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A Method to Suppress Isobaric and Polyatomic Interferences for Measurements of Highly Siderophile Elements in Desilicified Geological Samples

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Abstract

Sample decomposition using inverse *aqua regia* at elevated temperatures and pressures (e.g., Carius tube

or high pressure asher) is the most common method used to extract highly siderophile elements (HSEs: Ru,

Rh, Pd, Re, Os, Ir, Pt and Au) from geological samples. Recently, it has been recognised that additional

HF-desilicification is necessary to better recover HSEs, potentially contained within silicate or oxide

minerals in mafic samples, which cannot be dissolved solely by inverse *aqua regia*. However, the

abundance of interfering elements tends to increase in the eluent when conventional ion-exchange

purification procedures are applied to desilicified samples. In this study, we developed an improved

purification method to determine HSEs in desilicified samples. This method enables the reduction of the

ratios of isobaric and polyatomic interferences, relative to the measured intensities of HSE isotope masses,

to less than a few hundred parts per million. Furthermore, the total procedural blanks are either comparable

to or lower than conventional methods. Thus, this method allows accurate and precise HSE measurements in mafic and ultramafic geological samples, without the need for interference corrections. Moreover, the problem of increased interfering elements, such as Zr for Pd, and Cr for Ru, is circumvented for the desilicified samples.

Highly siderophile elements (HSEs) are used as important geochemical tracers for understanding fundamental processes such as planetary differentiation, core segregation, late accretion, core-mantle interaction, meteorite impacts, metallogenesis and others. (e.g., Brandon *et al.* 1999, 2006, Becker *et al.* 2001, 2006, Horan *et al.* 2003, Brandon and Walker 2005, Dale *et al.* 2012a, Barnes and Ripley 2016, Becker and Dale 2016, Day *et al.* 2016a, Gannoun *et al.* 2016). Although numerous analytical methods for HSEs have been developed, further improvements in purification procedures have been reported in recent years that allow the collection of highly accurate and precise ICP-MS and TIMS data (e.g., Jarvis *et al.* 1997a, Rehkämper and Halliday 1997, Ely *et al.* 1999, Pearson and Woodland 2000, Meisel and Moser 2004a, b, Qi *et al.* 2004, Shinotsuka and Suzuki 2007, Savard *et al.* 2010, Fischer-Gödde *et al.* 2011, Ishikawa *et al.* 2014, Li *et al.* 2014, 2015, Chu *et al.* 2015a, Day *et al.* 2016b, Ren *et al.* 2016). Quantitative measurements of HSEs are hampered by the following: (1) extremely low abundances (typically < a few ng g^{-1}) in terrestrial rock samples, (2) achieving full sample-spike equilibrium without losing the volatile OsO_4, (3) sample heterogeneity caused by the nugget effect, (4) relatively high contribution of procedural blanks relative to the low HSE mass fractions, and (5) incomplete removal of matrix and isobaric and polyatomic interfering elements. To overcome these difficulties, the Carius tube (CT) method, using inverse *aqua regia*, coupled with the isotope dilution method was employed by most laboratories (e.g., Becker *et al.* 2006, Luguet *et al.*

2007, Shinotsuka and Suzuki 2007, Puchtel *et al.* 2008, Qi and Zhou 2008, Ishikawa *et al.* 2014, Li *et al.* 2014). However, one major potential limitation of the CT method is that inverse *aqua regia* cannot dissolve silicates and oxide minerals containing a small fraction of HSEs. To obtain complete or high recovery of HSEs from geological samples using the CT method, a desilicification step is necessary. Such as step was undertaken by adding HF before or after inverse *aqua regia* decomposition, and its effectiveness has been reported for mafic rock samples (Dale *et al.* 2009, Meisel *et al.* 2009, Ishikawa *et al.* 2014, Li *et al.* 2015, Day *et al.* 2016b). However, some analytical problems arise when applying desilicification. Day *et al.* (2016b) reported that the abundances of interfering elements in the desilicified sample elution were much higher than in the non-desilicified sample elution using an anion-exchange purification procedure. They also pointed out that HF treatment after CT decomposition increased blanks and modified Re/Os and Pt/Os concentration ratios in some analysed basalts. Ishikawa *et al.* (2014) reported that there were no distinguishable differences for interfering elements and blanks between with and without desilicification procedures. Moreover, they discussed the potential problem of Cr oxide for Ru measurement. To effectively suppress interfering elements in desilicified geological samples, the improvement of the purification procedure is a prerequisite for accurate HSE measurement results.

To separate HSEs from other elements in geological samples, previous studies have employed either an anion exchange resin (Jarvis *et al.* 1997b, Pearson and Woodland 2000, Meisel *et al.* 2001, Ishikawa *et al.* 2014, Chu *et al.* 2015a) or a cation exchange resin (Jarvis *et al.* 1997a, Ely *et al.* 1999, Meisel *et al.* 2003a, 2004a, b, Shinotsuka and Suzuki 2007, Fischer-Gödde *et al.* 2011, Li *et al.* 2014). Cation exchange resin has the advantage of a higher recovery of HSEs, when compared with anion exchange resin, but a larger volume of resin is required. The matrix elements can be removed using both types of resin. However, the aforementioned ion-exchange chromatographic methods are, unable to completely separate interfering elements (e.g., Cr, Y, Zr, Hf, Cd, Mo and W) from HSEs for subsequent mass spectrometric measurements. Therefore, several studies employed one or more purification steps (Shinotsuka and Suzuki 2007, Ishikawa *et al.* 2014, Li *et al.* 2014, Chu *et al.* 2015a). In geological samples, the concentrations of interfering

elements are considerably higher than those of HSEs, making it difficult to sufficiently purify HSEs to avoid interferences. Therefore, isobaric and polyatomic interference corrections have been generally applied during mass spectrometric measurements (e.g., Ely *et al.* 1999, Pearson and Woodland 2000, Shinotsuka and Suzuki 2007, Ishikawa *et al.* 2014, Li *et al.* 2014).

In this study, we present a newly developed purification method for HSEs from geological samples using a cation exchange resin (AG50W-X12) and three additional ion-exchange purification steps, following CT decomposition, Os extraction, and HF desilicification. This method allows for the measurement of HSEs without interference corrections for geological samples. Using this improved method, the Ru, Pd, Re, Ir, Pt and Os mass fractions and ^{187}Os/^{188}Os ratios of geological RMs in ultramafic to mafic compositions were evaluated.

Experimental section

All experiments in this study were performed at the Pheasant Memorial Laboratory for Geochemistry and Cosmochemistry (PML), Institute for Planetary Materials, Okayama University at Misasa, Japan.

Reagents and materials

High purity water ($\geq$ 18.2 MΩ cm) was prepared using a Milli-Q system (Merck Millipore, Darmstadt, Germany). For the sample decomposition and purification, TAMAPURE-AA-10 grade 38% HF and 68% HNO$_3$, TAMAPURE-AA-100 grade 30% HCl (Tama Chemicals, Kawasaki, Japan), infinity pure-grade CCl$_4$ (Wako Pure Chemical Industries, Osaka, Japan), and analytical grade 48% HBr (Kanto Chemical, Tokyo, Japan) were utilised. The HBr was further purified twice by distillation, as in Makishima and Nakamura (2001). We employed a HSE mixed spike solution containing ^{101}Ru, ^{105}Pd, ^{185}Re, ^{189}Os, ^{191}Ir and ^{195}Pt enriched isotopes prepared as described by Nakamura *et al.* (2003). The mass fractions of the HSE mixed spike solution were calibrated by the reverse isotope dilution method using the Precious

Metals plasma standard solution from Specpure® (Alfa Aesar, Lancashire, UK; the certified concentrations: 100.0 ± 0.5 µg ml^{-1} of Au, Ir, Os, Pd, Pt, Re, Rh and Ru, are directly traceable to the NIST SRMs). The geological RMs UB-N (serpentinite, CRPG), JP-1 (harzburgite, GSJ), TDB-1 (diabase, CCRMP) (Meisel *et al.* 2003b, Meisel and Moser 2004b), MUH-1 (harzburgite, IAG) and OKUM (komatiitic basalt, IAG) were analysed in this study. The ultramafic RMs UB-N and JP-1 from purchased batches were further pulverised in our laboratory. Of the five RMs, MUH-1 and OKUM are new ultramafic RMs prepared by IAGeo Limited, which have been distributed for interlaboratory comparisons of HSE and Os isotopic compositions (Meisel *et al.* 2013, Meisel and Horan 2016). The major and trace elements were already certified via IAGeo Limited (Burnham *et al.* 2010).

Powdered samples were decomposed with inverse *aqua regia* in a borosilicate CT (2.5 mm thick and 20 cm long main body with 7 cm neck), similar to that described by Shirey and Walker (1995). Before decomposition, the CT was cleaned in detergent (TMSC, Tama Chemicals, Kawasaki, Japan), subsequently rinsed with water and a mixture of 9.5 mol l^{-1} HCl (4 ml) and 16 mol l^{-1} HNO$_3$ (8 ml) was added. The CT was flame-sealed, and finally cleaned at 240 °C for ~ 48 h, following the procedure described by Day and Walker (2015).

Sample decomposition and chemical separation procedures

The workflow of the sample decomposition and subsequent chemical purification procedures is shown in Figure 1. Approximately 1 g of powdered sample, a corresponding weighed amount of HSE mixed spike solution, 2.5 ml of 9.5 mol l^{-1} HCl and 7.5 ml of 16 mol l^{-1} HNO$_3$ were transferred into a pre-cleaned CT, which was then flame-sealed. To reduce the vapour pressure of the reagents and to prevent Os loss, the CT was placed in an ethanol-liquid N$_2$ slush kept at ~ -90 °C during the whole procedure. The CT was placed into a stainless-steel jacket, and heated at 240 °C for 72 h. The stainless-steel jacket was connected to the exhaust post of the laboratory, to prevent leakage of any gas into the oven, which might cause the CT to explode during heating.

After cooling of the CT, the supernatant solution was transferred into a Savillex PFA vial (25 ml vol.). Osmium was extracted from the inverse *aqua regia* by adding 3 ml of CCl_4 and shaking the vial (Cohen and Waters 1996, Shen *et al.* 1996), and then back-extracted from CCl_4 into 4 ml of 8.8 mol l^{-1} HBr. To achieve high recovery of Os, this process was repeated three times. The HBr solution (4ml) was pipetted from CCl_4 into a PFA vial (7 ml vol.) and dried at 100 °C. Finally, Os was purified by microdistillation (Birck *et al.* 1997). The Os-bearing residue was added to 20 µl of H_2SO_4-CrO_3 solution (8% *m/v* of CrO_3 solution in 12 mol l^{-1} H_2SO_4) in the cap of a conical PFA vial (5 ml vol.). Osmium was vaporised and trapped into 20 µl of 8.8 mol l^{-1} HBr placed in the tip of the conical vial.

The Os-extracted inverse *aqua regia* solution, with or without an insoluble residue, was used for quantitative treatment of Ru, Pd, Re, Ir and Pt. For the desilicification procedure, the residue in the CT was mixed with the Os-extracted inverse *aqua regia* solution in a PFA vial (25 ml vol.), and then centrifuged. After removing the supernatant solution, the residue was digested in 5 ml of 20 mol l^{-1} HF (Ishikawa *et al.* 2014). The HF solution and the supernatant solution were dried at 120 °C, and both fractions were then again dissolved with 6 mol l^{-1} HCl and dried at 120 °C, repeating this procedure three times. Finally, the two solutions were mixed and dried down at 100 °C. For the non-desilicification procedure, only the Os-extracted inverse *aqua regia* solution was used for mass spectrometric measurement.

Purification of the HSE-bearing solution, to remove matrix elements and interfering elements, was performed in four steps of the ion chromatographic separation procedure, which is summarised in Table 1. The digested sample fraction, dissolved in 10 ml of 0.5 mol l^{-1} HCl was loaded onto a Bio-Rad polypropylene column (Econo-Pac® Chromatography column with 20 ml bed volume and a 10-ml reservoir), which was packed with Bio-Rad AG®50W-X12 resin (200-400 mesh) (Bio-Rad Laboratories, Hercules, CA, USA). The HSE-rich solution, eluted with 0.5 mol l^{-1} HCl, was evaporated to near dryness and again dissolved in 0.5 mol l^{-1} HCl. The solution was then loaded onto a custom-made low-density polyethylene (LDPE) column (0.5 ml bed volume and a 3-ml reservoir), packed with Eichrom-LN resin

(100–150 µm) (Eichrom Technologies, Lisle, IL, USA) to separate Y, Zr and Hf. The HSE-rich fraction was eluted with 0.5 mol l^{-1} HCl and evaporated to near dryness, then dissolved in 0.5 mol l^{-1} HNO$_3$. The HNO$_3$ solution was subsequently loaded onto a custom-made LDPE column (0.1 ml bed volume and a 3-ml reservoir), packed with Bio-Rad Chelex®100 resin (200–400 mesh) to separate the remaining Zr and Cd ions from Pd. Using Chelex100 resin, Ru-Re-Ir-Pt-rich and Pd-rich fractions were eluted with 0.5 mol l^{-1} HNO$_3$ and 8 mol l^{-1} HCl, respectively. The Ru-Re-Ir-Pt-rich fraction was evaporated to near dryness at 100 °C and dissolved in 0.5 mol l^{-1} HNO$_3$, which was further purified to remove Cr, using a custom-made LDPE column (0.3 ml bed volume and a 3-ml reservoir), packed with Bio-Rad AG®50W-X8 resin (200–400 mesh).

The recovery yields of HSEs and interfering elements after each ion chromatography step were examined using matrix-containing synthetic samples. The matrix powder, ultramafic-mafic in composition (SiO$_2$ = 46.3, TiO$_2$ = 1.2, Al$_2$O$_3$ = 7.1, Fe$_2$O$_3$ = 11.5, MgO = 25.3, CaO = 5.1, Na$_2$O = 1.1, and K$_2$O = 0.4 g 100g^{-1}) was prepared using chemical reagents (amorphous SiO$_2$, Ti solution in 5% HNO$_3$, Al solution in 5% HCl, Fe$_2$O$_3$, MgO, CaCO$_3$, NaCl, and KNO$_3$). For the recovery experiments concerning HSEs and interfering elements, a mixture of ~ 100 ng of HSEs dissolved in HCl and a mixture of ~ 2500 µg of Cr, ~ 50 µg of Y, ~ 200 µg of Zr, ~ 500 ng of Cd and ~ 5µg of Hf dissolved in HCl were mixed with ~ 1 g of matrix powder, respectively. Recovery experiments were performed for both desilicification and non-desilicification procedures using the aforementioned two sets (i.e., HSEs and interfering elements) of starting materials. After decomposing the starting materials by inverse *aqua regia*, each set of samples was added to 5 ml of 20 mol l^{-1} HF and re-dissolved by 6 mol l^{-1} HCl for the desilicification procedure. For the non-desilicification procedure, each set of samples was only treated with 6 mol l^{-1} HCl. Then, each sample was treated using the same procedures as for the RMs. Finally, each sample solution was eluted following the procedures shown in Table 1. The recovery yields of HSEs and interfering elements after each ion chromatography step were determined by isotope dilution and calibration curve methods, respectively.

Mass spectrometric measurements

Ruthenium, Pd, Re, Ir and Pt intensities were measured using ICP-MS (ThermoScientific Element XR), and Os isotope ratios were measured as OsO_3^- by TIMS (ThermoFinnigan TRITON). The ICP-MS measurements were performed using three analytical protocols: Ru-Ir-Pt, Re, and Pd analyses. Among these protocols, Ru-Ir-Pt and Pd fractions were measured with dry plasma using a desolvating nebulizer system (CETAC Aridus II^{TM}). For the Re measurements, a wet plasma was used because it is more effective in eliminating the memory effect as described by Fischer-Gödde *et al.* (2011). The desolvating nebulizer system effectively increases the intensities of target elements with decreasing interference oxide intensities for: $^{53}Cr^{16}O_3^+$ on $^{101}Ru^+$, $^{89}Y^{16}O^+$ on $^{105}Pd^+$, $^{90}Zr^{16}O^+$ on $^{106}Pd^+$, $^{177}Hf^{16}O^+$ on $^{193}Ir^+$, $^{178}Hf^{16}O^+$ on $^{194}Pt^+$, and $^{179}Hf^{16}O^+$ on $^{195}Pt^+$. The monitored mass to charge ratio (m/z) of the analytes and interferences for the Ru-Ir-Pt and Re fractions are m/z 53 (Cr), 99 (Ru), 101 (Ru), 178 (Hf), 185 (Re), 187 (Re), 188 (Os), 191 (Ir), 193 (Ir), 194 (Pt), 195 (Pt), and for the Pd fraction are m/z 89 (Y), 90 (Zr), 105 (Pd), 106 (Pd), 112 (Cd) (Table 2). The CrO_3^+/Cr^+, YO^+/Y^+, ZrO^+/Zr^+ and HfO^+/Hf^+ ratios were monitored using 200 ng g^{-1} of Cr solution, 1 ng g^{-1} of Y solution, and 20 ng g^{-1} of a Zr and Hf mixed solution dissolved in 0.5 mol l^{-1} HNO$_3$, which was prepared from commercially-available 100–1000 μg g^{-1} standard solutions. When using a desolvating nebulizer system, the production of oxide species was typically ~ 0.1% for $^{89}Y^{16}O^+/^{89}Y^+$ and $^{90}Zr^{16}O^+/^{90}Zr^+$, ~ 0.02% for $^{178}Hf^{16}O^+/^{178}Hf^+$, and the intensity of $^{53}Cr^{16}O_3$ was under the detection limit (< 50 cps). All measurements were performed in pulse-counting mode and low resolution mode with intensities < 5–6 × 10^6 cps.

For Os isotope measurements, purified Os was loaded on Pt filaments (0.5 mm × 0.025 mm; purity 99.999% m/m; H.Cross Company, Moonachie, USA) which had been cleaned previously with 16 mol l^{-1} HNO$_3$ and baked in air at 3 A for 2 min. Os dissolved in 8.8 mol l^{-1} HBr was loaded slowly onto the filament and covered with 0.5 μl of a Ba(OH)$_2$-NaOH activator (Creaser *et al.* 1991, Völkening *et al.* 1991) and subsequently heated in air under a heat lamp.

A gain calibration of the amplifiers was performed at the beginning of every daily measurement session. Oxygen gas was bled into the ion source, maintained at $\sim 3 \times 10^{-5}$ Pa during measurements. Employing a static multi-ion-collection mode using Faraday cups with 10^{11} Ω amplifiers, $^{184}Os^{16}O_3^-$ (10^{12} Ω), $^{186}Os^{16}O_3^-$, $^{188}Os^{16}O_3^-$, $^{189}Os^{16}O_3^-$, $^{190}Os^{16}O_3^-$ and $^{192}Os^{16}O_3^-$ were simultaneously measured. These signals were collected over 10 blocks of 10 cycles with an 8 s integration time and a 3 s idle time. When measuring low quantities of Os (< 1 ng), a secondary electron multiplier (SEM) in peak-jumping mode was applied. The measurement in peak-jumping mode consisted of five blocks with ten cycles per block, each cycle containing six masses including $^{192}Os^{16}O_3^-$, $^{190}Os^{16}O_3^-$, $^{189}Os^{16}O_3^-$, $^{188}Os^{16}O_3^-$, $^{187}Os^{16}O_3^-$ and $^{186}Os^{16}O_3^-$, with integration times of 2, 1, 2, 4, 8 and 2 s, respectively. The idle time was 3 s for mass 240 and 0.5 s for all other masses. Interfering ions ($^{196}Pt^{16}O^{2-}$, $^{198}Pt^{16}O^{2-}$, $^{183}W^{16}O^{3-}$, $^{185}Re^{16}O^{3-}$, $^{194}Pt^{16}O^{3-}$) were measured in peak-jumping mode using a 4 s integration time for one block of ten cycles, before and after Os measurements, and the time-drifted interference intensities were used for Os data reduction.

Data reduction was performed in the following order on the raw data: correction for interferences, oxygen correction using $^{17}O/^{16}O$ and $^{18}O/^{16}O$ ratios measured during each analytical session, spike reduction, and instrumental mass fractionation correction using $^{192}Os/^{188}Os = 3.083$ (Nier 1937) via the exponential law. The $^{17}O/^{16}O$ and $^{18}O/^{16}O$ ratios were determined in-run measurements on masses 236 ($^{188}Os^{16}O_3^-$), 238 ($^{190}Os^{16}O_3^-$), 239 ($^{190}Os^{16}O_2^{17}O^-$), 240 ($^{192}Os^{16}O_3^-$), 241 ($^{192}Os^{16}O_2^{17}O^-$) and 242 ($^{192}Os^{16}O2^{18}O^-$), similar to those described by Luguet *et al.* (2008). The $^{186}Os/^{188}Os$, $^{187}Os/^{188}Os$ and $^{190}Os/^{188}Os$ ratios for DROsS (Durham *Romil* Osmium Standard supplied by *IAGeo Limited*) yielded 0.11994 ± 0.00006 (0.52‰), 0.16092 ± 0.00005 (0.31‰) and 1.98381 ± 0.00010 (0.05‰), respectively, using 50 ng of Os measured in static mode (2 s and 2 RSD, n = 20); 0.11993 ± 0.00018 (1.5‰), 0.16091 ± 0.00012 (0.78‰) and 1.98385 ± 0.00020 (0.10‰), respectively, using 1 ng of Os by static mode (2 s and 2 RSD, n = 21); and 0.11983 ± 0.00097 (8.1‰), 0.16079 ± 0.00029 (1.8‰) and 1.98451 ± 0.00377 (1.9‰), respectively, using 0.1 ng of Os by a peak-jumping mode (2 s and 2 RSD, n = 12). These results agreed well with the previously published data for the same material (Luguet *et al.* 2008, Wittig *et al.* 2010, Liu and Pearson 2014, Chatterjee and Lassiter 2015, Chu *et al.* 2015b).

Results and discussion

Chemical separation of HSEs

Step 1, AG50W-X12 resin: Most studies that separate matrix elements from HSEs by cation-exchange chromatography used AG50W-X8 resin (e.g., Meisel *et al.* 2003a, Shinotsuka and Suzuki 2007, Fischer-Gödde *et al.* 2011, Li *et al.* 2014). In this study, we selected an AG50W-X12 resin because it has a greater cation capacity than AG50W-X8. HSE elution curves using 3 ml of AG50W-X8 and -X12 were compared. Although X12 recorded larger tailing for Pt and worse separation of the interfering element Cr than X8, it was able to reduce the tailing of Ru and more effectively separate the interfering elements Zr, Hf and Cd (Figure 2). Theoretically, >11 ml (calculation based on ion exchange capacity) of AG50W-X12 resin is necessary to retain all cations in an appropriate bearing solution for ~ 1 g of natural silicate rock, ranging in composition from rhyolite to peridotite. In this study, we used 20 ml of resin to avoid the breakthrough of cations (Table 1). The recovery yields of HSEs after the first column were also examined by a calibration curve method using a non-matrix containing synthetic sample (i.e., HSE synthetic solution was prepared from the Precious Metals plasma standard solution). The recoveries of HSEs from both matrix bearing and non-matrix bearing synthetic samples did not change significantly, resulting in > 92% (Figure 3) and > 95% yields, respectively, while the major cations were reduced to almost negligible amounts. Figure 3 shows that there were no significant differences with regard to the recoveries of interfering elements in the HSE cut between desilicified and non-desilicified matrix-containing synthetic samples: ~ 6% for Cr, < 0.2% for Y, ~ 5–8% for Zr, ~ 21–23% for Cd, and ~ 1–6% for Hf. The cation exchange resin retains Cr^{3+}, mainly forming $Cr(H_2O)_6^{3+}$, but it cannot adsorb Cr^{6+} mostly present in anion complexes such as $Cr_2O_7^{2-}$ or CrO_4^{2-} (Korkish 1989). Therefore, it is important to suppress the formation of Cr^{6+} in sample solution to retain Cr in the cation exchange resin. The Cr concentration in HSE-bearing solution significantly increased when the sample solution dissolved in HCl was evaporated at >110 ˚C. Thus, the evaporation temperature was set at 100 ˚C before sample loading. The majority of Cr was separated from HSEs through the first column, and further separation of Cr was achieved at the final purification step, as we will discuss in a later section.

Step 2, LN resin: Molecular interferences of ZrO^+ and HfO^+ are significant for Pd and Ir-Pt, respectively, because of the elevated Zr/Pd, Hf/Ir and Hf/Pt ratios in terrestrial rock samples. To separate Zr and Hf from HSEs, LN resin was used because it can selectively retain Zr and Hf chloro-complexes (Münker *et al.* 2001). Calculations of the distribution coefficient (K_d) for the distribution of HSEs, Zr and Hf between LN resin and 0.5 mol l^{-1} HCl using batch method (Table 3) yielded extremely high K_d values for Zr and Hf ($> 10^6$) and low values for HSEs (< 2 for Ru, Pd, Ir and Pt and 11 for Re). This suggests that a low molarity of HCl effectively separates Zr, Hf and Y ($K_d = \sim 500$) from HSEs. The recoveries of HSEs after the second column were ~ 83–96% and ~ 90–100% from desilicified and non-desilicified matrix-containing synthetic samples, respectively. Interfering elements Zr and Hf were completely removed by LN resin for the non-desilicified matrix-containing synthetic sample. However, $\sim 6\%$ of Zr and $\sim 3\%$ of Hf remained in HSE cut for the desilicified matrix-containing synthetic sample (Figure 3). This reveals that fluoro-complexes of Zr and Hf, which are more stable than chloro-complexes of these elements (Makishima *et al.* 2009), remained in the solution even after repeated addition of HCl. Because the K_d values of Zr, Hf and HSEs are nearly identical between LN resin and 0.5 mol l^{-1} HF, it is difficult to separate these elements by the second column (Table 3). Pearson and Woodland (2000) also mentioned the hardness to separate fluoro-complexes of Zr and Hf from HSEs using common anion exchange resin AG1-X8. Although using diluted HF to remove Zr and Hf as much as possible, several amounts of these stable anionic fluoro-complexes were still strongly retained with HSEs in AG1-X8 resin, thus leading to severe oxide interferences especially on Pd in some cases (e.g., low Pd concentrations in Zr-rich terrestrial rocks) (Table 2). On the other hand, the first and second columns effectively separated Y from the HSE cut for the desilicified matrix-containing synthetic sample ($\sim 0.2\%$ and $< 0.01\%$ after first and second columns, respectively), because of the higher K_d for Y between LN resin and 0.5 mol l^{-1} HF than for HSEs (Table 3). Nearly all Cr and Cd were eluted in the HSE cut for both desilicified and non-desilicified matrix-containing synthetic samples during the second column (Figure 3).

Step 3, Chelex 100 resin: Chelex 100 resin is an organic ion exchanger containing weakly acidic iminodiacetic functional groups with strong chelating properties, and forms chelate complexes with numerous metal cations. The actual form of the functional group when acting as a cation exchanger or anion exchanger depends on the pH of the medium. In this study, Chelex 100 resin was conditioned in an acidic medium. The K_d values of the target elements with various reagents are shown in Table 3. The elution profiles of LN resin and Chelex 100 resin using ~ 1 g of desilicified TDB-1 are shown in Figure 4a–b. The elution profiles of Hf and Y are not shown in Figure 4a–b, because the quantities of Hf and Y in the loading solution were reduced to almost negligible levels (< 100 pg) in the HSE cut after the second column (Figure 4a). The behaviour of Hf and Y is similar to that of Zr, as suggested by the K_d values of these elements between Chelex 100 resin and 0.5 mol l^{-1} HNO_3 and HF (Table 3). Figure 4b shows that interfering elements Zr and Cd were eluted with Ru-Re-Ir-Pt cut by 0.5 mol l^{-1} HNO_3, whereas Pd was retained in Chelex 100 resin, which was collected by 8 mol l^{-1} HCl. Thus, the third column could effectively remove the Zr fluoro-complex and Cd from Pd. Figure 3 indicates that nearly 100% of Ru, Re, Ir and Pt were eluted for the non-desilicified matrix-containing synthetic sample through the third column. However, recoveries of Ru, Re, Ir and Pt for the desilicified matrix-containing synthetic sample were ~ 63–80%. This might be attributed to the presence of fluoro-complexes of HSEs in the loading solution, because K_d values of HSEs between Chelex 100 resin and 0.5 mol l^{-1} HF are higher than those for 0.5 mol l^{-1} HNO_3 (Table 3). The recoveries of Pd for both desilicified and non-desilicified matrix-containing synthetic samples reveal that ~ 20 % of the loaded Pd were retained in the third column, which could occur due to a strong affinity of Pd in anionic form to Chelex 100 resin.

Our results indicate that it is better to minimise the formation of fluoro-complexes prior to the use of the second and third columns, in order to enhance recoveries of HSEs and remove Hf. Figure 3 shows that recovery of Hf in the Ru-Re-Ir-Pt cut after the third column for the desilicified matrix-containing synthetic sample was ~ 3% while that of the desilicified TDB-1 was almost negligible. The difference of recovery between matrix-containing synthetic sample and RM could be caused by the desilicification procedure. For

TDB-1, desilicification was only performed for the residue after inverse *aqua regia* decomposition, whilst it was performed for both the supernatant solution and residue for matrix-containing synthetic sample. We also found that the recovery of Hf in the Ru-Re-Ir-Pt cut increased when desilicification was performed for both solution and residue for TDB-1, following inverse *aqua regia* decomposition. Therefore, HF-desilicification was only applied for the sample residue for geological RMs.

[Insert Figure 4a-b]

Step 4, AG50W-X8 resin: It was found that ~ 6% of Cr still remained in both desilicified and non-desilicified matrix- containing synthetic samples after the third column (Figure 3). Ru concentrations in terrestrial rock samples are much lower than Cr concentrations (typically Cr/Ru > 400,000 for basalt and peridotite) and the Cr/Ru ratio might possibly increase during HF desilicification, as Cr is hosted in silicates or oxide minerals in rocks. Therefore, it would be advisable to further reduce Cr concentration, because Cr multi-oxide probably interferes with Ru in terrestrial rock samples, when no further purification is conducted. Figure 5 shows the elution profiles of HSEs and the interfering element Cr using 0.3 ml of AG50W-X8 resin. In this study, ~ 60–85% of Ru, Re, Ir and Pt were collected, and > 99% of Cr was removed for both desilicified and non-desilicified matrix-containing synthetic samples after the final column (Figure 3), which was modified from the method in Yamakawa *et al.* (2009).

Recovery yields of HSEs, interfering elements, and blanks

The recovery yields of HSEs from RM UB-N determined by a calibration curve method, both with and without desilicification, were ~ 60–80% for Ru, Re, Ir and Pt and ~ 80–90% for Pd, which is almost consistent with the results determined by matrix-containing synthetic samples (Figure 3). Several studies previously reported the recoveries of HSEs from geological RMs. Using an anion exchange resin, variable yields (~ 30–90%) of HSEs from mafic and ultramafic RMs were reported by Pearson and Woodland (2000) and Chu *et al.* (2015a). Using a cation exchange resin, Shinotsuka and Suzuki (2007) showed ~ 70–90% of

HSEs for TDB-1 and JP-1. Therefore, the recovery yields achieved in this study were comparable to or better than those reported in the previous studies.

Table 4 shows the ratios of interference intensities relative to the measured intensities of HSE isotope masses during ICP-MS measurement for RMs. The ratios were negligible, as follows: < 1 parts per million (ppm) for $^{53}Cr^{16}O_3^+$ on m/z 101 (Ru) and for $^{89}Y^{16}O^+$ on m/z 105 (Pd), < 2 ppm for $^{178}Hf^{16}O^+$ on m/z 194 and for $^{179}Hf^{16}O^+$ on m/z 195 (Pt), and < 26 ± 20 ppm for $^{177}Hf^{16}O^+$ on m/z 193 (Ir). The sum of $^{106}Cd^+$ and $^{90}Zr^{16}O^+$ exceeded 100 ppm (23–249 ppm) for m/z 106 (Pd), which despite no interference correction, did not affect the result. Therefore, it is concluded that no interference correction is necessary for Ru, Pd, Re, Ir and Pt measurements in our analytical method. Because this method can effectively purify Pd with high recovery (~ 80–90%), it has great potential for application to precise Pd isotope analysis.

Total procedural blanks of HSEs (n >10) were 0.9–2.5 pg for Ru, 8.8–25 pg for Pd, 0.01–0.5 pg for Re, 0.05–0.4 pg for Ir, 1.2–18 pg for Pt and 0.9–3.9 pg for Os. Figure 6 shows the comparison of the total procedural blanks in this study with those previously published. The mean values of the Re, Ir and Pt blanks tended to be somewhat lower than those obtained by both CT and high pressure asher (HPA) methods. The main source of Pd in the blank from this study could have come from Chelex 100 resin. This is similar behaviour to that reported in the studies that used an anion exchange resin such as AG1X-8, which contains considerable amounts of Pd (e.g., Pearson and Woodland 2000). Therefore, minimising the contamination of resin blanks using sufficient cleaning procedures is important to keep consistent blank levels (e.g., Becker *et al.* 2006, Ishikawa *et al.* 2014). In this study, the proportions of HSEs in blanks were 0.8–3.5% for Os and < 1% for other HSEs for TDB-1; 0.8–2% for Pd, 0.02–1.3% for Re and < 1% for other HSEs for JP-1; and < 1% for all HSEs for UB-N, MUH-1 and OKUM. Although the proportions of blanks were low, all mass fractions and isotopic compositions were blank-corrected based on the measurement of blanks that were undertaken along with the measurement of the samples.

HSE mass fractions and Os isotope ratios of reference materials

The HSE mass fractions and Os isotope ratios of RMs UB-N, JP-1, MUH-1, OKUM and TDB-1 were determined by our analytical method (Table 5 and 6). The primitive upper mantle (PUM)-normalised HSE patterns for these RMs are shown in Figure 8.

UB-N: This reference material a serpentinised fertile lherzolite, is recognised as a relatively homogeneous ultramafic RM for HSE analysis (Meisel and Moser 2004b), and has been determined by many laboratories. All HSE mass fractions determined in our study showed no considerable differences between desilicification and non-desilicification procedures, within a 1s intermediate precision (Table 5 and Figure 8). The Ru, Pd and Ir mean mass fractions were in good agreement with the range of the published data (Figure 7a). The deviations of their mean mass fractions from the published data were < 10%. The Re and Pt mean mass fractions were relatively more variable (the discrepancy for Re and Pt was > 15%) between laboratories, especially for those showing > 100% higher intermediate precision values than those in our study, such as Re (0.210 ± 0.018 ng g^{-1}, 1s and n = 9) in CT data (Ishikawa *et al.* 2014) and (0.201 ± 0.012 ng g^{-1}, 1s and n = 8) in HPA data (Fischer-Gödde *et al.* 2011), and Pt (8.07 ± 1.17 ng g^{-1}, 1s and n = 6) in CT data (Luguet *et al.* 2007) (Figure 7a). The high variances of the Re and Pt measurement results may be due to other artificial effects other than lab bias. It should be noted that UB-N is distributed only in course grained batches, and powders are presumably further pulverised among independent laboratories. It was observed that Cr concentrations vary systematically from batch to batch, possibly causing the differences in HSE concentrations (Meisel and Horan 2016). The Os mean mass fraction (Note that Os mass fraction and $^{187}Os/^{188}Os$ ratio data were collected prior to desilicification and thus no desilicified data are presented in Figure 7a–c) was < 15% lower than the published mean values. The mean $^{187}Os/^{188}Os$ ratio fell within the range of the previously reported data (Figure 7a). The reproducibility of $^{187}Os/^{188}Os$ ratios (0.48% RSD) was comparable to that of Ishikawa *et al.* (2014), but slightly worse than other previous studies. The Ru, Ir and Os (5.0–13.6% RSD) were more heterogonous than Pt, Pd and Re (1.8–5.2% RSD) in UB-N (Table 5), which may be due to the nugget effect at the ~ 1 g test portion size used in this study. On the other hand,

Ru, Ir and Os may also reside in alloys or laurite (Ru, Os, Ir)S_2, which are difficult to digest in both *aqua regia* and HF (Meisel *et al.* 2003a, b).

JP-1: This is a highly depleted harzburgite, which has been used as an ultramafic RM for HSE analysis in a very limited number of studies (e.g., Meisel and Moser 2004b, Ishikawa *et al.* 2014). Our results did not display systematic differences between the data for the desilicified and non-desilicified samples, within a 1*s* intermediate precision (Table 5 and Figure 8). The Pd, Pt, and Os mean mass fractions were in good agreement with the range of the previously reported data (Figure 7b). The desilicified mean mass fraction of Ir also fell within the range of data reported in the literature, but the non-desilicified value did not. Both desilicified and non-desilicified mean mass fractions of Ru were lower than the literature values. The Re mean mass fractions with and without desilicification were consistently ~ 20% higher compared with the published data, except for that reported by Meisel and Moser (2004b), which was one order of magnitude higher and with a large intermediate precision (0.29 ± 0.36 ng g^{-1}, 1*s* and *n* = 9) (Figure 7b). The reason for the significant variance of Re values is uncertain. It may reflect the nugget effect. The mean $^{187}Os/^{188}Os$ ratio was only ~ 0.25% lower than that reported by Ishikawa *et al.* (2014). Our Pd and Re data (6.8–12% RSD) were more reproducible than Ru, Ir, Os and Pt data (15–27% RSD) (Table 5). The large variations in Ru, Ir, Os and Pt data may result from the retention of these elements by the refractory laurite and Pt-rich alloy phases distributed in JP-1. The inclusion of a desilicification step for UB-N and JP-1 did not yield any major differences when compared with non-desilicified data, as demonstrated by our results. A similar finding was reported by Meisel *et al.* (2003b) and Ishikawa *et al.* (2014).

MUH-1: The HSE mass fractions of ultramafic RM MUH-1 (a depleted harzburgite) showed no significant differences between those involving desilicification and non-desilicification procedures (Figure 8). Thus, desilicification is not necessary for HSE extractions from MUH-1. The Re mean mass fraction for desilicified samples was < 8% higher than that for non-desilicified samples within a 1*s* intermediate precision (Table 5), the reason for which remains obscure. The minor bias was not expected to be the effect

of desilicification, as some measured quantity values for non-desilicified samples overlapped with the range of the desilicified values.

OKUM: The ultramafic RM OKUM (a komatiite) displayed systematically higher mass fractions of Ru, Ir and Pt in desilicified samples than those in non-desilicified samples, while the mass fractions of Pd and Re were identical among these samples (Table 6 and Figure 8). Moreover, the desilicified mean mass fractions of Ru, Ir, and Pt were higher than non-desilicified values by ~ 11%, ~ 24%, ~ 13%, respectively. The Pd and Re mean mass fractions with and without desilicification, were in good agreement with the range of non-desilicified HPA data reported by Savard *et al.* (2010) (Pd = 12.20 ± 6.0% RSD; Re = 0.566 ± 6.3% RSD) and Wang and Becker (2014) (Pd = 11.8 ± 4% RSD; Re = 0.4 ± 21% RSD). However, the desilicified mean mass fractions of Ru (4.39 ± 1.2% RSD), Ir (0.951 ± 9.3% RSD) and Pt (11.5 ± 1.7% RSD) seemed more consistent with HPA data from both Savard *et al.* (2010) (Ru = 4.15 ± 2.0% RSD; Ir = 0.943 ± 3.9% RSD; Pt = 11.44 ± 1.9% RSD) and Wang and Becker (2014) (Ru = 4.44 ± 2% RSD; Ir = 0.897 ± 8% RSD) (Table 6). This could be explained by incomplete digestion of OKUM by the CT method used in this study (i.e., Ru, Ir and Pt may be released more completely from the sample matrix at elevated temperatures with prolonged heating, even without HF treatment). Nevertheless, desilicification is somewhat useful to liberate Ru, Ir and Pt from sample residues following CT decomposition. Furthermore, it should be noted that Pt (46% RSD) and Os (97% RSD) in OKUM reported by Wang and Becker (2014) were particularly heterogeneous (at 0.5–1 g test portion size), which demonstrates that Pt and Os concentrations may be significantly influenced by the nugget effect. The variance of Os data was also observed in our study, but they were more reproducible (15% RSD). As shown in Figure 8, it is evident that the homogeneity of HSEs in harzburgites JP-1 and MUH-1 are generally much worse than those in lherzolite UB-N and komatiite OKUM, due to the nugget effect. Most of the HSEs in harzburgite are hosted in difficult to digest minerals such as laurite and alloys, which increases sample heterogeneity, whereas the dominant HSE-bearing phases in lherzolite and komatiite are base metal sulfides (Meisel *et al.* 2013).

TDB-1: This mafic RM, a diabase, is a widely used for HSE measurements (e.g., Meisel and Moser 2004a, b, Ishikawa *et al.* 2014). Our results demonstrate that the mean mass fractions of Ru and Re from the desilicification procedure were higher than those from the non-desilicification procedure, by ~ 30% and ~ 10%, respectively, while the mean mass fractions of Pd, Ir and Pt were identical between these two procedures, within a 1*s* intermediate precision (Table 6 and Figure 8). The problems of incomplete recovery of HSEs in TDB-1 during acid digestion have been pointed out elsewhere (e.g., Dale *et al.* 2009, Meisel *et al.* 2009). Dale *et al.* (2012b) showed the efficient extraction of Ru and Re from TDB-1 using HF-desilicification following HPA decomposition. Ishikawa *et al.* (2014) examined the effectiveness of different digestion methods and conditions on HSE extractions in TDB-1. Both Ishikawa *et al.* (2014) and Meisel and Horan (2016) concluded that Re in TDB-1 could be completely extracted from the sample matrix at elevated temperatures over prolonged heating in *aqua regia*, even without additional desilicification. By contrast, the full extraction of Ru was dependent on HF treatment. Therefore, the result of the higher desilicified Ru and Re values, relative to non-desilicified values obtained in this study, also supports the previous theory that desilicification is useful to enhance Ru and Re extractions from TDB-1 (e.g., Meisel *et al.* 2009, Dale *et al.* 2009, 2012b, Ishikawa *et al.* 2014, Ackerman *et al.* 2016, Jonášová *et al.* 2016). Instead, the identical Pd, Ir and Pt values with and without desilicification imply that they were completely extracted from the sample matrix during non-desilicification procedure. The Os mean mass fraction was consistent with the reported data of both CT and HPA methods, except for those of Ishikawa *et al.* (2014), Qi and Zhou (2008) and Savard *et al.* (2010). The large variance in Os data observed between laboratories could result from the nugget effect. The ^{187}Os/^{188}Os ratios agreed well with the previously reported CT and HPA data, within a 1*s* intermediate precision (Figure 7c).

Conclusions

An effective analytical method was developed for the determination of HSE mass fractions and Os isotopic compositions in geological samples, by high-resolution ICP-MS and N-TIMS, respectively. The procedure enabled the use of the same aliquot for both ICP-MS and N-TIMS measurements and utilised an isotope

dilution method. This study presents two new methodologies for the ion-exchange separation of Ru, Pd, Re, Ir and Pt: (1) The cation exchange resin AG50W-X12 can more effectively separate HSEs, in particular Ru, from matrix elements than the -X8, generally used in previous studies, (2) When the HF-desilicification was performed following sample decomposition, trace amounts of Zr, forming stable fluoro-complex, cannot be removed by LN resin. Chelex 100 resin, however, can effectively separate Pd from the Zr fluoro-complex, because the K_d of Pd is ~ 1000–3000 times higher than that for Zr in both diluted HF and HNO_3. Furthermore, the Cr multi-oxide interference in Ru measurements, rarely discussed in previous studies, was critically evaluated. In this method, with careful purification and utilisation of a desolvating nebulizer system, the ratios of the interference intensities relative to the measured intensities of HSE isotope masses: CrO_3^+/Ru^+ (101), YO^+/Pd^+ (105), Cd^+/Pd^+(106), ZrO^+/Pd^+ (106), HfO^+/Ir^+(193) and HfO^+/Pt^+ (194,195), were reduced by less than a few hundred parts per million. Thus, no interference correction is required for the measurements of Ru, Pd, Re, Ir and Pt for both desilicified and non-desilicified geological samples. The contributions of the total procedural blank of HSEs in RMs were < 1% and did not significantly affect the measurement results.

Our data for HSE mass fractions and Os isotopic compositions of RMs UB-N, JP-1 and TDB-1, commonly used between laboratories, were in good agreement with or comparable to the literature data, demonstrating the validation of our analytical method. Furthermore, the effectiveness of HF-desilicification on the Ru, Pd, Re, Ir and Pt extractions from the sample matrix was evaluated for UB-N, JP-1, TDB-1, and two new CRMs MUH-1 and OKUM. Our results indicate that desilicification, followed by CT decomposition using inverse *aqua regia*, more effectively extracted Ru and Re for the mafic RM TDB-1, but not for the ultramafic RMs UB-N and JP-1, the results of which are consistent with previous studies. The ultramafic RM MUH-1, similar to UB-N and JP-1, does not require HF treatment. The ultramafic RM OKUM gave a different result. In this study, the systematically higher Ru, Ir and Pt values for the desilicified samples, compared with those of non-desilicified samples, demonstrate that desilicification improved the liberation of Ru, Ir and Pt from OKUM. Knowing that this study used a ~ 1 g test portion size, among four ultramafic RMs, the homogeneity

of HSEs in harzburgites JP-1 and MUH-1 are generally worse than those in lherzolite UB-N and komatiite OKUM.

Acknowledgements

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Figure captions

Figure 1. The Workflow diagram for separations and determination of HSE mass fractions and Os isotope ratios developed in this study.

Figure 2. Elution profiles of HSEs and interfering elements (non-matrix containing synthetic solutions) for 3 ml of AG50W-X8 (broken line) and -X12 (solid line). The insert for HSEs shows the tailing of Ru, Pd, Re, Ir and Pt eluting from 6 to 12 ml for both X8 and X12.

Figure 3. Recovery yields of HSEs and interfering elements (Cr, Y, Zr, Cd and Hf) for each column using a matrix-containing synthetic sample (a) without and (b) with desilicification. 1: AG50W-X12 resin, 2: LN resin, 3: Chelex 100 resin, 4: AG50W-X8 resin. For the third column, two fractions were collected, the Ru-Re-Ir-Pt cut, and the other the Pd cut (Figure 4b). The recoveries shown for the third column are: Ru, Re, Ir, Pt, Hf and Cr for the Ru-Re-Ir-Pt cut and Pd, Zr, Y and Cd for the Pd cut.

Figure 4. Elution profiles of HSEs and interfering elements (desilicified RM TDB-1) for (a) the second column LN resin and (b) third column Chelex100 resin: Pd was successfully separated from Zr and Cd.

Figure 5. Elution profiles of HSEs and the interfering element Cr (non-matrix containing synthetic solutions: 10 ng of HSEs and 10 μg of Cr, respectively) for the fourth column AG50W-X8 resin.

Figure 6. The range of total procedural blanks from this study and previous studies, CT: Carius tube digestion method, HPA: high-pressure asher digestion method.

Figure 7. HSE mass fractions and Os isotope ratios for RMs (a) UB-N, (b) JP-1 and (c) TDB-1. Comparison with previous studies (error bar: 1*s*), CT: Carius tube without desilicification, CT-HF: Carius tube with post-Os desilicification, HPA: high-pressure asher without desilicification, HPA-HF:

high-pressure asher with post-Os desilicification. Os data of CT-HF represent Os data employing a CT from both the current study and previous studies.

Figure 8. PUM-normalised HSE patterns for RMs TDB-1, OKUM, UB-N, MUH-1 and JP-1, respectively with and without desilicification from this study. The grey lines denote HSE patterns of DS. The PUM data are from Becker *et al.* (2006). DS: HF-desilicification.

Table 1.
Separation scheme for Ru-Pd-Ir-Re-Pt purification

(1) Separation of Ru-Pd-Ir-Re-Pt from matrix elements	
Econo-Pac chromatography column packed with 20 ml AG50WX12, 200–400 mesh	
Column dimension: 15 mm wide $\times$ 120 mm long	
Resin cleaning	150 ml 6 mol l^{-1} HCl
Conditon	100 ml 0.5 mol l^{-1} HCl
Load sample	6 ml 0.5 mol l^{-1} HCl
Load and collect sample	4 ml 0.5 mol l^{-1} HCl
Collect sample	8 ml 0.5 mol l^{-1} HCl
(2) Separation of Ru-Pd-Ir-Re-Pt from Y, Zr, Hf	
LDPE column packed with 0.5 ml LN resin, 100–150 µm	
Column dimension: 4 mm wide $\times$ 45 mm long	
Resin cleaning	3 ml 0.5 mol l^{-1} HF
Resin cleaning	3 ml Mili-Q
Resin cleaning	6 ml 6 mol l^{-1} HCl
Resin cleaning	3 ml Mili-Q
Conditon	3 ml 0.5 mol l^{-1} HCl
Load and collect sample	0.5 ml 0.5 mol l^{-1} HCl
Collect sample	2.5 ml 0.5 mol l^{-1} HCl
(3) Separation of Pd from Cd and Zr fluoro-complex	
LDPE column packed with 0.1 ml Chelex100, 200–400 mesh, sodium form	
Column dimension: 4 mm wide $\times$ 10 mm long	
Resin cleaning	9 ml 9.5 mol l^{-1} HCl
Resin cleaning	3 ml Mili-Q
Conditon	3 ml 0.5 mol l^{-1} HNO$_3$
Load and collect sample	0.5 ml 0.5 mol l^{-1} HNO$_3$
Collect sample (Ru-Re-Ir-Pt fraction)	4 ml 0.5 mol l^{-1} HNO$_3$
Collect sample (Pd fraction)	3 ml 8 mol l^{-1} HCl
(4) Separation of Ru-Re-Ir-Pt from Cr	
LDPE column packed with 0.3 ml AG50WX8, 200–400 mesh	
Column dimension: 4 mm wide $\times$ 30 mm long	
Resin cleaning	6 ml 6 mol l^{-1} HCl
Resin cleaning	3 ml Mili-Q
Conditon	3 ml 0.5 mol l^{-1} HNO$_3$
Load and collect sample	0.3 ml 0.5 mol l^{-1} HNO$_3$
Collect sample	0.6 ml 0.5 mol l^{-1} HNO$_3$

Table 2.
Isobaric and potential polyatomic interferences for HSE measurements by ICP-MS

HSE isotope mass	Isobaric	Oxide	Others		
			Inteference — Polyatomic		
$^{99}Ru^+$				$^{62}Ni^{37}Cl^+$	$^{59}Co^{40}Ar^+$
				$^{64}Ni^{35}Cl^+$	$^{61}Ni^{38}Ar^+$
				$^{64}Zn^{35}Cl^+$	$^{63}Cu^{36}Ar^+$
$^{100}Ru^+$	$^{100}Mo^+$	$^{84}Sr^{16}O^+$		$^{65}Cu^{35}Cl^+$	$^{60}Ni^{40}Ar^+$
					$^{62}Ni^{38}Ar^+$
$^{101}Ru^+$		$^{53}Cr^{16}O_3^+$	$^{84}Sr^{16}O^1H^+$	$^{64}Ni^{37}Cl^+$	$^{61}Ni^{40}Ar^+$
		$^{85}Rb^{16}O^+$		$^{64}Zn^{37}Cl^+$	$^{65}Cu^{36}Ar^+$
				$^{66}Zn^{35}Cl^+$	
$^{105}Pd^+$		$^{89}Y^{16}O^+$	$^{88}Sr^{16}O^1H^+$	$^{68}Zn^{37}Cl^+$	$^{65}Cu^{40}Ar^+$
				$^{70}Ge^{35}Cl^+$	
$^{106}Pd^+$	$^{106}Cd^+$	$^{90}Zr^{16}O^+$	$^{89}Y^{16}O^1H^+$		$^{66}Zn^{40}Ar^+$
$^{108}Pd^+$	$^{108}Cd^+$	$^{92}Zr^{16}O^+$			$^{68}Zn^{40}Ar^+$
		$^{92}Mo^{16}O^+$			
$^{185}Re^+$		$^{169}Tm^{16}O^+$			
$^{187}Re^+$	$^{187}Os^+$	$^{171}Yb^{16}O^+$			
$^{191}Ir^+$		$^{175}Lu^{16}O^+$	$^{140}Ce^{35}Cl^{16}O^+$		
$^{193}Ir^+$		$^{177}Hf^{16}O^+$	$^{140}Ce^{37}Cl^{16}O^+$		
$^{194}Pt^+$		$^{178}Hf^{16}O^+$			
$^{195}Pt^+$		$^{179}Hf^{16}O^+$	$^{178}Hf^{16}O^1H^+$		
$^{196}Pt^+$	$^{196}Hg^+$	$^{180}Hf^{16}O^+$			
		$^{180}W^{16}O^+$			
		$^{180}Ta^{16}O^+$			
$^{198}Pt^+$	$^{198}Hg^+$				

Table 3.

Distribution coefficient (Kd) of HSEs and interfering elements in LN and Chelex 100 resins determined in this study

		Ru	Pd	Re	Ir	Pt	Y	Zr	Cd	Hf
LN resin	0.5 mol l^{-1} HCl	1	0.3	11	1	2	5.4×10^2	9×10^6	1	3×10^{11}
	0.5 mol l^{-1} HF	7	7	8	3	5	20	2	6	7
Chelex 100 resin	0.5 mol l^{-1} HNO$_3$	6	1.3×10^3	20	8	14	0.4	2	2	2
	0.5 mol l^{-1} HF	36	2.8×10^3	78	35	44	3	1	10	2
	8 mol l^{-1} HCl	4	8	30	5	26	2	7	18	7

Table 4.
Ratios of interference intensities relative to the measured intensities of HSE isotope masses (cps/cps in parts per million) during ICP-MS measurement

inteference/isotope	Non-desilicification					Desilicification				
	UB-N	JP-1	MUH-1	OKUM	TDB-1	UB-N	JP-1	MUH-1	OKUM	TDB-1
$^{53}Cr^{16}O_3{}^+/^{101}Ru^+$	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
$^{89}Y^{16}O^+/^{105}Pd^+$	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
$^{90}Zr^{16}O^+/^{106}Pd^+$	13 ± 2	66 ± 119	3 ± 2	0.8 ± 0.3	< 1	18 ± 6	53 ± 62	3 ± 1	1.6 ± 0.4	< 1
$^{106}Cd^+/^{106}Pd^+$	100 ± 149	172 ± 188	140 ± 95	224 ± 153	23 ± 23	47 ± 15	127 ± 76	110 ± 25	233 ± 188	249 ± 225
$^{177}Hf^{16}O^+/^{193}Ir^+$	< 1	< 1	< 1	< 1	3 ± 4	< 1	< 1	< 1	< 1	26 ± 20
$^{178}Hf^{16}O^+/^{194}Pt^+$	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	2 ± 2
$^{179}Hf^{16}O^+/^{195}Pt^+$	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	1.5 ± 1

Table 5.
HSE mass fractions (ng g^{-1}) and Os isotopic compositions of UB-N, JP-1 and MUH-1 from this study and the literature

	Digestion[a]	No.	Ru		Pd		Re		Ir		Pt		Os		$^{187}Re/^{188}Os$		$^{187}Os/^{188}Os$	
UB-N (serpentinite, CRPG)																		
This study	CT	1	6.76	10	5.37	8	0.198	2	3.48	4	7.02	10	3.51	5	0.272	5	0.12727	14
		2	6.49	10	5.47	8	0.193	2	2.82	3	6.42	8	3.45	5	0.270	5	0.12745	15
		3	6.29	9	5.51	8	0.193	2	3.32	4	6.89	9	3.35	5	0.278	5	0.12676	47
		4	6.02	9	5.44	8	0.182	2	3.37	4	7.08	10	3.27	5	0.269	5	0.12766	28
		5	5.77	8	5.70	7	0.190	2	2.55	2	6.86	8	3.02	4	0.303	5	0.12692	13
		6	6.17	7	5.85	11	0.198	2	3.05	3	7.25	9	3.41	5	0.280	5	0.12856	20
		7	5.86	7	5.67	11	0.194	2	3.39	4	7.65	10	3.47	5	0.270	5	0.12709	16
		8	6.01	7	5.84	10	0.193	2	3.06	3	7.32	8						
		mean, 1s	6.17	0.33	5.61	0.18	0.192	0.005	3.13	0.32	7.06	0.37	3.35	0.17	0.278	0.012	0.12739	0.00060
		% RSD		5.4		3.3		2.6		10		5.2		5.0		4.4		0.47
	CT-HF	1	6.72	10	5.62	8	0.198	2	2.94	3	6.73	9	3.09	4	0.309	5	0.12794	21
		2	6.80	10	5.51	8	0.189	2	3.84	5	6.75				0.277	5	0.12671	12
		3	6.50	10	5.68	9	0.199	2	3.71	4	6.91	10	3.47	5	0.288	5	0.12707	1
		4	6.27	9	5.58	8	0.185	2	3.14	3	7.00	9	3.11	4	0.282	5	0.12686	21
		5	6.62	10	5.64	9	0.190	2	3.81	5	6.65	9	3.25	5	0.263	4	0.12676	31
		6	6.16	7	5.60	10	0.194	2	2.95	3	6.61	7	3.57	5				
		7	7.14	9	5.58	10	0.192	2	2.77	3	6.37	7			0.248	4	0.12660	35
		8	6.66	8	5.73	11	0.196	2	3.23	3	6.75	8	3.82	6	0.287	7	0.12601	114
		9	5.54	6	5.73	11	0.193	2	2.78	3	6.77	8	3.24	7	0.258	4	0.12738	23
		10	6.25	7	5.85	11	0.187	2	2.79	3	6.78	8	3.50	5				
		mean, 1s	6.46	0.44	5.65	0.10	0.192	0.005	3.20	0.43	6.73	0.17	3.38	0.25	0.277	0.020	0.12692	0.00057
		% RSD		6.8		1.8		2.4		14		2.5		7.5		7.1		0.45
Ishikawa et al. (2012)	CT	n=9, % RSD	6.85	5.9	5.55	3.1	0.210	8.6	3.47	6.7	6.98	5.0	3.97	9.6	0.257	15	0.12732	0.67
	CT-HF	n=4, % RSD	6.70	9.9	5.67	2.9	0.203	0.9	3.26	8.9	6.82	3.7	3.57	7.8	0.275	7.9	0.12720	0.40
Li et al. (2014)	CT	n=5, % RSD	7.09	16	5.66	6.3	0.197	6.6	3.56	16	7.56	4.0	3.42	11	0.280	7.6	0.12700	0.16
Fischier et al. (2011)	CT	n=8, % RSD	6.52	6.2	5.85	3.4	0.201	5.9	3.33	5.0	7.55	5.0	3.70	8.4			0.12704	0.20
Becker et al. (2006)	CT	n=4, % RSD	6.51	5.0	5.86	4.5	0.205	1.9	3.26	4.0	7.00	3.2	3.51	3.6	0.282	5.1	0.12737	0.25
Luguet et al. (2007)	CT	n=6, % RSD	6.48	4.5	6.17	4.1	0.205	3.4	3.24	10	8.07	14	3.66	4.1			0.12790	0.39
Puchtel et al. (2008)	CT	n=4, % RSD	6.93	3.4	5.70	1.1	0.213	2.6	3.58	5.6	7.47	1.1	3.85	4.2			0.1272	0.15
Kogiso et al. (2008)	CT	n=3, % RSD	6.23	1.0	6.05	1.3	0.190	1.1	3.38	1.0	7.40	2.7	3.56	2.6				
Fischier et al. (2011)	HPA	n=11,% RSD	6.36	5.7	5.86	3.5	0.184	14	3.02	5.0	7.16	6.5	3.46	5.7	0.257	13	0.12729	0.20
Meisel and Moser (2004b)	HPA	n=14,% RSD	6.30	4.6	6.11	2.9	0.206	2.4	3.38	6.4	7.42	4.0	3.71	7.2				

	Digestion[a]	No.	Ru		Pd		Re		Ir		Pt		Os		$^{187}Re/^{188}Os$		$^{187}Os/^{188}Os$	
JP-1 (harzburgite, GSJ)																		
This study	CT	1	4.61	*6*	1.35	*1*	0.0293	*3*	2.19	*3*	4.23	*4*	3.45	*5*	0.0411	*7*	0.12221	*11*
		2	3.84	*5*	1.46	*1*	0.0299	*3*	1.98	*2*	3.52	*3*	2.35	*3*	0.0613	*11*	0.11961	*38*
		3	3.65	*4*	1.32	*1*	0.0281	*3*	1.98	*2*	3.37	*3*	2.31	*3*	0.0589	*10*	0.11978	*38*
		4	3.08	*3*	1.51	*2*	0.0264	*3*	1.55	*1*	3.62	*3*						
		5	4.39	*5*	1.65	*1*	0.0306	*5*	2.72	*3*	5.38	*5*	3.52	*5*	0.0420	*9*	0.12187	*14*
		6	4.78	*8*	1.22	*1*	0.0307	*5*	2.84	*3*	4.61	*4*	3.84	*5*	0.0386	*8*	0.12183	*26*
		7	4.82	*5*	1.18	*1*	0.0275	*4*	2.56	*3*	4.43	*4*	3.04	*4*	0.0437	*9*	0.11930	*32*
		8	4.49	*5*	1.27	*1*	0.0255	*4*	2.25	*2*	3.83	*3*	2.75	*4*	0.0448	*9*	0.12019	*15*
		mean, 1s	4.21	0.62	1.37	0.16	0.0285	0.0019	2.26	0.43	4.12	0.67	3.04	0.60	0.0472	0.0091	0.12069	0.00124
		% RSD		15		12		6.8		19		16		20		19		1.0
	CT-HF	1	4.53	*5*	1.39	*1*	0.0266	*4*	2.52	*2*	4.45	*3*	2.73	*4*	0.0470	*9*	0.12051	*41*
		2	7.13	*8*	1.33	*1*	0.0277	*4*	4.13	*4*	4.42	*3*	2.46	*3*	0.0544	*11*	0.11945	*25*
		3	5.56	*6*	1.19	*1*	0.0282	*4*	1.82	*1*	6.69	*6*	3.86	*5*	0.0354	*7*	0.11883	*53*
		4	3.98	*4*	1.19	*1*	0.0307	*4*	2.38	*2*	4.42	*3*	4.04	*6*	0.0367	*7*	0.12173	*15*
		5	4.89	*8*	1.49	*1*	0.0292	*4*	2.63	*1*	5.89	*9*	3.15	*4*	0.0447	*9*	0.12061	*12*
		6	3.93	*6*	1.18	*1*	0.0301	*5*	2.16	*1*	3.90	*4*	2.35	*3*	0.0618	*13*	0.12139	*34*
		7	4.96	*8*	1.19	*1*	0.0221	*4*	2.69	*1*	3.93	*4*	2.57	*4*	0.0416	*9*	0.12047	*97*
		8	3.81	*5*	1.26	*1*	0.0282	*4*	2.09	*1*	3.81	*4*	3.78	*7*	0.0360	*9*	0.11988	*75*
		mean, 1s	4.84	1.12	1.28	0.11	0.0279	0.0027	2.55	0.70	4.69	1.04	3.12	0.69	0.0447	0.0095	0.12036	0.00096
		% RSD		23		9		10		27		22		22		21		0.8
Ishikawa et al. (2012)	CT	n=10, % RSD	5.64	13	1.50	16	0.0244	7.5	2.83	10	4.80	20	3.16	17	0.0382	23	0.12083	0.5
	CT-HF	n=5, % RSD	5.49	15	1.34	10	0.0234	7.2	2.68	16	4.10	18	2.98	22	0.0396	26	0.12082	0.7
Shinotsuka and Suzuki (2007)	CT	n=7, % RSD	5.98	7.9	1.42	10	0.0234	3.0	2.83	7.4	4.48	11	3.43	15				
Meisel and Moser (2004b)	HPA	n=9, % RSD	5.29	12	1.63	24	0.286	125	2.47	8.1	5.09	61	3.78	18				
MUH-1 (harzburgite, IAG)																		
This study	CT	1	5.56	*6*	10.5	*1*	0.166	*2*	2.31	*8*	7.36	*14*	3.43	*5*	0.234	*4*	0.12757	*4*
		2	7.54	*9*	7.14	*5*	0.172	*2*	2.64	*9*	7.23	*12*	4.54	*6*	0.183	*3*	0.12652	*15*
		3	5.87	*6*	7.98	*6*	0.175	*2*	2.20	*6*	7.22	*12*	2.93	*4*	0.287	*5*	0.12797	*5*
		4	5.04	*5*	8.32	*6*	0.170	*2*	2.49	*8*	10.3	*2*	3.31	*5*	0.248	*4*	0.12837	*15*
		5	7.65	*7*	9.60	*9*	0.179	*2*	2.70	*9*	9.01	*6*	4.17	*6*	0.207	*3*	0.12794	*4*
		mean, 1s	6.33	1.19	8.71	1.34	0.172	0.005	2.47	0.21	8.23	1.39	3.68	0.66	0.232	0.040	0.12767	0.00070
		% RSD		19		15		2.7		8.6		17		18		17		0.55
	CT-HF	1	7.33	*7*	7.95	*1*	0.187	*2*	2.08	*6*	7.72	*5*	3.58	*5*	0.252	*4*	0.12714	*17*
		2	5.61	*5*	10.3	*1*	0.189	*2*	2.50	*8*	9.33	*6*	3.12	*4*	0.293	*5*	0.12812	*14*
		3	6.45	*6*	8.49	*8*	0.177	*2*	2.20	*6*	7.01	*4*	4.64	*6*	0.185	*3*	0.12761	*1*
		4	6.36	*6*	8.02	*7*	0.185	*2*	2.46	*8*	7.60	*4*	3.53	*5*	0.253	*4*	0.12691	*10*
		mean, 1s	6.44	0.71	8.69	1.10	0.185	0.005	2.31	0.20	7.92	0.99	3.72	0.65	0.246	0.045	0.12744	0.00054
		% RSD		11		13		2.8		8.6		13		17		18		0.42

Uncertainties (2SE given in italic, refer to least significant digits) on each sample are calculated by error propagation, which includes uncertainties of isotope ratio, spike mass fraction and blank correction. [a]CT: Carius tube without desilicification; CT-HF: carius tube with post-Os desilicification; HPA: high pressure asher without desilicification

Table 6.

HSE mass fractions (ng g⁻¹) and Os isotopic compositions of OKUM and TDB-1 from this study and the literature

	Digestion[a]	No.	Ru		Pd		Re		Ir		Pt		Os		$^{187}Re/^{188}Os$		$^{187}Os/^{188}Os$	
OKUM (komatiite, IAG)																		
This study	CT	1	4.04	*4*	11.1	*1*	0.454	*4*	0.776	*9*	10.3	*2*	0.765	*11*	2.87	*5*	0.2642	*3*
		2	3.93	*4*	11.4	*1*	0.445	*4*	0.790	*8*	9.99	*20*	0.767	*11*	2.80	*5*	0.2629	*3*
		3	3.99	*4*	12.6	*1*	0.472	*5*	0.784	*9*	10.1	*2*	0.780	*11*	2.92	*5*	0.2632	*6*
		4	4.04	*4*	10.5	*1*	0.462	*5*	0.763	*8*	10.2	*2*	0.737	*10*	3.03	*5*	0.2741	*3*
		5	3.86	*4*	10.7	*1*	0.450	*4*	0.730	*8*	10.4	*2*	0.696	*10*	3.12	*5*	0.2791	*3*
		mean, 1s	3.97	0.08	11.3	0.83	0.456	0.011	0.769	0.024	10.2	0.1	0.749	0.034	2.95	0.13	0.2687	0.0074
		% RSD		1.9		7.3		2.4		3.1		1.4		4.5		4.3		2.8
	CT-HF	1	4.40	*4*	11.2	*1*	0.493	*5*	1.02	*1*	11.5	*1*	0.962	*13*	2.47	*4*	0.2302	*3*
		2	4.45	*4*	11.6	*1*	0.502	*5*	0.847	*10*	11.8	*1*	0.669	*9*	3.62	*6*	0.2912	*3*
		3	4.32	*4*	11.7	*1*	0.466	*5*	0.907	*12*	11.5	*1*	0.778	*11*	2.89	*5*	0.2576	*2*
		4	4.40	*4*	10.6	*1*	0.459	*5*	1.02	*1*	11.3	*1*	1.01	*1*	2.19	*4*	0.2266	*1*
		mean, 1s	4.39	0.05	11.3	0.5	0.480	0.021	0.951	0.088	11.5	0.2	0.855	0.160	2.80	0.62	0.2514	0.0299
		% RSD		1.2		4.4		4.3		9.3		1.7		19		22		12
Savard et al. (2010)	HPA	mean,% RSD	4.15	2.0	12.20	6.0	0.566	6.3	0.943	3.9	11.44	1.9	0.790					
Wang and Becker (2014)	HPA	n=6, % RSD	4.44	2.0	11.8	4.0	0.4	21	0.897	8.0	21.1	46	3.61	97			0.4185	35

TDB-1 (diabase, CCRMP) This study	CT	1	0.184	*2*	23.9	*12*	0.924	*10*	0.067	*0*	4.41	*4*	0.116	*2*	38.6	*7*	0.976	*2*
		2	0.184	*2*	25.0	*23*	0.924	*11*	0.061	*0*	4.13	*5*	0.111	*2*	40.0	*7*	0.972	*1*
		3	0.212	*2*	27.7	*18*	0.916	*10*	0.089	*0*	4.74	*5*						
		4	0.182	*2*	26.0	*18*	0.927	*10*	0.058	*0*	4.03	*4*						
		5	0.191	*2*	21.6	*7*	0.931	*19*	0.085	*0*	5.39	*6*	0.140	*2*	32.2	*8*	0.829	*1*
		6	0.185	*2*	21.3	*6*	0.895	*18*	0.069	*0*	4.50	*5*	0.118	*2*	36.6	*9*	0.917	*4*
		7	0.194	*2*	22.8	*6*	0.917	*17*	0.068	*0*	4.77	*4*	0.115	*2*	38.4	*9*	0.951	*3*
		8	0.191	*2*	21.9	*5*	0.916	*16*	0.072	*0*	4.51	*4*	0.120	*2*	37.0	*9*	0.915	*2*
		mean, 1s	0.190	0.010	23.8	2.3	0.919	0.011	0.071	0.011	4.56	0.42	0.120	0.010	37.1	2.7	0.927	0.055
		% RSD		5.2		9.7		1.2		15		9.3		8.4		7.4		5.9
	CT-HF	1	0.223	*2*	23.4	*10*	1.03	*2*	0.063	*0*	5.17	*4*	0.106	*2*	46.6	*10*	1.028	*2*
		2	0.270	*2*	23.1	*10*	1.12	*2*	0.089	*0*	4.92	*4*						
		3	0.245	*2*	24.3	*9*	0.969	*16*	0.097	*0*	5.23	*4*						
		4	0.233	*2*	23.5	*9*	0.977	*16*	0.068	*0*	4.61	*3*						
		5	0.255	*3*	21.8	*4*	0.978	*16*	0.072	*0*	4.38	*5*	0.118	*2*	40.2	*9*	0.924	*5*
		6	0.241	*2*	22.8	*4*	0.951	*16*	0.066	*0*	4.60	*5*	0.106	*2*	43.2	*10*	1.003	*2*
		7	0.269	*3*	22.9	*5*	0.973	*17*	0.085	*0*	4.89	*6*	0.128	*2*	36.7	*8*	0.813	*2*
		8	0.256	*3*	21.8	*4*	0.964	*16*	0.142	*1*	4.47	*5*	0.135	*2*	34.5	*8*	0.845	*2*
		mean, 1s	0.249	0.017	23.0	0.8	0.994	0.054	0.085	0.026	4.78	0.32	0.119	0.013	40.3	4.8	0.923	0.094
		% RSD		6.7		3.7		5.4		30		6.6		11		12		10
Ishikawa et al.(2012)	CT	n=20, % RSD	0.196	14	23.2	11	0.928	7.9	0.080	29	4.89	15	0.147	26	35.3	25	0.879	20
	CT-HF	n=8, % RSD	0.285	4.5	23.4	6.9	1.05	2.6	0.080	21	5.00	12	0.145	19	40.1	22	0.958	19
Shinotsuka and Suzuki (2007)	CT	n=7, % RSD	0.203	9.0	22.4	4.1	0.801	3.0	0.070	4.6	4.84	3.5	0.096	10				
Li et al.(2014)	CT	n=4, % RSD	0.192	8.2	21.0	9.9	0.847	3.2	0.067	13	4.84	6.2	0.109	13	42.0	15	0.918	12
Qi and Zhou(2008)	CT	n=6, % RSD	0.220	9.1	23.0	5.2	0.770	1.3	0.082	12	5.23	5.4	0.153	6.5				
Meisel and Moser (2004a)	HPA	n=7, % RSD	0.198	4.2	24.3	7.8	0.794	2.9	0.075	13	5.01	3.6	0.117	10			0.917	11
Meisel et al.(2001)	HPA	mean,% RSD	0.237	30	23.0	13	0.735	7.1	0.077	22	5.02	6.7	0.112	10				
Savard et al. (2010)	HPA	mean,% RSD	0.164	17	22.4	4.8	0.721	3.3	0.061	25	4.79	4.0	0.050	42				
Dale et al.(2012)	HPA	n=3, % RSD	0.196	4.6	23.9	5.1	0.835	4.2	0.063	6.3	4.81	3.3	0.114	7.5	39.2	6.8	0.937	3.3
	HPA-HF	n=2	0.277		22.0		1.04		0.058		4.54		0.099		56.5		1.013	

Uncertainties (2SE given in italic, refer to least significant digits) on each sample are calculated by error propagation, which includes uncertainties of isotope ratio, spike mass fraction and blank correction. [a]CT: Carius tube without desilicification; CT-HF: carius tube with post-Os desilicification; HPA: high pressure asher without desilicification; HPA-HF: high pressure asher with post-Os desilicification

Carius tube (sample+spike),
240 °C, 72 hours

Inverse *aqua regia*
(olivine, sulfide, metals)

AG50WX12

HSE in
0.5 mol l^{-1} HCl

HSE in
6 mol l^{-1} HCl

Non-
desilicification

HCl-HNO$_3$

CCl$_4$

CCl$_4$ **solvent**
extraction

CCl$_4$ (Os)

HSE-Y, Zr,
Hf, Cd, Cr

LN resin

Desilicification

residue

HBr

CCl$_4$

HSE-Cd, Cr, (Zr fluoro-complex)

Fluoride in
6 mol l^{-1} HCl

Silicate and
oxide minerals

HBr back
-extraction

Chelex 100

HBr (Os)

HSE-Cr, Cd,
(Zr fluoro-complex)

Pd

HBr

AG50WX8

OsO$_4$

H$_2$SO$_4$+CrO$_3$

Microdistillation

Ru-Re-Ir-Pt → HR-ICP-MS

N-TIMS