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Depleted mantle sources through time: Evidence from Lu–Hf and Sm–Nd isotope systematics of Archean komatiites

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ABSTRACT

In this study, we present Lu–Hf isotope systematics and Lu and Hf abundances for komatiites from the lowermost part of the 2.8 Ga Kostomuksha greenstone belt in the Baltic Shield and compare these, as well as available Sm–Nd isotope data, with those for the best characterized Archean komatiite systems. The Lu–Hf isotope compositions of four spatially associated differentiated lava flows from the Kostomuksha greenstone belt yield an isochron (MSWD = 1.6) with an age of 2931 ± 300 Ma, which represents the first Lu–Hf isochron obtained for a suite of co-magmatic komatiite lavas. The calculated mean initial ^{176}Hf/^{177}Hf for the Kostomuksha komatiite samples is 0.281107 ± 3 ($2\sigma_{mean}$), which corresponds to an initial ε^{176}Hf of +4.9 ± 0.1 ($2\sigma_{mean}$). Assuming that mantle differentiation occurred 10 Ma after Earth's accretion at 4.558 Ga, this precise initial ratio requires a time-integrated ^{176}Lu/^{177}Hf = 0.03759 ± 8, which is identical to the average time-integrated ^{176}Lu/^{177}Hf = 0.0375 ± 6 calculated for the best characterized late Archean komatiite systems. Together with the calculated average time-integrated ^{147}Sm/^{144}Nd = 0.2091 ± 4 for the same late Archean komatiite systems, these parameters represent our best estimate of the Lu/Hf and Sm/Nd properties in the late Archean mantle and indicate derivation of komatiite magmas from around the globe from long-term melt-depleted sources that were remarkably homogenous in terms of lithophile trace element systematics. These time-integrated ratios are identical to the respective values of 0.0375 and 0.209 calculated by Boyet and Carlson (2006) for the so-called Early Depleted Reservoir (EDR), and may indicate that the late Archean mantle was similar in composition to the putative EDR, whereas early Archean systems had higher, and Proterozoic systems lower time-integrated Lu/Hf and Sm/Nd ratios. The observed decrease in time-integrated Lu/Hf and Sm/Nd in komatiite sources over time is interpreted as strong evidence for the existence of a hidden enriched reservoir complementary to the EDR that has been gradually mixed back into the mantle over time. The overall depletion of the early mantle likely occurred very early in Earth's history as a result of either global magma ocean differentiation or extraction and subsequent long-term isolation of primordial terrestrial crust.

1. Introduction

Komatiites are unique high-MgO lavas that are mostly confined to Archean terranes. They provide key information in studies bearing on the origin and early evolution of the planet. About three decades ago, several authors (Nesbitt et al., 1979; Jahn and Gruau, 1981; Jahn et al., 1982) proposed to sub-divide komatiites into two main groups on the basis of their major and lithophile trace element geochemistry. The so-called Al-undepleted, or Munro-type, komatiites, found mostly in late Archean terranes, are characterized by primitive mantle-normalized Al/Ti, Ca/Al, Ti/Y, and Gd/Yb ratios that are close to unity. The Al-depleted/enriched, or Barberton-type, lavas, found largely in early Archean terranes, are characterized by depletions/enrichments in Al, Y, and heavy rare earth elements (HREE) compared to primitive mantle estimates. Because HREE, Al, and Y are elements that preferentially partition into garnet relative to silicate melt, it has been proposed that garnet was a fractionating phase during hot, anhydrous melting in deep mantle plumes that supposedly produced Al-depleted/enriched komatiites (Sun and Nesbitt, 1978; Nesbitt et al., 1979; Jahn et al., 1982; Sun, 1987). This hypothesis received support from experimental studies that demonstrated that majorite (pyrope-pyroxene, high-P solid solution) is a likely liquidus phase during mantle melting at depths greater than 450 km (Ohtani et al., 1986; Ito and Takahashi, 1987; Kato et al., 1988). Uncertainty has remained as to whether fractionation of majorite controlled the composition of Al-depleted/enriched komatiites at the time of mantle melting (Ohtani, 1984, 1990), or whether the source regions of Barberton-type komatiites were characterized by majorite enrichment or depletion originally caused by fractionation in, and subsequent solidification of, a primordial magma ocean (Gruau and Jahn, 1983; Ohtani et al., 1989). Attempts to test this hypothesis, using

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the Lu–Hf isotope system, were made, first, by Gruau et al. (1990) and, later, by Blichert-Toft and co-workers (Blichert-Toft and Arndt, 1999; Blichert-Toft et al., 2004). ^{176}Lu decays to ^{176}Hf with a half-life of ~36 Ga. Since Lu partitions more strongly into majorite than Hf (Green, 1994), a cumulate from a magma ocean enriched in majorite would likely have a superchondritic Lu/Hf ratio and, given sufficient time, would develop superchondritic ^{176}Hf/^{177}Hf. The magnitude of this enrichment in the mantle would substantially exceed that caused by continental crust extraction (Blichert-Toft and Albarède, 1997) and, hence, the two mechanisms should be readily distinguishable.

The 2.8 Ga Kostomuksha komatiites belong to the Al-depleted type, having Al/Ti and Gd/Yb ratios intermediate between those typical of the Barberton- and Munro-type komatiites (Puchtel et al., 1998b). Based on their geological context, lithophile trace element abundances, and Sm–Nd and Pb–Pb isotopic compositions, these komatiites were proposed to have been derived from a starting mantle plume at temperatures some 300 °C higher than those of the ambient mantle (Puchtel et al., 1997, 1998b). The time-integrated superchondritic Pt/Os and Re/Os of the Kostomuksha mantle source, calculated from the corresponding initial ^{186}Os/^{188}Os and ^{187}Os/^{188}Os of the komatiite lavas, were interpreted to have been derived from interactions between the plume source and the outer core (Puchtel et al., 2005).

It has recently been argued that radiogenic initial ^{187}Os/^{188}Os isotopic compositions of some Barberton-type komatiites, i.e., those from the 3.5 Ga Schapenburg Greenstone Remnant, could have been the result of these lavas being derived from re-melting of a majorite-enriched cumulate that formed during stratification of a primordial terrestrial magma ocean (Puchtel et al., 2009a). Since the Kostomuksha lavas belong to the Barberton-type komatiites, their ^{187}Os/^{188}Os-enriched signature, therefore, could have had the same origin. On the other hand, the accompanying radiogenic initial ^{186}Os/^{188}Os isotopic composition of the Kostomuksha komatiites may argue against this possibility, since majorite garnet is not expected to be an important host of Pt (decaying into ^{186}Os) as opposed to Re (decaying into ^{187}Os). In order to test this hypothesis, we analyzed the Lu–Hf isotope compositions of ten komatiite drill core samples from a number of differentiated lava flows within the Southern sequence of the Kostomuksha greenstone belt. Anomalously radiogenic ^{176}Hf/^{177}Hf decoupled from the known radiogenic ^{143}Nd/^{144}Nd and ^{187}Os/^{188}Os of the Kostomuksha komatiites, would favor the magma ocean scenario for their origin and, thus, majorite garnet controlling the observed Hf–Nd–Os isotope systematics. In contrast, a moderately radiogenic Hf isotopic composition, matching the radiogenic initial ^{143}Nd/^{144}Nd, would be consistent with derivation from the depleted mantle, hence leaving the radiogenic Os isotopic signature open to interpretation with respect to outer core influence.

Based on the new Lu–Hf isotope data presented here and placed in the context of existing Sm–Nd, Re–Os, and Pt–Os isotope data, as well as trace element concentrations, we show that there is no evidence for the direct involvement of ancient majorite garnet-bearing residues in the source of the Kostomuksha komatiites, nor in those of the similarly-aged late Archean Abitibi or Belingwe komatiites. We further demonstrate that these three mantle sources, located beneath three different continents (the Baltic Shield, the Canadian Shield, and the Kaapvaal Craton), are depleted and nearly identical, suggesting that the mantle was homogeneous at this time and may have been depleted by a large-scale process very early in Earth's history. Finally, we review the time-integrated Sm/Nd and Lu/Hf ratios in mafic and ultramafic rocks from different locations worldwide through the Archean and early Proterozoic, and show that the parent–daughter ratios of these magma sources changed over time (becoming progressively less depleted), but are closely similar at any given time. We speculate on the meaning of this time evolution in terms of an evolving depleted reservoir interacting with a major enriched reservoir, while at the same time being subjected to mixing and extraction processes.

2. Geological background, previous studies, and sampling

The Kostomuksha greenstone belt is located in the NW Karelian granite–greenstone terrane, which occupies a total area of ~350,000 km^2 in the SE Baltic Shield, Russia (for reference, see Fig. 1 in Puchtel et al., 1998b) and is composed of gneiss–migmatite and granite–greenstone units. The latter is made up of volcanic and plutonic rocks and sediments of Archean greenstone belts. These show a pronounced linear alignment, forming a pattern of NNW-trending outcrops of isolated synforms among the rocks of the gneiss–migmatite unit. The Kostomuksha greenstone belt consists of a number of conjugate synforms, including the largest of these, the Kostomuksha synform, and can be traced over a distance of >400 km (for reference, see Fig. 1 in Puchtel and Humayun, 2000). The Kostomuksha synform is composed of at least two distinct lithotectonic terranes, one mafic igneous and the other sedimentary. These are separated by a major structural unconformity interpreted to represent a detachment surface along which the two terranes were tectonically juxtaposed (for reference, see Fig. 2 in Puchtel et al., 1998b). The mafic terrane contains submarine-erupted komatiitic and basaltic lavas, mafic and ultramafic volcaniclastic sediments, and numerous gabbro and peridotite sills. The sedimentary terrane is composed of shelf-type rocks and banded iron formations. The details of the geology, petrology, mineralogy, lithophile trace element abundances, and Pb and Nd isotope systematics, as well as highly siderophile element (HSE) abundances and Os isotopic compositions for mafic and ultramafic lavas from the Kostomuksha greenstone belt have been reported on extensively by Puchtel and co-workers (Puchtel et al., 1998b, 2001, 2005; Puchtel and Humayun, 2000, 2005). The komatiites have $Ti/Zr = 110 \pm 6$ ($2\sigma_{mean}$), similar to that estimated for the primitive mantle (PM; $Ti/Zr = 112$) of Hofmann (1988), and show a moderate depletion in Al ($Al_2O_3/TiO_2 = 17.2 \pm 0.3$ vs. 22 in PM) and HREE (PM-normalized $Gd/Yb = 1.16 \pm 0.01$). The latter feature allowed Puchtel et al. (1998b) to classify these rocks as belonging to the group of Al-depleted, or Barberton-type, komatiites, although the authors acknowledged the fact that the degree of Al-depletion in the Kostomuksha komatiites is less pronounced compared to a typical Barberton-type komatiite. The komatiites and basalts have Sm–Nd and Pb–Pb whole rock isochron ages of 2843 ± 39 and 2813 ± 78 Ma, respectively (Puchtel et al., 1998b). The entire sequence is intruded and overlain by mafic and felsic subvolcanic, volcanic, and volcaniclastic rocks with a U–Pb zircon age of 2821 ± 1 Ma (Puchtel et al., 1998b). As a result of seafloor alteration and/or greenschist facies metamorphism, the igneous mineralogy of the lavas was almost completely replaced by serpentine–chlorite–magnetite assemblages at 2757 ± 113 Ma. However, primary volcanic textures, structures, and most of the chemical features have remained intact. The lithophile trace element and isotopic characteristics of the komatiites (e.g., $(La/Sm)_N = 0.48 \pm 0.03$, $(Nb/Th)_N = 1.6 \pm 0.1$, $\varepsilon^{143}Nd(T) = +3.0 \pm 0.1$, $\mu_1 = 8.77 \pm 0.02$) are consistent with those of the contemporary oceanic depleted mantle. On the basis of geological evidence and isotopic and geochemical data, Puchtel et al. (1998b, 2001) argued that the mafic terrane represented remnants of the upper crustal part of an Archean oceanic plateau derived from partial melting in a starting mantle plume head.

For the Kostomuksha komatiites, Puchtel et al. (2005) further reported Pt–Os and Re–Os isochron ages of, respectively, 2816 ± 190 and 2880 ± 83 Ma. The mean initial ^{186}Os/^{188}Os and ^{187}Os/^{188}Os are 0.1198341 ± 7 and 0.11042 ± 69, respectively, indicating that the mantle source region that gave rise to these komatiites evolved with time-integrated superchondritic Pt/Os and Re/Os. The coupled ^{186,187}Os enrichments in the Kostomuksha komatiite source are similar to those found in the sources of younger plume-derived lavas, such as the 250 Ma Siberian Traps (Walker et al., 1997), the 89 Ma Gorgona komatiites (Brandon et al., 2003), and recent Hawaiian picrites (Brandon et al., 1998; 1999). Based on isotopic and trace element modeling, Puchtel et al. (2005) concluded that the radiogenic Os isotopic signatures most likely were derived from the outer core.

For the present study, ten among the freshest drill core samples from four differentiated lava flows of the Kostomuksha Southern komatiite sequence were carefully selected using existing geochemical and isotopic data to help identify the best preserved samples (for sample locations, see Fig. 1 in Puchtel and Humayun, 2005). Of these, six samples (9493–94100) come from a single, 6.5 m thick lava flow (flow 17). The remaining samples come from flow 18 (94104), flow 19 (94114), and flow 26 (94123 and 94126). The flows consist of an upper spinifex zone (A) and a lower cumulate zone (B). The A-zone is capped by a flowtop breccia and upper chilled margin, which grade downward into a subzone of initially random, and then oriented olivine spinifex. A distinct feature of all komatiite flows studied at Kostomuksha, compared to those from, for example, the komatiite type locality at Pyke Hill (Pyke et al., 1973), is a smaller thickness of cumulate zones in the former, usually <20% of the total thickness of the flows, and widespread occurrence of spinifex textures, with subordinate amounts of massive, undifferentiated lava flows.

3. Analytical techniques

3.1. Sample preparation

For this study, we used the batches of sample powders that had been previously prepared for the HSE abundance and Pt–Re–Os isotopic work on the Kostomuksha komatiites (Puchtel and Humayun, 2005; Puchtel et al., 2005). These powders were made by grinding, first in an alumina shatter box and then in an alumina disk mill, of additional material from the same rock crushes from which batches of sample powders used in the Puchtel et al. (1997; 1998b; 2001) studies had been prepared. The new batches of sample powders were then recombined with the older ones, well mixed, and re-ground in the alumina disk mill to achieve complete homogenization.

3.2. Chemical separation and mass-spectrometry of Lu and Hf

Lutetium and Hf chemical separations were carried out following the methods outlined in Blichert-Toft et al. (1997) with minor modifications designed to process ultramafic (i.e., high-MgO) and Cr-rich rocks, such as komatiites, as described by Blichert-Toft (2001). Approximately 600 mg of sample powder and appropriate amounts of a >98% pure mixed ^{176}Lu–^{180}Hf spike were weighed out into high-pressure, stainless steel-jacketed Teflon vessels (Parr bombs) and digested in a mixture of 10:1 concentrated HF:HNO_3 in an oven at 160 °C for one week. The resultant fluorides in the dried-down residues from the dissolution procedure were then treated with concentrated $HClO_4$ on a hotplate in order to break down the fluorides, which, once accomplished, allowed for the conversion of the samples into chlorides using Parr bombs and 6 M HCl overnight in an oven at 160 °C. This step achieved complete sample dissolution and, hence, sample-spike equilibration. Fractions containing Hf and the REEs were subsequently separated on a cation-exchange column. Hafnium was further purified on an anion-exchange column and, as a last measure, separated from Ti on a cation-exchange column using H_2O_2 as a complexing agent. Lutetium, together with Yb (which, in its natural abundance in the samples, is used to correct the Lu isotopic composition for instrumental mass bias), were separated from the rest of the REEs on a di-(2-ethylhexyl) phosphoric acid (HDEHP)-coated column.

Lutetium and Hf isotopic compositions were measured by MC-ICP-MS using the Nu Plasma 500 HR at the Ecole Normale Supérieure in Lyon, following the protocols of Blichert-Toft et al. (1997) for Hf and Blichert-Toft et al. (1997; 2002) for Lu. The JMC-475 Hf standard was analyzed in alternation with the samples (every two samples) and gave, during the present single analytical session, an average $^{176}Hf/^{177}Hf$ value of 0.282169 ± 0.000006 ($2\sigma_{stdev}$; $n = 6$), which represents the most accurate estimate of the external precision of the Hf isotopic analyses and is equal to 0.0021% (or 21 ppm) relative. The in-run precision of the measured $^{176}Hf/^{177}Hf$ for all the samples was better than or equal to 0.000006 (Table 1). Therefore, we used the maximum 0.0021% obtained from the reproducibility of the Hf standard as uncertainty on the Hf isotopic composition for the isochron calculations. The uncertainty on the measured Lu/Hf ratio was 0.2% and this is the value we used for the isochron calculations. Total procedural blanks were less than 10 pg for both Lu and Hf.

For the isochron calculations, we used ISOPLOT 3.00 (Ludwig, 2003) and the ^{176}Lu decay constant of 1.867×10^{-11} year^{-1} (Söderlund et al., 2004). The ε^{176}Hf values were calculated as parts per 10,000 deviation of the $^{176}Hf/^{177}Hf$ in the source of the lavas at the time of their formation relative to that of the most recent chondritic reference defined as $^{176}Lu/^{177}Hf = 0.0336$ and $^{176}Hf/^{177}Hf = 0.282785$ (Bouvier et al., 2008).

4. Results

The Lu–Hf isotopic data, as well as the abundances of Lu and Hf for the ten komatiite samples analyzed in this study, are presented in Table 1 and plotted on the MgO variation diagrams in Fig. 1 and on the Lu–Hf isochron diagram in Fig. 2.

The abundances of Lu and Hf show tight inverse correlations with the corresponding MgO contents and plot on the regression lines that intersect the MgO axes at 50.8 ± 2.5% and 49.1 ± 3.3%, respectively (2σ). These MgO abundances are within the uncertainty of the average composition of the fractionating olivine in these lavas (Puchtel et al., 1998b), indicating that the trends in Fig.1 represent olivine control lines. This attests to the immobile behavior of both Lu and Hf during seafloor alteration and metamorphism of the Kostomuksha komatiites. One sole exception is the flowtop breccia sample 9493, which plots well above the regression line in the MgO vs. Lu diagram. Since flowtop breccias typically are *the* sub-units within komatiite flows that are the most susceptible to alteration, due to their vulnerable position at the contact between lava flows (e.g., Lahaye and Arndt, 1996), their fractured nature, and protracted period of surface exposure, a logical explanation would be that this is most likely owing to some late-occurring Lu enrichment event, which is not reflected in the time-integrated ingrowth of radiogenic ^{176}Hf, because the $^{176}Hf/^{177}Hf$ ratio of this sample is not only similar to those of the other komatiites, but slightly lower (Table 1).

The Lu and Hf abundances obtained in this study also correlate well with the respective Yb and Zr abundances from the Puchtel et al. (1998b) study. The slopes of the regression lines of 6.8 ± 0.6 (Lu vs. Yb) and 31 ± 3 (Hf vs. Zr) are similar to the PM-values of, respectively, 6.5 and 36 for Yb/Lu and Zr/Hf (Hofmann, 1988). Again, the one exception is sample 9493, which plots well below the Lu vs. Yb

Table 1
Lu and Hf abundances (ppm) and Lu–Hf isotope compositions of the Kostomuksha komatiites.

Sample	Hf	Lu	$^{176}Lu/^{177}Hf$	2σ	$^{176}Hf/^{177}Hf$	2σ	$\varepsilon^{176}Hf(T)$
9493	0.668	0.191	0.04063	0.00008	0.282656	0.000004	−18
9495	0.634	0.134	0.03008	0.00006	0.282732	0.000004	+4.9
9496	0.653	0.142	0.03092	0.00006	0.282779	0.000005	+4.9
9497	0.666	0.142	0.03026	0.00006	0.282744	0.000004	+5.0
9498	0.729	0.150	0.02920	0.00006	0.282686	0.000005	+4.9
94100	0.404	0.0873	0.03065	0.00006	0.282767	0.000005	+5.0
94104	0.585	0.127	0.03069	0.00006	0.282762	0.000005	+4.8
94114	0.574	0.126	0.03110	0.00006	0.282798	0.000004	+4.8
94123	0.698	0.146	0.02975	0.00006	0.282713	0.000005	+4.8
94126	0.422	0.0916	0.03078	0.00006	0.282767	0.000006	+4.9

Note. The initial ε^{176}Hf was calculated for the accepted emplacement age of the lavas of 2821 Ma.

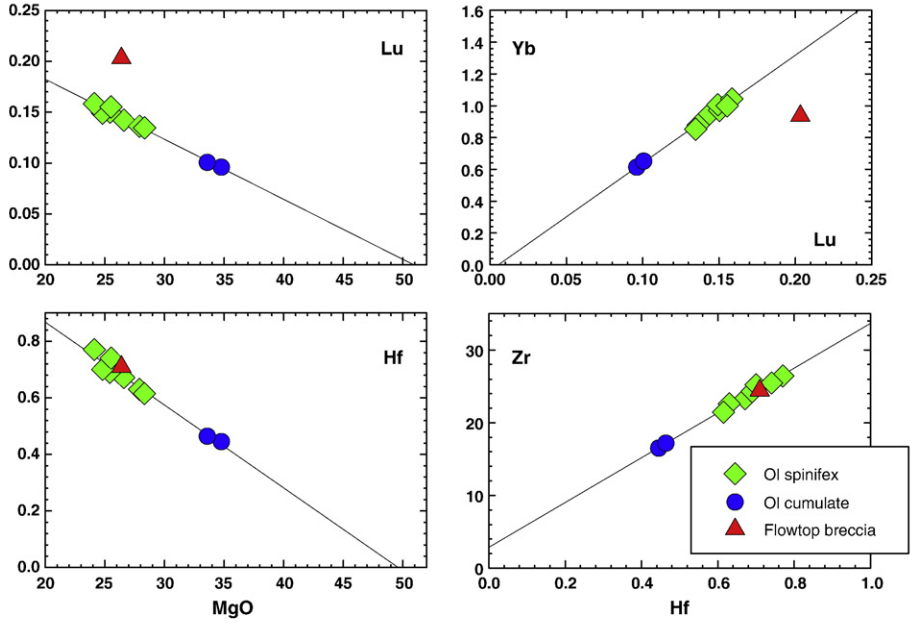

Fig. 1. Diagrams illustrating co-variations in the Lu, Hf, Yb, Zr, and MgO abundances in the Kostomuksha komatiites. The Lu and Hf data are from this study, and the Yb, Zr, and MgO data are from Puchtel et al. (1998b). With the exception of the Lu abundance in the flowtop breccia (sample 9493), the data define well-constrained regression lines representing olivine control lines.

regression line, due to the inferred recent post-magmatic Lu-enrichment that may have affected this sample because of its greater propensity for alteration. This enrichment of Lu relative to Yb is quite surprising considering the fact that both elements have very similar chemical properties and, for the most part, are well coupled in their partitioning behavior. Moreover, other elements that are usually more easily mobilized during alteration than Lu, such as the LREE, do not show any signs of mobility (Puchtel et al., 1998b), including the ^{146}Sm–^{142}Nd isotope systematics of this sample (Boyet and Carlson, 2006). For now, the issue of Lu enrichment and the question of which natural mechanism could have added Lu without also adding some Yb, remains unresolved.

In the Lu–Hf isochron diagram (Fig. 2), data for the komatiite samples (excluding sample 9493, which plots well below the regression line due to its much higher Lu/Hf ratio for a Hf isotopic composition nearly identical to those of the other samples; Table 1) define an isochron (MSWD = 1.6) with a slope corresponding to an age of 2931 ± 300 Ma and an initial ^{176}Hf/^{177}Hf = 0.28104 ± 0.00018 (ε^{176}Hf(T) = + 5.2 ± 6.4). To the best of our knowledge, this is the first statistically significant Lu–Hf isochron established for a suite of co-magmatic komatiite lavas. The large uncertainties on the age and the initial Hf isotopic composition are due to the limited variability of the Lu/Hf ratio in this rock suite. Because of this small spread in the Lu/Hf ratio between the samples, the slope of the regression line is greatly influenced by a single sample (sample 91114) that plots on the upper end and slightly above the regression line. Excluding this sample from the regression calculations reduces the scatter of the data about the regression line (MSWD = 0.63) and results in an isochron age of 2798 ± 220 Ma and a somewhat more precise initial ^{176}Hf/^{177}Hf = 0.28112 ± 0.00013 (ε^{176}Hf(T) = + 4.9 ± 4.6). Both ages are consistent, within the uncertainties, with the precise accepted emplacement age of these lavas of 2821 ± 1 Ma (Puchtel et al., 1998b). Based on this observation, and coupled with the established immobile behavior of both Lu and Hf, two highly refractory elements, we conclude that the calculated initial ^{176}Hf/^{177}Hf ratio represents that of the source of the lavas. The large uncertainty on this initial ^{176}Hf/^{177}Hf ratio is, as for the isochron age, due to the limited spread in the Lu/Hf ratios between the samples. A more accurate way of estimating the initial ^{176}Hf/^{177}Hf in the source of the lavas is to calculate a mean of the initial ^{176}Hf/^{177}Hf ratios for the individual samples using the well-established emplacement age of 2821 Ma and the measured ^{176}Hf/^{177}Hf and ^{176}Lu/^{177}Hf for each sample (Table 1). The calculated mean initial ^{176}Hf/^{177}Hf for the nine samples is 0.281107 ± 3 ($2\sigma_{mean}$), which corresponds to an initial ε^{176}Hf = + 4.9 ± 0.1 ($2\sigma_{mean}$). This represents our best estimate of the initial ^{176}Hf/^{177}Hf in the source of the Kostomuksha komatiites.

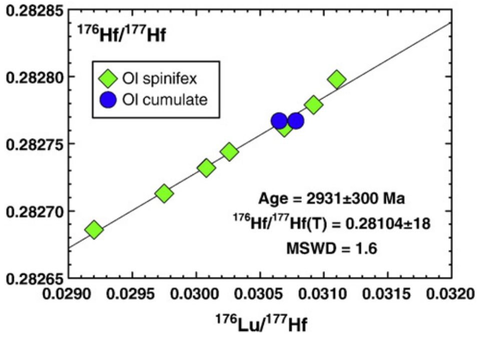

Fig. 2. ^{176}Lu/^{177}Hf vs. ^{176}Hf/^{177}Hf isochron diagram for the Kostomuksha komatiites. Sample 9493 plots well below the isochron and is not shown; this sample also was not included in the regression calculations.

5. Discussion

5.1. Parameters used in the present study

The two lithophile trace element isotope systems, ^{147}Sm–^{143}Nd and ^{176}Lu–^{176}Hf, when considered together, provide one of the most robust constraints on the Earth's chemical evolution. The two systems are much alike, with the parent isotopes being more compatible in the mantle residue during mantle melting than the respective daughter isotopes. The elements that constitute both isotope systems are highly refractory, implying that they are unlikely to have been fractionated by condensation processes in the early Solar System, and lithophile, meaning that they should not have been fractionated during core formation either.

For the purpose of modeling the Lu–Hf and Sm–Nd isotopic evolution of the Kostomuksha komatiite mantle source, key parameters must first be defined. In the present work, we used the most recent, well-defined ^{176}Lu decay constant value $\lambda = 1.867 \times 10^{-11}$ yr^{-1} (Scherer et al., 2001; Söderlund et al., 2004) obtained from terrestrial mineral isochrons. For the chondritic uniform reservoir (CHUR), we likewise used the most recent parameters obtained from unequilibrated chondrites of ^{176}Lu/^{177}Hf = 0.0336 ± 1 and ^{176}Hf/^{177}Hf = 0.282785 ± 11 (Bouvier et al., 2008), which are closely similar, within the uncertainties, to the original CHUR reference values of Blichert-Toft and Albarède (1997) of ^{176}Lu/^{177}Hf = 0.0332 ± 2 and ^{176}Hf/^{177}Hf = 0.282772 ± 29. The depleted mantle growth curve utilized in this study is based on the present-day depleted mantle ^{176}Hf/^{177}Hf = 0.283294, or ε^{176}Hf = +18 (Vervoort and Blichert-Toft, 1999). This requires that the depleted mantle evolved from the chondritic initial ^{176}Hf/^{177}Hf = 0.279801 starting at 4558 Ma with a time-integrated ^{176}Lu/^{177}Hf = 0.03933. Using these parameters, the Kostomuksha komatiite source is calculated to have evolved to its ^{176}Hf/^{177}Hf = 0.281107 at 2821 Ma with a time-integrated ^{176}Lu/^{177}Hf = 0.03759 ± 8, which is ca. 4% lower than that of the contemporary depleted mantle.

For the Sm–Nd isotopic system, the conventional present-day values have been used, which are as follows. CHUR: ^{147}Sm/^{144}Nd = 0.1967 (Jacobsen and Wasserburg, 1980), ^{143}Nd/^{144}Nd = 0.512638 (Hamilton et al., 1983). DM: ^{147}Sm/^{144}Nd = 0.2135, ^{143}Nd/^{144}Nd = 0.513151 (ε^{143}Nd = +10).

5.2. Origin of the Sm–Nd and Lu–Hf isotope systematics of the Kostomuksha komatiite source

Measured Nd and Hf isotopic compositions of modern and ancient volcanic rocks can potentially be used, with some assumptions, to calculate time-integrated Sm/Nd and Lu/Hf in the sources of these lavas, and, hence, to infer the time-integrated evolution of the Earth's mantle in terms of lithophile trace element characteristics. Presented in Table 2 and in Fig. 3 are time-integrated ^{147}Sm/^{144}Nd and ^{176}Lu/^{177}Hf in komatiitic and basaltic sources from worldwide-located occurrences through the Archean and early Proterozoic calculated using the respective initial ^{143}Nd/^{144}Nd and ^{176}Hf/^{177}Hf for sets of best preserved samples (i.e., unaffected by alteration and crustal contamination) and the model parameters specified above (see Section 5.1). Although the literature data are quite limited, several important observations can be made. First, there appears, over time, to be a gradual decrease in the time-integrated ^{147}Sm/^{144}Nd ratio, and possibly also the ^{176}Lu/^{177}Hf ratio, although the latter correlation is not as well defined as the former due to large uncertainties on ^{176}Lu/^{177}Hf for most localities. The early Archean sources have the highest ^{147}Sm/^{144}Nd and ^{176}Lu/^{177}Hf time-integrated ratios, both of which are identical to those of the model depleted mantle reservoir. This is a strong indication that as early as 3.5 Ga, which is the age of the oldest known komatiite occurrences, there existed ancient reservoirs in the terrestrial mantle that were already as strongly depleted in highly relative to less incompatible lithophile trace elements as the modern depleted mantle. The late Archean and early Proterozoic sources form two compact groups that plot distinctly below the DM line and can be clearly distinguished in terms of their time-integrated ^{147}Sm/^{144}Nd, although they overlap, within the uncertainties, with respect to the time-integrated ^{176}Lu/^{177}Hf. The similarity of late Archean komatiite sources in terms of time-integrated ^{147}Sm/^{144}Nd and ^{176}Lu/^{177}Hf is remarkable, with mean values of, respectively, 0.2091 ± 4 ($N = 6$) and 0.0375 ± 6 ($N = 3$) (Table 2).

Table 2
Time-integrated Sm/Nd and Lu/Hf ratios in the sources of Archean and Proterozoic komatiites and basalts and in the model terrestrial reservoirs.

Locality	Age, Ma	^{147}Sm/^{144}Nd	$2\sigma_{mean}$	^{176}Lu/^{177}Hf	$2\sigma_{mean}$
Ottawa Islands[1]	1900	0.20646	0.00109	0.03737	0.00064
Onega plateau[2]	1975	0.20583	0.00039		
Birimian terrain[3]	2100	0.20672	0.00063	0.03728	0.00033
Belingwe[4]	2692	0.20846	0.00019	0.03693	0.00038
Abitibi[5]	2725	0.20877	0.00019	0.03802	0.00063
Kostomuksha[6]	2821	0.20958	0.00046	0.03759	0.00008
Sum-Kenozero[7]	2875	0.20919	0.00053		
Volotsk[8]	2875	0.20891	0.00021		
Olondo[9]	3000	0.20995	0.00068		
Komati[10]	3470	0.21264	0.00197	0.03894	0.00220
Schapenburg[11]	3550	0.21543	0.00169	0.04012	0.00082
CHUR		0.1967		0.0336	
DM		0.2135		0.0393	

Note. The time-integrated ^{147}Sm/^{144}Nd and ^{176}Lu/^{177}Hf ratios in the sources of the lavas were calculated using the measured initial ^{143}Nd/^{144}Nd and ^{176}Hf/^{177}Hf in the respective sources and assuming separation from the CHondritic Undifferentiated Reservoir (CHUR) at 4558 Ma. The sources of the Sm–Nd and Lu–Hf isotopic data used in the calculations are as follows: (1) Blichert-Toft and Arndt, 1999. (2) Puchtel et al., 1998a; Puchtel et al., 1999a. (3) Abouchami et al., 1990; Blichert-Toft and Arndt, 1999. (4) Blichert-Toft and Arndt, 1999; Puchtel et al., 2009b. (5) Blichert-Toft and Arndt, 1999; Puchtel et al., 2009b. (6) Puchtel et al., 1998b; this study. (7) Puchtel et al., 1999b. (8) Puchtel et al., 2007. (9) Puchtel and Zhuravlev, 1993. (10) Blichert-Toft and Arndt, 1999; Chavagnac, 2004. (11) Lécuyer et al., 1994; Blichert-Toft et al., 2004. For explanation of the CHUR and DM parameters, see text, Section 5.1.

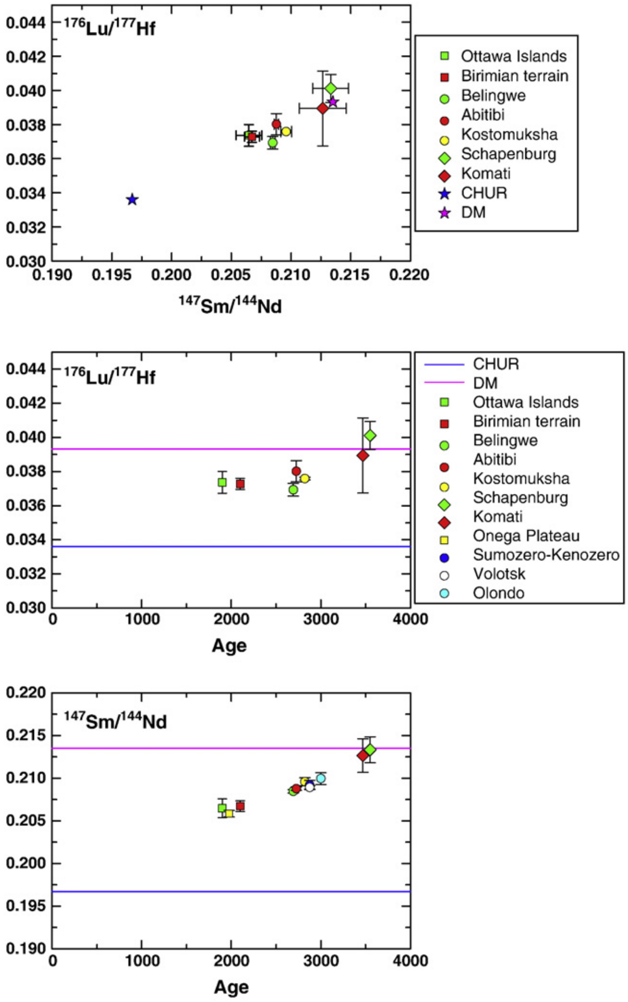

Fig. 3. ^{147}Sm/^{144}Nd and ^{176}Lu/^{177}Hf data for komatiites and basalts of various ages and from different geographic locations worldwide. See Table 2 for the sources of the data.

Second, as is evident from Fig. 3, the Kostomuksha komatiite source has both ^{147}Sm/^{144}Nd and ^{176}Lu/^{177}Hf time-integrated ratios that plot right in the middle of the narrow range for the late Archean komatiite sources. Short of some very unlikely coincidence, this implies a similar long-term lithophile trace element history of these sources. The coupled behavior of the ^{147}Sm/^{144}Nd and ^{176}Lu/^{177}Hf in these sources indicate that melt depletion was the most likely factor controlling their variations in REE and HFSE. This observation can be used to test the hypothesis of the formation of the Kostomuksha komatiites as a result of re-melting of a majorite-enriched domain formed very early in Earth's history via solidification of a primordial magma ocean.

Garnet is a major host for Lu, with a solid–liquid partition coefficient of ~10 (Green, 1994). As a result, in a rock containing 10% majorite garnet, the latter will control 50% of the total Lu budget. At the same time, with garnet–liquid D^{Hf} being close to or below unity (Green, 1994), only 5% of the total Hf budget will be controlled by garnet. In contrast, Sm and Nd have only a slightly different relative garnet–silicate melt partitioning behavior, and an order of magnitude lower absolute partition coefficients (0.4 and 0.1, respectively; Green, 1994). Consequently, a garnet-rich cumulate will have a significantly higher excess of Lu over Hf than Sm over Nd, and will with time develop substantially more radiogenic Hf than Nd compared to a melt-depleted residue. The presence of a majorite component in garnet has a substantial effect on the trace element partitioning between majorite garnet and silicate melt (Draper et al., 2003). According to these authors, a significant majorite component appears in garnet at pressures as low as 5 GPa, i.e., at depths greater than 150 km. With increasing depth and amount of majorite component, the garnet–silicate melt D values for HREE decrease markedly, whereas the effect on the LREE is much less pronounced, and D values for Hf show essentially no change (Draper et al., 2003).

Since Barberton-type komatiites are argued to form either by hydrous melting at depths >150 km (Grove et al., 1999) or by dry melting at depths >450 km (e.g., Herzberg, 1992) in equilibrium with garnet, the latter should have a very substantial majorite component irrespective of the mode of komatiite formation. Using the average partition coefficients from Draper et al. (2003), and assuming that solidification of the primordial magma ocean occurred within the first 100 Ma of Earth's history, we modeled the Sm–Nd and Lu–Hf evolution of the putative majorite-rich domain. We also assumed that the garnet in the source was completely converted into majorite, i.e., had the lowest possible D^{Lu}. Our calculations show that, in order for that domain to develop the observed ε^{176}Hf value of +4.9 by the time of komatiite formation, it should have contained a maximum of about 4% cumulate majorite garnet. At the same time, by 2.82 Ga this domain would have developed an ε^{143}Nd value of only +0.2, in sharp contrast to the observed initial ε^{143}Nd of +3.0 in the Kostomuksha komatiite source. Our modeling, thus, indicates that, when the coupled Sm–Nd and Lu–Hf isotope systematics are considered, melt depletion effects can be clearly distinguished from those created by majorite garnet fractionation. Secondly, as is evident from Fig. 3, the Kostomuksha komatiite source does not display Hf–Nd isotopic decoupling, which would be expected if derived from the re-melting of a majorite-rich fossil domain in the mantle, but instead plots on the trend defined by melt-depleted residues. Our modeling therefore rules out direct involvement of majorite-rich primordial magma ocean cumulates in the formation of the Kostomuksha komatiites.

5.3. Lithophile trace element composition of the Kostomuksha komatiite source

While the initial ^{143}Nd/^{144}Nd and ^{176}Hf/^{177}Hf in the Kostomuksha komatiite source provide a measure of its time-integrated Sm/Nd and Lu/Hf ratios, variations of lithophile trace element abundances in the Kostomuksha differentiated komatiite lava flows can be used to calculate the absolute abundances of these elements in their source at the time of komatiite magma formation. In order to do that, we used a modified projection technique of Puchtel and co-workers (Puchtel et al., 2004; Puchtel and Humayun, 2005). For a specific komatiite lava suite, the abundances of trace elements that are incompatible with respect to mantle residues plot on liquid lines of descent obtained via regression of the data for the lavas; source concentrations then can be calculated for a given MgO content in the source. Since the MgO content of the mantle is only little affected by variations in the degree of previous melt extractions, Puchtel et al. (2004) used an average MgO content of 38% for depleted spinel peridotites worldwide, which is also the accepted value for the putative Primitive Upper Mantle, PUM (McDonough and Sun, 1995).

The calculated trace element and some major element abundances in the Kostomuksha komatiite source, as well as in two other late Archean komatiite sources, Abitibi and Belingwe, for which both Sm–Nd and Lu–Hf isotope and lithophile trace and major element data are available, are presented in Table 3 and plotted as primitive mantle-normalized values in Fig. 4. All three sources are characterized by very similar relative lithophile element abundances with strong depletions in highly incompatible elements and generally unfractionated moderately incompatible element patterns. The Lu/Hf and Al/Ti in the Kostomuksha source are a little lower, and the Gd/Yb ratio is a little higher than in the PM or the other two late Archean komatiite sources. These features may be interpreted as the result of involvement of small amounts of majorite garnet in the petrogenesis of the Kostomuksha komatiites, although the differences between the three komatiite sources in this respect are statistically insignificant. The time-integrated ^{176}Lu/^{177}Hf ratios for all three komatiite sources, however, are very similar and indicate that majorite garnet fractionation in the Kostomuksha source, if any, occurred during the komatiite formation. The calculated Sm/Nd ratios in all three late Archean komatiite sources are variable and substantially higher than the calculated time-integrated ^{147}Sm/^{144}Nd. The latter phenomenon can be explained by a two-stage plume model of komatiite formation as proposed by Puchtel et al. (2009b). According to these authors, the moderate LREE depletion in the sources of the komatiites initially occurred within the first 100 Ma of Earth's history. The komatiite formation, preceded by derivation of basaltic magmas, was a result of second-stage, large-degree dynamic melting in mantle plume heads.

The possibility of an early-Earth differentiation event has recently been investigated via ^{146,147}Sm–^{142,143}Nd and ^{176}Lu–^{177}Hf studies of a wide range of terrestrial rocks and chondritic meteorites (e.g., Boyet

Table 3
Calculated absolute lithophile element abundances in late Archean komatiite sources.

Sample	Kostomuksha	Abitibi	Belingwe
Th	0.033 ± 0.002	0.023 ± 0.007	0.031 ± 0.002
Nb	0.39 ± 0.03	0.29 ± 0.08	0.29 ± 0.01
La	0.40 ± 0.07	0.26 ± 0.02	0.302 ± 0.007
Ce	1.20 ± 0.16	0.86 ± 0.08	0.87 ± 0.08
Nd	1.16 ± 0.08	0.89 ± 0.06	0.86 ± 0.07
Sm	0.45 ± 0.02	0.41 ± 0.03	0.33 ± 0.03
Hf	0.34 ± 0.04	0.32 ± 0.06	0.25 ± 0.01
Zr	13.0 ± 0.6	12.1 ± 2.1	9.4 ± 0.2
TiO_2	0.23 ± 0.02	0.23 ± 0.02	0.17 ± 0.01
Gd	0.66 ± 0.03	0.64 ± 0.05	0.49 ± 0.02
Dy	0.82 ± 0.04	0.83 ± 0.06	0.62 ± 0.04
Y	5.0 ± 0.5	5.1 ± 0.6	3.9 ± 0.2
Er	0.53 ± 0.03	0.55 ± 0.04	0.41 ± 0.02
Yb	0.51 ± 0.03	0.54 ± 0.04	0.41 ± 0.02
Lu	0.076 ± 0.007	0.083 ± 0.008	0.064 ± 0.001
Al_2O_3	4.0 ± 0.3	4.3 ± 0.2	3.23 ± 0.08
^{147}Sm/^{144}Nd[a]	0.235 ± 0.016	0.275 ± 0.019	0.231 ± 0.021
^{147}Sm/^{144}Nd[b]	0.2096 ± 0.0005	0.2088 ± 0.0002	0.2085 ± 0.0002
^{176}Lu/^{177}Hf[a]	0.032 ± 0.003	0.036 ± 0.003	0.037 ± 0.001
^{176}Lu/^{177}Hf[b]	0.0376 ± 0.0001	0.0380 ± 0.0006	0.0369 ± 0.0004
Al_2O_3/TiO_2	17.8 ± 1.5	18.4 ± 1.6	19.3 ± 0.5
$(Ce/Sm)_N$	0.64 ± 0.08	0.51 ± 0.05	0.64 ± 0.06
$(Gd/Yb)_N$	1.05 ± 0.06	0.96 ± 0.07	0.95 ± 0.05

Note. [a]Ratios derived from the calculated Sm, Nd, Lu, and Hf abundances in the sources, as opposed to the time-integrated ratios[b] derived from the Sm–Nd and Lu–Hf isotope systematics (Table 2). The abundances were calculated using the projection technique of Puchtel et al. (2004). The sources of the data, in addition to those cited in the footnotes to Table 2, are as follows: Abitibi — Lahaye et al., 1995. Belingwe — Nisbet et al., 1987; Jochum et al., 1991; Bickle et al., 1993. Except for the major elements TiO_2 and Al_2O_3 (wt.%), all trace element abundances are in ppm.

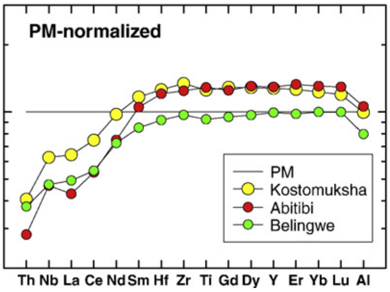

Fig. 4. Lithophile element abundances in the calculated source of the 2.8 Ga Kostomuksha komatiites normalized to the primitive mantle values of Hofmann (1988). The calculated sources of the Abitibi and Belingwe (2.7 Ga) komatiites are plotted for comparison. The sources of the data are listed in the footnotes to Tables 2 and 3.

et al., 2003; Caro et al., 2003, 2006; Boyet and Carlson, 2006; Bennett et al., 2007). Boyet and Carlson (2006) suggested that both oceanic and continental crust may have been derived from a mantle reservoir that had been depleted in highly incompatible elements very early in Earth's history. The highly incompatible elements would, shortly after Earth's formation, have been incorporated into a hidden reservoir, which would hence be enriched in nature, possibly a primordial terrestrial crust that was unstable at Earth's surface. The resulting so-called Early Depleted Reservoir (EDR) likely would have persisted throughout Earth's history, and would currently occupy between 75 to >90% of the mantle (Carlson and Boyet, 2008). Boyet and Carlson (2006) further noted that both the ^{142,143}Nd and Lu–Hf isotope systematics of the depleted mantle (with present-day ε^{143}Nd and ε^{176}Hf values of, respectively, +10 and +18) can be accounted for by an early differentiation event if it left the EDR with ^{147}Sm/^{144}Nd = 0.209 and ^{176}Lu/^{177}Hf = 0.0375. Our calculated average ^{147}Sm/^{144}Nd = 0.2091 ± 4 and ^{176}Lu/^{177}Hf = 0.0375 ± 6 for the sources of late Archean komatiites are identical to these estimates and suggest that the presumed EDR may have been the source of late Archean komatiites.

If the model of Boyet and Carlson (2006) is correct and a chondritic composition for the Bulk Silicate Earth is assumed, the Earth must contain a lithophile incompatible trace element-enriched reservoir that is complementary to the EDR. Such an enriched reservoir, presumably hidden somewhere in the Earth, was also evoked by Blichert-Toft and Albarède (1997) based on coupled Hf–Nd isotope systematics of terrestrial basalts and continental crust compared with chondritic meteorites. The fact that our calculated time-integrated ^{147}Sm/^{144}Nd and ^{176}Lu/^{177}Hf ratios for komatiite sources decrease over time, with those in the early Archean sources being higher and Proterozoic sources being lower than estimated for the EDR, is inconsistent with a single homogenous source that evolved with constant parent–daughter ratios. Instead, this observation may indicate that the Hadean mantle was characterized by even higher depletions in incompatible lithophile elements than currently observed for the early Archean mantle and that the observed decrease in the time-integrated ^{147}Sm/^{144}Nd and ^{176}Lu/^{177}Hf in komatiite sources over time is due to the alleged enriched component being mixed back into the mantle. This seems to be the only mechanism that satisfactorily explains the observed change in Lu/Hf and Sm/Nd in komatiite sources over time. Although recycling of either increasingly larger volumes of crust or progressively more evolved crust over time, or both, could also be envisaged to have caused the observed decrease in time-integrated Lu/Hf and Sm/Nd in younger mantle reservoirs, the very strong time-integrated depletions of the early Archean rocks in LREE (Fig. 3) inclines us towards the first process involving re-integration of the hidden enriched reservoir. Given that we cannot close the time-integrated Hf–Nd budget for the Earth's crust and modern mantle (Blichert-Toft and Albarède, 1997), and faced with the conspicuous ^{142}Nd excess of the Earth relative to chondrites (Boyet and Carlson, 2005), this process may not yet have gone to completion, implying that part of this early enriched reservoir still exists. In order to place more robust constraints on the hypotheses speculated on here, additional high-precision Sm–Nd and Lu–Hf isotope data for well-preserved and well-studied Archean komatiite systems are required.

The last point raised by the present data set is that of the similar time-integrated parent–daughter ratios at different locations worldwide at any given time during the Archean and early Proterozoic, indicating that the depleted mantle was homogeneous on a global scale. This can be explained by the stirring effect of mantle convection, which is believed to have been more vigorous in the past (Blichert-Toft and Albarède, 1994) and, hence, particularly efficient during Earth's early history at remixing heterogeneities arising from the combination of continuous crust extraction and recycling, and the hypothesized re-incorporation of the enriched hidden reservoir as discussed above. Because the residence times for Lu, Hf, Sm, and Nd in the mantle are longer than their respective mixing times (Albarède, 2005), this will lead to what seems to be a homogeneous mantle.

6. Concluding remarks

Well-preserved, uncontaminated komatiites are scarce in the geological record, but, when found, such rocks serve as valuable sources of information about how the Earth has formed and evolved. The Kostomuksha komatiites are in many ways unique rocks. In particular, this is the only known Archean komatiite system that records super-chondritic initial Os for both the ^{186}Os/^{188}Os and ^{187}Os/^{188}Os ratios. This observation, together with the lithophile isotope, trace element, and HSE abundance data, have been interpreted as evidence for the existence of whole-mantle convection and core–mantle interaction via ascent from the core–mantle boundary of a starting mantle plume some 2.8 Ga ago (Puchtel and Humayun, 2005; Puchtel et al., 2005). These data also have allowed placing constraints on the timing of the onset of inner core crystallization and the mechanism of core–mantle exchange (Puchtel et al., 2005).

It has been argued recently, however, that an enriched ^{187}Os/^{188}Os isotopic composition of some komatiites could have been the result of derivation from re-melting of a majorite-enriched domain that formed deep in the mantle during the solidification of a primordial terrestrial magma ocean, and persisted over several billions of years (Puchtel et al., 2009a). In order to test this hypothesis with respect to the Kostomuksha komatiite system, we studied the Lu–Hf isotope system in a set of Kostomuksha komatiites. The results obtained in this study indicate that the lithophile trace element and Sm–Nd and Lu–Hf isotope systematics of the Kostomuksha komatiite system are remarkably similar to other well-studied late Archean komatiite systems, namely, Abitibi, Belingwe, Sumozero–Kenozero, Volotsk, and Olondo, and show no evidence of formation from re-melting of the majorite-enriched domain of a former magma ocean. When considered together, these komatiite systems provide our best estimate for the lithophile trace element composition of the contemporary late Archean mantle. This mantle was characterized by average time-integrated ^{147}Sm/^{144}Nd = 0.2091 ± 4 and ^{176}Lu/^{177}Hf = 0.0375 ± 6. These time-integrated ratios are identical to the respective ratios of 0.209 and 0.0375 calculated by Boyet and Carlson (2006) for the Early Depleted Reservoir (EDR) on the basis of ^{146,147}Sm–^{142,143}Nd and Lu–Hf isotopic studies of a range of terrestrial and extraterrestrial materials and may indicate that the late Archean mantle was similar in composition to the putative EDR. The observed decrease in the time-integrated Sm/Nd and Lu/Hf in komatiite sources over time is interpreted as strong evidence for the existence of the hidden enriched reservoir that was first postulated by Blichert-Toft and Albarède (1997) and later by Boyet and Carlson (2006) to be complementary to the EDR, possibly a primordial terrestrial crust, that has gradually been re-assimilated and mixed back into the mantle.

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References

Abouchami, W., Boher, M., Michard, A., Albarède, F., 1990. A major 2.1 Ga event of mafic magmatism in West Africa: an early stage of crustal accretion. J. Geophys. Res. 95 (B11), 17605–17629.

Albarède, F., 2005. The survival of mantle geochemical heterogeneities. Earth's deep mantle: Structure, composition, and evolution: In: van der Hilst, R.D., Bass, J.D., Matas, J., Trampert, J. (Eds.), AGU Geophysical Monograph Series, 160, pp. 27–46.

Bennett, V.C., Brandon, A.D., Nutman, A.P., 2007. Coupled ^{142}Nd–^{143}Nd isotopic evidence for Hadean mantle dynamics. Science 318 (5858), 1907–1910.

Bickle, M.J., Arndt, N.T., Nisbet, E.G., Orpen, J.L., Martin, A., Keays, R.R., Renner, R., 1993. Geochemistry of the igneous rocks of the Belingwe Greenstone Belt: alteration, contamination and petrogenesis. The Geology of the Belingwe Greenstone Belt, Zimbabwe. A study of the evolution of Archaean continental crust: In: Bickle, M.J., Nisbet, E.G. (Eds.), Geol. Soc. Zimbabwe Spec. Publ. , pp. 175–213.

Blichert-Toft, J., 2001. On the Lu–Hf isotope geochemistry of silicate rocks. Geostand. Newsl. 25 (1), 41–56.

Blichert-Toft, J., Albarède, F., 1994. Short-lived chemical heterogeneities in the Archean mantle with implications for mantle convection. Science 263, 1593–1596.

Blichert-Toft, J., Albarède, F., 1997. The Lu–Hf isotope geochemistry of chondrites and the evolution of the mantle–crust system. Earth Planet. Sci. Lett. 148 (1–2), 243–258.

Blichert-Toft, J., Arndt, N.T., 1999. Hf isotope compositions of komatiites. Earth Planet. Sci. Lett. 171 (3), 439–451.

Blichert-Toft, J., Arndt, N.T., Gruau, G., 2004. Hf isotopic measurements on Barberton komatiites: effects of incomplete sample dissolution and importance for primary and secondary magmatic signatures. Chem. Geol. 207 (3–4), 261–275.

Blichert-Toft, J., Boyet, M., Télouk, P., Albarède, F., 2002. Sm-147–Nd-143 and Lu-176–Hf-176 in eucrites and the differentiation of the HED parent body. Earth Planet. Sci. Lett. 204 (1–2), 167–181.

Blichert-Toft, J., Chauvel, C., Albarède, F., 1997. Separation of Hf and Lu for high-precision isotope analysis of rock samples by magnetic sector multiple collector ICP-MS. Contrib. Mineralog. Petrol. 127 (3), 248–260.

Bouvier, A., Vervoort, J.D., Patchett, P.J., 2008. The Lu–Hf and Sm–Nd isotopic composition of CHUR: constraints from unequilibrated chondrites and implications for the bulk composition of terrestrial planets. Earth Planet. Sci. Lett. 273 (1–2), 48–57.

Boyet, M., Blichert-Toft, J., Rosing, M., Storey, M., Télouk, P., Albarède, F., 2003. ^{142}Nd evidence for early Earth differentiation. Earth Planet. Sci. Lett. 214 (3–4), 427–442.

Boyet, M., Carlson, R.W., 2005. ^{142}Nd evidence for early (>4.53 Ga) global differentiation of the silicate Earth. Science 309, 576–581.

Boyet, M., Carlson, R.W., 2006. A new geochemical model for the Earth's mantle inferred from ^{146}Sm–^{142}Nd systematics. Earth Planet. Sci. Lett. 250 (1–2), 254–268.

Brandon, A.D., Norman, M.D., Walker, R.J., Morgan, J.W., 1999. ^{186}Os–^{187}Os systematics of Hawaiian picrites. Earth Planet. Sci. Lett. 174 (1–2), 25–42.

Brandon, A.D., Walker, R.J., Morgan, J.W., Norman, M.D., Prichard, H.M., 1998. Coupled ^{186}Os and ^{187}Os evidence for core–mantle interaction. Science 280 (5369), 1570–1573.

Brandon, A.D., Walker, R.J., Puchtel, I.S., Becker, H., Humayun, M., Revillon, S., 2003. ^{186}Os–^{187}Os systematics of Gorgona Island komatiites: implications for early growth of the inner core. Earth Planet. Sci. Lett. 206 (3–4), 411–426.

Carlson, R.W., Boyet, M., 2008. Composition of the Earth's interior: the importance of early events. Philos. Trans. R. Soc. A Math. Phys. Eng. Sci. 366 (1883), 4077–4103.

Caro, G., Bourdon, B., Birck, J.-L., Moorbath, S., 2003. ^{146}Sm–^{142}Nd evidence from Isua metamorphosed sediments for early differentiation of the Earth's mantle. Nature 423, 428–432.

Caro, G., Bourdon, B., Birck, J.-L., Moorbath, S., 2006. High-precision ^{142}Nd/^{144}Nd measurements in terrestrial rocks: constraints on the early differentiation of the Earth's mantle. Geochim. Cosmochim. Acta 70 (1), 164–191.

Chavagnac, V., 2004. A geochemical and Nd isotopic study of Barberton komatiites (South Africa): implication for the Archean mantle. Lithos 75 (3–4), 253–281.

Draper, D.S., Xirouchakis, D., Agee, C.B., 2003. Trace element partitioning between garnet and chondritic melt from 5 to 9 GPa: implications for the onset of the majorite transition in the martian mantle. Phys. Earth Planet. Inter. 139 (1–2), 149–169.

Green, T.H., 1994. Experimental studies of trace-element partitioning applicable to igneous petrogenesis — Sedona 16 years later. Chem. Geol. 117 (1–4), 1–36.

Grove, T.L., Parman, S.W., Dann, J.C., 1999. Conditions of magma generation for Archean komatiites from the Barberton Mountainland, South Africa. Mantle Petrology: Field Observations and High Pressure Experimentation: A Tribute to Francis R. Boyd. Fei, Y., Bertka, C. M. and Mysen, B. O. : Geochem. Soc. Spec. Publ. No. 6, pp. 155–167.

Gruau, G., Chauvel, C., Arndt, N.T., Cornichet, J., 1990. Al-depletion in komatiites and garnet fractionation in the Early Archean mantle: Hf-isotopic constraints. Geochim. Cosmochim. Acta 54 (11), 3095–3101.

Gruau, G., Jahn, B.M., 1983. Significance of REE typology of komatiites: argument for early mantle stratification. Terra Cognita 3, 130.

Hamilton, P.J., O'Nions, R.K., Bridgwater, D., Nutman, A.P., 1983. Sm–Nd studies of Archaean metasediments and metavolcanics from West Greenland and their implications for the Earth's early history. Earth Planet. Sci. Lett. 62 (2), 263–272.

Herzberg, C.T., 1992. Depth and degree of melting of komatiites. J. Geophys. Res. 97 (B4), 4521–4540.

Hofmann, A.W., 1988. Chemical differentiation of the Earth: the relationship between mantle, continental crust and oceanic crust. Earth Planet. Sci. Lett. 90 (3), 297–314.

Ito, E., Takahashi, E., 1987. Melting of peridotite at uppermost lower-mantle conditions. Nature 328 (6130), 514–517.

Jacobsen, S.B., Wasserburg, G.J., 1980. Sm–Nd isotopic evolution of chondrites. Earth Planet. Sci. Lett. 50, 139–155.

Jahn, B.M., Gruau, G., 1981. Possible significance of REE typology of komatiites to Archean mantle differentiation: Terra Cognita Spec. Issue 19.

Jahn, B.M., Gruau, G., Glikson, A.Y., 1982. Komatiites of the Onverwacht Group, South Africa: REE geochemistry, Sm–Nd age and mantle evolution. Contrib. Mineralog. Petrol. 80 (1), 25–40.

Jochum, K.P., Arndt, N.T., Hofmann, A.W., 1991. Nb–Th–La in komatiites and basalts: constraints on komatiite petrogenesis and mantle evolution. Earth Planet. Sci. Lett. 107 (2), 272–289.

Kato, T., Ringwood, A.E., Irifune, T., 1988. Experimental determination of element partitioning between silicate perovskite, garnet and liquid: constraints on early differentiation of the mantle. Earth Planet. Sci. Lett. 89 (1), 123–145.

Lahaye, Y., Arndt, N.T., 1996. Alteration of a komatiite flow from Alexo, Ontario. J. Petrol. 37 (6), 1261–1284.

Lahaye, Y., Arndt, N.T., Byerly, G., Chauvel, C., Fourcade, S., Gruau, G., 1995. The influence of alteration on the trace-element and Nd-isotopic compositions of komatiites. Chem. Geol. 126 (1), 43–64.

Lécuyer, C., Gruau, G., Anhaeusser, C.R., Fourcade, S., 1994. The origin of fluids and the effect of metamorphism on the primary chemical compositions of Barberton komatiites: new evidence from geochemical (REE) and isotopic (Nd, O, H, ^{39}Ar/^{40}Ar) data. Geochim. Cosmochim. Acta 58 (2), 969–984.

Ludwig, K.R., 2003. ISOPLOT 3.00. A geochronological toolkit for Microsoft Excel: Berkeley Geochronology Center Spec. Publ. No. 4. 70 pp.

McDonough, W.F., Sun, S.-s., 1995. The composition of the Earth. Chem. Geol. 120 (3–4), 223–253.

Nesbitt, R.W., Sun, S.S., Purvis, A.C., 1979. Komatiites: geochemistry and genesis. Can. Mineralog. 17 (2), 165–186.

Nisbet, E.G., Arndt, N.T., Bickle, M.J., Cameron, W.E., Chauvel, C., Cheadle, M., Hegner, E., Kyser, T.K., Martin, A., Renner, R., Roedder, E., 1987. Uniquely fresh 2.7 Ga komatiites from the Belingwe greenstone belt, Zimbabwe. Geology 15 (12), 1147–1150.

Ohtani, E., 1984. Generation of komatiite magma and gravitational differentiation in the deep upper mantle. Earth Planet. Sci. Lett. 67 (2), 261–272.

Ohtani, E., 1990. Majorite fractionation and genesis of komatiites in the deep mantle. Precambrian Res. 48 (3), 195–202.

Ohtani, E., Kato, T., Sawamoto, H., 1986. Melting of a model chondritic mantle to 20 GPa. Nature 322 (6077), 352–353.

Ohtani, E., Kawabe, I., Moriyama, J., Nagata, Y., 1989. Partitioning of elements between majorite garnet and melt and implications for petrogenesis of komatiite. Contrib. Mineralog. Petrol. 103 (3), 263–269.

Puchtel, I.S., Arndt, N.T., Hofmann, A.W., Haase, K.M., Kröner, A., Kulikov, V.S., Kulikova, V.V., Garbe-Schönberg, C.-D., Nemchin, A.A., 1998a. Petrology of mafic lavas within the Onega plateau, central Karelia: Evidence for 2.0 Ga plume-related continental crustal growth in the Baltic Shield. Contrib. Mineralog. Petrol. 130 (2), 134–153.

Puchtel, I.S., Brandon, A.D., Humayun, M., Walker, R.J., 2005. Evidence for the early differentiation of the core from Pt–Re–Os isotope systematics of 2.8-Ga komatiites. Earth Planet. Sci. Lett. 237 (1–2), 118–134.

Puchtel, I.S., Brügmann, G.E., Hofmann, A.W., 1999a. Precise Re–Os mineral isochron and Pb–Nd–Os isotope systematics of a mafic–ultramafic sill in the 2.0 Ga Onega plateau (Baltic Shield). Earth Planet. Sci. Lett. 170 (4), 447–461.

Puchtel, I.S., Brügmann, G.E., Hofmann, A.W., 2001. ^{187}Os-enriched domain in an Archaean mantle plume: evidence from 2.8 Ga komatiites of the Kostomuksha greenstone belt, NW Baltic Shield. Earth Planet. Sci. Lett. 186 (3–4), 513–526.

Puchtel, I.S., Hofmann, A.W., Amelin, Y.V., Garbe-Schönberg, C.-D., Samsonov, A.V., Shchipansky, A.A., 1999b. Combined mantle plume–island arc model for the formation of the 2.9 Ga Sumozero–Kenozero greenstone belt, SE Baltic Shield: isotope and trace element constraints. Geochim. Cosmochim. Acta 63 (21), 3579–3595.

Puchtel, I.S., Hofmann, A.W., Jochum, K.P., Mezger, K., Shchipansky, A.A., Samsonov, A.V., 1997. The Kostomuksha greenstone belt, NW Baltic Shield: remnant of a Late Archean oceanic plateau? Terra Nova 9, 87–90.

Puchtel, I.S., Hofmann, A.W., Mezger, K., Jochum, K.P., Shchipansky, A.A., Samsonov, A.V., 1998b. Oceanic plateau model for continental crustal growth in the Archaean: a case study from the Kostomuksha greenstone belt, NW Baltic Shield. Earth Planet. Sci. Lett. 155 (1–2), 57–74.

Puchtel, I., Humayun, M., 2000. Platinum group elements in Kostomuksha komatiites and basalts: implications for oceanic crust recycling and core–mantle interaction. Geochim. Cosmochim. Acta 64 (24), 4227–4242.

Puchtel, I.S., Humayun, M., 2005. Highly siderophile element geochemistry of ^{187}Os-enriched 2.8-Ga Kostomuksha komatiites, Baltic Shield. Geochim. Cosmochim. Acta 69 (6), 1607–1618.

Puchtel, I.S., Humayun, M., Campbell, A., Sproule, R., Lesher, C.M., 2004. Platinum group element geochemistry of komatiites from the Alexo and Pyke Hill areas, Ontario, Canada. Geochim. Cosmochim. Acta 68 (6), 1361–1383.

Puchtel, I.S., Humayun, M., Walker, R.J., 2007. Os–Pb–Nd isotope and highly siderophile and lithophile trace element systematics of komatiitic rocks from the Volotsk suite, SE Baltic Shield. Precambrian Res. 158 (1–2), 119–137.

Puchtel, I.S., Walker, R.J., Anhaeusser, C.R., Gruau, G., 2009a. Re–Os isotope systematics and HSE abundances of the 3.5 Ga Schapenburg komatiites, South Africa: hydrous melting or prolonged survival of primordial heterogeneities in the mantle? Chem. Geol. 262 (3–4), 391–405.

Puchtel, I.S., Walker, R.J., Brandon, A.D., Nisbet, E.G., 2009b. Pt–Re–Os and Sm–Nd isotope and HSE and REE systematics of the 2.7 Ga Belingwe and Abitibi komatiites. Geochim. Cosmochim. Acta 73 (20), 6367–6389.

Puchtel, I.S., Zhuravlev, D.Z., 1993. Petrology of mafic–ultramafic metavolcanics and related rocks from the Olondo greenstone belt, Aldan Shield. Petrology 1 (3), 263–299.

Pyke, D.R., Naldrett, A.J., Eckstrand, O.R., 1973. Archean ultramafic flows in Munro Township, Ontario. Geol. Soc. Am. Bull. 84 (3), 955–978.

Scherer, E., Munker, C., Mezger, K., 2001. Calibration of the lutetium–hafnium clock. Science 293 (5530), 683–687.

Söderlund, U., Patchett, J.P., Vervoort, J.D., Isachsen, C.E., 2004. The Lu-176 decay constant determined by Lu–Hf and U–Pb isotope systematics of Precambrian mafic intrusions. Earth Planet. Sci. Lett. 219 (3–4), 311–324.

Sun, S.-S., 1987. Chemical composition of Archaean komatiites: implications for early history of the Earth and mantle evolution. J. Volcanol. Geoth. Res. 32 (1–3), 67–82.

Sun, S.S., Nesbitt, R.W., 1978. Petrogenesis of Archaean ultrabasic and basic volcanics: evidence from rare-earth elements. Contrib. Mineralog. Petrol. 65 (3), 301–325.

Vervoort, J.D., Blichert-Toft, J., 1999. Evolution of the depleted mantle: Hf isotope evidence from juvenile rocks through time. Geochim. Cosmochim. Acta 63 (3–4), 533–556.

Walker, R.J., Morgan, J.W., Beary, E.S., Smoliar, M.I., Czamanske, G.K., Horan, M.F., 1997. Applications of the ^{190}Pt–^{186}Os isotope system to geochemistry and cosmochemistry. Geochim. Cosmochim. Acta 61 (22), 4799–4807.