A Quantitative Link Between Recycling and Osmium Isotopes

Alexander V. Sobolev[1,2]*, Albrecht W. Hofmann[2], Gerhard Brügmann[2,3], Valentina G. Batanova[1], Dmitry V. Kuzmin[2,4]

1-V.I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Acad. of Sciences, Kosygin 19, 119991, Moscow, Russia;
2-Max Planck Institute for Chemistry, Post Office Box 3060, 55020 Mainz, Germany;
3-Institut für Geowissenschaften, Johannes Gutenberg-Universität Mainz, Becherweg 21, 55099 Mainz, Germany;
4-V.S. Sobolev Institute of Geology and Mineralogy, Siberian Branch of Russian Acad. of Sciences, Koptuyga 3, 630090, Novosibirsk, Russia.

*- corresponding author, e-mail sobolev@geokhi.ru

Recycled subducted ocean crust has been traced by elevated $^{187}Os/^{188}Os$ in some studies and by high nickel and low manganese contents in others. Here we show that these tracers are linked for Quaternary lavas of Iceland, strengthening the recycling model. An estimate of the osmium isotopic composition of both the recycled crust and the mantle peridotite implies that Icelandic Quaternary lavas are derived in part from an ancient crustal component with model ages between 1.1 × 10^9 and 1.8 × 10^9 years and from a peridotitic end-member close to present day oceanic mantle.

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Alexander V. Sobolev,[1,2]* Albrecht W. Hofmann,[2] Gerhard Brügmann,[2,3]
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Formation, subduction, and incomplete mixing of oceanic crust produces chemical and isotopic heterogeneity in Earth's mantle (*1*, *2*). The signature of these processes in the mantle over time and the importance of recycling in explaining the origins and compositions of volcanic rocks remain major questions. Recently, osmium isotopes have proved to be an important tracer (*3*, *4*). Basaltic ocean crust has much higher Re/Os ratios than mantle peridotite, from which it is derived through partial melting, because osmium remains mostly in the solid (mantle residue), whereas Re preferentially enters the melt. The decay of long-lived ^{187}Re to stable ^{187}Os therefore generates increased ^{187}Os/^{188}Os ratios in such crustal rocks. Elevated ^{187}Os/^{188}Os values have been recently found in Icelandic basalts, where they are correlated with the relative abundances of other isotopes (*5*, *6*). These data support the notion that the mantle source of Icelandic basalts contains oceanic crust that has been recycled by subduction and mantle convection (*7*). However, it has been difficult to assess this model because independent estimates of the proportions of components and their Os isotopic compositions were lacking.

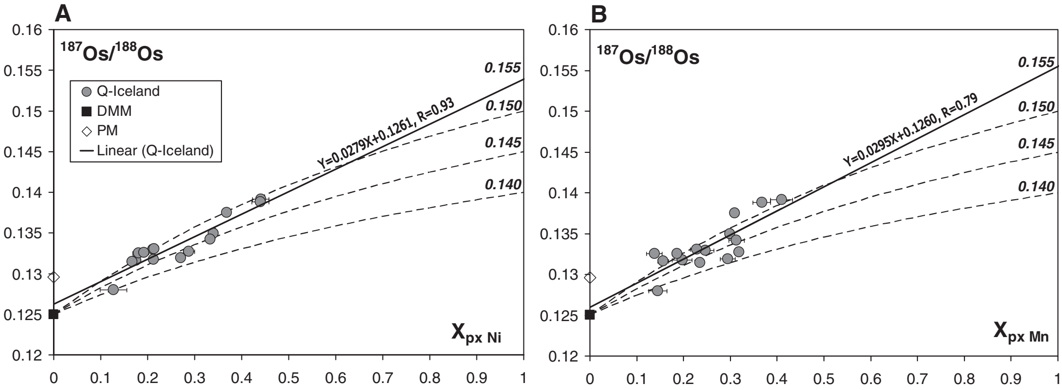

Fig. 1. (**A** and **B**) Measured bulk rock ^{187}Os/^{188}Os versus estimated proportion of pyroxenite derived melt (X_{px}) (table S1). X_{px} is defined as a following linear functions of average olivine composition (*10*): $X_{px\ Ni} = 10.54 \times \text{NiO}/(\text{MgO}/\text{FeO}) - 0.4368$; $X_{px\ Mn} = 3.483 - 207.139 \times (\text{Mn}/\text{Fe})$. Solid lines represent linear regression with parameters shown. DMM and PM stand for depleted and primitive present day mantle estimates, respectively (*4*). Dashed lines indicate mixing of melt derived from peridotite with ^{187}Os/^{188}Os = 0.125 and from pyroxenite with ^{187}Os/^{188}Os ratio indicated in italics (*10*).

Sobolev *et al.* (*8*, *9*) recently proposed that the abundances of Mn and Ni in early-formed olivine crystals in oceanic basalts such as Hawaii and Iceland can provide these estimates. The method makes use of fundamental differences in chemical composition, mineralogy, and melting behavior between recycled (oceanic) crust and mantle. Whereas mantle peridotite invariably contains large proportions of olivine, recycled (eclogitic) crust reacts with the surrounding peridotite and forms an olivine-free hybrid, pyroxenite (*8*). A similar hybrid component, a mixture of ancient recycled crust and peridotites, was also proposed on the basis of Os-He isotope relationships in Icelandic picrites (*6*). Because olivine and pyroxene partition Ni and Mn differently (olivine prefers Ni and pyroxene, Mn), Ni and Mn abundances in equilibrium melts formed from these contrasting lithologies will retain the memory of their respective source compositions. When a source contains both peridotite and pyroxenite, both lithologies contribute to the resulting melt, and their proportions can be reconstructed by using Mn/Fe or Ni/(Mg/Fe) ratios in olivine phenocrysts formed from these hybrid melts.

We combined data for averaged compositions of olivine phenocrysts for olivine-rich lavas and bulk rock ^{187}Os/^{188}Os ratios from Iceland to obtain the proportion of pyroxenite-derived melt by both Ni excesses and Mn deficits in olivine (Fig. 1). These parameters indeed show strong linear correlations, and this permits quantitative assessment of the end-member isotope ratios: peridotitic mantle ($X_{px} = 0$) and pyroxenite from recycled crust ($X_{px} = 1$). The best correlation based on Ni (Fig. 1A) yields a (peridotitic) intercept of ^{187}Os/^{188}Os = 0.126 ± 0.002 (2σ), similar to estimates of present-day oceanic mantle ^{187}Os/^{188}Os = 0.125 (*4*). The calculated isotopic composition of pyroxenite is ^{187}Os/^{188}Os = 0.140 to 0.155. The analogous correlation based on Mn (Fig. 1B) is consistent with this result, although the scatter is slightly greater. These values can be modeled as 1.1- to 1.8-billion-year-old oceanic crust reacted with present-day oceanic peridotite shortly before final melting (*10*). The calculated age range for recycled component in Icelandic mantle is consistent with similar age estimations from Pb isotopes (*11*) and Os and He isotope relationships (*6*). The obtained isotopic compositions of the peridotitic and pyroxenitic components for Iceland also support independently "olivine-based" estimates of source proportions (*9*), as well as the qualitative idea of the presence of ancient recycled materials in Icelandic mantle sources (*5*–*7*, *11*).

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Materials and Methods
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[1] V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, Kosygin Street 19, 119991, Moscow, Russia. [2] Max Planck Institute for Chemistry, Post Office Box 3060, 55020 Mainz, Germany. [3] Institut für Geowissenschaften, Johannes Gutenberg-Universität Mainz, Becherweg 21, 55099 Mainz, Germany. [4] V. S. Sobolev Institute of Geology and Mineralogy, Siberian Branch of Russian Academy of Sciences, Koptuyga prospect 3, 630090, Novosibirsk, Russia.

*To whom correspondence should be addressed. E-mail: sobolev@geokhi.ru

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*To whom correspondence should be addressed. E-mail: sobolev@geokhi.ru

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- Table S1
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Materials and Methods

Samples

All samples are Icelandic picrites and olivine basalts less than about 2 Ma old. Olivine analyses and bulk rock ^{187}Os/^{188}Os ratios are reported for the same samples (8 cases) or for the same localities and flows (7 cases).

Os isotope analyses

Eight samples were newly analyzed for Os concentrations and ^{187}Os/^{188}Os at Max-Planck Institute for Chemistry, Mainz. These measurements were made on bulk rock powder, following the techniques described in *(S1)*. The total procedural blanks for Os were less than 1 pg. The error (2σ) for ^{187}Os/^{188}Os ratio was less than 0.5%.

Proportion of pyroxenite derived melt

The proportion of pyroxenite derived melt in lavas was defined as a function of Mn/Fe of average olivine phenocrysts (*S2*). The relation of this proportion with Ni/(Mg/Fe) of olivine (see Fig. 1 caption) was defined in the same way using olivine-melt Ni partition after Kinzler et al (*S3*).

End-members

Peridotite. The X_{px} = 0 intercepts yield **^{187}Os/^{188}Os = 0.126±0.002** (2σ) for Ni and ^{187}Os/^{188}Os = 0.126±0.004 for Mn estimates and are close to the present-day value for the depleted mantle ^{187}Os/^{188}Os = 0.125 *(S4)*.

Pyroxenite. According to Sobolev et al, 2005 (*S5*), high-Si melt from recycled oceanic crust (in the form of eclogite) reacts with peridotite to produce a hybrid pyroxenite shortly before melting. The amount of melt required to create such pyroxenite is roughly equal to the content of olivine in peridotite (approximately 60%). The Os concentration in eclogite-derived melt has been estimated using 60% degree of melting *(S5)* and (Kd) for Os between restite and melt of 3 (sulfur undersaturated *(S1)*). We assume sulfur undersaturated conditions of melting for eclogites and (later on) pyroxenite because of their high degrees of melting (over 50%) which makes any existence of sulfide melt in the restite highly unlikely. Using these constraints and the compositions of recycled oceanic crust and mantle from Brandon et al, 2007 (*S6*), we obtain an **Os** content for pyroxenite of about **1.33 ppb** (for **3.3 ppb** for **Os** in peridotite). Modeling of melting of these sources yields **Os** concentrations of **0.4 ppb** and **0.7 ppb** for peridotite-derived and pyroxenite-derived melts respectively, assuming degrees of melting of 10-20% for peridotite and 50-60% for pyroxenite and bulk distribution coefficient (Kd) for Os between restite and melt Kd =10 (sulfur saturated) for peridotite and 3 (sulfur undersaturated) for pyroxenite (*S1*). Mixing lines of calculated melts are shown on Fig 1 (for ^{187}Os/^{188}Os = 0.125 of peridotite-derived melt) and ^{187}Os/^{188}Os = 0.140-0.150 of pyroxenite-derived melt).

According to Fig 1A Icelandic Quaternary picrites feature pyroxenitic source with **^{187}Os/^{188}Os = 0.140-0.150** and up to **0.155** if consider linear correlation as an extreme. Using these estimates for pyroxenite Os isotope composition, pyroxenite reaction model (see above) and initial concentrations of Os, Re and Pt in the recycled crust and depleted mantle after Brandon et al, 2007 (*S6*), we obtain recycled crust **ages** of **1.1-1.8 Ga**. These estimates do not depend significantly on Re/Os ratios of lavas and a newly formed reaction pyroxenite because of their young ages.

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Table S1. Average olivine compositions and ^{187}Os/^{188}Os in Quaternary rocks of Iceland

Sample	locality	Lat, Long	n	Fo	Mn/Fe	Ni#	Xpx Mn	±2σ	Xpx Ni	±2σ	Ref1	187Os/188Os	±2σ	Ref2
03-140	Kistufel, MVZ	64°47'51.67"N; 17°12'12.15"W	46	88.55	0.0153	0.069	0.318	0.008	0.288	0.012	*(S6)*	0.13275	0.00047	new
03-137	Kistufel, MVZ	64°47'41.24"N; 17°13'25.06"W	100	88.24	0.0154	0.067	0.294	0.016	0.270	0.009	new	0.13193	0.00023	new
03-122	Skridufel, ERZ	64° 7'3.01"N; 19°56'26.03"W	291	88.98	0.0153	0.076	0.309	0.006	0.368	0.006	new	0.13752	0.00020	new
03-122b	Skridufel, ERZ	64° 7'3.01"N; 19°56'26.03"W	100	87.37	0.0148	0.083	0.410	0.023	0.441	0.018	new	0.13913	0.00022	new
03-122a	Skridufel, ERZ	64° 7'3.01"N; 19°56'26.03"W	97	87.71	0.0150	0.083	0.367	0.019	0.440	0.018	new	0.13879	0.00016	new
03-101	Lagafell, WRZ	63°52'54.42"N; 22°32'28.44"W	51	90.14	0.0160	0.058	0.157	0.011	0.176	0.010	new	0.13163	0.00019	new
03-102	Lagafell, WRZ	63°52'54.36"N; 22°32'36.66"W	51	90.04	0.0161	0.059	0.138	0.017	0.180	0.012	new	0.13254	0.00034	new
Avg (4)	Haleabunga, WRZ	63°48'56.72"N; 22°38'45.72"W	304	90.09	0.0159	0.062	0.197	0.021	0.213	0.004	new	0.13174	0.00046	*(S6)*
Avg (6)	Hengill, Maelifell, WRZ	64° 6'9.45"N; 21°10'30.08"W	443	87.84	0.0156	0.061	0.246	0.018	0.211	0.005	new	0.13296	0.00035	*(S6)*
Avg (6)	Hengill, Midfell, WRZ	64°10'25.52"N; 21° 4'4.83"W	394	88.49	0.0157	0.062	0.270	0.014	0.213	0.007	new	0.13305	0.00020	*(S6)*
Avg (5)*	Borgarhraun, NRZ	65°49'46.10"N; 16°59'48.53"W	118	91.65	0.0161	0.054	0.145	0.020	0.127	0.028	new	0.12800	0.00030	*(S7)*
Avg (5)	Langavitishraun, NRZ	65°56'16.51"N ; 16°52'23.37"W	341	90.15	0.0157	0.057	0.236	0.008	0.167	0.004	new	0.13145	0.00030	*(S7)*
Avg (2)	Storavitishraun, NRZ	65°50'36.81"N ; 17°0'2.47"W	46	85.61	0.0153	0.073	0.313	0.017	0.333	0.007	new	0.13420	0.00030	*(S7)*
01-41	Theistareykirhraun, NRZ	65°57'32.83"N; 17° 4'7.18"W	55	88.63	0.0154	0.074	0.299	0.009	0.340	0.007	*(S6)*	0.13497	0.00061	*(S6)*
01-56-1	Laufrandarhraun, NRZ	65°56'16.62"N; 17° 5'22.46"W	100	89.77	0.0159	0.060	0.186	0.010	0.192	0.010	new	0.13256	0.00024	new

Notes for Table S1. Fo= Mg/Mg+Fe in atomic %, Ni#= NiO/(MgO/FeO) in wt%. Standard error for olivine (σ) – is the standard error of the mean for the number (n) of olivine grains measured for a particular sample or for the shown number of samples. Uncertainty for ^{187}Os/^{188}Os ratios corresponds to the in-run 2-sigma error of the measurement, except for samples from Haleabunga, Hengill and Longavitishraun where the quoted error is the standard error of the mean for the averaged samples. Avg (m) - stands for average of olivine averages from m samples from the same locality, in these cases n indicate total amount of considered olivine grains.

*- for Borgarhraum flow only high –Mg olivine (Fo> 91) was considered for X_{px} calculations because of very early crystallization of clinopyroxene, which leads to significant overestimation of X_{px}. WRZ, ERZ, NRZ – Western, Eastern and Northern rift zones respectively. MVZ - Mid-Icelandic Volcanic Zone. Ref1 - reference for olivine composition; Ref2 - reference for ^{187}Os/^{188}Os data; new - newly analyzed in this work.