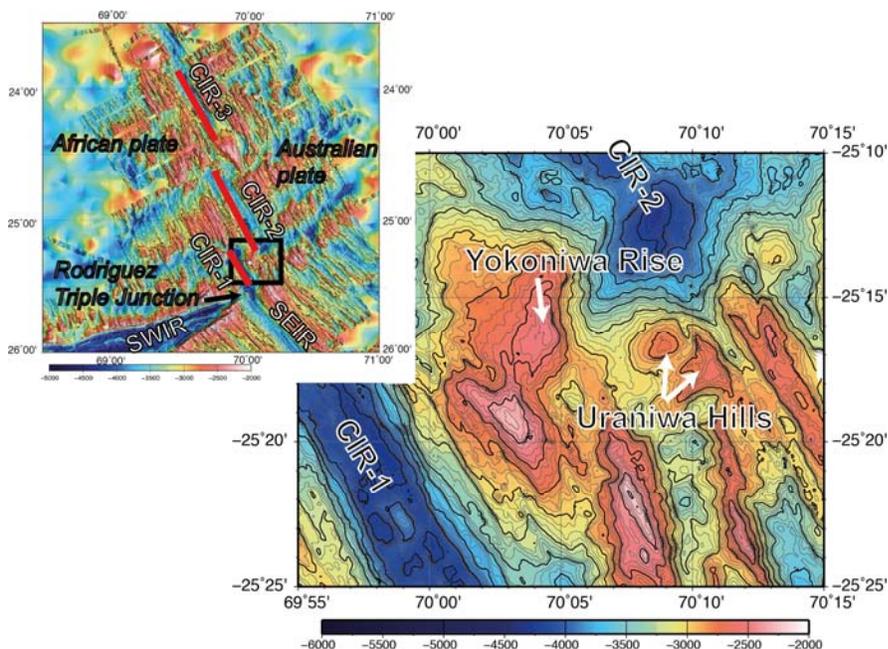


## Rhenium-osmium isotope fractionation at the oceanic crust-mantle boundary

Alessio Sanfilippo, Tomoaki Morishita, and Ryoko Senda

## Sample locations and geographical coordinates

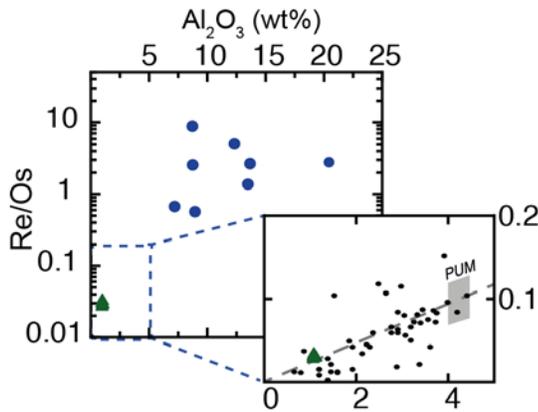


Location of the Uraniwa Hills and Yokoniwa Rise in the southernmost portion of the Central Indian Ridge (CIR). CIR-1; CIR-2 and CIR-3 indicates different segments (see details in Morishita et al., 2015). Note that collected mantle peridotites and troctolites are spatially unrelated.

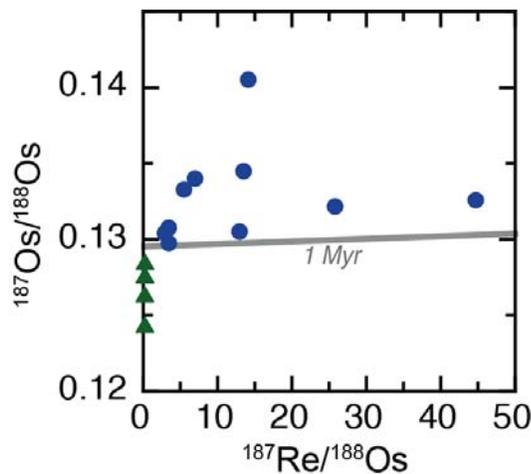
## Sample locations

Sample Name	Area	Cruise ID	Submersible	DiveNo.	Latitude	Longitude	Depth
1170-R01	Yokoniwa Rise	YK05-13_leg3	SHINKAI 6500	1170	-25.2497	70.1021	3420
1170-R20	Yokoniwa Rise	YK05-13_leg3	SHINKAI 6500	1170	-25.2518	70.0821	2783
1170-R25	Yokoniwa Rise	YK05-13_leg3	SHINKAI 6500	1170	-25.2524	70.0783	2635
1176-R09	Yokoniwa Rise	YK05-13_leg3	SHINKAI 6500	1176	-25.2741	70.0857	2763
925-R03	URANIWA-Hills	YK05-16_leg1	SHINKAI 6500	925	-25.2483	70.1504	3556
925-R04	URANIWA-Hills	YK05-16_leg1	SHINKAI 6500	925	-25.2536	70.1499	3338
925-R06	URANIWA-Hills	YK05-16_leg1	SHINKAI 6500	925	-25.2536	70.1499	3338
925-R09	URANIWA-Hills	YK05-16_leg1	SHINKAI 6500	925	-25.2573	70.1500	3190
925-R10	URANIWA-Hills	YK05-16_leg1	SHINKAI 6500	925	-25.2573	70.1500	3190
925-R12	URANIWA-Hills	YK05-16_leg1	SHINKAI 6500	925	-25.2590	70.1499	3168
922-R05	URANIWA-Hills	YK05-16_leg1	SHINKAI 6500	922	-25.3069	70.1660	2837
922-R07	URANIWA-Hills	YK05-16_leg1	SHINKAI 6500	922	-25.3058	70.1645	2712

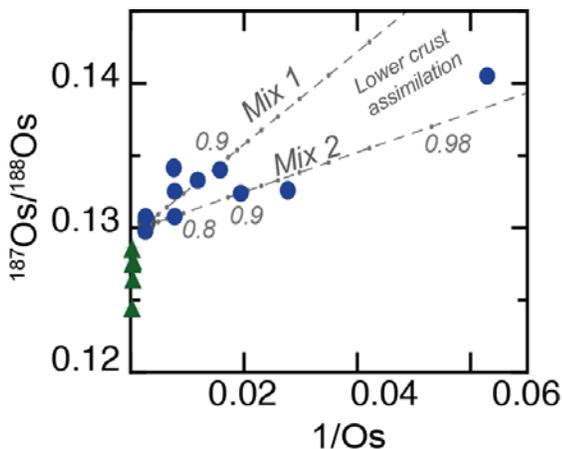
## Additional Figures



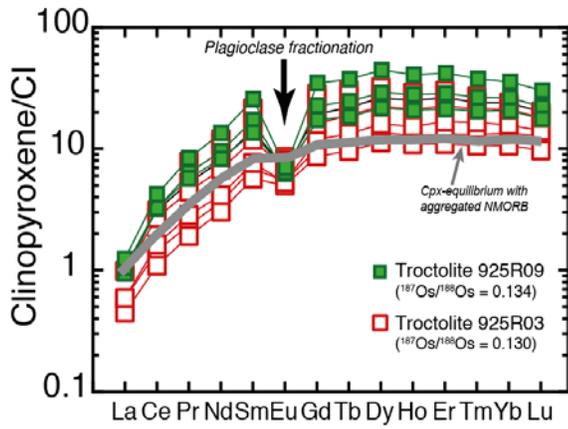
**Figure DR1-**  $\text{Al}_2\text{O}_3$  versus Re/Os variations of CIR-troctolites (blue dots) and harzburgites (green triangle). The inset shows the compositions of the harzburgites compared to peridotites worldwide (green triangles) and primitive upper mantle (PUM) from Becker et al. (2006) and references therein).



**Figure DR2-**  $^{187}\text{Re}/^{188}\text{Os}$  versus  $^{187}\text{Os}/^{188}\text{Os}$  variations of CIR troctolites and harzburgites. The grey line indicates the 1 Ma isochrone (initial  $^{187}\text{Os}/^{188}\text{Os}$  0.129) roughly corresponding to the magnetic age of the Uraniwa Hills (Okino et al., 2015). The plot clearly shows that radiogenic Os cannot have been acquired through  $^{187}\text{Re}$  decay over time. Symbols as Fig. DR1.



**Figure DR3-**  $1/\text{Os}$  versus  $^{187}\text{Os}/^{188}\text{Os}$  ratios. Dashed grey lines represent mixing between mantle melt similar to that crystallizing the most primitive troctolite ( $\text{Os} = 400 \text{ pg/g}$ ;  $^{187}\text{Os}/^{188}\text{Os} = 0.129$ ) and altered lower oceanic crust similar to the Hole ODP 735B gabbros ( $\text{Os} \sim 10 \text{ pg/g}$ ;  $^{187}\text{Os}/^{188}\text{Os} = 0.17\text{-}0.145$ ; Blusztajn et al., 2000). Symbols as Fig. DR1.



**Figure DR4-** REE compositions of clinopyroxenes from two troctolite samples having different Os isotopic ratios (data from Sanfilippo et al., Lithos). The compositions of clinopyroxene at the equilibrium with NMORB were calculated through average NMORB compositions of Hofmann (1988) and clinopyroxene/basalt partition coefficients from Hart and Dunn (1993). Increasing Eu anomaly at increasing REE concentrations is due to plagioclase fractionation.

## Details of analytical methods

### *Re-Os isotopes and Platinum Group Elements*

Osmium isotopes were determined by negative thermal ionization mass spectrometry (N-TIMS) using TRITON (Thermo-Fischer Scientific). Rhenium and PGE concentrations were determined by Q-pole type inductively coupled plasma mass spectrometer (ICP-QMS; Agilent 7700s).

The analytical method used for this study is identical to that reported in Ishikawa et al. (2014). In particular, Carius tube digestion method (Shirey & Walker, 1995), organic extraction method (Roybarman, & Allegre, 1995), micro-distillation method (Cohen and Waters, 1996) and anion exchange method (Pearson and Woodland, 2000) were adopted for Os, PGE and Re extraction with isotope dilution. One gram of whole-rock sample powders combined with enriched isotopes of  $^{99}\text{Ru}$ ,  $^{105}\text{Pd}$ ,  $^{185}\text{Re}$ ,  $^{191}\text{Ir}$ ,  $^{190}\text{Os}$ , and  $^{196}\text{Pt}$  solutions and inverse aqua regia solution (total 10 mL) were sealed in Pyrex glass tubes. The tubes were heated in an oven at  $240^{\circ}\text{C}$  for 72 hours. After heating, carbon tetra chloride was used for extraction of Os from the acid solution three times. Then the Os was back-extracted into HBr and purified by micro-distillation. Purification of Re and other PGE was accomplished by two kinds of anion-exchange column and solvent extraction using N-benzoyl-N-phenylhydroxylamine. Measurements of Os isotopes were done by negative thermal ionization mass spectrometry (N-TIMS) using TRITON (Thermo-Fischer Scientific). Peak jumping method using an axial secondary electron multiplier (SEM) for Os. Analyses of DROsS osmium standard solution (0.2-0.4ng) measured by SEM peak jumping gave  $^{187}\text{Os}/^{188}\text{Os} = 0.16096 \pm 19$  (2SD, n=8). Rhenium and other PGE isotopes were measured by the Q-pole type inductively coupled plasma mass spectrometer (ICP-QMS, Agilent 7700 s), installed in JAMSTEC. Total procedure blanks were  $0.97 \pm 0.28$  pg Os,  $0.39 \pm 0.12$  pg Re,  $1.87 \pm 0.28$  pg Ru,  $68.9 \pm 8.4$  pg Pd,  $0.61 \pm 0.92$  pg Ir, and  $202.5 \pm 63.1$  pg Pt respectively (n=7, 1 standard deviation (SD)). The blank correction for each samples are 0.02~1.6% Ir, 0.02~6.0% Ru, 1.7~60% Pt, and 2.1~54% Pd, respectively, Os and Re data are in the Table DR1. Average of Os isotope ratios of procedural blanks was  $^{187}\text{Os}/^{188}\text{Os} = 0.141 \pm 0.025$ .

As sulfides are the main carrier of PGE, it has been argued that bulk-rock Re-Os isotope compositions of peridotites are affected by the heterogeneous distribution of different sulfides populations at a sample scale (see for instance Alard et al., 2005; Harvey et al., 2006; 2011). To evaluate this possibility, we performed duplicate analysis on two different sample splits for four samples. These duplicates have Re-Os isotopic ratios almost undistinguishable from the original determinations, although they testify a local variability in terms of absolute PGE concentrations (see Table DR1). In addition we analyzed reference materials with our method in parallel to the unknowns. These analyses are furnished in Table DR2 where they are compared with literature data.

#### *Bulk rock major and trace elements*

Bulk-rock major and trace elements analyses were determined at JAMSTEC. The major element compositions were measured by X-ray fluorescence spectrometer (XRF), following the fused glass bead method described in detail by Tani et al. (2006). Trace elements compositions were determined by inductively coupled plasma-mass spectrometry (ICP-MS) using Agilent 7500ce. Sample powders (~50 g) were digested by HF and HClO<sub>4</sub> using the method reported in Nakamura and Chang (2007) and Senda et al. (2014). Compositons are reported in Table DR1.

#### **Additional references (if not cited in the main text)**

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- Tani, K., Kawabata, H., Chang, Q., Sato, K. and Tatsumi, Y., 2006, Quantitative analyses of silicate rock major and trace elements by X-ray fluorescence spectrometer: Evaluation of analytical precision and sample preparation. *Frontier Research on Earth Evolution*, 2 (CD-ROM)

## Reactive crystallization model

The reactive crystallization model (Fig. 1) predicts the Os composition of a mantle derived melt evolving through the preferential assimilation of interstitial radiogenic sulfides and synchronous fractionation of magmatic sulphides (see also Sen et al., 2011). Given the dependence of PGE compositions on the amount of sulfides accumulated in the silicate matrix, this model is used to verify whether increasing  $^{187}\text{Os}/^{188}\text{Os}$  ratios can be acquired by melt-mantle interaction, rather than reproduce the exact Os versus  $^{187}\text{Os}/^{188}\text{Os}$  correlation of our troctolites.

Experimental studies show that Os is mostly partitioned between crystalline sulphides and molten sulphide melt, where immiscible sulfide melt droplets are physically entrained in silicate melt (Ballhaus et al., 2006; Bockrath et al., 2004). Using  $D_{\text{Os}}$  sulphide melt/silicate melt of  $4.8 \times 10^4$  and initial Os composition of (500 pg/g) from Burton et al. (2002) we calculated the Os versus  $^{187}\text{Os}/^{188}\text{Os}$  composition of the melt produced at each step of the reaction. At each step, the initial melt interacts with 1 wt% of peridotite, crystallizing the same amount of silicate phases ( $M_{\text{a}}/M_{\text{c}} \sim 1$ ), in agreement with thermodynamic calculations on melt-mantle reactions (see Kelemen et al., 1997; Collier and Kelemen, 2010) and with our previous study on Uraniwa troctolites (Sanfilippo et al., 2015). Considering a mean  $^{187}\text{Os}/^{188}\text{Os}$  ratios of 0.120 and 0.150 for unradiogenic and radiogenic sulfides in AP (Alard et al., 2005; Harvey et al., 2006; Warren and Shirey, 2012) and supposing that sulfides constitute  $\sim 0.05$  wt% of the rock (Luguet et al., 2003), we assume that radiogenic sulfides of the reacted peridotite ( $^{187}\text{Os}/^{188}\text{Os}=0.1265$ ) constitute  $\sim 0.01$  wt% of the rock mass. Hence, each step of interaction corresponds to assimilation of  $\sim 0.0001\%$  interstitial radiogenic sulfides, followed by the same amount of sulfide segregation. Table DR3 reports the initial parameters and the compositions of the reacting melts. Here follows a brief explanation of the equations used.

*Interstitial sulphides assimilation:*

- The *Os* concentration is given by the mixture between the two end-members (*A*, initial melts and *B*, radiogenic sulphides) calculated as weighted average of the two components.
- The  $^{187}\text{Os}/^{188}\text{Os}$  ratio is calculated based on mixing equations in Faure (1998). Equation 1 describes the variation in the  $^{187}\text{Os}/^{188}\text{Os}$  ratio to be expected in a mixture generated by combining various proportions of *Os* from two different end-members with different  $^{187}\text{Os}/^{188}\text{Os}$  ratios:

$$\left(\frac{^{187}\text{Os}}{^{188}\text{Os}}\right)_{mix} = \frac{a}{[\text{Os}]_{mix}} + b \quad (\text{Eq. 1})$$

The slope of the mixing line is calculated from equation 2:

$$a = \frac{[\text{Os}]_A * [\text{Os}]_B * \left\{ \left(\frac{^{187}\text{Os}}{^{188}\text{Os}}\right)_B - \left(\frac{^{187}\text{Os}}{^{188}\text{Os}}\right)_A \right\}}{[\text{Os}]_A - [\text{Os}]_B} \quad (\text{Eq. 2})$$

and the y-intercept from Equation 3:

$$b = \frac{[\text{Os}]_A * \left(\frac{^{187}\text{Os}}{^{188}\text{Os}}\right)_A - [\text{Os}]_B * \left(\frac{^{187}\text{Os}}{^{188}\text{Os}}\right)_B}{[\text{Os}]_A - [\text{Os}]_B} \quad (\text{Eq. 3})$$

*Magmatic sulphides fractionation:*

- The *Os* concentration of the reacting melt is calculated from Rayleigh equation (Eq. 4) using initial melt *Os* composition and the extent sulphide fractionation (*F*) at each step of the *Interstitial Sulphides Assimilation* process.

$$\text{Os} (\text{react. melt}) = \text{Os} * \frac{1}{(1-F)*(1-D)+D} \quad (\text{Eq. 4})$$