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Evidence for the early differentiation of the core from Pt–Re–Os isotope systematics of 2.8-Ga komatiites

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Abstract

Komatiite samples from the 2.8-Ga Kostomuksha greenstone belt in the Baltic Shield define Pt–Os and Re–Os isochrons with ages of 2816 ± 190 and 2880 ± 83 Ma, respectively. The mean initial $^{186}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios calculated at $T=2821$ Ma are 0.1198341 ± 7 and 0.11042 ± 69 ($\gamma^{187}\text{Os}=+2.5 \pm 0.6$), respectively. This Os isotopic composition characterizes that of the source of the Kostomuksha komatiite and is 53 ± 6 ppm and $2.5 \pm 0.6\%$ more radiogenic in $^{186}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$, respectively, than the putative contemporary convecting mantle. The coupled ^{186}Os – ^{187}Os enrichment cannot be the result of incorporation of the material of aged recycled oceanic crust into the source of the plume, as five to six times more crustal component is required to create the ^{186}Os -enrichment than the ^{187}Os -enrichment observed. Moreover, the radiogenic $^{186}\text{Os}/^{188}\text{Os}$ ratio combined with the subchondritic Pt/Os in this source calculated from the HSE abundance data is inconsistent with any model of Os isotopic evolution that involves crustal recycling, as these models require substantially suprachondritic Pt/Os in the hybrid sources. The coupled ^{186}Os – ^{187}Os enrichment in the source of the Kostomuksha komatiite is best explained via derivation of most of the Os from the outer core. This is most consistent with the Kostomuksha komatiites originating from a mantle plume that arose from the core–mantle boundary (CMB). If this interpretation is correct, the data provide minimum constraints on the $^{186}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios of the outer core at 2.8 Ga. The existing models of core crystallization based on experimentally determined solid metal–liquid metal partition coefficients for Pt, Re, and Os can adequately explain the Os isotopic composition of the Kostomuksha mantle source, although require the onset of inner core crystallization several hundred million years prior to formation of the Kostomuksha plume. Based on thermodynamic models, such an early onset of inner core crystallization would require a relatively low heat flux across the CMB of ~ 3 TW and the presence of >100 ppm K in the core. The results of this study combined with the HSE abundance data for the source of komatiites at Kostomuksha indicate that core–mantle interaction, at

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least in this instance, could occur in the form of isotopic exchange without significant mass transfer from the core to the mantle.

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1. Introduction

The Earth's core constitutes one third of the total mass of the planet yet contains >99% of the entire inventory of highly siderophile elements (HSE: Ru, Rh, Pd, Re, Os, Ir, Pt, and Au). It consists of the liquid outer core and the solid inner core, the latter representing ~5.5% of the total mass of the core. Crystallization of the inner core over much of the Earth's history has resulted in the production of energy in the form of latent heat that enables thermal convection in the outer core and in the mantle. In the silicate portion of the Earth, this heat may initiate thermal plumes rising from the core–mantle boundary (CMB) and also contributes to plate tectonics, both of which may be responsible for chemical exchange within the mantle and between the core and mantle.

Timing of the onset of crystallization of the inner core and its growth rate are matters of considerable debate (e.g., [1–3]). Until now, the issue has been largely addressed via thermal calculations and paleomagnetic studies. Another potential way to constrain the timing of inner core growth would be to assess the timing of the appearance and magnitude of geochemical indicators of core differentiation that might be present in putative plume-derived rocks. For example, coupled enrichments of $^{186}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios in young plume-derived lavas have been interpreted to be evidence of core–mantle interaction and core differentiation (e.g., [4–9]). If correct, then similar, though muted, signatures in ancient plume-derived lavas could be used to infer the timing of the onset of inner core crystallization. A record of such changes through time could be used to calculate the pace of inner core growth over the Earth's history.

In this study, Pt–Re–Os isotopic data for 2.8 Ga old komatiites from the Kostomuksha greenstone belt are presented. These komatiites were previously shown to have an initial $^{187}\text{Os}/^{188}\text{Os}$ ratio ~3% more radiogenic than the contemporary convecting mantle [10]. The new data are considered within the framework of the

possible timing of core differentiation and, when combined with the HSE abundance data for the source of these komatiites [11], on the possible mechanisms of core–mantle exchange.

2. Sampling

Seven samples from five komatiite lava flows were analyzed for HSE abundances and Os isotopic compositions. Four cumulate samples (9455, 9464, 9490, and 9490A) come from the Munro-type [11] lava flows #2, 6, and 13, the first two of which are massive throughout, and the last one is differentiated. Three others come from the Kostomuksha-type differentiated lava flows #17 and 19 (see Fig. 1 in [11] for sample locations). Out of these three, 9493 and 94111 are A₁-flowtop breccia samples, and 9496 is an A₃-spinfex sample. Details about field geology, petrology, and mineralogy, as well as trace element, HSE, Pb-, Nd-, and earlier $^{187}\text{Os}/^{188}\text{Os}$ -isotope systematics of the Kostomuksha komatiites have been previously provided by Puchtel et al. [10,12] and Puchtel and Humayun [11,13].

3. Analytical techniques

3.1. Sample preparation

For this study, batches of sample powders that had been previously utilized by Puchtel and Humayun [11,13], were re-analyzed. These batches were made by grinding new portions of the same rock crushes from which powder batches used by Puchtel et al. [10,12] were made. The new batches of powder were then combined with the older ones and re-ground.

Three separate sets of Carius tube digestions were carried out at the University of Chicago (UC) and at the University of Maryland (UMD) in order to: (1) determine HSE abundances on ~1.5 g aliquants spiked with the UC mixed HSE spike #000531, (2) determine $^{186}\text{Os}/^{188}\text{Os}$ ratios on ~30 g unspiked aliquants and

Pt/Os ratios on ~5% aliquants obtained by sub-sampling of the solutions of unspiked aliquants and spiked with the UC mixed HSE spike #000531, and (3) obtain Re–Os isotopic data on ~2 g aliquants spiked with the UMD mixed Re–Os spike. The analytical procedures mostly follow those described by Puchtel et al. [14].

3.2. HSE analysis

The HSE analyses were carried out at the University of Chicago using the techniques of Puchtel et al. [15]. Approximately 1.5 g of whole rock powder, an appropriate amount of the mixed UC HSE spike #000531, and ~7 mL of inverse aqua regia (15 N HNO₃:12 N HCl=2:1) were placed in a chilled to 0 °C Pyrex™ borosilicate glass Carius tube, and sealed. Samples were digested at 270 °C for ~72 h. Osmium was extracted from the aqua regia solution into CCl₄ [16] and then back-extracted into HBr, followed by purification via microdistillation [17]. The residual aqua regia solution was dried, the residue converted into chloride form, and Ir, Ru, Pt, Pd, and Re were separated from the rock matrix and further purified by cation exchange chromatography. The resulting eluate was used directly for ICP-MS analysis.

Measurements of Os, Ir, Ru, Pt, Pd, and Re isotopic compositions were performed on a Finnigan Element™ single-collector, magnetic sector ICP-MS at the University of Chicago. The sample solutions were introduced into the ICP-MS torch via a CETAC MCN6000 desolvating nebulizer for the PGE measurements or an ESI™ low-flow nebulizer for the Re measurements. Typical count rates were 10⁵–10⁶ cps for PGEs and 10⁴–10⁵ cps for Re, and the internal precisions of individual runs were better than 0.5% relative ($2\sigma_{\text{mean}}$). Long-term reproducibilities of the in-house 0.5 ppb Ir–Ru–Pd–Pt and Re standard solutions and a 1 ppb Os standard solution, which characterize the external precision of the analysis, were 1–2% ($2\sigma_{\text{stdev}}$) on all isotope ratios. Mass fractionation for Ru, Pd, Ir, Pt, and Re was corrected using $^{99}\text{Ru}/^{102}\text{Ru}=0.4044$, $^{110}\text{Pd}/^{106}\text{Pd}=0.4288$, $^{191}\text{Ir}/^{193}\text{Ir}=0.5942$, $^{198}\text{Pt}/^{195}\text{Pt}=0.2130$, and $^{185}\text{Re}/^{187}\text{Re}=0.5975$ relative to those measured in the standard solutions that were run alternately with the samples. The measured $^{190}\text{Os}/^{192}\text{Os}$ ratios in the samples

were corrected for fractionation using a linear law and $^{192}\text{Os}/^{188}\text{Os}=3.083$. The average total analytical blank was 5 pg Os, 0.5 pg Ir, 3 pg Ru, 31 pg Pt, 7 pg Pd, and 10 pg Re. Blank corrections applied were <0.1% for Os, Ir, Ru, and Pd, ~0.3% for Pt, and ≤20% for Re.

3.3. Pt–Os isotope study

Chemical treatment of the samples for the Pt–Os isotopic study was performed at the University of Chicago. To obtain the amount of osmium required for the high-precision measurements of the $^{186}\text{Os}/^{188}\text{Os}$ ratio, each of the six samples studied was processed in eight to twelve Carius tubes. No spike was added to the initial digestions, in which ~3–4 g of sample powder and ~13 mL of inverse aqua regia were placed into a chilled to 0 °C 25 mL Pyrex™ borosilicate glass Carius tube, and sealed. The samples were digested at 250 °C for 96 h. After the tubes were opened, ~5% of the sample solution from each of the Carius tubes making a single sample were transferred into a new Carius tube for precise determination of the Pt/Os ratio. Before the transfer procedure, the Carius tube was chilled to 0 °C and an appropriate amount of the UC mixed HSE spike #000531 was added to it, followed by ~5 mL of inverse aqua regia after the sample solution transfer was completed. In this work, we utilized the same UC mixed HSE spike #000531 used by Puchtel et al. [14] in their study of Pyke Hill komatiites. This promotes a more direct comparison of initial $^{186}\text{Os}/^{188}\text{Os}$ ratios of the Pyke Hill and Kostomuksha komatiite sources by eliminating a potential bias in Pt/Os ratios stemming from discrepancies in spike calibrations. The new tube was then sealed and heated at ~250 °C for 24 h to achieve sample-spike equilibration. After opening the tube, the spiked solution was processed to obtain the Pt/Os ratio using the same procedure utilized in the HSE analysis. From the remaining 95% of the unspiked aqua regia sample solution, Os was extracted and purified. The clean Os cuts from each of the unspiked Carius tube digestions for the sample were combined into one cut and used for the precise measurements of the $^{186}\text{Os}/^{188}\text{Os}$ ratio.

Measurements of Os and Pt isotopic compositions of the spiked aliquants, for the determination of Pt/Os ratios, were performed at the University of Chicago

by ICP-MS and followed the same procedure utilized in the HSE analysis. The high-precision measurements of the $^{186}\text{Os}/^{188}\text{Os}$ ratios were performed by negative thermal ionization mass-spectrometry (N-TIMS) in static mode on an eight-Faraday collector ThermoFinnigan Triton[®] mass spectrometer at the Johnson Space Center. Signals of 130–180 mV on mass 234 ($^{186}\text{Os}^{16}\text{O}_3^-$) and 235 ($^{187}\text{Os}^{16}\text{O}_3^-$) were generated for ≥ 180 ratios to reach the desired run precision of ± 20 ppm or better ($2\sigma_{\text{mean}}$) for the $^{186}\text{Os}/^{188}\text{Os}$ ratio. The interference of $^{186}\text{W}^{16}\text{O}_3^-$ on $^{186}\text{Os}^{16}\text{O}_3^-$ was monitored by measuring $^{184}\text{Os}^{16}\text{O}_3^-$ ($^{184}\text{W}^{16}\text{O}_3^-$). The mean of 26 runs of the Johnson–Matthey Os standard during the analytical campaign was 0.0013092 ± 11 for $^{184}\text{Os}/^{188}\text{Os}$, 0.1198462 ± 21 for $^{186}\text{Os}/^{188}\text{Os}$ and 0.1137893 ± 45 for $^{187}\text{Os}/^{188}\text{Os}$ ($2\sigma_{\text{stddev}}$). Each sample load was run one to four times. To calculate the age, Pt–Os data were regressed using the ISOPLOT program [18] and the ^{190}Pt decay constant (λ) of $1.477 \times 10^{-12} \text{ yr}^{-1}$ [19]. Error input was determined from the precision of the averages of the individual runs. All errors on age and initial isotopic ratios are quoted at $2\sigma_{\text{mean}}$.

3.4. Re–Os isotope study

For a more direct comparison between Pt–Os and Re–Os systematics and with the Re–Os data obtained by Puchtel et al. [10] on different aliquants of sample powders, it was decided to also study the Re–Os isotopic compositions of each sample used in the Pt–Os study and of one additional sample with a low Re/Os ratio at the Isotope Geochemistry Labo-

ratory, University of Maryland. About 2 g of sample powder, an appropriate amount of the UMD mixed Re–Os spike, and 7 mL of inverse aqua regia were weighed into a chilled to 0 °C 25 mL Pyrex[™] borosilicate glass Carius tube. Samples were digested at 270 °C for 96 h. Osmium extraction and purification procedures were identical to those used in the HSE analysis at the University of Chicago. Rhenium was recovered from the residual aqua regia solution and purified by anion exchange chromatography. A 2 mL quartz column filled with Bio-Rad[®] AG 1-X8 resin was used to separate Re from the bulk of the rock matrix. A second, 100 μL Teflon column was used for purification of the Re fraction.

Isotopic compositions of Os were measured in static mode on Faraday cups via N-TIMS on a VG Sector-54 instrument. The effects of fractionation during Os runs were eliminated by normalizing the Os isotope ratios to $^{192}\text{Os}/^{188}\text{Os}=3.083$. The mean of five runs of the Johnson–Matthey Os standard during the analytical campaign was 0.11381 ± 3 for $^{187}\text{Os}/^{188}\text{Os}$ ($2\sigma_{\text{stddev}}$). Rhenium isotopic compositions were measured in static mode on SEM detectors on a Nu Plasma multi-collector ICP-MS. Measured Re-isotopic ratios were corrected for fractionation and instrumental bias using $^{185}\text{Re}/^{187}\text{Re}=0.5975$ relative to those measured in the 0.2 ppb Re standard solution that was run alternately with the samples. The average total analytical blank was 5 μg Re and 4 μg Os. Blank corrections applied were $<0.1\%$ for Os and $<10\%$ for Re. Analytical uncertainties on Re and Os isotopic compositions are 1% and 0.2%, respectively, and include uncertainty on

Table 1
Re–Os isotopic data

Sample	Re (ppb)	Os (ppb)	Re/Os	$^{187}\text{Re}/^{188}\text{Os}$	$^{187}\text{Os}/^{188}\text{Os}$	$\gamma^{187}\text{Os}$ (T)
9455	0.2134	4.1806	0.0510	0.2457	0.12068	1.11
9464	0.1215	3.3347	0.0364	0.1753	0.11796	1.73
9490	0.0392	5.1348	0.0076	0.0367	0.10999	0.52
9490A	0.0283	4.6113	0.0061	0.0295	0.11015	0.99
9493	0.5771	2.0933	0.2757	1.3360	0.17163	−0.30
9496	0.1485	2.0915	0.0710	0.3420	0.12711	2.77
94111	0.9557	1.9325	0.4945	2.4107	0.21678	−6.40

The data obtained on 2-g sample aliquants spiked with the UMD mixed Re–Os spike. The $\gamma^{187}\text{Os}$ values for individual samples calculated at $T=2821$ Ma. The Re and Os abundances are re-calculated on an anhydrous basis. The estimated errors on the measured $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios are 1% and 0.2%, respectively, and include uncertainties on both blank correction and instrumental bias and mass-fractionation corrections.

the blank correction and on instrumental bias and mass fractionation corrections. To calculate the age, the Re–Os data were regressed using the ISOPLOT program [18]. All errors on age and initial isotopic ratios are quoted at $2\sigma_{\text{mean}}$. The initial $\gamma^{187}\text{Os}$ values were calculated as the per cent deviation of the initial $^{187}\text{Os}/^{188}\text{Os}$ ratio relative to the chondritic reference at that time [20]. The chondritic Os isotopic composition at the time T was calculated using the ^{187}Re decay constant (λ) of $1.666 \times 10^{-11} \text{ yr}^{-1}$, the starting solar system $^{187}\text{Os}/^{188}\text{Os}=0.09531$, and the present-day chondritic composition ($^{187}\text{Re}/^{188}\text{Os}=0.40186$, $^{187}\text{Os}/^{188}\text{Os}=0.1270$ [20,21]).

3.5. Major and minor element analysis

Major and minor (Cr, Ni) element abundances in whole rock samples 9455 and 9464, not previously reported by Puchtel et al. [12] and Puchtel and Humayun [11], were determined on pressed powder pellets by wavelength-dispersive X-ray fluorescence spectrometry using a VRA-20R spectrometer at the Institute of Geology and Geophysics (IGG) in Novosibirsk, Russia. The accuracy and reproducibility of the analyses were $\sim 1\%$ and $\sim 3\%$ (relative) for major and minor elements, respectively. Major and minor element abundances in the other five samples, reported in [11], and for the sake of completeness presented here, were also determined at the IGG using the same technique.

4. Results

4.1. Re–Os and Pt–Os isotopic data

The Re–Os isotopic data for the seven komatiite samples analyzed are presented in Table 1 and plotted on the $^{187}\text{Re}/^{188}\text{Os}$ vs. $^{187}\text{Os}/^{188}\text{Os}$ isochron diagram in Fig. 1A. Regression of the data for all samples but flow top breccia 94111, which plots well below the regression line, yields an isochron with an age of 2862 ± 214 Ma and an initial $^{187}\text{Os}/^{188}\text{Os}$ of 0.10888 ± 0.00099 , corresponding to a $\gamma^{187}\text{Os}(T)=+1.4 \pm 0.9$. Also plotted in Fig. 1 are the Re–Os data from [10]. Addition of these data into the regression dataset (with the exception of sample 94111, which again plots off the regression line) yields an isochron with an age of 2880 ± 83

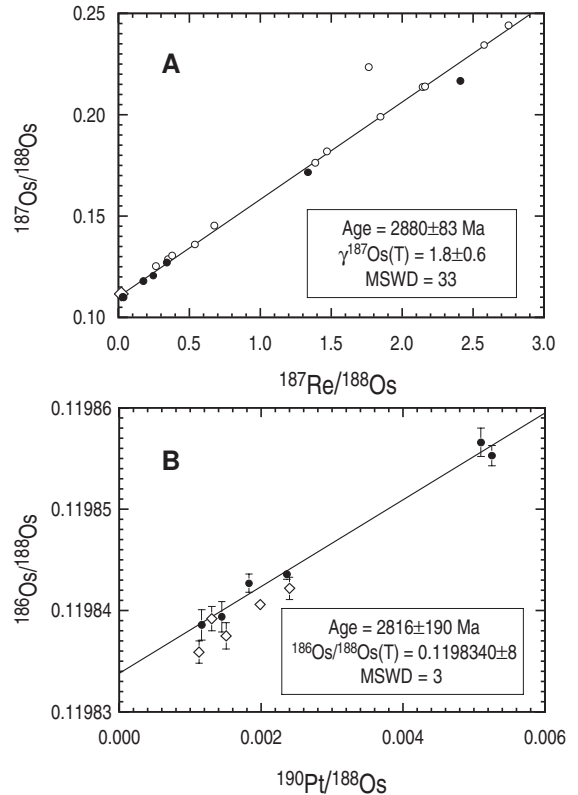


Fig. 1A. Re–Os isochron diagram for Kostomuksha komatiites. Solid circles—whole rock data from this study, open circles and an open diamond—whole rock and chromite data, respectively, from [10]. Flow top breccia sample 94111 analyzed in both studies plots off the isochron and was not included into the regression calculations. 1B. Pt–Os isochron diagram for Kostomuksha komatiites (solid circles). The Pt–Os age was calculated using the ^{190}Pt decay constant (λ) of $1.477 \times 10^{-12} \text{ yr}^{-1}$ [19]. Data for Pyke Hill komatiites (open diamonds) from [15] are plotted for comparison. Note that with the exception of sample PH30, the Pyke Hill komatiites have a distinctly less radiogenic initial $^{186}\text{Os}/^{188}\text{Os}$ ratio.

Ma and an initial $^{187}\text{Os}/^{188}\text{Os}$ of 0.10916 ± 0.00067 , corresponding to a $\gamma^{187}\text{Os}(T)=+1.8 \pm 0.6$. Finally, the mean initial $^{187}\text{Os}/^{188}\text{Os}$ of these samples re-calculated at $T=2821$ Ma (the best age estimate for the Kostomuksha lavas [12]) is 0.11042 ± 0.00069 ($\gamma^{187}\text{Os}=+2.5 \pm 0.6$).

The precise Pt–Os isotopic data for the six samples analyzed are listed in Table 2 and plotted on the $^{190}\text{Pt}/^{188}\text{Os}$ vs. $^{186}\text{Os}/^{188}\text{Os}$ isochron diagram in Fig. 1B. The data define a regression line with a slope corresponding to an age of 2816 ± 190 Ma and an initial $^{186}\text{Os}/^{188}\text{Os}$ of 0.1198340 ± 8 using the ^{190}Pt

Table 2
Precise Os isotopic data and Pt–Os abundance ratios

Sample	Pt/Os	¹⁹⁰ Pt/ ¹⁸⁸ Os	¹⁸⁴ Os/ ¹⁸⁸ Os	¹⁸⁶ Os/ ¹⁸⁸ Os	¹⁸⁷ Os/ ¹⁸⁸ Os
9455			0.0013067 ± 10	0.1198432 ± 15	0.1216968 ± 14
			0.0013073 ± 16	0.1198423 ± 18	0.1216963 ± 17
Average	1.919 ± 22	0.001828 ± 21	0.0013070 ± 06	0.1198427 ± 09	0.1216966 ± 06
9464			0.0013045 ± 12	0.1198433 ± 17	0.1163619 ± 20
			0.0013030 ± 14	0.1198438 ± 15	0.1163623 ± 19
Average	2.482 ± 13	0.002364 ± 12	0.0013038 ± 15	0.1198436 ± 05	0.1163621 ± 04
9490			0.0013061 ± 14	0.1198378 ± 15	0.1099955 ± 16
			0.0013104 ± 10	0.1198393 ± 17	0.1099942 ± 15
Average	1.219 ± 10	0.001161 ± 10	0.0013083 ± 43	0.1198386 ± 15	0.1099948 ± 13
9490A			0.0013106 ± 10	0.1198389 ± 15	0.1101089 ± 17
			0.0013074 ± 08	0.1198374 ± 16	0.1101100 ± 14
			0.0013079 ± 14	0.1198408 ± 16	0.1101125 ± 16
			0.0013072 ± 12	0.1198403 ± 17	0.1101107 ± 17
Average	1.518 ± 23	0.001445 ± 23	0.0013083 ± 15	0.1198394 ± 15	0.1101105 ± 15
9493	5.353 ± 81	0.005098 ± 77	0.0013043 ± 11	0.1198566 ± 14	0.1731327 ± 17
94111			0.0013056 ± 12	0.1198558 ± 17	0.2145642 ± 24
			0.0013054 ± 11	0.1198548 ± 15	0.2145599 ± 21
Average	5.516 ± 60	0.005253 ± 57	0.0013055 ± 02	0.1198553 ± 10	0.2145620 ± 42

The Os isotopic compositions were determined by N-TIMS on 30-g unspiked sample aliquants. The Pt–Os ratios were determined by ID-ICP-MS on 5% spiked aliquants obtained by post-dissolution subsampling of the 30-g unspiked aliquants and spiked with the UC mixed HSE spike #000531.

decay constant of $1.477 \times 10^{-12} \text{ yr}^{-1}$ [19]. The mean initial ¹⁸⁶Os/¹⁸⁸Os ratio of the samples re-calculated at $T=2821 \text{ Ma}$ is 0.1198341 ± 7 .

4.2. Major, minor, and highly siderophile element abundances

The major, minor and highly siderophile element data for the seven samples studied are presented in

Tables 3 and 4 and plotted on the variation diagrams in Fig. 2. Also plotted in Fig. 2 are compositions of olivine from Abitibi komatiites adopted from [15]. We aimed at obtaining as wide a spread in the Re/Os and Pt/Os ratios as possible, which was vital for obtaining more precise isochrons, and, thus, more precise initial Os isotope ratios. In order to do so, we have chosen samples with the largest possible range of MgO abundances (25–37%) collected from

Table 3
Major (wt.%) and minor (ppm) element data

Sample	9455	9464	9490	9490A	9493	9496	94111
SiO ₂	44.0	43.9	43.4	44.2	44.7	45.0	46.2
TiO ₂	0.301	0.335	0.261	0.264	0.459	0.489	0.416
Al ₂ O ₃	5.15	5.37	4.48	4.53	7.91	7.89	7.15
Fe ₂ O ₃	11.8	12.0	11.0	10.5	13.2	13.8	11.7
MnO	0.18	0.19	0.17	0.18	0.17	0.18	0.16
MgO	34.7	33.1	37.3	37.1	26.4	25.4	27.4
CaO	3.73	4.91	3.32	3.08	6.98	7.12	6.95
Na ₂ O	0.01	0.11	0.01	0.11	0.09	0.01	0.04
K ₂ O	0.02	0.01	0.01	0.01	0.02	0.02	0.02
P ₂ O ₅	0.05	0.05	0.03	0.08	0.06	0.07	0.08
LOI	9.81	10.1	11.6	11.0	6.27	5.65	6.39
Cr	3083	3062	2466	2409	3120	2968	3009
Ni	1818	1724	2119	2077	1244	1103	1401

Abundances are re-calculated on an anhydrous basis. Data for samples 9455 and 9464 from this study, and for the rest of the samples—from [11] and [12].

Table 4
HSE abundance data (ppb)

Sample	Re	Os	Ir	Ru	Pt	Pd	Re/Os	Pt/Os
9455*	0.234	4.23	3.76	6.24	8.41	7.56	0.055	1.99
9455*	0.245	4.37	3.83	6.28	8.10	7.50	0.056	1.85
9464	0.126	3.31	2.89	6.02	8.34	7.50	0.038	2.52
9490*	0.040	5.11	4.15	5.75	6.24	4.97	0.008	1.22
9490*	0.045	5.26	4.26	5.87	7.12	6.60	0.009	1.35
9490A	0.051	4.55	3.79	5.95	6.84	5.95	0.011	1.50
9493*		2.02	1.85	5.98	11.3	10.7		5.60
9493*	0.546	1.96	1.77	5.93	11.3	10.1	0.279	5.76
9493*	0.604	2.22	1.98	5.97	11.0	9.87	0.272	4.95
9496	0.145	1.85	1.60	5.64	10.5	10.5	0.078	5.70
94111*		1.71	1.67	5.65	10.3	11.0		6.04
94111*	0.895	1.89	1.76	5.82	10.4	10.7	0.473	5.51
94111*	0.920	1.81	1.67	5.76	10.2	10.4	0.507	5.64

Analyses are re-calculated on an anhydrous basis.

* Replicate digestions of the same sample powder aliquants. Boldfaced values—data from this study, obtained by the Carius tube digestion ID-ICP-MS technique. Data for the rest of the samples from [11].

both Kostomuksha- and Munro-type flows [11]. The Re/Os ratios obtained in the Re–Os study vary between 0.006 and 0.495 and agree to within 10% for all samples measured in the HSE study but 9490A (45%). The largest discrepancies are observed for samples with the lowest Re abundances (0.030–0.040 ppb) and are likely due to an imprecise determination of these in the HSE study as a result of overspiking and a relatively low count rate. On the other hand, the discrepancies for samples with the higher Re abundances (e.g., 9493 and 94111) are <1%. The Pt/Os ratios determined on the same samples for both the HSE abundance study and the Pt–Os isotope study agree to within 5%. Although this range of variation in the Pt/Os ratios observed between replicate analyses is relatively small, it still justifies the determination of precise Pt/Os ratios on the same digestions that were performed for obtaining precise $^{186}\text{Os}/^{188}\text{Os}$ ratios.

As can be seen in Fig. 2, all samples analyzed plot on the bulk differentiation trends for major, minor elements, and PGEs defined by Puchtel and Humayun [11] for both the Munro- and Kostomuksha-type komatiite flows. These samples, thus, display the same type of immobile, magmatic behavior for these elements, as did the entire set of the Kostomuksha komatiite samples. The Re abundances, on the other hand, show a totally irregular behavior.

5. Discussion

5.1. Os isotopic composition of the mantle source of the Kostomuksha komatiite

The initial Os isotopic composition of a lava can be regarded as representing that of its mantle source unless one of the following natural processes had affected its Re–Os and/or Pt–Os isotopic systems prior to or during/after emplacement: (1) contamination of the magma with upper crustal rocks, and (2) seafloor alteration and/or metamorphism of the lava.

As the abundance of Os in an average upper continental crust is about two orders of magnitude lower than that in komatiites, i.e., 20–30 ppt [22] vs. 2 ppb, the Os isotopic composition of komatiites can only be affected by crustal contamination when the mass fraction of a contaminant is substantial, i.e., 10% or more. Komatiite lavas that assimilate smaller amounts of crustal material may still develop strongly fractionated HSE abundance patterns (e.g., [23]) and inherit the lithophile element systematics from upper crustal rocks (e.g., [24]), but will essentially retain their mantle Os isotopic signature [25]. For instance, Puchtel et al. [24,25] have shown that assimilation of 10% of upper crustal material aged for 700 Ma by a komatiite melt will increase its initial $^{187}\text{Os}/^{188}\text{Os}$ ratio by <1 gamma unit, whereas decreasing its initial $^{143}\text{Nd}/^{144}\text{Nd}$ by ~ 4 epsilon units and its Nb/Th by a factor of seven. The possibility that the emplaced komatiite lavas at Kostomuksha could have had their Os isotopic composition inherited from that of crustal contaminant can be discarded on the grounds that they have lithophile trace element and isotope characteristics (e.g., $(\text{Nb}/\text{Th})_n = 1.5\text{--}2.1$, $\epsilon\text{Nd}(T) = +2.8 \pm 0.2$, $\mu_1 = 8.77 \pm 0.02$) similar to those of the contemporary oceanic mantle and show no evidence of contamination by the material of continental crust [12].

The mafic–ultramafic lavas at Kostomuksha have Sm–Nd and Pb–Pb whole rock isochron ages of 2843 ± 39 and 2813 ± 78 Ma, respectively, and are intruded and overlain by felsic subvolcanic, volcanic and volcanoclastic rocks with a U–Pb zircon age of 2821 ± 1 Ma [12]. The Re–Os and Pt–Os ages obtained in this study or in combination with the Re–Os data from [10] are, thus, consistent with the existing geochronological information. This implies that either the Re–Os and Pt–Os systems have

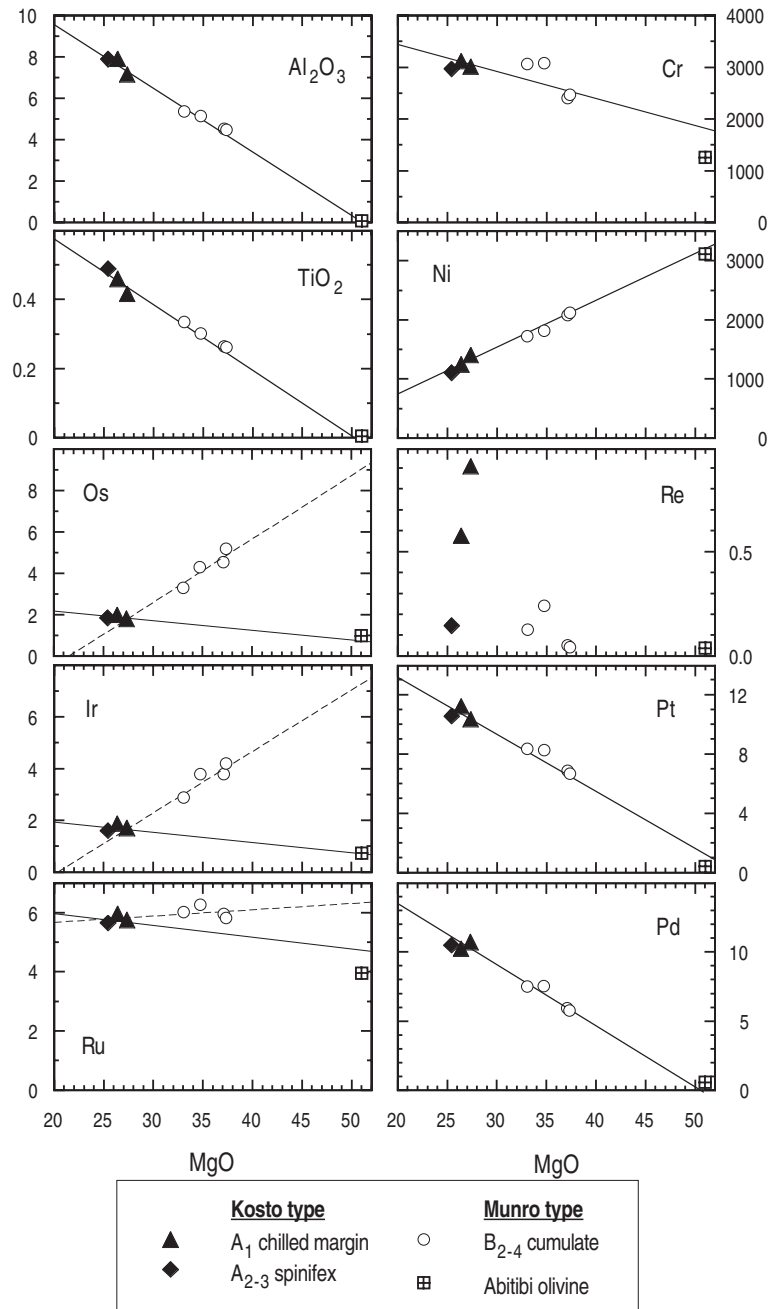


Fig. 2. Variation diagrams of MgO (wt.%) vs. major, minor elements, and HSE in the seven komatiite samples studied. The linear trends are best fit lines drawn linear law through the data for all komatiite samples of both Kostomuksha-type (solid line) and Munro-type (dashed line) from [11]. Note that samples from this study plot on or near the corresponding differentiation trends indicating the lack of postmagmatic disturbance for all elements but Re. Abitibi olivine composition from [15].

remained closed after lava emplacement, or they were disturbed during or shortly after emplacement but remained closed ever since. These two scenarios can be constrained using the Re, Pt, and Os variations in the lavas. In terms of the Re–Os system, the fact that the Re abundances exhibit a totally irregular behavior on the MgO vs. Re plot (Fig. 2) favors a postmagmatic disturbance. It has also been proposed that Re can escape as volatile Re-oxide or Re-chloride species during magma degassing prior to or during subaerial eruption (e.g., [26]). However, although this might be an additional factor contributing to the generally low Re abundances in some of the samples, it is unlikely that this factor entirely controlled the observed Re variations in the lavas. First, the komatiites at Kostomuksha were emplaced as submarine, not subaerial lavas [12], and, therefore, Re-degassing should have been limited. Second, the lavas display large variations in Re content even within individual flows. Moreover, the deepest parts of the flows that are expected to have experienced least degassing, have the lowest Re content, which does not fit the degassing scenario. On the other hand, these cumulate parts of the flows mostly consist of olivine and devitrified glass and are more susceptible to alteration and Re-loss.

In addition to the geochemical factors such as contamination and secondary alteration discussed above, it is also important to consider various analytical issues that could have led to obtaining a biased result. One potential concern might be that the samples were not completely digested and therefore not all Os and Pt carriers were accessed. However, as has been argued by Puchtel et al. [14], as long as individual phases in the sample are in isotopic equilibrium with the bulk rock (e.g., the isotopic system has not been disturbed since the time of lava emplacement on the scale of the samples), and as far as determinations of Os isotopic compositions and Pt/Os ratios have been performed on the same digestions, incomplete dissolution of resistant phases only moves the whole rock analyses along the isochron, having no effect on the calculated initial Os isotopic ratio. In addition, Puchtel et al. [15] and Puchtel and Humayun [11] demonstrated by time/temperature-series experiments for the KAL-1 komatiite standard and the GP-13 and UB-N peridotite standards that the PGE data obtained by methods used therein do

not reflect incomplete digestion, and that these data are consistent with those obtained in other labs using both Carius tube and high pressure ashing (HPA) digestion techniques.

Second, errors in the determination of the precise Pt/Os ratios could also bias the result. For one thing, the Pt/Os ratios of the 5%-spiked aliquants may not be the same as those of the unspiked digestions of bulk rocks due to the ubiquitous presence of undissolved silicate sludge. However, comparison of the Pt/Os ratios presented in Tables 2 and 4 shows that these agree within 5% and do not reveal any systematic deviations. Finally, discrepancies in analytical procedures, e.g., errors in spike calibrations, may also bias results for ancient rocks. However, the Os isotopic data for Kostomuksha komatiites that we compare with those for Pyke Hill komatiites were obtained using the identical HSE spike and analytical procedures, thus eliminating procedural bias as a potential cause of the more radiogenic Os isotopic composition in the Kostomuksha komatiites.

Osmium and Pt abundances vary in a regular fashion in all samples, including 94111, which is consistent with these variations being controlled by magmatic differentiation. This indicates that both Os and Pt were immobile during postmagmatic processes, as was also established by Puchtel and Humayun [11] on the basis of their study of a larger set of samples. Thus, the combination of immobile behavior of Pt and Os, and the fact that the Pt–Re–Os isotopic data yield isochrons are consistent with the interpretation that the mean initial Os isotopic composition of the Kostomuksha komatiites ($^{186}\text{Os}/^{188}\text{Os}=0.1198341 \pm 7$, $^{187}\text{Os}/^{188}\text{Os}=0.11042 \pm 69$, $\gamma^{187}\text{Os}(2821 \text{ Ma})=+2.5 \pm 0.6$) represents that in their mantle source region.

In Table 5, the initial $^{187}\text{Os}/^{188}\text{Os}$ ratio of the Kostomuksha komatiite source is compared with those of the contemporary convecting upper mantle (DMM) as represented by compositions of selected mantle-derived materials [14], which is identical to the chondritic reference of Shirey and Walker [20], and with the contemporary primitive upper mantle (PUM) as defined by Meisel et al. [27] on the basis of their worldwide study of mantle xenoliths. The initial $^{187}\text{Os}/^{188}\text{Os}$ ratio of the Kostomuksha source is $2.5 \pm 0.6\%$ more radiogenic than that of DMM and $1.6 \pm 0.6\%$ more radiogenic than that of PUM. For comparison, the initial $^{187}\text{Os}/^{188}\text{Os}$ ratio of the source

Table 5
Initial Os isotopic compositions of reference reservoirs and of Kostomuksha komatiites

Initial ratio (at 2821 Ma)	DMM	PUM	Kostomuksha	Δ Kosto (DMM)	Δ Kosto (PUM)
$^{187}\text{Os}/^{188}\text{Os}$	0.10770	0.10869 ^a	0.11042 ± 69^b	$2.5 \pm 0.6\%$	$1.6 \pm 0.6\%$
$^{186}\text{Os}/^{188}\text{Os}$	0.1198277	0.1198317 ^c	0.1198341 ± 7^b	53 ± 6 ppm	20 ± 6 ppm

^a Calculated from the global data on fertile mantle peridotites [27].

^b Mean initial Os isotopic compositions of samples.

^c Mean for the Pyke Hill samples [14] excluding PH30.

of Archean komatiites at Belingwe is $2.8 \pm 0.8\%$ more radiogenic than DMM [28].

The present-day $^{186}\text{Os}/^{188}\text{Os}$ and $^{190}\text{Pt}/^{188}\text{Os}$ ratios for DMM were established by Walker et al. [5] and Brandon et al. [7,29,30] to be 0.1198350 ± 10 and 0.00174 , respectively, on the basis of their measurements of the Allende carbonaceous chondrite, abyssal peridotites, ophiolitic Os–Ir alloys, and chromitites. This composition of modern DMM projects to the solar system initial $^{186}\text{Os}/^{188}\text{Os}$ ratio of 0.1198232 ± 10 and to a $^{186}\text{Os}/^{188}\text{Os}$ ratio of 0.1198277 ± 10 at the time of the emplacement of the Kostomuksha lava (2821 Ma). Further, Puchtel et al. [14] established the Pt–Os evolution curve for PUM on the basis of their study of Pyke Hill komatiites, which had an initial $^{187}\text{Os}/^{188}\text{Os}$ ratio similar to that of contemporary PUM. Using this evolution curve, the calculated PUM contemporary to the Kostomuksha komatiites had $^{186}\text{Os}/^{188}\text{Os} = 0.1198317 \pm 6$. Therefore, the initial $^{186}\text{Os}/^{188}\text{Os}$ ratio of the Kostomuksha komatiite source was 53 ± 6 ppm more radiogenic than that of the contemporary DMM and 20 ± 6 ppm more radiogenic than that of the contemporary PUM (Table 5).

5.2. Origin of the coupled $^{186}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ enrichments in the source of the Kostomuksha komatiite

Puchtel et al. [10] previously discussed possible causes of the suprachondritic initial $^{187}\text{Os}/^{188}\text{Os}$ ratio in the Kostomuksha komatiites. These included the possibility that it is an intrinsic feature of the lower mantle, the result of contamination by older oceanic crust onto which the oceanic plateau lavas erupted, oceanic crust recycling into the mantle source of the komatiites, and entrainment of outer core material into the source of the putative Kostomuksha plume. The new data obtained here, as well as results reported by

Brandon et al. [9], Puchtel et al. [14,15] and Puchtel and Humayun [11], allow new constraints to be placed on these possibilities. The possibility that the ^{187}Os -enrichment in the source of the Kostomuksha plume was the result of primordial mantle heterogeneities in Re/Os that survived to the present was ruled out by Puchtel et al. [10]. They argued that if these heterogeneities were created as a result of initial separation of the Earth's core, the HSE abundances in the Kostomuksha source should have been two orders of magnitude lower than they calculated [13]. This conclusion has now been reinforced by a more accurate determination of HSE composition of the Kostomuksha komatiite source by Puchtel and Humayun [11], which was shown to be similar to that of the average depleted spinel lherzolite (ADSL) of Puchtel et al. [15].

The hypothesis of the origin of the ^{187}Os -enrichment in the source of the Kostomuksha plume as a result of mixing the komatiite lava with pre-existing oceanic crust onto which the oceanic plateau lavas erupted or incorporation of aged recycled oceanic crust into the source of the plume, in addition to the mass-balance arguments put forward by Puchtel and Humayun [13] and Puchtel et al. [10], can now also be ruled out on the basis of the $^{187}\text{Os}/^{188}\text{Os}$ vs. $^{186}\text{Os}/^{188}\text{Os}$ systematics and the HSE abundance data for the Kostomuksha komatiite source [11]. As can be seen in Fig. 3, addition of <10% of an Archean oceanic crustal component, with a residence time of 1 b.y., to the source of the Kostomuksha komatiite, is required to increase its initial $^{187}\text{Os}/^{188}\text{Os}$ ratio by 1.6% relative to PUM observed. At the same time, this amount of oceanic crustal material in the Kostomuksha source will increase its initial $^{186}\text{Os}/^{188}\text{Os}$ ratio by only ~1 ppm. To account for the ~20 ppm increase relative to PUM observed, 50–55% crustal component will be required. This result is similar to the findings of Brandon et al. [7,9], who have argued that the $^{186}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ iso-

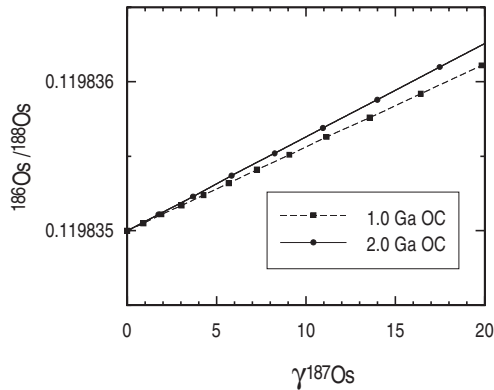


Fig. 3. Diagram illustrating the effect of incorporation of Archean oceanic crust (komatiite:basalt=1:10), aged for 1–2 b.y., into a mantle plume source with a chondritic Os isotopic composition. The composition of the Archean oceanic crust from [10,13]. Tick marks drawn in 5% increments.

topic data for the Hawaii, Gorgona, and Noril'sk lavas plot on the trends with the slopes corresponding to high Pt/Re ratios that are not usually observed in crustal materials (90–110 vs. 10–20). These trends converge to a common isotopic component that appears to be present in the sources of plumes worldwide. This component was inferred to be the outer core.

Second, any model explaining radiogenic Os isotopic composition of plume-derived lavas by mixing crustal materials into their mantle sources, be they fragments of oceanic lithosphere (e.g., [31]), metalliferous sediments [32,33], or mantle pyroxenite [34], would ultimately require substantially suprachondritic Re/Os and Pt/Os ratios in the resulting hybrid sources. However, Puchtel and Humayun [11] established a HSE pattern for the Kostomuksha source with a subchondritic Pt/Os ratio of 1.40. Thus, the radiogenic initial $^{186}\text{Os}/^{188}\text{Os}$ ratio combined with the subchondritic Pt/Os in the Kostomuksha komatiite source is inconsistent with any model of Os isotopic evolution that involves crustal recycling. We argue that the observed coupled ^{186}Os – ^{187}Os enrichment is an outer core signature.

5.3. Why are some plumes enriched in ^{186}Os – ^{187}Os isotopes while others are not? Implications for tectonic setting of komatiites

There is a long-standing debate on whether komatiites are the products of hydrous (i.e., subduction-

related) melting or dry (i.e., plume-related) melting of the mantle (e.g., [35,36]). Dry melting would imply that Archean komatiites came from a mantle that was 200–300 °C hotter than the present-day mantle, whereas wet melting requires mantle temperatures in the Archean to be similar to the present-day temperatures. This debate has far-reaching implications for the thermal and chemical evolution of the Earth and tectonic styles in the Archean. Although resolving these issues is beyond the scope of this paper, some conclusions can be drawn from the Os isotopic data pertaining to the tectonic setting of the Kostomuksha komatiites. The possible outer core signature found in the Kostomuksha komatiites implies that these magmas were formed in a starting mantle plume that originated at the CMB, and not in a subduction-related environment. These komatiites and associated abundant basaltic lavas were emplaced onto oceanic crust to form part of an Archean oceanic plateau [12]. Due to its excessive buoyancy, this oceanic plateau was then subducted to and obducted onto the continent, adding to the mass of the existing Archean continental crust. Thus, this study supports the notion that at least some komatiites were formed via dry melting in deep mantle plumes and that formation and accretion of oceanic plateaux in the Archean was an important mechanism of heat release and continental crustal growth. As observed by Arndt et al. [35], ultramafic lavas represent a broad range of magma types that form in different tectonic settings. It is important, when discussing the origin of any particular komatiite, to recognize this diversity.

Although many mafic–ultramafic lavas have been probably derived from partial melting of mantle material captured by mantle plumes, only a few show ^{187}Os -enrichments, whereas most of them do not. This in part may be explained by differences in the depths of plume initiation, and in part by different tectonic settings of lava emplacement. Plumes that have never seen the CMB and have instead risen from the 670-km discontinuity or above, would never have had a chance to acquire the core signature. For instance, Kostomuksha and Pyke Hill komatiites have similar lithophile trace element and isotopic characteristics, but differ in their Os isotopic compositions. And, although Kostomuksha komatiites were likely derived via a deeper mantle melting than their Pyke Hill counterparts, this fact alone does not explain these

differences, as the depth of origin of a komatiite melt may have nothing to do with the depth of origin of the plume itself. Therefore, the occasional appearance of coupled ^{186}Os – ^{187}Os enrichments in the Archean as well as in younger lavas is most suggestive of different locations/depths for plume initiation.

5.4. Implications for the rate and the timing of the onset of inner core crystallization

Brandon et al. [9] evaluated four different crystallization models for the Earth's core using the Os isotopic data for Hawaii, Gorgona, and Norilsk lavas and assuming that the point of convergence of these data in the $^{186}\text{Os}/^{188}\text{Os}$ vs. $^{187}\text{Os}/^{188}\text{Os}$ space corresponds to the Os isotopic composition of the modern outer core. These four crystallization models are illustrated in Figs. 4 and 5. In Models 1 to 3, the inner core crystallization begins at 4.4 Ga following the hypothesis of Stacey and Loper [37] that the inner core has been present and growing for most of the Earth's history. In Model 4, it is delayed until 3.5 Ga

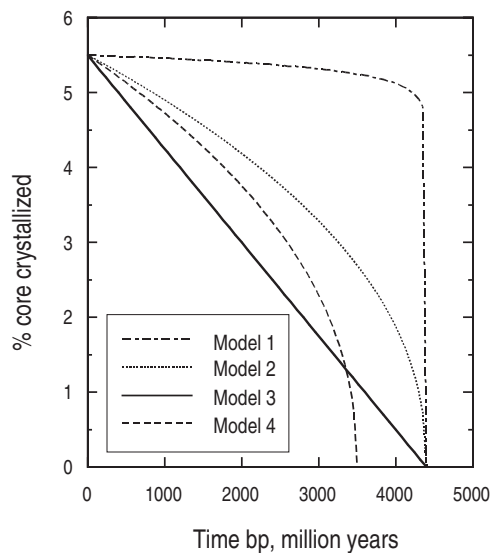


Fig. 4. Diagram illustrating the timing of the onset and the rate of inner core crystallization in Models 1 to 4 discussed in the text. Model parameters from [9]. The solid metal–liquid metal partition coefficients for Os and Re were modified as described in the text to incorporate the adjustments in the starting mantle composition assumed to be PUM [14] and are as follows. Model 1: 26.6 and 18.3; Model 2: 34.4 and 22.7; Model 3: 41.8 and 26.2; Model 4: 38.4 and 24.1 for Os and Re, respectively.

based on the observation that the Earth's magnetic field is at least 3.5 b.y. old [38]. In Model 1, most of the inner core crystallizes by 4.3 Ga; in Models 2 and 4, the inner core undergoes rapid crystallization during the Archean, followed by slower but constant post-Archean growth. Finally, in Model 3, the inner core crystallizes at a constant rate over Earth's history. For these models, the solid metal–liquid metal partition coefficients for Re and Os necessary to produce $^{186}\text{Os}/^{188}\text{Os}=0.1198700$ and $\gamma^{187}\text{Os}=+18$, corresponding to the convergence point of the available Os isotopic data, were adjusted assuming a solid metal–liquid metal D_{Pt} of 2.9 [5]. Because the Os isotopic composition of the primitive mantle [14] we used in our modeling is slightly more radiogenic than that adopted by Brandon et al. [9], the required D_{Os} we used in our calculations are 5–8% lower than those utilized by Brandon et al. [9] and, thus, even better fit those determined in experimental studies [39]. Also plotted in Fig. 5 are Os isotopic data for lavas at Kostomuksha as well as at several other localities, including those with radiogenic Os isotopic compositions from Belingwe [28] and Pechenga [40]. Several conclusions can be drawn from these results. First, all four models can explain the Os isotopic composition of the Kostomuksha source, and, for that matter, the Os isotopic composition of the source of lavas at Belingwe and Pechenga. Second, in Models 3 and 4, the Os isotopic compositions of the Archean sources were totally dominated by that of the outer core, whereas in Models 1 and 2, the Archean sources inherited only part of that signature.

Using the initial $^{186}\text{Os}/^{188}\text{Os}$ ratio of the Kostomuksha source and assuming that it is entirely determined by that of the outer core, we calculate the latest possible time of the onset of inner core crystallization necessary to build up the $^{186}\text{Os}/^{188}\text{Os}$ radiogenic ratio of this magnitude in the outer core. For these calculations, in each model from Fig. 4, we used solid metal–liquid metal D_{Pt} of 2.9. As Models 2 and 4 differed only in the timing of the onset of inner core crystallization, these were combined into one model (Model 2). Thus, for Models 2 and 3, we used the highest $D_{\text{Os}}=41.8$ from the adjusted models in Fig. 5, and for Model 1, a moderately high $D_{\text{Os}}=35$. The results of the calculations are presented in Fig. 6. For Model 1, the onset of inner core crystallization could be as late as 3.0 Ga. Model 2 places the onset of inner core

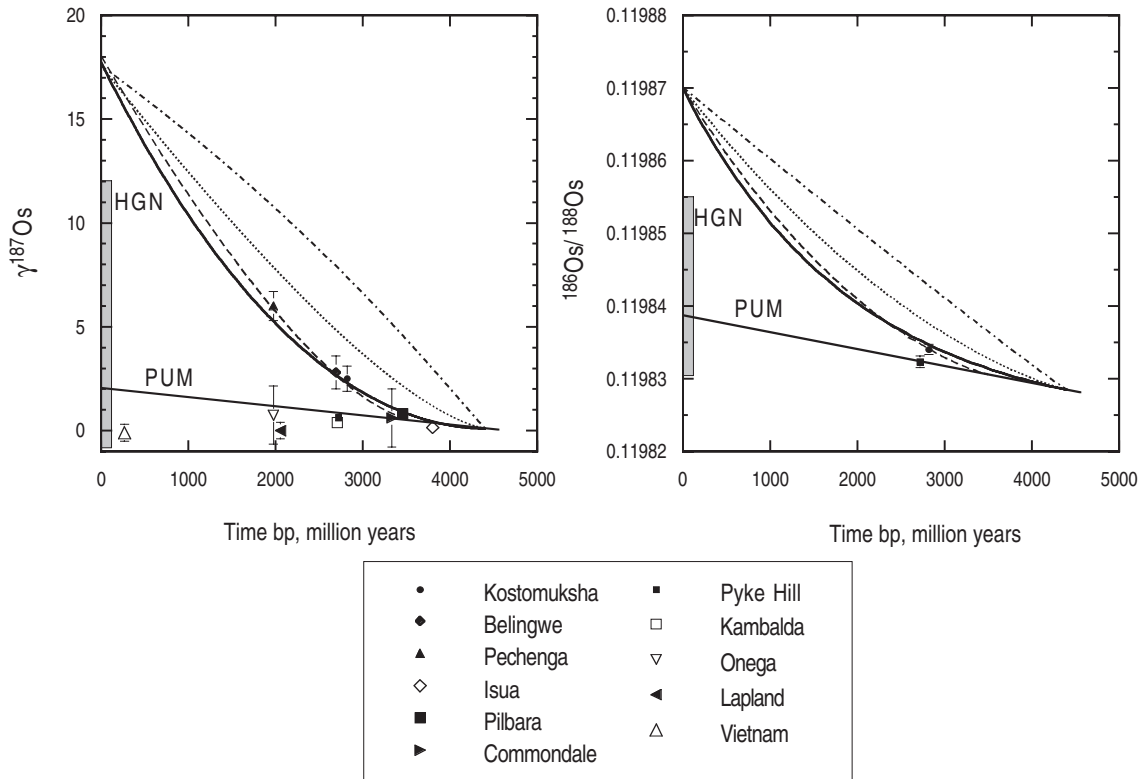


Fig. 5. Variations of $^{186}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ vs. time in the outer core for the four core crystallization models of Brandon et al. [9]. The $^{186}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ vs. time evolution of PUM (straight solid lines) from [14] and [27]. The Os composition of Greenland peridotites [50], Pilbara [50], Kambalda [51], Vetryny Belt [25], Finnish Lapland [52], and Vietnam [53] komatiites, Commondale boninites [54], and Onega plateau picrites [55], as well as for Hawaii [7], Gorgona [9], and Noril'sk [5] lavas (HGN) are plotted for comparison. Note that Os isotopic composition of the Kostomuksha source as well as those of Belingwe komatiites [28] and Pechenga picrites [40] are consistent with all four models.

crystallization at 3.4 Ga and Model 3—at 4.2 Ga. These results, thus, require that the inner core started to crystallize at least several hundred million years prior to melting of the Kostomuksha source. Assuming 3.4 Ga as an upper limit for the onset of inner core crystallization, the average age of the inner core (the time in the past when 50% of the inner core has crystallized) would be 2.3 Ga [9].

Numerous recent articles have attempted to constrain the rate of heat flow out of the core today and in the past, and the implications this heat flow has for the age of the inner core (e.g., [1,2,41–43]). A minimum constraint on core/mantle heat flow is based on estimates of how much heat flow is required to drive the geodynamo. Estimates of the heat transported by plumes and simple boundary layer theory also provide constraints on core/mantle heat flow. The large ma-

ajority of these models suggest minimum heat flow across the core/mantle boundary of ~ 3 TW, with higher heat flow in the range of 5–12 TW suggested by boundary layer models and estimates of plume heat transport. All core thermal models consistently show that, given heat flow in this range, the average age of the material within the inner core must be between 1 and 2 Ga unless the core contains substantial quantities of heat-producing elements, e.g., potassium (e.g., [44]). Recent experimental studies have shown that the core is likely to contain up to 130 ppm K if formed from a Fe-sulfide liquid with $\sim 10\%$ sulfur [45]. A maximum K content of 250 ppm in the core would be achieved if core formation involved a Fe-sulfide liquid with 4–8% O. Cosmochemical models based on the volatility of S have argued that the S content of the core may only be $< 2\%$ [46], indicating that an Fe–S–

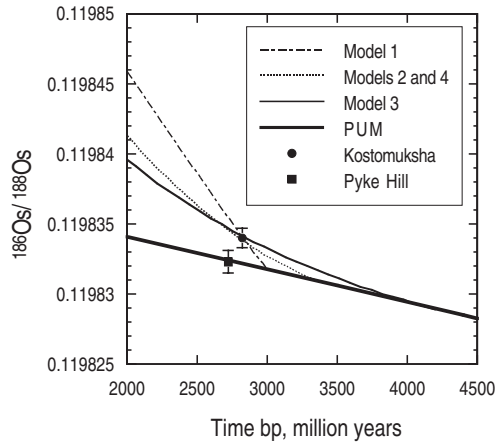


Fig. 6. Diagram illustrating the latest possible timing of the onset of inner core crystallization to account for the Os isotopic composition of the Kostomuksha source assuming the latter was derived from the outer core. The $^{186}\text{Os}/^{188}\text{Os}$ vs. time evolution curve of PUM from [14]. See text for further explanations.

O composition of the core is consistent with the presence of some heat-producing elements. In summary, given the uncertainties in the estimates for the present heat flux at the CMB, ranging from 3 to 10 TW [2] and in the current knowledge of the partition coefficients for radioactive elements at the CMB conditions, the estimates of the age of the inner core in these models allow for a large range between 1.0 and 3.5 Ga. We argue that Os isotopic studies of Archean komatiites allow tighter constraints to be placed on the timing of the onset of inner core crystallization, supporting an early crystallization of the core.

5.5. Implications for the mechanisms of core–mantle interaction

There are two types of models of core–mantle exchange that are currently being discussed in the literature. The first one, introduced by Walker et al. [6], implies a physical addition of $\leq 1\%$ of the outer core liquid metal into the silicate lower mantle. Because the outer core has up to three orders of magnitude higher HSE abundances compared to the mantle, the Os isotopic composition of the resulting hybrid mantle source will be dominated by that of the outer core. This process should have resulted in an order of magnitude higher HSE abundances in the hybrid mantle sources compared to those in the convecting

upper mantle (e.g., [13,47]). The fact that the lavas derived from these hybrid sources (e.g., Hawaiian picrites) did not show such an HSE enrichment was explained by the difficulty of deducing the abundances of HSE in the mantle source due to the compatible nature of HSE during mantle melting and complex differentiation histories of basalts and picrites (e.g., [20,48]). Puchtel and Humayun [11,13] and Puchtel et al. [15] developed a technique for accurate determination of HSE abundances in the sources of high-degree partial melts such as komatiites. These melts derive a substantial portion of HSE inventory from the mantle and experience little or no differentiation en route to the surface, thus delivering a clear message about the HSE abundances in their mantle sources. Comparison of HSE abundances in komatiites at Kostomuksha and Abitibi showed that mantle sources of these lavas contained essentially the same abundances of HSE, despite different initial Os isotopic compositions. Assuming that the conclusion of Puchtel et al. [10] was correct and the $\sim 3\%$ enrichment in $^{187}\text{Os}/^{188}\text{Os}$ in the Kostomuksha komatiite source was the outer core signature, this observation led Puchtel and Humayun [11,13] to propose a model of core–mantle interaction by isotopic exchange at the CMB without physical addition of the outer core to the silicate lower mantle. Further, precise measurements of the Fe/Mn ratio of Hawaiian picrites revealed that the mantle source under Hawaii had a high Fe/Mn relative to other lavas, which was interpreted to be the result of chemical exchange of FeO between the outer core and lower mantle [49].

The HSE abundance data from [11] combined with the coupled ^{186}Os – ^{187}Os enrichment in the Kostomuksha komatiite source established in this study lend further support to this hypothesis. The radiogenic initial $^{186}\text{Os}/^{188}\text{Os}$ ratio of 0.1198341 ± 7 in the Kostomuksha source implies that it has evolved with a $^{190}\text{Pt}/^{188}\text{Os}$ ratio of 0.00238 (Pt/Os=2.50). This ratio is $\sim 1.5 \times$ chondritic as compared to the subchondritic Pt/Os=1.40 calculated from the HSE abundance data [11]. This indicates that parentless Os is present in the Kostomuksha mantle source region, consistent with isotopic exchange of a chondritic mantle with a ^{186}Os – ^{187}Os -enriched reservoir, potentially the Earth's differentiated outer core. Thus, this work validates the conclusions of Puchtel and Humayun [11,13] and confirms that the core–mantle interaction,

at least in this instance, could occur in the form of isotopic exchange without significant mass transfer from the core to the mantle. At present, the exact mechanism of this exchange and the time scales it operates on are not clear.

6. Conclusions

1. The mantle source of komatiite lavas at Kostomuksha had $^{186}\text{Os}/^{188}\text{Os}=0.1198341 \pm 7$ and $^{187}\text{Os}/^{188}\text{Os}=0.11042 \pm 69$ ($\gamma^{187}\text{Os}=+2.5 \pm 0.6$) at the time of lava emplacement (2821 Ma). These Os isotopic ratios are 53 ± 6 ppm and $2.5 \pm 0.6\%$ more radiogenic, respectively, than those of the contemporary depleted mantle (DMM) and 20 ± 6 ppm and $1.6 \pm 0.6\%$ more radiogenic, respectively, than those of primitive mantle (PUM).
2. The observed coupled ^{186}Os – ^{187}Os enrichment in the source of the Kostomuksha komatiite was derived from the outer core. Other potential mechanisms of creating this enrichment have been discarded on the basis of mass-balance calculations and combined Os isotopic and HSE abundance data for the Kostomuksha komatiite source.
3. The existing models of core crystallization based on the experimentally determined solid metal–liquid metal partition coefficients can adequately explain the Os isotopic composition of the Kostomuksha plume source. The data obtained place the onset of inner core crystallization several hundred million years prior to the formation of the Kostomuksha plume. Based on thermodynamic models, such an early onset of inner core crystallization would require a relatively low heat flux across the CMB of ~ 3 TW and the presence of > 100 ppm K in the core.
4. The results of this study combined with the HSE abundance data for the source of komatiites at Kostomuksha confirm that the core–mantle interaction, at least in this instance, could occur in the form of isotopic exchange without significant mass transfer from the core to the mantle.

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