haiyang Liu (2019M652497). Haiyang Liu is partly supported by the postdoctoral innovation project of Shandong province, the postdoctoral applied research program of Qingdao City, the Taishan Scholar Program of Shandong (ts201712075), AoShan Talents Cultivation Program Supported by Qingdao National Laboratory for Marine Science and Technology (2017ASTCP-OS07) and Qingdao National Laboratory for Marine Science and Technology (2017ASKJ02). Wei-Dong Sun, Ying-Yu Xue, Jian Huang, Dongyong Li, Yangyang Wang and Hongqiong Wan are thanked for helpful discussions during manuscript preparation. Discussion of our compositional data with Bill Leeman over the years and his suggestions how to proceed with interpretations is also greatly appreciated. We thank Dr. Paul Tomascak and Dr. Ming Tang for thorough and helpful reviews that greatly improved the manuscript. The associate editor Stephen Parman is acknowledged for efficient editorial handling. The data supporting our work are provided in the “*GEOROC*” and “*EarthChem Library*” data bases (<https://doi.org/10.26022/IEDA/111529>).

References:

- Agostini, S., Ryan, J. G., Tonarini, S., & Innocenti, F. (2008). Drying and dying of a subducted slab: Coupled Li and B isotope variations in Western Anatolia Cenozoic Volcanism. *Earth and Planetary Science Letters*, 272(1-2), 139-147.
<https://doi.org/10.1016/j.epsl.2008.04.032>
- Auer, S., Bindeman, I., Wallace, P., Ponomareva, V., & Portnyagin, M. (2009). The origin of hydrous, high-delta O-18 voluminous volcanism: diverse oxygen isotope values and high magmatic water contents within the volcanic record of Klyuchevskoy volcano, Kamchatka, Russia. *Contributions to Mineralogy and Petrology*, 157(2), 209-230.
<https://doi.org/10.1007/s00410-008-0330-0>
- Balesta, S. T. (1991). Earth crust structure and magma chambers of the areas of present Kamchatka volcanism. *Active Volcanoes of Kamchatka. Nauka, Moscow*, 36-45.
- Bebout, G. E., Bebout, A. E., & Graham, C. M. (2007). Cycling of B, Li, and LILE (K, Cs, Rb, Ba, Sr) into subduction zones: SIMS evidence from micas in high-P/T metasedimentary rocks. *Chemical Geology*, 239(3-4), 284-304.
<https://doi.org/10.1016/j.chemgeo.2006.10.016>
- Bebout, G. E., & Nakamura, E. (2003). Record in metamorphic tourmalines of subduction-zone devolatilization and boron cycling. *Geology*, 31(5), 407-410.
[https://doi.org/10.1130/0091-7613\(2003\)031<0407:Rimtos>2.0.Co;2](https://doi.org/10.1130/0091-7613(2003)031<0407:Rimtos>2.0.Co;2)
- Bebout, G. E., Agard, P., Kobayashi, K., Moriguti, T., & Nakamura, E. (2013). Devolatilization history and trace element mobility in deeply subducted sedimentary rocks: Evidence

from Western Alps HP/UHP suites. *Chemical Geology*, 342, 1-20.

<https://doi.org/10.1016/j.chemgeo.2013.01.009>

Bebout, G. E., Ryan, J. G., Leeman, W. P., & Bebout, A. E. (1999). Fractionation of trace elements by subduction-zone metamorphism — effect of convergent-margin thermal evolution. *Earth and Planetary Science Letters*, 171(1), 63-81.

[https://doi.org/10.1016/S0012-821X\(99\)00135-1](https://doi.org/10.1016/S0012-821X(99)00135-1)

Benton, L. D., Ryan, J. G., & Savov, I. P. (2004). Lithium abundance and isotope systematics of forearc serpentinites, Conical Seamount, Mariana forearc: Insights into the mechanics of slab-mantle exchange during subduction. *Geochemistry, Geophysics, Geosystems*, 5(8). <https://doi.org/10.1029/2004GC000708>

Bergal-Kuvikas, O., Nakagawa, M., Kuritani, T., Muravyev, Y., Malik, N., Klimenko, E., Amma-Miyasaka, M., Matsumoto, A., & Shimada, Shunjiro. (2017). A petrological and geochemical study on time-series samples from Klyuchevskoy volcano, Kamchatka arc.

Contributions to Mineralogy and Petrology, 172(5), 35.

<https://doi.org/10.1007/s00410-017-1347-z>

Bouvier, A. S., Métrich, N., & Deloule, E. (2010). Light elements, volatiles, and stable isotopes in basaltic melt inclusions from Grenada, Lesser Antilles: Inferences for magma genesis.

Geochemistry, Geophysics, Geosystems, 11(9). <https://doi.org/10.1029/2010GC003051>

Brenan, J. M., Neroda, E., Lundstrom, C. C., Shaw, H. F., Ryerson, F. J., & Phinney, D. L. (1998). Behaviour of boron, beryllium, and lithium during melting and crystallization:

Constraints from mineral-melt partitioning experiments. *Geochimica Et Cosmochimica*

Acta, 62(12), 2129-2141. [https://doi.org/10.1016/S0016-7037\(98\)00131-8](https://doi.org/10.1016/S0016-7037(98)00131-8)

Brenan, J. M., Ryerson, F. J., & Shaw, H. F. (1998). The role of aqueous fluids in the slab-to-mantle transfer of boron, beryllium, and lithium during subduction: Experiments and models. *Geochimica Et Cosmochimica Acta*, 62(19-20), 3337-3347. [https://doi.org/10.1016/S0016-7037\(98\)00224-5](https://doi.org/10.1016/S0016-7037(98)00224-5)

Cao, Y-T., Liu, L., Chen, D-L., Wang, C., Yang, W-Q., Kang, L., & Zhu, X-H. 2017. Partial melting during exhumation of Paleozoic retrograde eclogite in North Qaidam, western China. *Journal of Asian Earth Science*, 148: 223-240. <https://doi.org/10.1016/j.jseaes.2017.09.009>

Chan, L. H., Leeman, W. P., & You, C. F. (2002). Lithium isotopic composition of Central American volcanic arc lavas: implications for modification of subarc mantle by slab-derived fluids: correction. *Chemical Geology*, 182(2-4), 293-300. [https://doi.org/10.1016/S0009-2541\(01\)00298-4](https://doi.org/10.1016/S0009-2541(01)00298-4)

Chan, L. H., Lassiter, J. C., Hauri, E. H., Hart, S. R., & Blusztajn, J. (2009). Lithium isotope systematics of lavas from the Cook–Austral Islands: Constraints on the origin of HIMU mantle. *Earth and Planetary Science Letters*, 277(3–4), 433-442. <http://dx.doi.org/10.1016/j.epsl.2008.11.009>

Chen, S., Hin, R. C., John, T., Brooker, R., Bryan, B., Niu, Y., & Elliott, T. (2019). Molybdenum systematics of subducted crust record reactive fluid flow from underlying slab serpentine dehydration. *Nat Commun*, 10(1), 4773. <http://doi.org/10.1038/s41467-019-12696-3>

-
- Churikova, T., Dorendorf, F., & Worner, G. (2001). Sources and fluids in the mantle wedge below Kamchatka, evidence from across-arc geochemical variation. *Journal of Petrology*, 42(8), 1567-1593. <https://doi.org/10.1093/petrology/42.8.1567>
- Churikova, T., Wörner, G., Mironov, N., & Kronz, A. (2007). Volatile (S, Cl and F) and fluid mobile trace element compositions in melt inclusions: implications for variable fluid sources across the Kamchatka arc. *Contributions to Mineralogy and Petrology*, 154(2), 217-239. <https://doi.org/10.1007/s00410-007-0190-z>
- Dorendorf, F., Wiechert, U., & Wörner, G. (2000). Hydrated sub-arc mantle: a source for the Kluychevskoy volcano, Kamchatka/Russia. *Earth and Planetary Science Letters*, 175(1–2), 69-86. [http://dx.doi.org/10.1016/S0012-821X\(99\)00288-5](http://dx.doi.org/10.1016/S0012-821X(99)00288-5)
- Du, L., Long, X., Yuan, C., Zhang, Y., Huang, Z., Sun, M., & Xiao, W. 2018. Petrogenesis of Late Paleozoic diorites and A-type granites in the central Eastern Tianshan, NW China: Response to post-collisional extension triggered by slab breakoff. *Lithos*, 318-319: 47-59. <https://doi.org/10.1016/j.lithos.2018.08.006>
- Du, L., Zhang, Y., Huang, Z., Li, X-P., Yuan, C., Wu, B., & Long, X. 2019. Devonian to carboniferous tectonic evolution of the Kangguer Ocean in the Eastern Tianshan, NW China: Insights from three episodes of granitoids. *Lithos*: 105243. <http://doi.org/10.1016/j.lithos.2019.105243>
- Eiler, J. M., Schiano, P., Kitchen, N., & Stolper, E. M. (2000). Oxygen-isotope evidence for recycled crust in the sources of mid-ocean-ridge basalts. *Nature*, 403(6769), 530-534. <https://doi.org/10.1038/35000553>

-
- Elliott, T., Jeffcoate, A., & Bouman, C. (2004). The terrestrial Li isotope cycle: light-weight constraints on mantle convection. *Earth and Planetary Science Letters*, 220(3-4), 231-245. [https://doi.org/10.1016/S0012-821x\(04\)00096-2](https://doi.org/10.1016/S0012-821x(04)00096-2)
- Elliott, T., Plank, T., Zindler, A., White, W., & Bourdon, B. (1997). Element transport from slab to volcanic front at the Mariana arc. *Journal of Geophysical Research: Solid Earth*, 102(B7), 14991-15019. <https://doi.org/10.1029/97jb00788>
- Fedotov, S. A., & Masurenkov, Y. P. (1991). Active Volcanoes of Kamchatka. Moscow: Nauka Pub, 2 volumes.
- Ferlito, C. (2011). Bimodal geochemical evolution at Sheveluch stratovolcano, Kamchatka, Russia: Consequence of a complex subduction at the junction of the Kuril Kamchatka and Aleutian island arcs. *Earth-Science Reviews*, 105(1-2), 49-69. <https://doi.org/10.1016/j.earscirev.2010.12.003>
- Geist, E. L., & Scholl, D. W. (1994). Large-Scale Deformation Related to the Collision of the Aleutian Arc with Kamchatka. *Tectonics*, 13(3), 538-560. <https://doi.org/10.1029/94tc00428>
- Gorbatov, A., Kostoglodov, V., Suarez, G., & Gordeev, E. (1997). Seismicity and structure of the Kamchatka subduction zone. *Journal of Geophysical Research-Solid Earth*, 102(B8), 17883-17898. <https://doi.org/10.1029/96jb03491>
- Halama, R., Bebout, G. E., John, T., & Schenk, V. (2010). Nitrogen recycling in subducted oceanic lithosphere: The record in high- and ultrahigh-pressure metabasaltic rocks. *Geochimica Et Cosmochimica Acta*, 74(5), 1636-1652.

<http://dx.doi.org/10.1016/j.gca.2009.12.003>

Halama, R., John, T., Herms, P., Hauff, F., & Schenk, V. (2011). A stable (Li, O) and radiogenic (Sr, Nd) isotope perspective on metasomatic processes in a subducting slab. *Chemical Geology*, 281(3–4), 151-166. <http://dx.doi.org/10.1016/j.chemgeo.2010.12.001>

Halama, R., McDonough, W. F., Rudnick, R. L., Keller, J., & Klaudius, J. (2007). The Li isotopic composition of Oldoinyo Lengai: Nature of the mantle sources and lack of isotopic fractionation during carbonatite petrogenesis. *Earth and Planetary Science Letters*, 254(1–2), 77-89. <https://doi.org/10.1016/j.epsl.2006.11.022>

Halama, R., Savov, I. P., Rudnick, R. L., & McDonough, W. F. (2009). Insights into Li and Li isotope cycling and sub-arc metasomatism from veined mantle xenoliths, Kamchatka. *Contributions to Mineralogy and Petrology*, 158(2), 197-222. <https://doi.org/10.1007/s00410-009-0378-5>

Hattori, K. H., Arai, S., & Clarke, D. B. (2002). Selenium, Tellurium, Arsenic and Antimony contents of primary mantle sulfides. *The Canadian Mineralogist*, 40(2), 637-650. <http://doi.org/10.2113/gscanmin.40.2.637>

Hofmann, A. W. (2014). Sampling Mantle Heterogeneity through Oceanic Basalts: Isotopes and Trace Elements. *Treatise on geochemistry*, 67-101. <https://doi.org/10.1016/b978-0-08-095975-7.00203-5>

Hofmann, A. W., Jochum, K. P., Seufert, M., & White, W. M. (1986). Nb and Pb in oceanic basalts: new constraints on mantle evolution. *Earth and Planetary Science Letters*, 79(1), 33-45. [https://doi.org/10.1016/0012-821X\(86\)90038-5](https://doi.org/10.1016/0012-821X(86)90038-5)

Huang, J., Zhang, X. C., Chen, S., Tang, L. M., Wörner, G., Yu, H. M., & Huang, F. (2018).

Zinc isotopic systematics of Kamchatka-Aleutian arc magmas controlled by mantle melting. *Geochimica Et Cosmochimica Acta*, 238, 85-101.

<https://doi.org/10.1016/j.gca.2018.07.012>

Ionov, D. A., & Seitz, H. M. (2008). Lithium abundances and isotopic compositions in mantle xenoliths from subduction and intra-plate settings: Mantle sources vs. eruption histories.

Earth and Planetary Science Letters, 266(3–4), 316-331.

<https://dx.doi.org/10.1016/j.epsl.2007.11.020>

Ishikawa, T., & Tera, F. (1999). Two isotopically distinct fluid components involved in the Mariana arc: Evidence from Nb/B ratios and B, Sr, Nd, and Pb isotope systematics.

Geology, 27(1), 83-86. [https://doi.org/10.1130/0091-7613\(1999\)027<0083:Tidfci>2.3.Co;2](https://doi.org/10.1130/0091-7613(1999)027<0083:Tidfci>2.3.Co;2)

Ishikawa, T., & Nakamura, E. (1994). Origin of the slab component in arc lavas from across-arc variation of B and Pb isotopes. *Nature*, 370(6486), 205-208.

<https://doi.org/10.1038/370205a0>

Ishikawa, T., Tera, F., & Nakazawa, T. (2001). Boron isotope and trace element systematics of the three volcanic zones in the Kamchatka arc. *Geochimica Et Cosmochimica Acta*,

65(24), 4523-4537. [https://doi.org/10.1016/S0016-7037\(01\)00765-7](https://doi.org/10.1016/S0016-7037(01)00765-7)

Jochum, K. P., & Hofmann, A. W. (1997). Constraints on earth evolution from antimony in mantle-derived rocks. *Chemical Geology*, 139(1), 39-49.

[https://doi.org/10.1016/S0009-2541\(97\)00032-6](https://doi.org/10.1016/S0009-2541(97)00032-6)

-
- Jochum, K. P., & Verma, S. P. (1996). Extreme enrichment of Sb, Tl and other trace elements in altered MORB. *Chemical Geology*, 130(3), 289-299. [https://doi.org/10.1016/0009-2541\(96\)00014-9](https://doi.org/10.1016/0009-2541(96)00014-9)
- Jochum, K. P., Hofmann, A. W., & Seufert, H. M. (1993). Tin in mantle-derived rocks: constraints on Earth evolution. *Geochimica Et Cosmochimica Acta*, 57(15), 3585-3595. [https://doi-org-443.webvpn.las.ac.cn/10.1016/0016-7037\(93\)90141-I](https://doi-org-443.webvpn.las.ac.cn/10.1016/0016-7037(93)90141-I)
- Kepezhinskas, P., McDermott, F., Defant, M. J., Hochstaedter, A., Drummond, M. S., Hawkesworth, C. J., . . . Bellon, H. (1997). Trace element and Sr-Nd-Pb isotopic constraints on a three-component model of Kamchatka arc petrogenesis. *Geochimica Et Cosmochimica Acta*, 61(3), 577-600. [https://doi.org/10.1016/S0016-7037\(96\)00349-3](https://doi.org/10.1016/S0016-7037(96)00349-3)
- Kersting, A. B., & Arculus, R. J. (1994). Klyuchevskoy Volcano, Kamchatka, Russia: The Role of High-Flux Recharged, Tapped, and Fractionated Magma Chamber(s) in the Genesis of High-Al₂O₃ from High-MgO Basalt. *Journal of Petrology*, 35(1), 1-41. <https://doi.org/10.1093/petrology/35.1.1>
- Kersting, A. B., & Arculus, R. J. (1995). Pb isotope composition of Klyuchevskoy volcano, Kamchatka and North Pacific sediments: Implications for magma genesis and crustal recycling in the Kamchatkan arc. *Earth and Planetary Science Letters*, 136(3-4), 133-148. [http://dx.doi.org/10.1016/0012-821X\(95\)00196-J](http://dx.doi.org/10.1016/0012-821X(95)00196-J)
- Khrenov, A. P., Antipin, V. S., Chuvashova, L. A., & Smirnova, E. V. (1989). Petrochemical and geochemical peculiarity of basalts of the Kluchevskoy volcano. *Volcanology and*

Seismology, **3**, 3-15.

- Konrad-Schmolke, M., Halama, R., & Manea, V. C. (2016). Slab mantle dehydrates beneath Kamchatka—Yet recycles water into the deep mantle. *Geochemistry, Geophysics, Geosystems*, *17*(8), 2987-3007. <https://doi.org/10.1002/2016GC006335>
- Koulakov, I. Y., Kukarina, E. V., Gordeev, E. I., Chebrov, V. N., & Vernikovskiy, V. A. (2016). Magma sources in the mantle wedge beneath the volcanoes of the Klyuchevskoy group and Kizimen based on seismic tomography modeling. *Russian Geology and Geophysics*, *57*(1), 82-94. <http://dx.doi.org/10.1016/j.rgg.2016.01.006>
- Leeman, W. P., Tonarini, S., & Turner, S. (2017). Boron isotope variations in Tonga-Kermadec-New Zealand arc lavas: Implications for the origin of subduction components and mantle influences. *Geochemistry Geophysics Geosystems*, *18*(3), 1126-1162. <https://doi.org/10.1002/2016GC006523>
- Leeman, W. P., Tonarini, S., Chan, L. H., & Borg, L. E. (2004). Boron and lithium isotopic variations in a hot subduction zone—the southern Washington Cascades. *Chemical Geology*, *212*(1–2), 101-124. <http://dx.doi.org/10.1016/j.chemgeo.2004.08.010>
- Leeman, W. P., Wörner, G., Churikova, T., Tonarini, S., & Heuser, A. (2001). *Boron and Fluid-Mobile Element (FME) Fluxes Across Kamchatka* (Vol. 6).
- Leeman, W. P. (1996). Boron and Other Fluid-mobile Elements in Volcanic Arc Lavas: Implications for Subduction Processes. In *Subduction* (pp. 269-276).
- Liu, H. Y., Sun, H., Xiao, Y. L., Wang, Y. Y., Zeng, L. S., Li, W. Y., Guo, H. H., Yu, H. M., & Pack, A. (2019a). Lithium isotope systematics of the Sumdo Eclogite, Tibet: Tracing

-
- fluid/rock interaction of subducted low-T altered oceanic crust. *Geochimica Et Cosmochimica Acta*, 246, 385-405. <https://doi.org/10.1016/j.gca.2018.12.002>
- Liu, H. Y., Xiao, Y. L., van den Kerkhof, A., Wang, Y. Y., Zeng, L. S., & Guo, H. H. (2019b). Metamorphism and fluid evolution of the Sumdo eclogite, Tibet: Constraints from mineral chemistry, fluid inclusions and oxygen isotopes. *Journal of Asian Earth Sciences*, 172, 292-307. <https://doi.org/10.1016/j.jseaes.2018.09.013>
- Liu, S. A., Huang, J., Liu, J. G., Worner, G., Yang, W., Tang, Y. J., et al. (2015). Copper isotopic composition of the silicate Earth. *Earth and Planetary Science Letters*, 427, 95-103. <https://doi.org/10.1016/j.epsl.2015.06.061>
- Magna, T., Wiechert, U., Grove, T. L., & Halliday, A. N. (2006). Lithium isotope fractionation in the southern Cascadia subduction zone. *Earth and Planetary Science Letters*, 250(3–4), 428-443. <http://dx.doi.org/10.1016/j.epsl.2006.08.019>
- Marschall, H. R., Pogge von Strandmann, P. A. E., Seitz, H. M., Elliott, T., & Niu, Y. L. (2007). The lithium isotopic composition of orogenic eclogites and deep subducted slabs. *Earth and Planetary Science Letters*, 262(3-4), 563-580. <https://doi.org/10.1016/j.epsl.2007.08.005>
- Marschall, H. R., Altherr, R., & Rüpke, L. (2007). Squeezing out the slab — modelling the release of Li, Be and B during progressive high-pressure metamorphism. *Chemical Geology*, 239(3–4), 323-335. <http://dx.doi.org/10.1016/j.chemgeo.2006.08.008>
- Marschall, H. R., Wanless, V. D., Shimizu, N., Pogge von Strandmann, P. A. E., Elliott, T., & Monteleone, B. D. (2017). The boron and lithium isotopic composition of mid-ocean

-
- ridge basalts and the mantle. *Geochimica Et Cosmochimica Acta*, 207, 102-138.
<https://doi.org/10.1016/j.gca.2017.03.028>
- McDonough, W. F., & Sun, S. S. (1995). The composition of the Earth. *Chemical Geology*, 120(3), 223-253. [https://doi.org/10.1016/0009-2541\(94\)00140-4](https://doi.org/10.1016/0009-2541(94)00140-4)
- Moriguti, T., & Nakamura, E. (1998). Across-arc variation of Li isotopes in lavas and implications for crust/mantle recycling at subduction zones. *Earth and Planetary Science Letters*, 163(1-4), 167-174. [https://doi.org/10.1016/S0012-821x\(98\)00184-8](https://doi.org/10.1016/S0012-821x(98)00184-8)
- Moriguti, T., Shibata, T., & Nakamura, E. (2004). Lithium, boron and lead isotope and trace element systematics of Quaternary basaltic volcanic rocks in northeastern Japan: mineralogical controls on slab-derived fluid composition. *Chemical Geology*, 212(1-2), 81-100. <https://doi.org/10.1016/j.chemgeo.2004.08.005>
- Münker, C., Wörner, G., Yogodzinski, G., & Churikova, T. (2004). Behaviour of high field strength elements in subduction zones: constraints from Kamchatka–Aleutian arc lavas. *Earth and Planetary Science Letters*, 224(3–4), 275-293.
<http://dx.doi.org/10.1016/j.epsl.2004.05.030>
- Newsom, H. E., & Palme, H. (1984). The depletion of siderophile elements in the Earth's mantle: new evidence from molybdenum and tungsten. *Earth and Planetary Science Letters*, 69(2), 354-364. [https://doi.org/10.1016/0012-821X\(84\)90194-8](https://doi.org/10.1016/0012-821X(84)90194-8)
- Newsom, H. E., Sims, K. W. W., Noll, P. D., Jaeger, Windy L., Maehr, S. A., & Beserra, T. B. (1996). The depletion of tungsten in the bulk silicate earth: Constraints on core formation. *Geochimica Et Cosmochimica Acta*, 60(7), 1155-1169.

[https://doi.org/10.1016/0016-7037\(96\)00029-4](https://doi.org/10.1016/0016-7037(96)00029-4)

Noll, P. D., Newsom, H. E., Leeman, W. P., & Ryan, J. G. (1996). The role of hydrothermal fluids in the production of subduction zone magmas: Evidence from siderophile and chalcophile trace elements and boron. *Geochimica Et Cosmochimica Acta*, 60(4), 587-611. [https://doi.org/10.1016/0016-7037\(95\)00405-X](https://doi.org/10.1016/0016-7037(95)00405-X)

Penniston-Dorland, S. C., Bebout, G. E., Pogge von Strandmann, P. A. E., Elliott, T., & Sorensen, S. S. (2012). Lithium and its isotopes as tracers of subduction zone fluids and metasomatic processes: Evidence from the Catalina Schist, California, USA. *Geochimica Et Cosmochimica Acta*, 77, 530-545. <https://doi.org/10.1016/j.gca.2011.10.038>

Penniston-Dorland, S. C., Sorensen, S. S., Ash, R. D., & Khadke, S. V. (2010). Lithium isotopes as a tracer of fluids in a subduction zone mélange: Franciscan Complex, CA. *Earth and Planetary Science Letters*, 292(1–2), 181-190. <http://dx.doi.org/10.1016/j.epsl.2010.01.034>

Penniston-Dorland, S., Liu, X. M., & Rudnick, R. L. (2017). Lithium isotope geochemistry. *Reviews in Mineralogy and Geochemistry*, 82(1), 165-217. <https://doi.org/10.2138/rmg.2017.82.6>

Pitcairn, I. K., Teagle, D. A. H., Craw, D., Olivo, G. R., Kerrich, R., & Brewer, T. S. (2006). Sources of Metals and Fluids in Orogenic Gold Deposits: Insights from the Otago and Alpine Schists, New Zealand. *Economic Geology*, 101(8), 1525-1546. <http://doi.org/10.2113/gsecongeo.101.8.1525>

-
- Portnyagin, M., Hoernle, K., Avdeiko, G., Hauff, F., Werner, R., Bindeman, I., Uspensky, V., & Garbe-Schonberg, D. (2005). Transition from arc to oceanic magmatism at the Kamchatka-Aleutian junction. *Geology*, 33(1), 25-28. <https://doi.org/10.1130/G20853.1>
- Portnyagin, M., Hoernle, K., Plechov, P., Mironov, N., & Khubunaya, S. (2007). Constraints on mantle melting and composition and nature of slab components in volcanic arcs from volatiles (H₂O, S, Cl, F) and trace elements in melt inclusions from the Kamchatka Arc. *Earth and Planetary Science Letters*, 255(1-2), 53-69. <https://doi.org/10.1016/j.epsl.2006.12.005>
- Ryan, J. G., Morris, J., Tera, F., Leeman, W. P., & Tsvetkov, A. (1995). Cross-Arc Geochemical Variations in the Kurile Arc as a Function of Slab Depth. *Science*, 270(5236), 625-627. <http://doi.org/10.1126/science.270.5236.625>
- Renkin, M. L., & Sclater, J. G. (1988). Depth and Age in the North Pacific. *Journal of Geophysical Research-Solid Earth and Planets*, 93(B4), 2919-2935. <https://doi.org/10.1029/Jb093ib04p02919>
- Richter, F. M., Davis, A. M., DePaolo, D. J., & Watson, E. B. (2003). Isotope fractionation by chemical diffusion between molten basalt and rhyolite. *Geochimica Et Cosmochimica Acta*, 67(20), 3905-3923. [https://doi.org/10.1016/S0016-7037\(03\)00174-1](https://doi.org/10.1016/S0016-7037(03)00174-1)
- Rudnick, R. L., Tomascak, P. B., Njo, H. B., & Gardner, L. R. (2004). Extreme lithium isotopic fractionation during continental weathering revealed in saprolites from South Carolina. *Chemical Geology*, 212(1-2), 45-57. <https://doi.org/10.1016/j.chemgeo.2004.08.008>

-
- Ryan, J. G., & Chauvel, C. (2014). The subduction-zone filter and the impact of recycled materials on the evolution of the mantle. *Treatise on geochemistry*, 479-508. <https://doi.org/10.1016/B978-0-08-095975-7.00211-4>
- Salters, V. J. M., & Stracke, A. (2004). Composition of the depleted mantle. *Geochemistry Geophysics Geosystems*, 5. <https://doi.org/10.1029/2003gc000597>
- Savov, I. P., Ryan, J. G., D'Antonio, M., Kelley, K., & Mattie, P. (2005). Geochemistry of serpentinized peridotites from the Mariana Forearc Conical Seamount, ODP Leg 125: Implications for the elemental recycling at subduction zones. *Geochemistry, Geophysics, Geosystems*, 6(4). <http://doi.org/10.1029/2004GC000777>
- Schmidt, M. W., & Poli, S. (1998). Experimentally based water budgets for dehydrating slabs and consequences for arc magma generation. *Earth and Planetary Science Letters*, 163(1–4), 361-379. [http://dx.doi.org/10.1016/S0012-821X\(98\)00142-3](http://dx.doi.org/10.1016/S0012-821X(98)00142-3)
- Simons, K. K., Harlow, G. E., Brueckner, H. K., Goldstein, S. L., Sorensen, S. S., Hemming, N. G., & Langmuir, C. H. (2010). Lithium isotopes in Guatemalan and Franciscan HP–LT rocks: Insights into the role of sediment-derived fluids during subduction. *Geochimica Et Cosmochimica Acta*, 74(12), 3621-3641. <http://dx.doi.org/10.1016/j.gca.2010.02.033>
- Sims, K. W. W., & Gladney, E. S. (1991). Determination of arsenic, antimony, tungsten and molybdenum in silicate materials by epithermal neutron activation and inorganic ion exchange. *Analytica Chimica Acta*, 251(1), 297-303. [https://doi.org/10.1016/0003-2670\(91\)87150-6](https://doi.org/10.1016/0003-2670(91)87150-6)

-
- Sun, H., Gao, Y. J., Xiao, Y. L., Gu, H. O., & Casey, J. F. (2016). Lithium isotope fractionation during incongruent melting: Constraints from post-collisional leucogranite and residual enclaves from Bengbu Uplift, China. *Chemical Geology*, 439, 71-82.
<http://dx.doi.org/10.1016/j.chemgeo.2016.06.004>
- Sun, S. S., & McDonough, W. F. (1989). Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. *Geological Society, London, Special Publications*, 42(1), 313-345. <https://doi.org/10.1144/gsl.sp.1989.042.01.19>
- Tang, M., Rudnick, R. L., & Chauvel, C. (2014). Sedimentary input to the source of Lesser Antilles lavas: A Li perspective. *Geochimica Et Cosmochimica Acta*, 144(0), 43-58.
<http://dx.doi.org/10.1016/j.gca.2014.09.003>
- Tang, M., Rudnick, R. L., McDonough, W. F., Bose, M., & Goreva, Y. (2017). Multi-mode Li diffusion in natural zircons: Evidence for diffusion in the presence of step-function concentration boundaries. *Earth and Planetary Science Letters*, 474(Supplement C), 110-119. <https://doi.org/10.1016/j.epsl.2017.06.034>
- Tang Y. J., Zhang H. F., & Ying J. F. (2009). Discussion on Fractionation Mechanism of Lithium Isotopes. *EarthScience-Journal of China University of Geosciences*, 34(1), 43-55.
- Teng, F. Z., McDonough, W. F., Rudnick, R. L., & Wing, B. A. (2007). Limited lithium isotopic fractionation during progressive metamorphic dehydration in metapelites: A case study from the Onawa contact aureole, Maine. *Chemical Geology*, 239(1-2), 1-12.
<https://doi.org/10.1016/j.chemgeo.2006.12.003>
- Tian, Y., Xiao, Y. L., Chen, Y. X., Sun, H., Liu, H. Y., Tong, F. T. (2019). Serpentine-derived

-
- low $\delta^7\text{Li}$ fluids in continental subduction zones: Constraints from the fluid metasomatic rocks (whiteschist) from the Dora-Maira Massif, Western Alps. *Lithos*, 348-349, 105177. <https://doi.org/10.1016/j.lithos.2019.105177>
- Tomanikova, L., Savov, I. P., Harvey, J., de Hoog, J. C. M., Churikova, T. G., Gordeychik, B., & Yogodzinski, G. M. (2019). A limited role for metasomatized subarc mantle in the generation of boron isotope signatures of arc volcanic rocks. *Geology*. <https://doi.org/10.1130/G46092.1>
- Tomascak, P. B., Langmuir, C. H., le Roux, P. J., & Shirey, S. B. (2008). Lithium isotopes in global mid-ocean ridge basalts. *Geochimica Et Cosmochimica Acta*, 72(6), 1626-1637. <http://dx.doi.org/10.1016/j.gca.2007.12.021>
- Tomascak, P. B., Ryan, J. G., & Defant, M. J. (2000). Lithium isotope evidence for light element decoupling in the Panama subarc mantle. *Geology*, 28(6), 507-510. [https://doi.org/10.1130/0091-7613\(2000\)28<507:Liefle>2.0.Co;2](https://doi.org/10.1130/0091-7613(2000)28<507:Liefle>2.0.Co;2)
- Tomascak, P. B., Tera, F., Helz, R. T., & Walker, R. J. (1999). The absence of lithium isotope fractionation during basalt differentiation: New measurements by multicollector sector ICP-MS. *Geochimica Et Cosmochimica Acta*, 63(6), 907-910. [https://doi.org/10.1016/S0016-7037\(98\)00318-4](https://doi.org/10.1016/S0016-7037(98)00318-4)
- Tomascak, P. B., Widom, E., Benton, L. D., Goldstein, S. L., & Ryan, J. G. (2002). The control of lithium budgets in island arcs. *Earth and Planetary Science Letters*, 196(3-4), 227-238. [https://doi.org/10.1016/S0012-821x\(01\)00614-8](https://doi.org/10.1016/S0012-821x(01)00614-8)
- Tomascak, P. B., Magna, T., & Dohmen, R. (2016). Advances in Lithium Isotope Geochemistry.

In: Springer.

Tsvetkov, A. A., Gladkov, N. G., & Volynets, O. N. (1989). Problem of Sediment Subduction and Be-10 Isotope in Lavas of Kuril Islands and Kamchatka Peninsula. *Doklady Akademii Nauk Sssr*, 306(5), 1220-1225.

Usui, T., Nakamura, E., Kobayashi, K., Maruyama, S., & Helmstaedt, H. (2003). Fate of the subducted Farallon plate inferred from eclogite xenoliths in the Colorado Plateau. *Geology*, 31(7), 589-592. [https://doi.org/10.1130/0091-7613\(2003\)031<0589:FOTSFP>2.0.CO;2](https://doi.org/10.1130/0091-7613(2003)031<0589:FOTSFP>2.0.CO;2)

Volynets, A. O., Churikova, T. G., Wörner, G., Gordeychik, B. N., & Layer, P. (2010). Mafic Late Miocene–Quaternary volcanic rocks in the Kamchatka back arc region: implications for subduction geometry and slab history at the Pacific–Aleutian junction. *Contributions to Mineralogy and Petrology*, 159(5), 659-687. <https://doi.org/10.1007/s00410-009-0447-9>

Walker, J. A., Teipel, A. P., Ryan, J. G., & Syracuse, E. (2009). Light elements and Li isotopes across the northern portion of the Central American subduction zone. *Geochemistry, Geophysics, Geosystems*, 10(6). <https://doi.org/10.1029/2009GC002414>

White, W. M., & Klein, E. M. (2014). Composition of the Oceanic Crust. *Treatise on geochemistry*, 457-496. <http://doi.org/10.1016/b978-0-08-095975-7.00315-6>

Wu, F. Y., Li, X. H., Zheng, Y. F., & Gao, S. (2007). Lu-Hf isotopic systematics and their applications in petrology. *Acta Petrologica Sinica*, 23(2), 185-220.

Wunder, B., Meixner, A., Romer, R. L., & Heinrich, W. (2006). Temperature-dependent

isotopic fractionation of lithium between clinopyroxene and high-pressure hydrous fluids. *Contributions to Mineralogy and Petrology*, 151(1), 112-120.

<https://doi.org/10.1007/s00410-005-0049-0>

Wunder, B., Deschamps, F., Watenphul, A., Guillot, S., Meixner, A., Romer, R. L., & Wirth, R. (2010). The effect of chrysotile nanotubes on the serpentine-fluid Li-isotopic fractionation. *Contributions to Mineralogy and Petrology*, 159(6), 781-790.

<https://doi.org/10.1007/s00410-009-0454-x>

Xiao, Y. L., Hoefs, J., Hou, Z. H., Simon, K., & Zhang, Z. M. (2011). Fluid/rock interaction and mass transfer in continental subduction zones: constraints from trace elements and isotopes (Li, B, O, Sr, Nd, Pb) in UHP rocks from the Chinese Continental Scientific Drilling Program, Sulu, East China. *Contributions to Mineralogy and Petrology*, 162(4), 797-819. <https://doi.org/10.1007/s00410-011-0625-4>

Yi, W., Halliday, A. N., Lee, D. C., & Christensen, J. N. (1995). Indium and tin in basalts, sulfides, and the mantle. *Geochimica Et Cosmochimica Acta*, 59(24), 5081-5090. [https://doi.org/10.1016/0016-7037\(95\)00342-8](https://doi.org/10.1016/0016-7037(95)00342-8)

Yogodzinski, G. M., Lees, J. M., Churikova, T. G., Dorendorf, F., Woerner, G., & Volynets, O. N. (2001). Geochemical evidence for the melting of subducting oceanic lithosphere at plate edges. *Nature*, 409(6819), 500-504. <https://doi.org/10.1038/35054039>

Yogodzinski, G., Kay, R. W., Volynets, O. N., Koloskov, A. V., & Kay, S. M. (1995). Magnesian andesite in the western Aleutian Komandorsky region: implications for slab melting and processes in the mantle wedge. *Geological Society of America Bulletin*, 107(5),

505-519. [https://doi.org/10.1130/0016-7606\(1995\)107<0505:MAITWA>2.3.CO;2](https://doi.org/10.1130/0016-7606(1995)107<0505:MAITWA>2.3.CO;2)

Zack, T., Kronz, A., Foley, S. F., & Rivers, T. (2002). Trace element abundances in rutiles from eclogites and associated garnet mica schists. *Chemical Geology*, 184(1), 97-122.
[https://doi.org/10.1016/S0009-2541\(01\)00357-6](https://doi.org/10.1016/S0009-2541(01)00357-6)

Zhang, L. P., Zhang, R. Q., Hu, Y. B., Liang, J. L., Ouyang, Z. X., He, J. J., Chen, Y. X., Guo, J., Sun, W. D. (2017). The formation of the Late Cretaceous Xishan Sn-W deposit, South China: Geochronological and geochemical perspectives. *Lithos*, 290, 253-268.
<http://doi.org/10.1016/j.lithos.2017.08.013>

Zhang, L. P., Zhang, R. Q., Chen, Y. X., Sun, S. J., Liang, J. L., & Sun, W. D. (2019). Geochronology and geochemistry of the Late Cretaceous Xinpeng granitic intrusion, South China: Implication for Sn-W mineralization. *Ore Geology Reviews*, 113, 103075.
<http://doi.org/10.1016/j.oregeorev.2019.103075>

Zhou, S. H., Yu, S. Y., Zhou, T., Lan, J. B., Kang, J., Chen, L. M., & Hu, J. H. (2018). Lithium elemental and isotopic disequilibrium in minerals from peridotite xenoliths from Shangzhi, NE China: products of recent melt/fluid-peridotite interaction. *Acta Geochimica*, 37(5), 769-789. <https://doi.org/10.1007/s11631-018-0276-5>

Table. 1 Li isotope compositions of representative samples in Kamchatka arc. Depths to Benioff zone after Gorbatov et al. (1997).

Sample	Setting	Li ($\mu\text{g/g}$)	$\delta^7\text{Li}$	2SD
GAM-96-07	EVF	1.87	4.1	0.5
GAM-96-14	EVF	1.45	2.9	0.4
GAM-96-26	EVF	2.46	5.4	0.1
GAM-96-28	EVF	1.52	4.0	0.1
SHM-96-01	EVF	9.56	4.1	0.1
SHM-96-03	EVF	7.68	4.3	0.1
SHM-96-04	EVF	6.08	4.3	0.1
KOM-96-05	EVF		4.0	0.2
KOM-96-06	EVF	5.16	1.8	0.1
KOM-96-09	EVF	16.7	5.2	0.2
KOM-96-11/2	EVF	15.1	3.5	0.2
KOM-96-02/2	EVF	6.78	3.7	0.1
KIZ-96-01/1	EVF	14.2	4.0	0.3
KIZ-96-19	EVF	3.84	2.1	0.2
KIZ-96-24	EVF	8.55	4.8	0.2
KLU-96-03	CKD	8.27	5.2	0.1
KLU-96-06	CKD	8.06	8.6	0.1
KLU-96-07	CKD	8.63	5.1	0.2
KLU-96-12	CKD	13.9	5.1	0.1
KLU-96-14	CKD	13.5	4.8	0.2
KLU-96-15	CKD	9.76	4.5	0.4
TOL-96-01	CKD	15.8	4.7	0.5
TOL-96-2/1	CKD	10.9	3.6	0.2
TOL-96-03	CKD	14.5	4.5	0.1
ESO-96-08	SR	3.13	3.9	0.2
ICH-96-02	SR	11.5	4.1	0.1
ICH-96-05	SR	5.63	3.5	0.1
ICH-96-69	SR	8.05	3.6	0.1
SHIV-01-01	NCKD	12.4	4.3	0.3
SHIV-01-05	NCKD	7.50	3.3	0.1
SHIV-01-12	NCKD	11.0	2.7	0.1

Figure 1. (a) Sketch map showing the location of Kamchatka Peninsula, modified after Kersting et al. (1995) and Churikova et al. (2001). The location of the trench is denoted by a solid line with triangles. (b) The enlarged area of Kamchatka shows the location from east to west: Eastern Volcanic Front (EVF), Central Kamchatka Depression (CKD) and North Central Kamchatka Depression (NCKD), Sredinny Range (SR). Studied volcanoes (orange squares - EVF: Gamchen (GAM), Shmidt (SHM), Komarov (KOM), Kizimen (KIZ); red triangles - CKD: Klyuchevskoy (KLU), Tolbachik (TOL); blue diamonds - NCKD Shiveluch (SHIV); green circles – SR of back-arc: Ichinsky (ICH), Eso (ESO)) are marked by symbols. The depth to Benioff zone in km (dashed lines) is from (Gorbatov et al. 1997).

Figure 2. (a) As/Ce, (b) Sb/Ce, (c) Pb/Ce, (d) W/Th, (e) Mo/Ce and (f) Sn/Sm vs depth of slab surface (km) for Kamchatka lavas (Table S5). N-MORB values are from Sun and McDonough (1989).

Figure 3. (a) As/Ce vs $\delta^{18}\text{O}$, (b) B/La vs $\delta^{18}\text{O}$, (c) U/Th vs B/La, (d) $^{87}\text{Sr}/^{86}\text{Sr}$ vs B/Zr, (e) As/Ce vs B/La and (f) Sb/Ce vs B/Zr for Kamchatka lavas. The endmembers are designated primarily by chalcophile elements ratios, B/La and $\delta^{18}\text{O}$ values (See text for details).

Figure 4. $\delta^7\text{Li}$ vs Li ($\mu\text{g/g}$) for Kamchatka lavas. Additional Li isotope data of Kamchatka lavas (Halama et al., 2009) and Avacha xenoliths (Ionov et al., 2008) are shown for comparison (Table S3, S4). The $\delta^7\text{Li}$ reference values of fresh N-MORB are from Tomascak et al. (2008) and Marschall et al. (2017). The compositional field for altered oceanic crust (AOC) is from Chan et al. (2002) and Bouman et al. (2004).

Figure 5. (a) $\delta^7\text{Li}$ vs $\text{MgO (wt\%)}$ and (b) $\delta^7\text{Li}$ vs $\text{LOI (wt\%)}$ for Kamchatka lavas. The $\delta^7\text{Li}$ values of fresh N-MORB are from Tomascak et al. (2008) and Marschall et al. (2017).

Figure 6. $\delta^7\text{Li}$ vs Sr/Y ratio values for Kamchatka lavas. The $\delta^7\text{Li}$ values of fresh N-MORB are from Tomascak et al. (2008) and Marschall et al. (2017).

Figure 7. (a) Li/Y and (b) $\delta^7\text{Li}$ vs slab depth (km) for Kamchatka lavas. Li isotope data for Kamchatka lavas from Halama et al, (2009) and for Avacha xenoliths from Ionov et al, (2008) are shown for comparison. The $\delta^7\text{Li}$ values of fresh N-MORB are from Tomascak et al. (2008) and Marschall et al. (2017). The Li/Y ratio of fresh N-MORB data is from Sun and McDonough, (1989).

Figure 8. (a) U/Th and (b) La/Sm vs slab depth (km) for Kamchatka lavas (Tables S1 and S5). The U/Th ratio of fresh N-MORB data is from Sun and McDonough, (1989).

Figure 9. $\delta^7\text{Li}$ vs U/Th for Kamchatka lavas (Table S1). The $\delta^7\text{Li}$ values of fresh N-MORB are from Tomascak et al. (2008) and Marschall et al. (2017).

Figure 10. Modeling the Li and $\delta^7\text{Li}$ during progressive metamorphic dehydration. Endmembers for modeling are: N-MORB from Tomascak et al, (2008) and Marschall et al, (2017); Serpentine from Benton et al, (2004); AOC from Chan et al., 2002; 2006; Bouman et al., 2004. Theoretical evolution trends of weathering, partial melting and fluid addition are represented schematically by arrows. For AOC and serpentinite, the elemental and isotopic Li compositions of dehydrated residues and of the extracted dehydration fluids are calculated using a Rayleigh dehydration model (Liu et al., 2019a; Marschall et al., 2007a; Simons et al., 2010). Thick lines represent the composition of the dehydrated residue of AOC (purple) and serpentinite (green). Thin lines represent the extracted fluids of AOC (purple) and serpentinite (green).

Figure 11. Schematic model showing the relationship between the factors that influence the observed geochemical signatures in the Kamchatka transect. Arc lavas in the EVF zone are enriched in B, As, Sb and Pb, indicating the breakdown of sulfide, serpentine and/or amphibole. Below CKD area, the high U/Th, Li/Y, La/Sm and B/Nb ratios, together with high $\delta^{18}\text{O}$ values, of the arc basalts suggest that lawsonite and serpentine breakdown reactions dominate the water release. In subduction zone, W, Mo and Sn are generally immobile and may remain in the subducted slab. Slab-derived fluids are initially enriched in Li and ^7Li , while during transit through mantle peridotite, anomalous Li isotope compositions were equilibrated within the sub-arc mantle (Tomascak et al., 2002). Therefore, subduction zones in general should act as a filter for Li and finally may result in the decoupling of Li isotope systems from other fluid-mobile elements.