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Earth and Planetary Science Letters 236 (2005) 182–194

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Slab devolatilization and Os and Pb mobility in the mantle wedge of the Kamchatka arc

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Received 15 September 2004; received in revised form 15 April 2005; accepted 18 May 2005
Available online 27 June 2005
Editor: E. Boyle

Abstract

Os-, Nd-, and Pb-isotope measurements were performed on a suite of eleven Kamchatka peridotite mantle xenoliths in volcanics from the southern (Avachinsky) and central (Sheveluch and Kharchinsky) segments of the Kamchatka peninsula. Peridotites with higher Os content (1.3–5.2 ppb) show a narrow $^{187}Os/^{188}Os$ range between 0.1182 and 0.1272 while the xenoliths with lower Os content (<1 ppb) show a wider variation and more radiogenic $^{187}Os/^{188}Os$ values (0.1287–0.1585). $^{187}Os/^{188}Os$ and $^{3}He/^{4}He$ (R/R_a) values of the xenoliths indicate that the xenoliths are metasomatized by the slab-derived fluids from the subducting altered oceanic crust. The original Os signature of some of the mantle wedge xenoliths seems to be eradicated and imprinted by the slab fluids from the subducting crust. The Nd-isotopic (+8.7–+9.3) and Pb-isotopic ratios ($^{206}Pb/^{204}Pb = 18.25$–$18.76$; $^{207}Pb/^{204}Pb = 15.43$–$15.55$; $^{208}Pb/^{204}Pb = 37.68$–$38.24$) of the xenoliths are similar to those of the Pacific MORB. Pb and Ba contents of the xenoliths increase with increasing $^{187}Os/^{188}Os$. Thus the mantle-wedge beneath Kamchatka was infiltrated by slab-derived fluids with Os, Pb, and other volatile and fluid-mobile elements.

Keywords: Os; Pb isotopes; slab devolatilization; mantle-wedge; arc volcanoes

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0012-821X/$ - see front matter
doi:10.1016/j.epsl.2005.05.018

1. Introduction

Subduction zones are the only tectonic settings where both new continental crust is formed as well as materials from the surface (altered oceanic crust and sediments) are buried into the Earth's interior. Fluid fluxes from the subducting oceanic slab to the mantle wedge by devolatilization are generally believed to cause arc volcanism. One of the most direct methods for studying the effect of the geochemical fluxes from the subducted slab to the mantle wedge is through the study of rare mantle xenoliths such as those reported from the Kamchatka arc [1,2]. Since sediment input into the Kamchatka arc is limited [3,4], xenoliths from this location may allow an examination of the effect of slab devolatilization into the mantle wedge.

The Re–Os system offers a different perspective on the geochemical diversity found in the oceanic basalts due to the different chemical behavior of the Re–Os system compared to the Rb–Sr, Sm–Nd and U–Th–Pb systems. The Re–Os isotopic system has previously been used to assess recycled basaltic material as well as lithospheric material in producing the chemical and isotopic heterogeneities observed in ocean-island basalts [5,6]. Recently Re–Os studies on arc lavas [7,8] have shown that the Os-isotopic heterogeneity in the lavas might be due to mixing with radiogenic sediments and oceanic crust as well as disequilibrium processes during magma generation and ascent. Os mobility has been implicated for the radiogenic Os-isotope signatures in mantle xenoliths from arc settings, including the Kamchatka arc [2,9,10]. In this paper, we report Nd-, Pb-, and Os-isotopic ratios of some peridotite mantle xenoliths from the Kamchatka arc. We discuss these results along with the Sr and He isotopic ratios and some trace elements of the same xenoliths that were reported by us in a previous study [11]. Ba concentrations are also included in the current study since arc volcanics show large enrichments in Ba compared to MORBs. In our previous study of these mantle xenoliths [11], petrographic evidence as well as He–Sr isotopic, CO_2 and trace element concentration data were interpreted to indicate that fluids derived from seawater-altered lithosphere moved through the mantle wedge beneath Kamchatka. The Os and Pb-isotopic data of the xenoliths, combined with the He-isotopic data [11], indicate that the radiogenic Os-signature as well as the higher Ba and Pb concentration in these rocks are inherited from the devolatilized altered lithospheric slab.

2. Geologic setting of the Kamchatka arc and sample setting

The Kamchatka Peninsula, which is a part of the Kurile–Kamchatka arc, is located at the junction between the North American, Eurasian and the Pacific plates (Fig. 1). The peridotite xenoliths of this study were collected from the Avachinsky, Kharchinsky and Sheveluch volcanoes [11]. The Sheveluch and Kharchinsky volcanoes, located in the central part of the peninsula, are situated in a graben parallel to the Central Kamchatka Depression (CKD) The Avachinsky volcano is situated in the southern part of the Eastern Volcanic Front (EVF) that is located to the south of the CKD, trench-ward. The southern and central sections of the Peninsula is associated with the subduction of the cold Mesozoic Pacific lithosphere (80–90 Ma) while the northern section formed when the young hot oceanic crust of the Komandorsky basin subducted beneath it [12,13]; this segment is currently inactive. The Sheveluch and Kharchinsky volcanoes are believed to be situated over the northern edge of the subducting Pacific slab [14,15]. The northern segment is underlain by ~18 km of thickened oceanic crust [16].

The track of the Hawaii hotspot is being subducted in the northernmost part of the peninsula but there is no direct geochemical evidence for its involvement in the source of the CKD magmas. However, a recent study has shown that lavas from the northernmost volcano of the CKD (Sheveluch) show involvement of slab melts in their source [15]. Some studies have shown that melts of subducted oceanic crust as well as that of the hydrated mantle contribute in the formation of the lavas in the CKD while only fluids fluxing from the subducted crust have affected the EVF lavas [4,14,17].

3. Samples and analytical techniques

Eleven xenoliths collected for this study are from the three Late Pleistocene–Holocene volcanoes, the

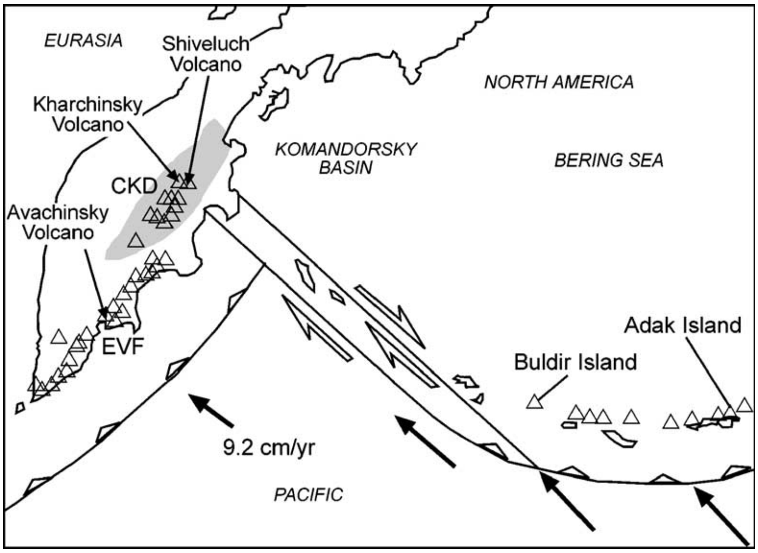

Fig. 1. Map of the Kamchatka and Aleutian arc, showing the subduction zone of the central Aleutians, the transform-type boundary in the western-most Aleutians, and the different subducting plates beneath the Kamchatka arc. Locations of the three volcanoes from which xenoliths for this study were collected are indicated by triangles along with the other associated volcanoes of the adjacent region. Also shown are Central Kamchatka Depression (CKD) and the Eastern Volcanic Front (EVF). Map modified after Yogodzinski et al. and Bindeman et al. [15,39].

Avachinsky, Kharchinsky, and Sheveluch. In Avachinsky the xenoliths are found in andesitic pyroclastics debris, at Sheveluch the xenoliths occur in Holocene calc-alkaline lava deposits while the Kharchinsky xenoliths were collected from the basaltic trachy-andesite lava dome. The xenoliths are spinel peridotites with a dominant olivine mineralogy, followed by variable amounts of orthopyroxenes, clinopyroxenes; trace amounts of amphiboles and phlogopites are occasionally found. All these peridotites show different degrees of plastic deformation and recrystallization and these deformation textures are quite similar to textures commonly found in mantle peridotite xenoliths hosted in alkali basalts and kimberlites. These textures range from protogranular through porphyroclastic to tabular mosaic and equigranular varieties [11]. Although some of these xenolith samples have been described as wehrlites in the literature, we prefer to call these rocks pryoxene-bearing peridotites that predominantly include harzburgites. Wehrlites are olivine–clinopyroxene rocks with at least 25% clinopyroxene. None of the samples of this study show this high amount of clinopyroxene and most show about 5% clinopyroxene with variable amounts of amphibole, spinel and phlogopite. The rare earth element patterns of these rocks [11] indicate a depleted upper mantle origin. However, these depleted mantle peridotites have been subsequently metasomatized by fluids coming from the slab, and the current study is about geochemical documentation of this metasomatism.

$^3He/^4He$ (R/R_a) and $^{87}Sr/^{86}Sr$ data as well as trace element data for the samples were measured in a previous study [11]. For this study Os-, Nd-, and Pb-isotopic ratios were measured in the same samples studied in the paper by Basu et al. [11]. He–Os–Nd–Pb isotopic data as well as certain trace element concentrations for the studied samples are given in Table 1.

The chemical separation of Re and Os, the mass spectrometric determination of Re and Os concentrations as well as $^{187}Os/^{188}Os$ isotopic ratios were analyzed at Harvard University following established procedures [18]. Whole-rock powders were made in a metal-free environment using an alumina-grinding mill. 1–2 g of rock samples was spiked with ^{190}Os and ^{185}Re tracer solutions. The xenolith samples were digested in aqua regia by the Carius tube-method [19] and heated in the oven at 200–230 °C for 5 days. Re and Os were then separated by the solvent extraction method where Os was extracted into CCl_4 while Re remained in the aqua regia. Os was back-extracted

Table 1
Os-, He-, Nd-, and Pb-isotopic and trace element concentrations of the peridotite xenoliths from the Kamchatka arc

Sample	Ba (ppm)[a]	Sr (ppm)[a]	$^{87}Sr/^{86}Sr$[a]	$^{3}He/^{4}He$ (R/R_a)[a]	Os (ppb)[b]	Re (ppt)[c]	$^{187}Re/^{188}Os$	$^{187}Os/^{188}Os$[d]	Nd (ppm)[a]	Sm (ppm)[a]	$^{143}Nd/^{144}Nd$ (0)[e]	$\varepsilon_{(Nd)}$[f]	Pb (ppm)[a]	$^{206}Pb/^{204}Pb$[g]	$^{207}Pb/^{204}Pb$[g]	$^{208}Pb/^{204}Pb$[g]
Avachinsky																
AV3	2.9	1.25	0.704045	7.3	4.8	–		0.1182						18.602	15.523	38.095
					5.2	–										
AV3-XLB	18.6	4.64	0.704056	6.8	0.49	7	0.07	0.1415	0.23	0.08	0.513110	9.2		18.453	15.460	37.678
				6.8	0.28	40	0.14	0.1449								
Kharchinsky																
KH8846-11A	43.1	28.7	0.703406	3.3	0.26	50	0.91	0.1416	1.29	0.46	0.513101	9.0	0.22	18.259	15.430	37.680
KH8846-11B	27.8	16.4			0.27	73	1.27	0.1303	0.63	0.26	0.513086	8.7	0.08	18.250	15.465	37.819
KH8846-11C	50.1	34.4			0.35	–		0.1303	0.65	1.68	0.513088	8.8	0.22	18.488	15.550	38.076
KH8846-12	67.5	33.9	0.703556	1.8	0.30	31	0.49	0.1442					0.78	18.432	15.519	38.005
KH8846-13	11.2	4.7			0.51	55	0.52	0.1287					0.21	18.557	15.503	38.244
KH8846-14		38.6	0.703674	0.6	0.0427	36	2.59	0.1514	0.92	0.37	0.513115	9.3		18.266	15.443	37.731
				0.6	0.0917	50	4.02	0.1344								
KH8846-15	30.2	50.1	0.703542	1.5	0.0187	8	2.04	0.1585					0.45	18.299	15.485	37.838
	30.2			1.5	0.0165			0.1585					0.45			
KHX98-1	20.6	5.0	0.703565	5.3	1.3	12	0.04	0.1272					0.16	18.312	15.474	37.805
	20.6			5.3	0.9	14	0.07	0.1265					0.16			
Shiveluch																
SH98X-1	1.3	1.8	0.703522	7.1	5.1	25	0.20	0.1265					0.15	18.759	15.543	37.911
	1.3			7.1	4.1	15	0.20	0.1268								

All rock samples are pyroxene-bearing peridotites dominated mostly by olivine with variable amounts of ortho and clinopyroxenes and spinel ± amphibole.

[a] Data taken from Basu et al. [59]. The He-isotopic ratios are normalized to atmospheric composition expressed as (R/R_a) and are corrected assuming that the Neon in the sample is of atmospheric origin. Measured $^{87}Sr/^{86}Sr$ ratios were normalized to $^{86}Sr/^{88}Sr = 0.1194$. The trace elements were measured by ICPMS and analytical uncertainties were within 5%.

[b] Os concentration measured by NTIMS using isotope dilution method with ^{190}Os spike.

[c] Re concentration measured by ICP-MS using isotope dilution method with ^{185}Re spike.

[d] Measured $^{187}Os/^{188}Os$ ratios were corrected for oxides and mass fractionation. MPI Os Standard analyzed during the course of this study yielded $^{187}Os/^{188}Os = 0.11988 \pm 16$ (2σ) $(n=7)$ [56]. Measured ratios have $2\sigma_{mean}$ values of less than 10 corresponding to the last two digits, except AV3-XLB, KH8846-13 and KH8836-15, which have less than 35.

[e] Measured $^{143}Nd/^{144}Nd$ ratios were normalized to $^{146}Nd/^{144}Nd = 0.7219$. La Jolla Nd Standard analyzed during the course of this study yielded $^{143}Nd/^{144}Nd = 0.511850 \pm 26$ (2σ) $(n=3)$. Measured ratios have $2\sigma_{mean}$ values of less than 25 corresponding to the last two digits.

[f] Calculated using present-day bulk-earth value of $^{143}Nd/^{144}Nd = 0.512638$ and $^{147}Sm/^{144}Nd = 0.1967$.

[g] For Pb isotopic analyses, mass fractionation was monitored by analysis of the NBS-981 Pb standard and was typically ~0.12% per amu. Pb-isotopic ratios were measured by TIMS and have $2\sigma_{mean}$ values of less than 10 corresponding to the last two digits of $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ and 20 for the last two digits of $^{208}Pb/^{204}Pb$.

into HBr and purified by microdistillation [20]. Re was purified using the AGI-X8 anion exchange column chemistry. Os was measured as oxides by negative thermal mass spectrometry (N-TIMS) on a Finnigan MAT 262. Measured ratios were corrected for oxides and for mass fractionation. Re was measured with quadrupole ICP-MS (a VG PQ II Plus). Os and Re processing blanks were <5 pg ($^{187}Os/^{188}Os=0.175$) and <8 pg, respectively. All the samples were blank corrected for Re and samples with Os concentration<1 ppb were blank-corrected for Os.

Nd-, Sr-, and Pb isotopes were measured with a VG Sector multi-collector TIMS using the procedures established in the laboratory at the University of Rochester [21,22]. Filament temperature during Pb-isotope ratio measurements was monitored continuously and raw ratios were calculated as weighted averages of the ratios measured at 1150, 1200, and 1250 °C, respectively. The reported Pb-isotopic data are corrected for mass fractionation of $0.12 \pm 0.03\%$ per amu based on replicate analyses of the NBS-982 Equal Atom Pb Standard measured in the same fashion. The laboratory procedural blanks were <200 pg for both Nd and Pb and <300 pg for Sr. No blank correction was necessary for these elements in Table 1.

4. Geochemical data

Plots of 1/Os, $^{3}He/^{4}He$, Ba/Os and Pb/Os versus $^{187}Os/^{188}Os$ are shown for the Kamchatka xenoliths in Figs. 2 and 3. These data are compared with estimates for the depleted mantle $^{187}Os/^{188}Os$ of ~0.120 to 0.127 [23,24], and Os concentration of 0.8–9 ppb [25]. The depleted mantle is indicated in Fig. 2 in $^{3}He/^{4}He$ with R/R_a ~8 ± 1 (the measured $^{3}He/^{4}He$ values are expressed with respect to the atmospheric $^{3}He/^{4}He$ as R/R_a.), and in Fig. 3 in Ba/Os ~200 and Pb/Os ~4. Altered ocean crust is shown in Figs. 2 and 3 with a range in $^{187}Os/^{188}Os$ ~0.142 to 0.439 and Os concentrations of ~20 ppt (range 5.5 to 363 ppt [26]). $^{3}He/^{4}He$ of the altered oceanic crust is taken as ~0.5 ± 0.25 (R/R_a) and its Ba/Os ~640,000, Pb/Os ~25,000 with their Pb and Ba concentrations taken from the study of Hofmann [27,34].

The Re–Os isotopic measurements for the Kamchatka xenoliths are reported in Table 1. The peridotite xenoliths exhibit a wide range of Os concentrations and $^{187}Os/^{188}Os$ ratios, from ~0.02 to 5.2 ppb and 0.1182 to 0.1585, respectively. Three of the samples (AV3, KHX98-1, and SH98X-1) in Table 1 show higher Os abundances (1–5 ppb) that may suggest presence of sulfides in these rocks. Repeat measurements of samples with high Os concentrations showed similar isotopic ratios, while samples with less than 1 ppb Os showed substantial differences in the measured $^{187}Os/^{188}Os$ ratios. This is probably due to the coarse grain size and inhomogeneity in the modal mineralogy (nugget effect) of the xenoliths. The Re concentrations in the peridotites are generally low, ranging from 7 to 55 ppt. The $^{187}Re/^{188}Os$ range from 0.2 to 4.02 and there is no correlation between the $^{187}Os/^{188}Os$ ratios and the $^{187}Re/^{188}Os$ ratios. The xenoliths from different volcanoes are shown by separate symbols. In the 1/Os versus $^{187}Os/^{188}Os$ diagram (Fig. 2a), samples with high Os concentrations have a less radiogenic $^{187}Os/^{188}Os$ signature than those with low Os concentration. Re–Os data from a previous study of xenoliths from the Kamchatka arc by Widom et al. [2] exhibit essentially the same ranges in Os concentration and isotopic composition as in our samples (Fig 2a). The $^{187}Os/^{188}Os$ data for arc volcanics from Kamchatka were reported by earlier workers [2,8]. The arc basalts generally show radiogenic $^{187}Os/^{188}Os$ signature with low Os concentration, most data have $^{187}Os/^{188}Os$ values above 0.2. A single xenolith from the Avachinsky (AV3) plots below the depleted mantle region with a $^{187}Os/^{188}Os$ value of 0.1182, which is similar to the least radiogenic abyssal peridotite published, $^{187}Os/^{188}Os=0.1183$ (sample number 16-71-22 from paper of Standish et al. [24]). Thus, we consider this sample to be part of the depleted mantle. The Os concentrations and isotopic ratios of the analyzed samples fall in the range from the depleted mantle reservoir to seawater-altered MORB. However, radiogenic Os from subducted sediment could also contribute to the slab Os-isotope signature. We discuss this possibility later in connection with the Pb-isotopic data of the xenoliths.

A plot of $^{187}Os/^{188}Os$ ratios versus the $^{3}He/^{4}He$ (R/R_a) values for the Kamchatka xenoliths is shown in Fig. 2b. The xenoliths show roughly a negative correlation between the $^{3}He/^{4}He$ (R/R_a) and

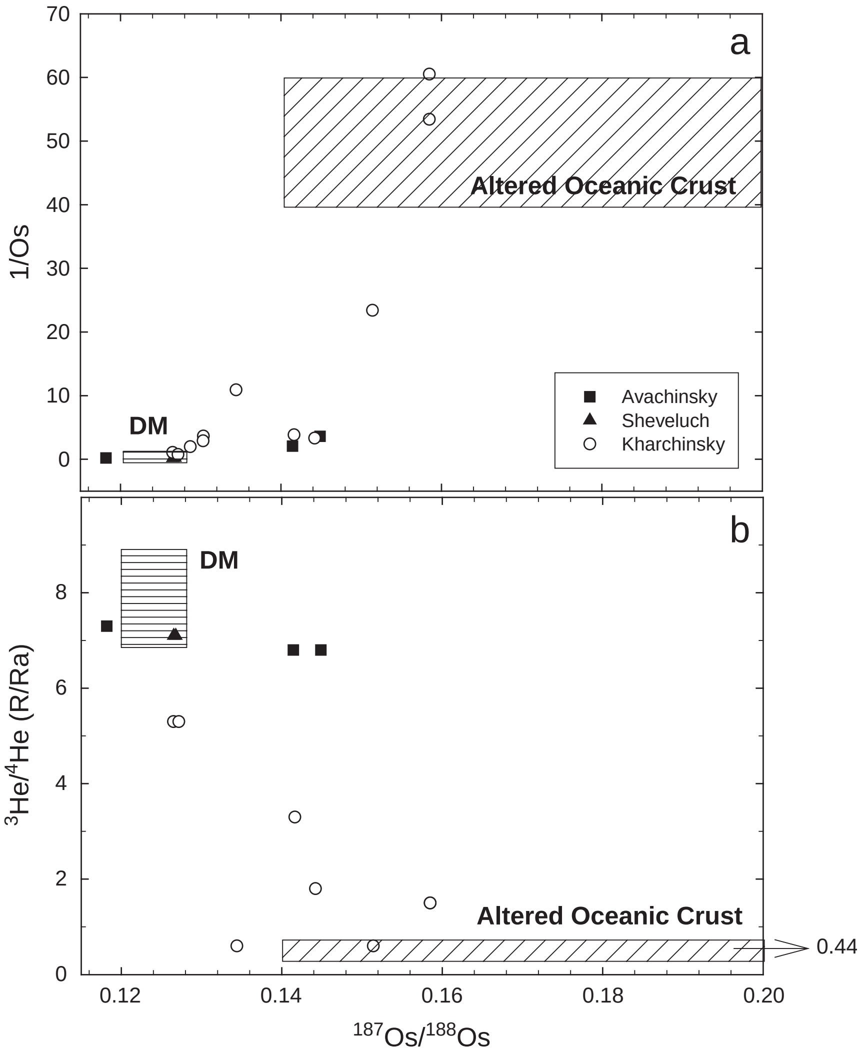

Fig. 2. a) The inverse value of the Os concentration (ppb) of the peridotite xenoliths versus their $^{187}Os/^{188}Os$ ratios. Os-isotopic data from previously studied xenoliths from the Kamchatka arc by Widom et al. [2] and arc volcanics from Kamchatka [2], cover essentially the same range as indicated by the xenolith data of this study. The xenoliths define a non-linear trend between samples with values similar to the depleted mantle (DM) and similar to altered ocean crust [23–26]. b) The $^{187}Os/^{188}Os$ plotted versus $^3He/^4He$ (R/R_a) for the mantle xenoliths. Two xenoliths, one each from Avachinsky and Sheveluch are similar to the depleted mantle (DM). The other peridotite samples show different degrees of metasomatism and a trend toward the signature of altered ocean crust. Radiogenic in-growth of Os within old seawater altered ocean crust ($^{187}Re/^{188}Os=400$, initial $^{187}Os/^{188}Os=0.123$, age = 180 Ma) could give present-day $^{187}Os/^{188}Os$ values of ~1.2. The highest measured $^{187}Os/^{188}Os$ in altered ocean crust is 0.44 [26], as indicated by the arrow at the bottom right hand corner of this diagram.

$^{187}Os/^{188}Os$ ratios. The single Sheveluch sample, one Kharchinsky and one Avachinsky sample plot near the depleted mantle field while one Avachinsky and four Kharchinsky samples plot away from the depleted mantle towards the field of the seawater-altered ocean crust.

In Fig. 3a, a rough positive correlation is seen between the ratio of large-ion-lithophile elements (LILE), Ba and Pb relative to Os, and the $^{187}Os/^{188}Os$ values. The Ba concentration varies between 1.3 and 67.5 ppm while the Pb concentration varies between 0.08 and 0.78 ppm. Sheveluch shows

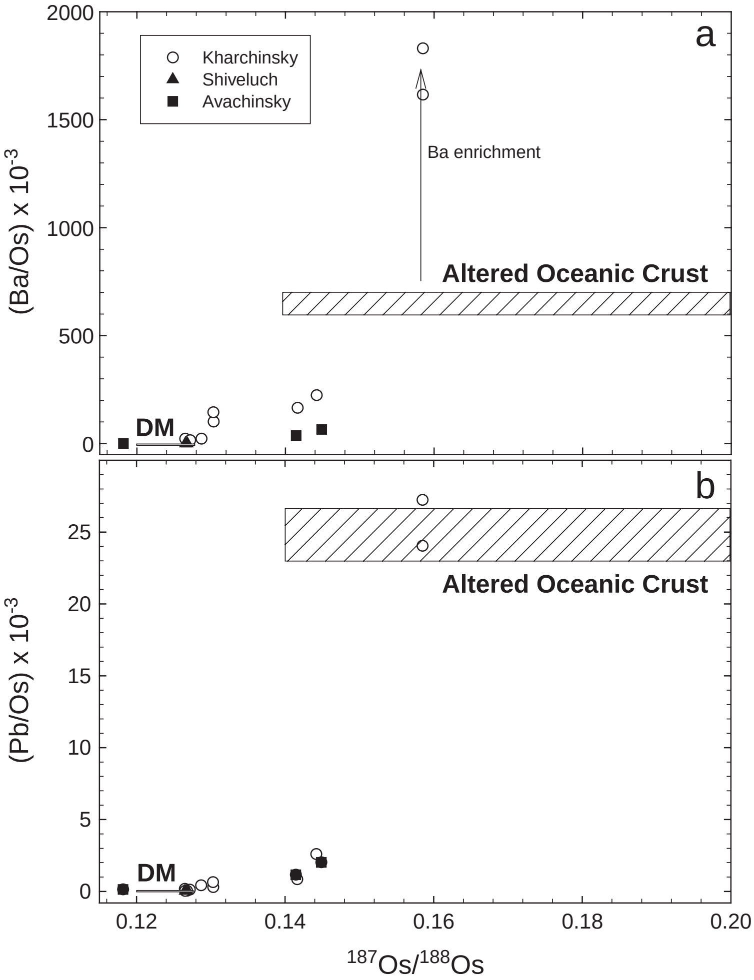

Fig. 3. $^{187}Os/^{188}Os$ plotted against Ba (a) and Pb (b) concentrations in the Kamchatka xenoliths. Positive correlations between the concentrations of these two large ion lithophile (LILE) elements and the $^{187}Os/^{188}Os$ indicate that radiogenic Os signatures along with these two LILE were carried by the slab-fluids. Reservoirs for mid-ocean-ridge basalts (MORB) and depleted mantle (DM) are from the paper of Hoffman and the study by Salters and Stracke [27,28].

the lowest LILE concentrations while Kharchinsky samples show variable Ba concentrations. In general, Ba and Sr concentrations (Table 1) in the xenoliths show a positive correlation with the radiogenic Os-isotopic ratios. Ba/Os shows a trend toward a component that has a Ba/Os ratio higher than altered oceanic crust. A high Ba/Os mixing component that extends to values higher than altered oceanic crust (Fig. 3a) could implicate the high Ba source from sediments.

The $^{206}Pb/^{204}Pb$ versus $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ isotopic ratios for the Kamchatka xenoliths are shown in Fig. 4 and compared with different mantle and crustal reservoirs: the depleted mantle (DM), enriched mantle (EMI and EMII) and HIMU, the Northern Hemisphere Reference Line (NHRL), the 4.55 Ga Geochron [29], an average of globally subducting sediments (GLOSS [30]) and the field of Pacific MORB [31]. Also shown are Pb-isotopic ratios of arc volcanics from the CKD (gray triangles) and the EVF (gray crosses: data compiled in GEOROC [32]). The xenoliths from Kharchinsky and Sheveluch show a range of $^{206}Pb/^{204}Pb$ values from 18.25 to 18.76 while the Avachinsky xenoliths

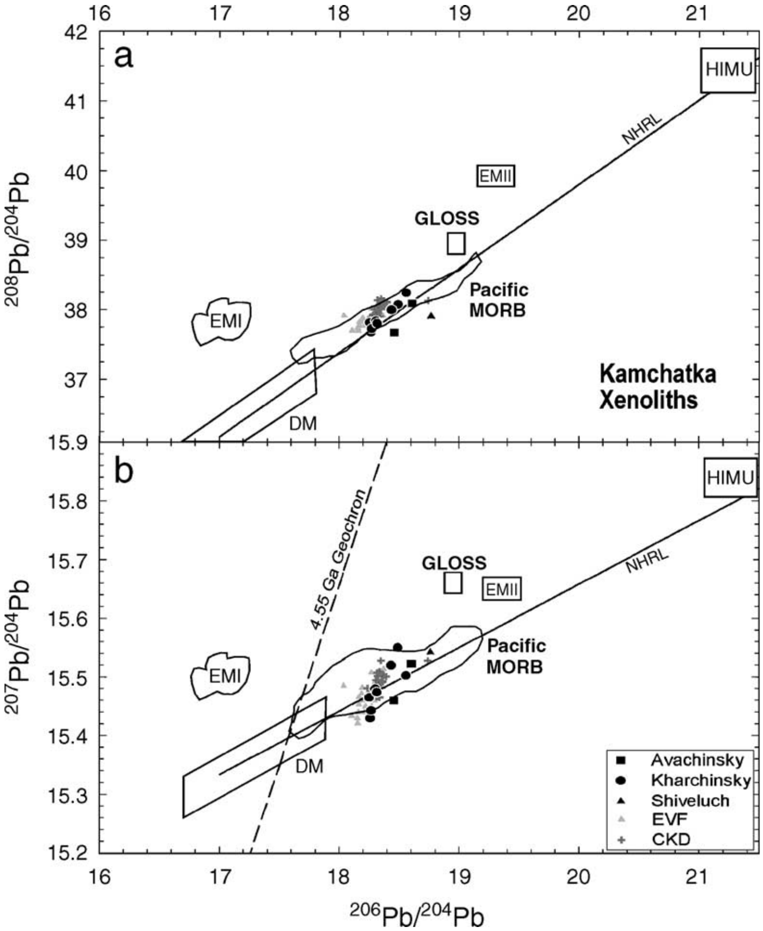

Fig. 4. Pb–Pb isotopic data for the mantle xenoliths. For comparison are shown the various mantle reservoirs, NHRL, 4.55 Ga Geochron and the GLOSS [30], the average global ocean sediments in subduction zones. Also shown are the fields of the Pacific MORB [33] and arc volcanic rocks from the CKD and EVF of the Kamchatka peninsula (Fig. 1) (data compiled in GEOROC [32]). All the peridotite samples fall within or near the field of the Pacific MORB. The Kharchinsky samples indicate a possible mixing between a Pacific MORB end-member and GLOSS. The Sheveluch and Avachinsky samples also show a similar trend. This trend, especially of a slightly more radiogenic $^{207}Pb/^{204}Pb$ signature toward GLOSS is thought to be affected by some sediment component in the fluid fluxing from the subducting oceanic slab.

have $^{206}Pb/^{204}Pb$ values of 18.45 to 18.60. Most of the peridotite xenoliths fall within the field of the Pacific MORB, showing a slight hint of a trend towards GLOSS; interestingly, the xenolith trend is similar to one exhibited by the volcanic rocks from the CKD and EVF of the Kamchatka arc (Fig. 1). The ϵ_{Nd} values of +8.7 to +9.3 (Table 1) for the xenoliths are similar to those exhibited by the Pacific MORB [33]. The isotopic ratios of Pb in the xenoliths (Table 1), however show no strong correlation with the Os-isotopic ratios.

5. Discussion

The xenoliths from this study as well as from Widom et al. [2] do not show a straight line relationship in the $^{187}Os/^{188}Os$ vs. 1/Os plot (Fig. 2a). This observation suggests that the radiogenic isotopic signatures of the xenoliths are not a result of a simple two-component mixing. The non-linear trend defined by the xenoliths in the 1/Os versus $^{187}Os/^{188}Os$ space is consistent with infiltration and alteration of a depleted mantle by a MORB-derived fluid carrying the Os isotopic signature [35–37] of the subducted altered oceanic crust.

The andesite host magma for the xenoliths could be a possible contaminating end-member. However, the Sr-isotopic ratios ($^{87}Sr/^{86}Sr$=0.70354–0.70367) and the chondrite-normalized rare earth element plots for the xenoliths as well as the host basalts ($^{87}Sr/^{86}Sr$=0.70358) and the He-isotopic ratios of these xenoliths having values much different from andesites (R/R_a as low as 0.6) clearly show that the xenoliths have not been affected by the host magma [11]. Hence it can be concluded that the Os isotopic signatures of the xenoliths are not affected by that of the host magma. Radiogenic ingrowth of Os due to Re-decay in the xenoliths could possibly account for the radiogenic Os signature of the xenoliths. Considering sample KH8846-14, with the highest measured value of $^{187}Re/^{188}Os$=4.02 and assuming it had an initial $^{187}Os/^{188}Os$ value of 0.1272 (KHX98-1) and a final $^{187}Os/^{188}Os$ value of 0.1514 (Table 1), the ingrowth period for this xenolith would be more than 365 Ma. Other xenoliths that have much lower values of $^{187}Re/^{188}Os$ (0.02–2.59) would require a longer period of time to attain their respective present-day $^{187}Os/^{188}Os$ radiogenic signatures. This observation requires that the mantle wedge should remain isolated for at least 365 Ma. Considering the young oceanic and volcanic arc terranes of the area [38] and the tectonic activity in the area during the Mesozoic and Cenozoic [39,40] it is highly unlikely for this mantle wedge to remain isolated. One possibility is that the xenoliths initially had higher $^{187}Re/^{188}Os$ values and recent metasomatic events caused the loss of Re from the xenoliths. Another strong possibility for the radiogenic $^{187}Os/^{188}Os$ values in xenoliths is fluids from the subducting oceanic slab, which would also impart a radiogenic $^{187}Os/^{188}Os$ signature to the xenoliths. MORBs are considered to be highly radiogenic, due to seawater alteration ($^{187}Os/^{188}Os$ ~1) and radiogenic ingrowth of Os because of high $^{187}Re/^{188}Os$ (100–5000 in the paper of Shirey and Walker [25]). The following discussion would indicate that the latter situation is a more viable possibility.

Fig. 2b shows the $^{3}He/^{4}He$ (R/R_a) versus the $^{187}Os/^{188}Os$ signature of the xenoliths studied. $^{3}He/^{4}He$ (R/R_a) values have been measured in 8 samples — 2 from Avachinsky 1 from Sheveluch and 5 from Kharchinsky [11,59]. The high $^{3}He/^{4}He$ (R/R_a) values of 6.8 to 7.3 are similar to those found in arcs that have a high component of their He derived from the mantle (94% for ~7.5) [41] while the lower $^{3}He/^{4}He$ (R/R_a) values are indicative of a crustal component ($^{3}He/^{4}He$ <0.1 R_a) or old oceanic crust [41]. The Sheveluch sample along with a Kharchinsky and Avachinsky sample, a total of 3 samples, are similar to the depleted mantle end member while the other 4 Kharchinsky xenoliths and 1 Avachinsky xenolith plot towards the altered ocean crust (Fig. 2b). This indicates that the $^{3}He/^{4}He$ (R/R_a) and the $^{187}Os/^{188}Os$ values of the xenoliths were affected by the altered ocean crust signature, which was probably carried by the fluids that derived from the dehydration of the subducting slab. Correlated values for $^{3}He/^{4}He$ (R/R_a) and $CO_2/^{3}He$ for the xenoliths have also shown that there is interaction between two reservoirs—the depleted mantle and a variably-altered ocean crust, the low R/R_a values requiring significant crustal input for ^{4}He [11,59].

Fig. 3 shows the relation between Ba/Os and Pb/Os ratios versus $^{187}Os/^{188}Os$ ratios of the xenoliths. Large ion lithophile elements (LILE; e.g., Ba, Pb) are known to be mobile in slab fluids while the high field strength elements (HFSE; Nb, Ta) are immobile e.g., refer to studies by Gill and Peacock [42,43]. In Fig. 3, the Ba/Os and Pb/Os ratios show a positive correlation with $^{187}Os/^{188}Os$ ratios of the xenoliths. The Sheveluch sample shows less metasomatism while the Kharchinsky samples indicate variable degrees of metasomatism.

In a Pb-isotope ratio plot for these peridotite mantle xenoliths (Fig. 4), it is observed that all the xenoliths plot close together towards the right of the Geochron, near or within the area of the Pacific MORB. The Kharchinsky samples fall on a mixing line between the Pacific MORB end-member and the GLOSS. The Avachinsky and Sheveluch samples show a similar trend. Several studies have shown that the volcanoes within the Kamchatka arc have very little sediment component [3,4,44], less than 1%. However when the overall trends of the CKD (Central Kamchatka Depression) and EVF (eastern Volcanic Front) volcanics are examined, a sediment component (especially in the $^{207}Pb/^{204}Pb$ ratios) seems to be the possible explanation for the Pb-isotopic trends observed. The Pb-isotopic ratios of the source of the arc volcanics as well as those of the mantle wedge peridotites might have been affected during the passage of the fluid from the subducting ocean crust into the subarc mantle wedge. Pb being a fluid-mobile element (e.g., [45,46]) and the Pb concentration of depleted mantle being low (23.2 ppb; [28]), a very low amount of sediment component within the fluid would affect the Pb-isotopic ratios of the mantle wedge. Thus the observed range in the Pb-isotopic ratios of the mantle xenoliths can be due to metasomatism by the devolatilized fluid derived from the subducting ocean crust with some sediment component. This is a possibility that is also supported by the Ba/Os ratios in a couple of samples that are significantly higher than the same ratios in altered oceanic crust (Fig. 3a).

Nd isotopic ratios in five of the ultramafic xenoliths were measured with $\epsilon_{Nd}(0)$ values from +8.7 to +9.3. These values are within the range observed for the Pacific MORB. We consider the Nd isotopic ratios of these peridotite xenoliths to be the original signature of the mantle wedge. These Nd isotopic signatures clearly indicate that the mantle wedge beneath Kamchatka is LREE-depleted, as has been previously observed [14,47] and the REE pattern of the samples of this study also clearly show such a depletion [11,59].

Is it possible that the peridotite xenoliths of this study represent overlying arc lithospheric mantle rather than the circulating mantle wedge? Although we have not carried out any definitive thermobarometric study of these xenoliths to decipher their temperatures and pressures of equilibration which may itself be a contentious issue given the limited mineralogical variations in the xenoliths, our geochemical data as presented here can be useful in determining a circulating mantle wedge origin for the xenoliths. It is important to note also that the central segments of the Kamchatka arc on which the xenolith bearing volcanoes were built exhibit a crustal thickness of 30–40 km with the development of a granulite facies lower crust [5]. Thus it is expected that the lithospheric mantle beneath this thickened crust should have a complex geological evolution with multiple episodes of chemical depletion and enrichment due to melt percolation, addition and extraction. Therefore, it is highly unlikely that some of the xenoliths of this study, if they are representative of this mantle beneath Kamchatka, could have retained present day MORB like or depleted asthenospheric Nd, Pb, Os and He-isotopic signatures (Table 1). Thus we believe that the xenolith samples of this study represent variably metasomatized circulating mantle wedge samples of the Kamchatka arc.

As already mentioned, the xenoliths were affected by fluids derived from the altered ocean crust. The consideration of $^{3}He/^{4}He$ (R/R_a) and the $^{187}Os/^{188}Os$ ratios of the xenoliths indicate that the infiltration of slab-derived fluids through the peridotite mantle wedge affected the He and Os-isotopic ratios of this wedge. It is interesting that some of the metasomatized mantle xenoliths of this study have lost all traces of the depleted mantle Os-isotopic signature and is overwhelmingly replaced by the altered oceanic crust Os-isotopic signature. It has been suggested that Os might be scavenged from the sub-arc mantle [48,49] when Os-undersaturated fluid/melt from the slab reacts with a relatively Os rich peridotite in the more oxidizing conditions of a mantle wedge [48, 50,51]. Also the solubility of Os has been shown to be high in Cl-rich fluids and this solubility increases with higher oxygen fugacity [52]. Silicate melts or fluids could be oxidizing agents in the mantle [48] and they could also mobilize ambient Os in the mantle. Thus, slab fluids or silicate melts from the subducted crust could have removed the original Os-isotopic signature of the mantle wedge replacing it with the Os isotopic signature of the altered oceanic crust. The Kamchatka xenoliths do not contain any sulfides [1,53], which are usually believed to contain the bulk of the Os in peridotites [54]. A generally high oxidizing conditions of the mantle wedge, with oxygen fugacity up to about 1.4 log units above the FMQ buffer [48], would indicate that sulfur is in the form of SO_4^{-2} dissolved in the fluids [55]. We suggest here that this process caused the removal of sulfides from the Kamchatka peridotites and hence created an environment for the slab fluids to imprint their signatures on the xenoliths. This process maybe inhomogeneous and may fail to remove all sulfides. Widom et al. [2] observed similar behavior of the Re–Os systematics of the Kamchatka xenoliths and attributed it to Os removal by the slab fluids or slab melts. The correlation between the high $^{187}Os/^{188}Os$ with enrichment in Pt, which is known to be fluid mobile [57], lead them to conclude that the $^{187}Os/^{188}Os$ values of the peridotite xenoliths were imparted by the slab-fluid infiltration.

There is experimental evidence, however, for even greater mobility of Re in oxidizing Cl-rich environments and yet most of the Kamchatka xenoliths have very low Re abundances, as noted also by Widom et al. [2]. The observed low concentration of Re in arc basalt has been used as an argument against slab fluid origin of radiogenic Os in arc mantle [58]. Radiogenic Os as measured in many arc volcanic rocks has been interpreted [58] by crustal interaction rather than by subduction fluid with high radiogenic Os-isotopic composition. The isotopic data presented in this and another recent study completed [59] by us clearly rule out such a crustal interaction process for the trace element and isotopic evolution for the Kamchatka xenoliths. This conclusion is based on He and Sr-isotopes as well as the trace elements, including the REE, distribution patterns.

Thus the isotopic data indicate that except for the Nd isotopic ratios, all other isotopic ratios of the Kamchatka xenoliths measured in this study have been affected by the fluid devolatilizing from the subducting slab. Several studies have indicated that the mantle wedge beneath the Central Kamchatka Depression (CKD) in the Kamchatka peninsula (Fig. 1) possibly has a slab melt component in it while the Eastern Volcanic Front (EVF) mantle wedge is only affected by fluids fluxing from the subducting slab [4,14]. The results of the present study and another recently completed by us [59] indicate that the Kamchatka mantle wedge beneath the CKD and EVF were similarly affected by the infiltrating Os, He and Pb by slab-derived fluids.

6. Conclusions

1. Slab fluids from the subducting seawater-altered ocean crust have metasomatized the mantle xenoliths in the Kamchatka arc. The Os–He isotopic ratios as well as trace element concentrations indicate that the depleted mantle signature of the mantle wedge have been affected by the slab-fluid.
2. The original Os was scavenged from the mantle wedge peridotites by the slab fluid, possibly due to a high oxygen fugacity of the fluids infiltrating the mantle that would mobilize Os as well as destabilize sulfides. However, the infiltrating slab fluids left behind their Os and Os-isotopic signatures in the mantle wedge, as represented by the xenoliths of this study.
3. The Pb isotopic ratios of the shallow mantle beneath the Kamchatka arc have been only slightly affected by the slab fluids. A very small component of the sediment within the slab fluid could have affected the Pb isotopic ratios, displacing them towards more radiogenic $^{207}Pb/^{204}Pb$ values without altering the Nd isotopic ratios.
4. The Nd isotopic ratio of the mantle wedge beneath Kamchatka is similar to the values observed in Pacific MORBs.
5. Thus, the mantle wedge beneath Kamchatka was metasomatized by slab-derived fluids, resulting in high Ba concentrations and exchange of Os and He isotopes.

Acknowledgements

This research was supported by NSF EAR-0310185 to ARB and by NASA and NSF grants to SBJ. We are grateful to Cin-Ty Lee and Elizabeth Widom for their careful and thoughtful reviews which considerably improved the presentation of data and arguments.

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