Determination of Platinum-Group Elements and Re-Os Isotopes using ID-ICP-MS and N-TIMS from a Single Digestion after Two-Stage Column Separation

Jie **Li** (1), Xiao-Ying **Jiang** (1, 2), Ji-Feng **Xu** (1)*, Li-Feng **Zhong** (3), Xuan-Ce **Wang** (4), Gui-Qin **Wang** (1) and Pei-Pei **Zhao** (1, 2)

(1) State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China
(2) University of Chinese Academy of Sciences, Beijing, 100049, China
(3) Key Laboratory of Marginal Sea Geology, South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou, 510301, China
(4) Department of Applied Geology, ARC Centre of Excellence for Core to Crust Fluid Systems (CCFS) and The Institute for Geoscience Research (TIGeR), Curtin University, GPO Box U1987, Perth, 6845, Australia
* Corresponding author. e-mail: jifengxu@gig.ac.cn

We report an improved procedure for the determination of the platinum-group elements (PGE) and Re, and Os isotopes from a single sample aliquot by isotope dilution (ID) using inductively coupled plasma-mass spectrometry (ICP-MS) and negative thermal ionisation mass spectrometry (N-TIMS), respectively. A two-stage column method was used to purify PGE-Re from their sample matrix and interfering elements (e.g., Mo, Zr and Hf) after Os had been separated by CCl_4 solvent extraction. The first column separation step used cation exchange resin (AG50W-X8) to concentrate PGE-Re and some potential interfering elements (e.g., Mo, Zr and Hf). In the second step, *N*-benzoyl-*N*-phenylhydroxylamine (BPHA) extraction resin was used to separate PGE-Re from the remaining interfering elements, which all remained strongly absorbed to the resin. The method was used to determine the PGE and rhenium, and Os isotope ratios in a range of geochemical reference materials (TDB-1, WGB-1, BHVO-2 and UB-N). The obtained results agree well with those previously published. This new method enables PGE-Re abundances and Os isotopic ratios to be determined on the same sample digestion, and circumvents the problems created by sample heterogeneity when comparing PGE and Re-Os isotope data.

Keywords: platinum-group elements, Re-Os isotopes, *N*-benzoyl-*N*-phenylhydroxylamine extraction resin, cation exchange resin, ICP-MS, N-TIMS.

Nous décrivons une procédure améliorée pour la détermination des abondances des éléments du groupe du platine (EGP), du Re et des isotopes de l'Os à partir d'un même aliquot d'échantillon par dilution isotopique (ID) en utilisant respectivement la spectrométrie de masse à source plasma (ICP-MS) et la spectrométrie de masse par ionisation thermique négative (N-TIMS). Une méthode sur colonne en deux étapes a été utilisé pour purifier les EGP et le Re de la matrice de l'échantillon et des éléments interférents (par exemple, Mo, Zr et Hf) et ceci après que l'Os ait été séparé par extraction par solvant CCl_4. La première étape de séparation sur colonne utilise une résine échangeuse de cations (AG50W-X8) pour concentrer les EGP et le Re et certains éléments interférents potentiels (par exemple, Mo, Zr et Hf). Au cours de la seconde étape, la résine d'extraction N-benzoyl-N-phénylhydroxylamine (BPHA) a été utilisée pour séparer les EGP et le Re des éléments interférents restants, qui sont tous fortement absorbé par cette résine. La méthode a été utilisée pour déterminer les concentrations en PGE et Re, et les rapports isotopiques de l'Os dans une gamme de matériaux de référence géochimiques (TDB-1, WGB-1, BHVO-2 et UB-N). Les résultats obtenus sont en bon accord avec ceux publiés antérieurement. Cette nouvelle méthode permet la détermination des abondances en PGE et Re et des rapports isotopiques de l'Os sur la même portion d'échantillon digérée, et contourne ainsi les problèmes liés à l'hétérogénéité des échantillons lorsqu'on compare les données élémentaires des EGP et les données isotopiques Re-Os.

Mots-clés : éléments du groupe du platine, isotopes Re-Os, résine d'extraction N-benzoyl-N-phénylhydroxylamine, résine échangeuse de cations, ICP-MS, N-TIMS.

Platinum-group elements (PGE: Ru, Rh, Pd, Ir, Os and Pt) and rhenium (Re), a coherent group of highly siderophile elements (HSE), have attracted considerable interest in Earth and planetary sciences because of their unique geochemical properties. These elements provide unique insights into global-scale differentiation processes such as core-mantle segregation (e.g., Day *et al.* 2007), the late accretionary history (e.g., Rehkämper *et al.* 1997, Dale *et al.* 2012a) and core-mantle exchange (e.g., Puchtel and Humayun 2000). In addition, HSE abundances combined with variations in Os isotope ratios related to the long-lived ^{187}Re-^{187}Os decay scheme provide new constraints on the age of extraction of the continental crust and lithosphere and the origin of mantle heterogeneities (e.g., Morgan 1985, Puchtel *et al.* 2005, Pearson *et al.* 2007). Due to this broad range of applications, the determination of PGE and Re-Os isotopes in geological samples has been an important focus of research efforts in the field of geochemistry. Ideally, the analytical methods used for these types of elements should avoid problems related to sample heterogeneity (i.e., the 'nugget effect') when comparing PGE and Re-Os isotope data. Furthermore, it is advantageous to be able to compare Re-Os geochronological and source tracer information with that derived from interelement PGE fractionations (Dale *et al.* 2012b).

Although various analytical methods for PGE concentration and Re-Os measurements have been developed in the past two decades (e.g., Creaser *et al.* 1991, Volkening *et al.* 1991, Shirey and Walker 1995, Pearson and Woodland 2000, Meisel *et al.* 2001a, 2003a, Meisel and Moser 2004a, Suzuki *et al.* 2004, Qi *et al.* 2004, Shinotsuka and Suzuki 2007, Nozaki *et al.* 2012), simultaneous determination of PGE concentrations and Re-Os isotopic ratios on the same sample aliquot remains a significant challenge. Pearson and Woodland (2000) first described a procedure that allowed separation of PGE and Re from the same sample aliquot for the determination of PGE abundances and Re-Os isotopic ratios. In their method, anion exchange resin was used for separation of PGE and Re, as major elements pass through the anion exchange column while chloro-complex anions of PGE and ReO_4^- can be adsorbed by a small volume of resin. However, this method is relatively complex and does not have complete recovery of the PGE due to their variable affinity to the resin.

Cation exchange separation techniques have also been widely used for bulk separation of PGE-Re (e.g., Jarvis *et al.* 1997, Ely *et al.* 1999, Shinotsuka and Suzuki 2007). Both PGE and Re have a weak affinity to cation exchange resin, resulting in cations of major elements being retained on the column, while the former are eluted through the column and can be collected into the same fraction. Although, the cation

exchange separation technique is simple and has a high recovery for PGE-Re, it does not completely separate potential interferents (e.g., Mo, Zr and Hf) from the PGE, which can lead to molecular isobaric interferences during plasma source mass spectrometry. Recently, Shinotsuka and Suzuki (2007) presented a method for removing these potential interfering elements from PGE-Re, which involves solvent extraction using *N*-benzoyl-*N*-phenylhydroxylamine (BPHA) in chloroform after cation exchange separation. However, this method is not effective and is also environmentally hazardous. Yang and Pin (2002) employed a BPHA extraction chromatographic technique to pre-concentrate Zr, Hf, Nb and Ta from rock samples. This solid phase extraction method is simple and effective in separating Zr and Hf compared with the BPHA solvent extraction method. However, the potential of this BPHA extraction chromatographic method in separating Zr, Hf, Mo and W from PGE-Re has not yet been investigated.

In this study, we present a procedure for the determination of PGE-Re and Os isotope ratios on the same sample digestion by isotope dilution-inductively coupled plasma-mass spectrometry (ID-ICP-MS) and negative thermal ionisation mass spectrometry (N-TIMS), respectively. In contrast to previously developed methods (Pearson and Woodland 2000, Shinotsuka and Suzuki 2007), a two-stage column separation procedure using cation exchange and BPHA extraction resins was used to separate and purify the PGE and Re. Given that PGE and Re have no affinity for cation exchange and BPHA extraction resins, only matrix elements and interfering elements were removed from the samples. Therefore, apart from volatile Os and mono-isotopic Rh, all the PGE and Re could be simultaneously measured by ID-ICP-MS. Prior to PGE separation, Os was separated by CCl_4 solvent extraction from the same digested sample aliquot and determined by ID-N-TIMS. We evaluated the validity of our method by analysing international reference materials of ultramafic to mafic composition with a wide range of PGE concentrations.

Experimental procedures

Preparation of reagents and materials

Four geochemical reference materials of different lithologies and PGE concentrations were analysed in this study: TDB-1 (diabase, CCRMP), WGB-1 (gabbro, CCRMP), BHVO-2 (Hawaiian basalt, USGS) and UB-N (serpentine, CRPG).

All the acids used in this study (HNO_3, HBr and HCl) were purified by DST-1000 sub-boiling stills (Savillex

Corporation, Eden Prairie, MN USA). Before the sub-boiling distillation of HNO_3, it was heated to 350 °C and purged with clean air for *ca.* 2 hr in order to reduce its Os blank. Ultraclean water (18 MΩ cm) from a Millipore purification system was used. Ultrapure CCl_4 (HPLC grade; Tianjin, China) and hydrogen peroxide (Merck & Co. Inc, Whitehouse Station, NJ, USA) were used in the chemistry without further purification. An oxidising solution $Cr^{VI}O_3$–H_2SO_4 was prepared by dissolving 8 g of $Cr^{VI}O_3$ (Puratronic®, Alfa Aesar, Johnson Matthey Co. Ltd., UK) in 92 g of 6 mol l^{-1} H_2SO_4 (ACS grade, Thermo Fisher Scientific Inc., Waltham, MA, USA). This solution has an extremely high Os content and requires purification prior to use, which involves heating to *ca.* 100 °C and bubbling clean air through the solution to remove volatile OsO_4.

The BPHA extraction chromatographic resin was prepared by impregnating 10 g of Amberchrom CG-71 m chromatographic grade resin (Rohm and Hass company, Philadelphia, PA, USA) in 50–100 ml of chloroform solution containing 5 g of BPHA (AR grade; Aladdin Reagent Inc, China). The mixture was then gently stirred and evaporated to dryness at room temperature (25 °C) in a fume cupboard. Finally, the resin was stored in 0.5 mol l^{-1} HCl and ready for use.

Solutions of enriched isotopic spikes of the PGE ([99]Ru, [105]Pd, [185]Re, [190]Os, [191]Ir and [194]Pt) were prepared by Carius tube digestion of metallic spikes (obtained from the Oak Ridge National Laboratory, Oak Ridge, TN, USA) in *aqua regia*. The *aqua regia* spike solutions were evaporated and redissolved in 6 mol l^{-1} HCl. Osmium is in the octavalent state after Carius tube digestion and can be readily lost by evaporation. As such, Os in the solution was extracted into CCl_4 and back-extracted into concentrated HBr. Dilutions of an ICP multi-element standard solution of 100 mg ml^{-1} of Pt, Pd, Rh, Ru, Ir and Au (AccuStandard, Inc., New Haven, CT, USA) were also used as required throughout this study.

Conventional borosilicate glass Carius tubes, similar to those described by Shirey and Walker (1995), were used. The tubes had an inner volume of *ca.* 76 ml (220 mm × 250 mm). The tubes were pre-cleaned with 50% v/v *aqua regia* and heated to 300 °C for 6 hr. After rinsing with Milli-Q water, the tubes were dried. All the laboratory ware that the samples were exposed to was made of PFA (Savillex). PFA vials were cleaned with 50% v/v *aqua regia* and Milli-Q water, and then filled with concentrated HBr and heated overnight at 100 °C. This step helped to further clean the PFA and ensured that the

vials did not contribute Os blank during separation and microdistillation. Finally, all the laboratory ware was rinsed with Milli-Q water and air-dried.

Chemical separation

A schematic flow diagram of the method for the determination of the PGS and Re, and Os isotope ratios is shown in Figure 1. Approximately 1–2 g of powder were digested and equilibrated with a [99]Ru-[105]Pd-[185]Re-[190]Os-[191]Ir-[194]Pt-enriched spike using inverse *aqua regia* (2.5 ml of concentrated HCl and 7.5 ml of concentrated HNO_3) in a Carius tube (Shirey and Walker 1995). The Carius tube was carefully sealed, and the tube was heated in an oven at 240 °C for 24 hr. Osmium was extracted by CCl_4, back-extracted into HBr and further purified by microdistillation (Cohen and Waters 1996, Birck *et al.* 1997, Pearson and Woodland 2000).

The solution remaining after Os extraction was evaporated to dryness, and the residues were dissolved in 1 ml of 6 mol l^{-1} HCl. Following this, 1 ml of 30% H_2O_2 was slowly added in order to reduce Cr^{VI} to Cr^{III}, and the solution was dried down again. The residue was redissolved in 10 ml of 0.5 mol l^{-1} HCl and loaded onto the cation exchange columns (AG50W-X8, 200–400 mesh, Glass Econo-Column, 15 mm × 250 mm; Bio-Rad Laboratories, Inc., Berkeley, CA, USA). Before sample loading, the columns were rinsed and conditioned with 120 ml of 6 mol l^{-1} HCl and 100 ml of 0.5 mol l^{-1} HCl, respectively. The columns were eluted with 30 ml of 0.5 mol l^{-1} HCl, which was collected along with the loading solutions (Table 1).

The resulting PGE fraction was evaporated to near dryness, and the residues were dissolved in 1 ml of 0.5 mol l^{-1} HCl. These solutions were then loaded onto the BPHA extraction chromatographic column (Poly-Prep column, 8 mm × 40 mm; Bio-Rad Laboratories, Inc., Berkeley, CA, USA). Before sample loading, the columns were sequentially rinsed and conditioned with 6 ml of 6 mol l^{-1} HF, 6 ml of Milli-Q water and 5 ml of 0.5 mol l^{-1} HCl. The columns were eluted with 6 ml of 0.5 mol l^{-1} HCl, which was collected along with the loading solutions (Table 1). Finally, this PGE-bearing fraction was evaporated on a hot plate and then diluted with 3 ml of 2% HNO_3. This resultant solution was ready for Pt, Pd, Ir, Ru and Re determination by ID-ICP-MS.

Measurements

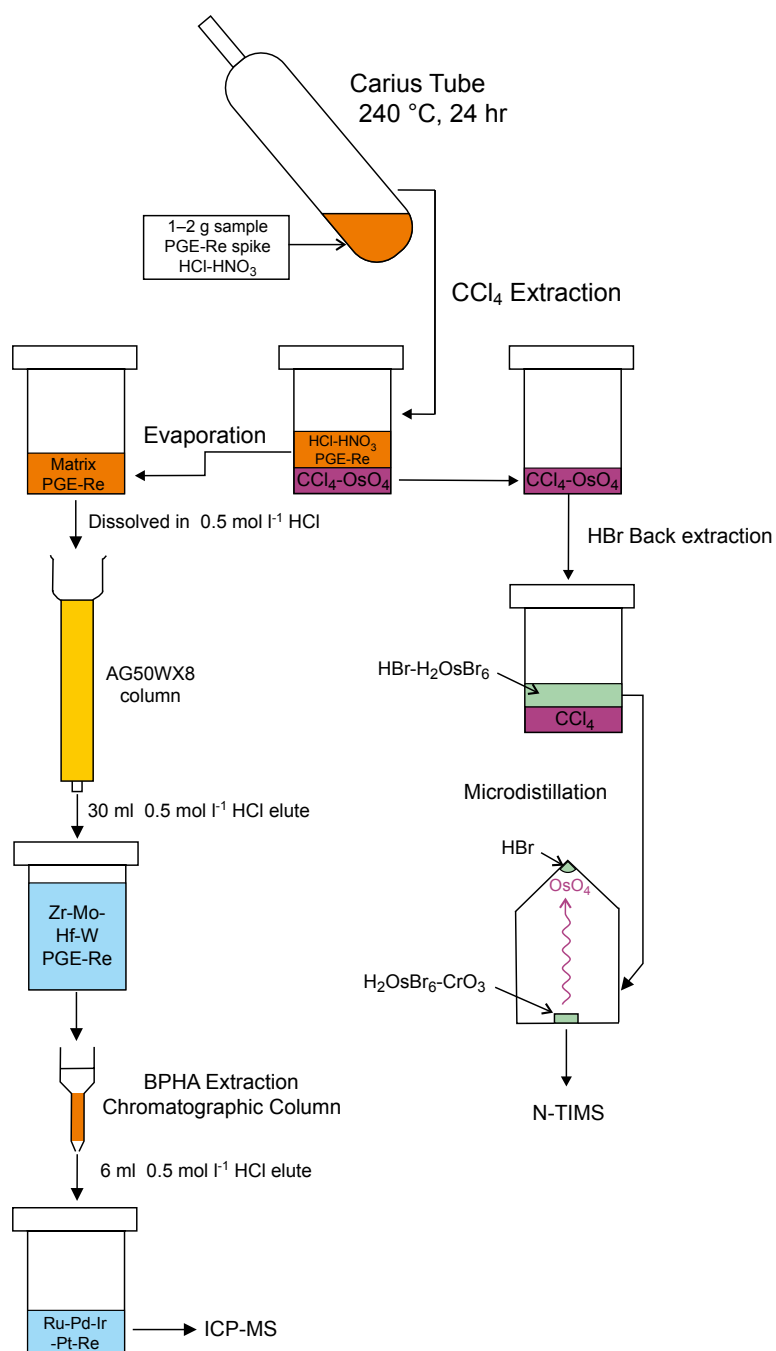**Os isotope measurements by N-TIMS:** Osmium isotope ratios were determined with a Thermo-Finnigan Triton

Figure 1. **Schematic flow diagram showing the method for the determination of PGE-Re concentrations and Os isotope ratios developed in this study.**

TIMS operated in the negative ion mode (N-TIMS). This instrument was equipped with nine Faraday collectors and a secondary electron multiplier (SEM). The ion optics used for the Os isotope measurements in this study was a system dedicated to negative ion Os isotope determinations and had never been exposed to Re or W filaments. Samples were loaded at *ca.* 0.9 A onto high-purity Pt filaments (99.999%, 1 mm × 0.025 mm; H. Cross Company, Moonachie, NJ, USA) that had previously been outgassed in air

for 3 min at *ca.* 4 A. Rhenium and Os blanks of the filaments were typically < 0.2 and < 0.04 pg (10^{-12} g), respectively. After complete evaporation, the sample was covered with 10 µg of Ba using a commercial standard solution of $Ba(NO_3)_2$ (10000 µg ml^{-1}, Claritas PPT®, SPEX CertiPrep, Ltd. Middlesex, UK; Kato *et al.* 2005). High-purity O_2 gas was introduced into the ion source via a leak valve to maintain a pressure of *ca.* 3 × 10^{-5} Pa. Osmium isotope ratios were determined by peak jumping on masses 235,

Table 1.
Summary of PGE-Re separation chemistry

Regent	Column	Volume (ml)
Cation column		
Resin	AG50WX8 (200–400 mesh)	44
Clean	6 mol l^{-1} HCl	120
Condition	0.5 mol l^{-1} HCl	100
Load and collect PGE-Re	0.5 mol l^{-1} HCl	10
Collect PGE-Re	0.5 mol l^{-1} HCl	30
BPHA column		
Resin	BPHA resin (100 mesh)	1
Clean	6 mol l^{-1} HF	6
Clean	18 MΩ cm H$_2$O	6
Condition	0.5 mol l^{-1} HCl	5
Load and collect PGE-Re	0.5 mol l^{-1} HCl	1
Collect PGE-Re	0.5 mol l^{-1} HCl	6

The resin-bed dimensions were 15 mm wide and 250 mm long for the cation column and 8 mm wide and 20 mm long for the BPHA column.

Table 2.
Isotope masses measured during mass spectrometry showing the spiked isotopes and potential isobaric interferences

Monitored isotopes	Spike composition (%)	Interference	
		Isobaric	Polyatomic
^{90}Zr$^+$			
^{95}Mo$^+$			
^{99}Ru$^+$	97.69		
^{100}Ru$^+$	0.74		
^{101}Ru$^+$	0.48		
^{105}Pd$^+$	98.4		^{89}Y^{16}O$^+$
^{106}Pd$^+$	1.5	^{106}Cd$^+$	^{90}Zr^{16}O$^+$
^{108}Pd$^+$	1.31	^{108}Cd$^+$	^{92}Zr^{16}O$^+$, ^{92}Mo^{16}O$^+$
^{111}Cd$^+$			^{95}Mo^{16}O$^+$
^{178}Hf$^+$			
^{185}Re$^+$	96.74		^{169}Tm^{16}O$^+$
^{187}Re$^+$	3.26	^{187}Os$^+$	^{171}Yb^{16}O$^+$
^{189}Os$^+$			^{173}Yb^{16}O$^+$
^{191}Ir$^+$	98.22		^{175}Lu^{16}O$^+$
^{193}Ir$^+$	1.78		^{177}Hf^{16}O$^+$
^{194}Pt$^+$	91.46		^{178}Hf^{16}O$^+$
^{195}Pt$^+$	6.75		^{179}Hf^{16}O$^+$
^{200}Hg$^+$			

236, 237, 238, 240 of the molecular ion OsO$_3^-$. Mass 233 (corresponding to ^{185}Re^{16}O$_3^-$) was measured throughout each run to monitor and correct for potential ^{187}Re^{16}O$_3^-$ interferences on ^{187}Os^{16}O$_3^-$ (mass 235). The data were corrected offline to remove oxygen and spike contributions.

PGE and Re concentration measurements by ICP-MS: An ICP-MS (Thermo-Scientific X series-2, Thermo Fisher Scientific Inc., Waltham, MA, USA) was used for isotope dilution (ID) analysis of Pt, Pd, Ir, Ru and Re. A conventional low-volume quartz impact bead spray chamber with a Peltier cooled (3 °C) and a 0.4 ml min^{-1} borosilicate nebuliser (MicroMist GE, West Melbourne, Australia) was used in the determinations. Ion lens settings, nebuliser gas flow rate and torch position were optimised daily using a 10-ng ml^{-1} tuning In-Ce standard solution in order to obtain the high instrumental sensitivity and low oxide production levels. A typical sensitivity of ~ 7 × 10^4 cps ng^{-1} for ^{115}In count rate and an oxide production rate of ~ 1.2% for the CeO$^+$/Ce$^+$ ratio were eventually obtained. A peristaltic pump was not used, as free aspiration of the nebuliser provided better signal stability.

The masses monitored during mass spectrometry and possible isobaric interferences for which corrections were made are listed in Table 2. Although these interferences should be reduced to insignificant levels by the chemical separation procedures, ^{95}Mo$^+$ and ^{111}Cd$^+$ were monitored to correct ^{100}Ru$^+$ and ^{108}Pd$^+$ signals, respectively. Similarly, ^{189}Os$^+$ was monitored to correct ^{187}Re$^+$. However, the ^{189}Os$^+$ signal was typically very small, and considering the large variation of ^{187}Os/^{189}Os ratios of natural samples, no

correction was necessary for this potential interference. Scanning was generally performed nine times.

All parts of the sample introduction system, such as the nebuliser, spray chamber, torch and cones, were carefully cleaned before use. The instrument background was monitored by measuring the signals of Pt, Pd, Ir, Ru and Re in a 2% HNO$_3$ rinse solution and was routinely < 5 cps. An instrumental mass bias correction was carried out by the calibrator-sample bracketing method using a 2 ng ml^{-1} synthetic PGE-Re standard solution during the determination of Re and the PGE. Measured PGE-Re isotopic ratios for the sample-spike mixtures were corrected using normalising factors calculated from the average measured ratios on the bracketed calibrators as compared with the 'true' IUPAC ratios (Rosman and Taylor 1998). Variations in these correction factors were found to be ~ 2% between the results of the initial and final standard runs. The precisions of the isotopic ratios for PGE-Re standard solutions were generally better than 1% (RSD, relative standard deviation). Isotope dilution calculations were performed offline on a commercial spreadsheet.

Results and discussion

Pre-concentration of PGE and Re by cation exchange chromatography

A synthetic PGE-Re standard solution (10 ng g^{-1}) and potential interfering elements (10 µg g^{-1} of Zr, Mo, Hf and W)

were used to optimise the chemical separation parameters in each stage of column purification. The solution was treated with the same procedures as those for the natural samples.

Previous studies have noted that PGE may experience hydrolytic loss at lower HCl molarities (0.1 mol l^{-1}) and that maximum recovery of PGE can be obtained at higher HCl molarities (0.5–0.6 mol l^{-1}; e.g., Strelow and Victor 1991, Ely *et al.* 1999, Shinotsuka and Suzuki 2007). We investigated the performance of the studied resins with different HCl molarities (0.1 and 0.5 mol l^{-1}). The elution profiles using the standard solution diluted in 0.1 and 0.5 mol l^{-1} HCl are shown in Figure 2. These profiles are different for PGE-Re (Figure 2). It is evident that the PGE-Re moved more rapidly through the column in 0.5 mol l^{-1} HCl than in 0.1 mol l^{-1} HCl. When 0.5 mol l^{-1} HCl was used as the eluant, > 95% of the PGE-Re were recovered in 30 ml of HCl, whereas when 0.1 mol l^{-1} HCl was used as the eluant, Pt-Pd-Re were completely recovered in 30 ml of HCl, but *ca.* 10% of the Ru-Ir were retained on the resin. A much greater volume of eluant (a further 30 ml) was required to achieve complete recovery of Ru-Ir. This probably reflects that fact that Ru-Ir chloro-complexes have different distribution coefficients on the resin as compared to the other PGE. Therefore, in the light of these tests, we elected to elute and collect 30 ml of 0.5 mol l^{-1} HCl to ensure high PGE yields and minimise the volume of eluant used.

Zr, Hf, Mo and W separation from PGE-Re by BPHA extraction chromatography

Molecular isobaric interferences from Zr, Hf, Mo and W on the PGE-Re are sometimes unavoidable after cation exchange separation (e.g., Jarvis *et al.* 1997, Ely *et al.* 1999, Shinotsuka and Suzuki 2007). The oxide interferences of $^{177,179}Hf^{16}O^{+}$ on $^{193}Ir^{+}$ and $^{195}Pt^{+}$, and of $^{90,92}Zr^{16}O^{+}$

and $^{92}Mo^{16}O^{+}$ on $^{106,108}Pd^{+}$ are particularly problematic during ID-ICP-MS analysis as the oxide formation rate of interfering elements is high. Although it is possible to mathematically correct for these interfering species, an increase in the uncertainty budget is still a consequence. Furthermore, the large ion beam peaks of W and Mo can tail onto small Re and Ru peaks (Shinotsuka and Suzuki 2007). Consequently, efficient and near-complete chemical separation of these interfering elements from the PGE-Re prior to ID-ICP-MS analysis is the most robust method to produce accurate concentration data. Shinotsuka and Suzuki (2007) investigated the use of solvent extraction using BPHA in chloroform to separate Zr, Hf, Mo and W from PGE-Re. BPHA is a typical chelating agent and selectively extracts group 4, 5 and 6 elements in the periodic table (e.g., Goguel 1992, Shinotsuka and Suzuki 2007, Li *et al.* 2010a). Although this method provides excellent separation of all the interfering elements, it does involve the use of toxic chloroform. As such, we developed a method using BPHA extraction chromatography for the separation of Zr, Hf, Mo and W from the PGE-Re.

An elution profile for PGE-Re and potential interfering elements on a BPHA column using 0.5 mol l^{-1} HCl is shown in Figure 3a and b, respectively. As expected, all the interfering elements were strongly absorbed on the resin, whereas the PGE-Re were largely eluted straight through the column. The effect of HCl molarity on the elution of the PGE-Re through the BPHA column was further examined. A synthetic standard solution of PGE-Re and interfering elements (i.e., Zr, Mo, Hf and W) was diluted with 1 ml of 0.5–4 mol l^{-1} HCl and loaded onto the BPHA columns, after the columns have been pre-conditioned with 5–10 ml of HCl at the same concentration as the loading solutions. The concentrations of PGE-Re and interfering elements in the eluants were measured by ICP-MS and compared with
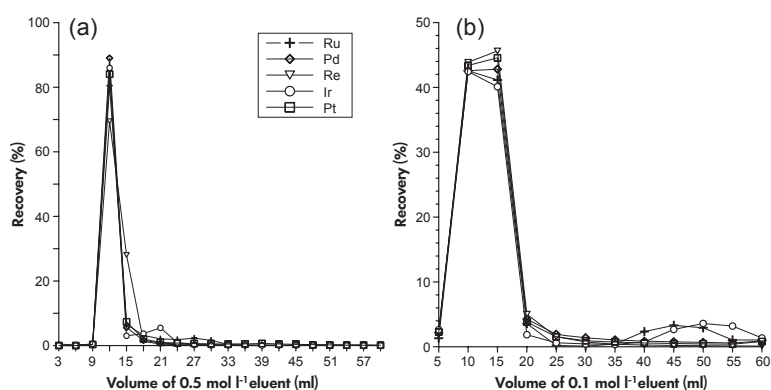

Figure 2. Elution profiles of PGE-Re (cumulative % recovery) during cation exchange separation using HCl of different molarity: (a) 0.5 mol l^{-1}; (b) 0.1 mol l^{-1}. The volume of cation resin was about 44 ml.
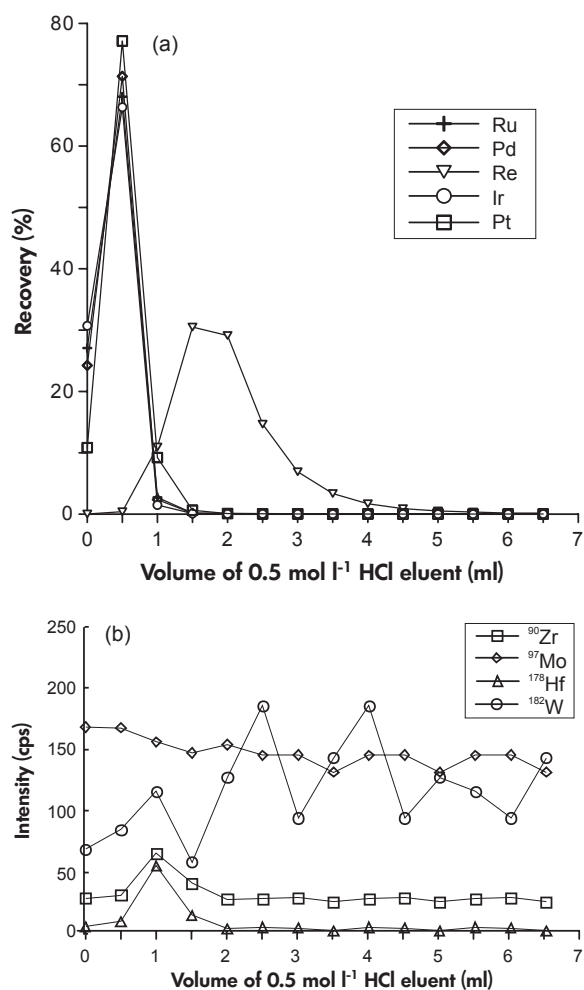
Figure 3. Elution profiles of PGE-Re (cumulative % recovery) (a) and the interfering elements (ICP-MS cps intensity); (b) during the BPHA extraction chromatographic separation in 0.5 mol l⁻¹ HCl. About 1 ml of BPHA resin and a synthetic PGE-Re standard solution (10 ng g⁻¹) and potential interfering elements (10 μg g⁻¹ of Zr, Mo, Hf and W) were used.

Table 3.
Recoveries of the PGE-Re and the interfering elements (Zr, Hf, Mo and W) using the BPHA extraction chromatographic separation in 0.5 mol l⁻¹ HCl

Analyte	Before BPHA column separation	After BPHA column separation	Recovery (%)
Ru	10 ng ml⁻¹	9.85 ng ml⁻¹	98.5
Pd	10 ng ml⁻¹	9.85 ng ml⁻¹	98.5
Re	10 ng ml⁻¹	9.91 ng ml⁻¹	99.1
Ir	10 ng ml⁻¹	9.88 ng ml⁻¹	98.8
Pt	10 ng ml⁻¹	9.81 ng ml⁻¹	98.1
Mo	10 μg ml⁻¹	0.029 ng ml⁻¹	0.00
Zr	10 μg ml⁻¹	0.017 ng ml⁻¹	0.00
Hf	10 μg ml⁻¹	0.015 ng ml⁻¹	0.00
W	10 μg ml⁻¹	0.067 ng ml⁻¹	0.00

The concentrations of the synthetic PGE-Re standard solution (10 ng ml⁻¹) and potential interfering elements (10 μg g⁻¹ of Zr, Mo, Hf and W) were measured by ICP-MS and compared with those in the loading solutions prior to BPHA column chemistry.

Procedural blanks

In contrast to other chemical separation procedures for PGE-Re purification, our method only required the use of concentrated acids for the digestion step and subsequently only used dilute HCl for the chemical separation. As such, the procedural blanks were largely controlled by the quality of acids used in the method. All the acids and reagents used in this study were carefully purified as described above. In addition, laboratory ware is also known to be a main source of blanks, and in particular, Os memory effects are a serious for PFA vials (e.g., Hirata 2000, Li *et al.* 2010b). We found that the Os blank was decreased dramatically by about one order of magnitude when PFA vials were cleaned with concentrated HBr. Osmium blanks during the course of this study ranged from 0.1 to 0.4 pg with a median value of 0.19 pg and $^{187}Os/^{188}Os$ ratio of 0.34. At such a low blank levels, it is possible to precisely measure Os concentrations and $^{187}Os/^{188}Os$ ratios in most igneous rocks by N-TIMS. Pearson and Woodland (2000) and Rehkämper *et al.* (1998) noted that the high Pt blank (*ca.* 200 pg) can originate from the borosilicate glass Carius tubes. Pearson and Woodland (2000) suggested that rigorous boiling of Carius tubes in *aqua regia* can improve blank levels to between 10 and 25 pg. We followed this cleaning method, and Pt blanks during the course of this study varied from 25 to 40 pg, with a median value of 32 pg. We also found that the main blank source of Pd and Re was from H_2O_2. The procedural blanks for Ru, Ir, Pd and Re were 7.0, 3.5, 7.6 and 8.1 pg, respectively. Although such contributions from the procedural blanks were negligible during this work, the

those in the loading solutions prior to column chemistry (Table 3). In all cases, from an HCl molarity of 0.5−3 mol l⁻¹, levels of the interfering elements were reduced to < 1%, and the PGE were quantitatively recovered in 2 ml of eluant. However, some retention of Re on the columns was observed, and a greater volume of eluant (6 ml) was necessary to completely elute Re. In all subsequent experiments, removal of interfering elements by BPHA extraction chromatography was carried out in 0.5 mol l⁻¹ HCl. After use of a column, the absorbed interfering elements can be removed from the resin by elution of 5–10 ml of 6 mol l⁻¹ HF, and the resin bed can be used more than twenty times in succession without any appreciable loss in the sorption efficiency.

Table 4.
Replicate determinations of PGE-Re concentrations (ng g^{-1}) and Os isotope ratios for geochemical reference materials UB-N, TDB-1, BHVO-2 and WGB-1, and literature data

Run No.	Digestion	Ru	Pd	Re	Os	Ir	Pt	$^{187}Os/^{188}Os$	2s	$^{187}Re/^{188}Os$	2s	Os/Ir	Pt/Ir
UB-N (Serpentine, CRPG)													
1[a]		7.37	6.27	0.195	2.92	2.94	7.39	0.1272	0.0003	0.29	0.01	1.00	2.5
2[a]		6.45	5.54	0.184	3.45	3.28	7.65	0.1268	0.0004	0.26	0.01	1.05	2.3
3[a]		5.62	5.36	0.189	2.96	3.22	7.22	0.1272	0.0003	0.31	0.02	0.92	2.2
4[b]		7.46	5.62	0.189	3.56	4.12	7.55	0.1270	0.0003	0.26	0.01	0.86	1.8
5[b]		8.57	5.50	0.217	3.74	4.22	8.02	0.1268	0.0003	0.28	0.02	0.89	1.9
Average		7.09 (16)[c]	5.66 (6.2)	0.197 (6.5)	3.42 (10)	3.56 (16)	7.56 (4.0)	0.1270	0.0002	0.28	0.02	0.96	2.1
Meisel and Moser (2004a), Meisel et al. (2003b)	HPA-S	6.30 (4.8)	6.11 (3.0)	0.206 (1.4)	3.71 (5.9)	3.38 (6.5)	7.42 (4.0)	0.1278	0.0002			1.10	2.2
Becker et al. (2006)	CT	6.51 (5.0)	5.85 (4.5)	0.205 (1.9)	3.51 (3.5)	3.26 (3.9)	7.00 (3.3)	0.1274	0.0003			1.08	2.1
Puchtel et al. (2008)	CT	6.93 (6.8)	5.70 (2.1)	0.213 (5.2)	3.85 (8.3)	3.58 (11.2)	7.47 (7.3)	0.1272	0.0004			1.08	2.1
Fischer-Gödde et al. (2011)	HPA-S	6.43 (5.9)	5.85 (3.4)	0.188 (13)	3.53 (7.0)	3.16 (7.0)	7.31 (6.4)	0.1272	0.0004	0.26		1.12	2.3
TDB-1 (Diabase, CCRMP)													
1		0.206	22.36	0.820	0.130	0.080	5.21	0.7542	0.0009	33.0	0.6	1.63	65.6
2		0.205	22.43	0.876	0.118	0.072	4.92	0.8585	0.0008	39.2	1.0	1.64	68.5
3		0.168	18.79	0.841	0.100	0.062	4.67	0.9809	0.0018	45.2	1.0	1.59	74.8
4		0.185	22.76	0.823	0.102	0.059	4.43	0.9497	0.0014	43.2	1.9	1.72	75.2
5		0.191	18.66	0.873	0.095	0.064	4.98	1.0477	0.0037	49.5	0.6	1.49	78.2
Average		0.192 (8.2)	21.00 (10)	0.847 (3.2)	0.109 (13)	0.067 (12)	4.84 (6.2)	0.9182	0.1100	42.0	6.3	1.63	69.9
Meisel and Moser (2004b)	HPA-S	0.198 (4.1)	24.3 (7.8)	0.794 (3.0)	0.117 (10)	0.075 (13)	5.01 (3.6)	0.9165	0.0895			1.56	66.8
Qi and Zhou (2008)	CT	0.220 (9.1)	23.0 (5.2)	0.770 (1.3)	0.153 (6.5)	0.082 (12)	5.23 (5.4)					1.87	63.8
Shinotsuka and Suzuki (2007)	CT	0.203 (9.1)	22.4 (4.1)	0.801 (3.0)	0.0965 (9.6)	0.070 (4.7)	4.84 (3.5)					1.37	68.8
Savard et al. (2010)	NiS-FA	0.253 (7.3)	22.82 (3.5)	0.063 (48)	0.159 (17)	0.084 (24)	4.64 (6.6)					1.89	55.2
Savard et al. (2010)	HPA-S	0.164 (17)	22.35 (4.8)	0.721 (3.4)	0.05 (42)	0.061 (25)	4.79 (3.9)					0.82	78.5
Becker et al. (2006)			24.8 (4.0)		0.122 (4.1)	0.078 (6.4)	4.40 (4.5)	0.8323	0.0040			1.56	56.4
Dale et al. (2012b)	HPA-S	0.231 (17)	22.3 (8.0)	1.01 (7)	0.106 (10)	0.059 (10)	4.74 (12)	0.973	0.128			1.80	80.3
BHVO-2 (Hawaiian basalt, USGS)													
1		0.101	2.90	0.587	0.089	0.069	6.73	0.1517	0.0003	31.8	0.7	1.29	97.2
2		0.098	2.89	0.560	0.063	0.065	14.21	0.1525	0.0006	42.8	1.0	0.97	218.0
3		0.097	2.99	0.572	0.068	0.064	7.58	0.1565	0.0005	40.5	1.5	1.07	119.0
4		0.100	2.68	0.508	0.071	0.055	5.10	0.1551	0.0005	34.6	1.4	1.29	92.9
5		0.117	2.81	0.522	0.087	0.071	5.70	0.1551	0.0022	28.2	0.5	1.23	80.9
Average		0.102 (8.0)	2.85 (4.1)	0.550 (6.1)	0.076 (15)	0.065 (9.5)	7.86 (49)	0.154	0.0022	37.4	5.0	1.10	117.6
Meisel and Moser (2004b)	HPA-S	0.129 (43)	2.94 (1.4)	0.543 (4.1)	0.101 (25)	0.058 (25)	10.1 (49)					1.74	174.1
Shinotsuka and Suzuki (2007)	CT	0.123 (18)	2.99 (1.7)	0.523 (2.4)	0.115 (40)	0.071 (31)	7.39 (17)					1.62	104.1
Li et al. (2011)	CT	0.138 (16)	3.14 (13)	0.554 (3.0)	0.083 (13)	0.06 (21)	8.56 (24)	0.1517	0.0007			1.38	142.7

Table 4 (continued).
Replicate determinations of PGE-Re concentrations (ng g^{-1}) and Os isotope ratios for geochemical reference materials UB-N, TDB-1, BHVO-2 and WGB-1, and literature data

Run No.	Digestion	Ru	Pd	Re	Os	Ir	Pt	^{187}Os/^{188}Os	2s	^{187}Re/^{188}Os	2s	Os/Ir	Pt/Ir
WGB-1 (Gabbro, CCRMP)													
1		0.128	15.81	1.10	0.386	0.198	4.09	0.188	0.0004	13.9	0.4	1.95	20.7
2		0.161	15.51	1.16	0.354	0.201	4.40	0.1792	0.0006	15.9	0.2	1.77	21.9
3		0.185	13.40	1.19	0.412	0.187	4.31	0.1931	0.0006	14.0	0.6	2.20	23.0
4		0.121	13.56	1.10	0.457	0.183	5.03	0.1827	0.0003	11.7	0.2	2.50	27.5
5		0.168	11.40	1.17	0.384	0.212	3.63	0.1863	0.0015	14.7	1.0	1.81	17.1
Average		0.153 (18)	13.94 (14)	1.14 (3.4)	0.399 (9.7)	0.196 (5.8)	4.29 (12)	0.1858	0.0061	13.9	1.6	2.03	21.9
Meisel and Moser (2004b)	HPA-S	0.144 (16)	13.9 (19)	1.15 (6.0)	0.54 (13)	0.211 (13)	6.39 (56)					2.56	30.3
Qi and Zhou (2008)	CT	0.130 (7.7)	13.0 (8.5)	1.14 (0.9)	0.37 (5.4)	0.160 (12)	6.34 (10)					2.31	39.6
Sun et al. (2009)	NiS-FA	0.159 (9.4)	10.6 (4.7)	1.06 (9.4)	0.602 (6.3)	0.183 (7.1)	5.38 (11)					3.29	29.4
Savard et al. (2010)	NiS-FA	0.182 (8.4)	12.42 (3.5)	0.33 (44)	0.544 (29)	0.199 (5.6)	4.71 (6.2)					2.73	23.7
Savard et al. (2010)	HPA-S	0.253 (77)	12.06 (17)	1.23 (8.6)	0.484 (7.7)	0.225 (21)	4.27 (12)					2.15	19.0
Peucker-Ehrenbrink et al. (2003)	NiS-FA		16.2 (4.0)		0.693 (25)	0.254 (26)	5.8 (22)	0.187	0.012				
Schmidt and Snow (2002)	NiS-FA				0.430 (4.7)			0.1582	0.0002				
Total procedure blanks (in pg, n = 4)		7	7.6	8.1	0.19	3.5	32						
Median value								0.34					

a Digestion temperature 240 °C.
b Digestion temperature 270 °C.
c Relative standard deviations (1s, %) are shown in parentheses. Uncertainties of Re-Os isotope quoted at 2s$_{mean}$.

Re blank was still slightly high; therefore, this method is probably unsuitable for accurate determination of Re-Os isotopes for some samples with very low Re content (e.g., lunar basalt).

PGE-Re concentration and Os isotope results for geochemical reference materials

The proposed method was used to determine the PGE-Re concentrations and Os isotope ratios of geochemical reference materials UB-N, TDB-1, WGB-1 and BHVO-2 (Table 4). The CI chondrite-normalised PGE-Re patterns for
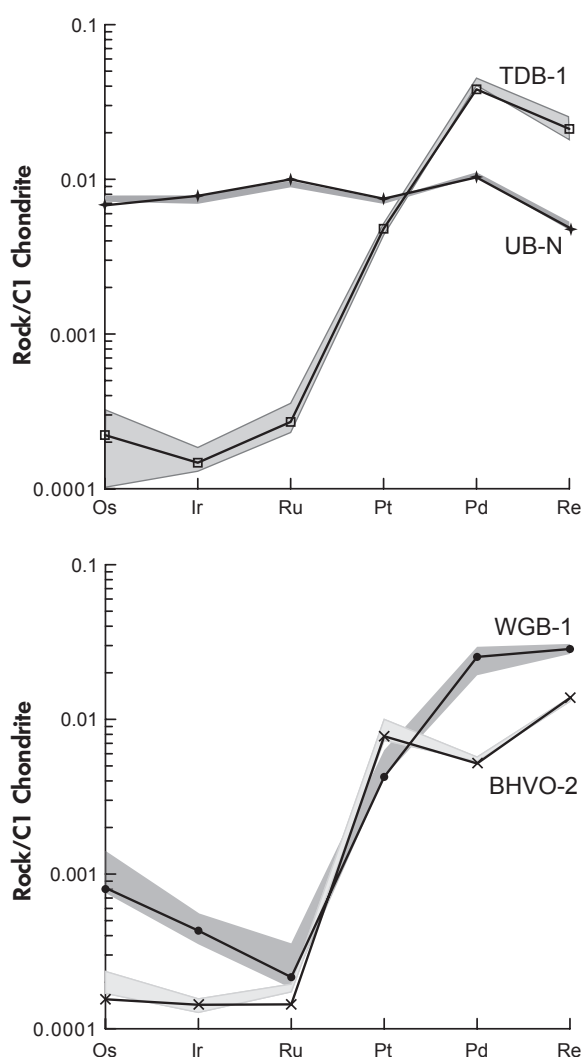
Figure 5. Replicate analyses of Re-Os isotope data for TDB-1 showing how binary mixing of two phases with different Os concentrations and isotopic ratios produces a linear trend in a plot of $1/Os$ vs. $^{187}Os/^{188}Os$.

Figure 4. CI chondrite-normalised PGE-Re patterns for reference materials UB-N, TDB-1, BHVO-2 and WGB-1. The concentrations of CI chondrites are from McDonough and Sun (1995). The reference fields (shaded areas) are from previously published values (given in Table 4).
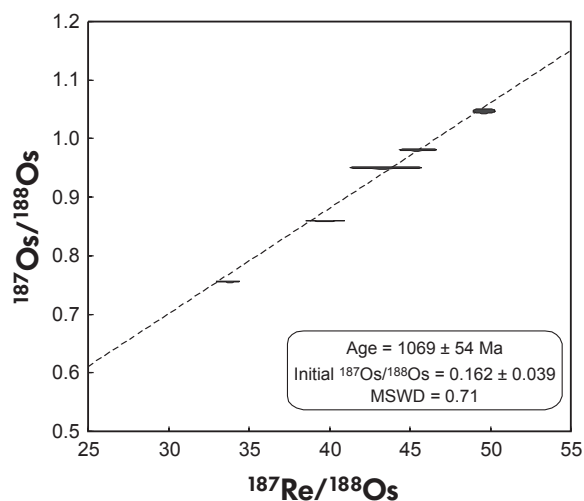
Figure 6. Replicate analyses of Re-Os isotope data for TDB-1 showing an isochron-type relationship.

these reference materials were plotted in Figure 4. Meisel and Moser (2004a) demonstrated that UB-N is the best reference rock reference material for PGE concentrations and is homogeneous at size fractions of 0.5–2 g. Platinum-group element concentrations and Os isotope ratios of UB-N have been determined by many laboratories (Table 4), making it an ideal reference material for evaluating our procedures. It should be noted that Meisel and Moser (2004a) concluded that the Carius tube digestion method was less efficient than the high-pressure asher (HPA-S) digestion technique for extracting PGE and, in particular, Os, Ir and Ru from the Mg-spinel-bearing peridotite UB-N.

To test our digestion method, we digested five aliquots of UB-N at different temperatures. The reproducibilities of Pd, Re and Pt concentrations were better than those of Ru, Ir and Os at temperatures of both 240 and 270 °C. Ratios of Os/Ir and Pt/Ir obtained at a temperature of 240 °C were higher than those at 270 °C. These results confirm that the Carius tube digestion is less efficient in dissolving PGE carriers in UB-N than the HPA-S digestion technique. It is thus possible that the somewhat poor reproducibility of our Ru, Ir and Os concentrations might be due to incomplete digestion rather than sample inhomogeneity. The use of a HPA-S system or Carius tube digestion at higher temperatures is thus advisable to avoid or minimise incomplete sample digestions. $^{187}Os/^{188}Os$ ratios measured for UB-N were reproducible to better than 0.2%, and our mean $^{187}Os/^{188}Os$ ratio was only 0.7% lower (0.1278 ± 2 vs. 0.1270 ± 3) (2 SE) than that reported by Meisel et al. (2003b) and is in excellent agreement with more recent studies of this reference material (0.1272 ± 4) (2 SE) (Fischer-Gödde et al. 2011).

Although previous studies have shown that PGE concentration in TDB-1 seems to be rather homogeneous (Meisel and Moser 2004a, Shinotsuka and Suzuki 2007), we observed poorer reproducibilities for Ir-Os concentrations and $^{187}Os/^{188}Os$ ratios in TDB-1. Our results for this reference material are consistent with those of Dale et al. (2012b), which may be due to sample heterogeneity. The Re-Os isotope system is highly sensitive to heterogeneous phase distribution in sample powders (Meisel et al. 2001b). This influence on Re-Os isotopic systematics is due to the irregular distribution of mineral phases such as osmiridium or sulfide in powder aliquots of the same rock sample and is referred to the 'nugget effect'. In a plot of $^{187}Os/^{188}Os$ vs. 1/Os for TDB-1, we observed a linear trend (Figure 5), which is indicative of mixing between two phases with different Os concentrations and Os isotopic compositions. Heterogeneous mixing of these two phases also produces a linear trend on a Re-Os isochron diagram, which appears to define a meaningful geological age (i.e., 1000–1200 Ma; Bell 1981; Figure 6).

The somewhat poorer reproducibility (RSD = 49%) for Pt concentrations of BHVO-2 was caused by a single discrepant analysis. This is consistent with the results of Meisel and Moser (2004b), who also obtained large RSD values for Pt concentrations in BHVO-2 (RSD = 49%). Meisel and Moser (2004b) concluded that even a 2 g sample aliquot was insufficient to allow determination of a precise average Pt concentration of a sample in the presence of Pt-rich nuggets and that a robust analysis requires digestion of a much larger aliquot. Our average Os concentration data for

BHVO-2 were lower than the ID-ICP-MS data reported by Meisel and Moser (2004b) and Shinotsuka and Suzuki (2007). Given the large variability in the data reported by these previous studies and the analytical difficulties in measuring low Os concentration by ICP-MS, it is likely that the superior reproducibility of our Os concentration measurements was partly due to use of the higher-sensitivity N-TIMS method. Our average $^{187}Os/^{188}Os$ ratios for BHVO-2 reproduce well and agree with those reported by Li et al. (2011). In contrast, Re and other PGE concentrations appear to be relatively homogeneously distributed in BHVO-2 with RSD values < ±10%.

Our PGE-Re concentrations obtained for WGB-1 agreed well with published data for this reference material that were obtained using different digestion techniques (Carius tube, HPA-S and NiS fire assay) within the analytical uncertainties of each other (Figure 4). The $^{187}Os/^{188}Os$ ratio determined in this study for WGB-1 was significantly more radiogenic (0.1858 vs. 0.1582) than N-TIMS data reported by Schmidt and Snow (2002), but was identical to values (0.1858 vs. 0.1870) reported by Peucker-Ehrenbrink et al. (2003). These differences may indicate Os isotope heterogeneity between the WGB-1 powder splits used in the different laboratories. Rhenium concentration data for WGB-1 reproduced well (RSD = 3.4%) and indicate that Re is relatively homogeneously distributed in WGB-1.

Conclusions

A simple and effective procedure was developed for the determination of platinum-group element and rhenium concentrations, and Os isotopes from the same sample digestion by ID-ICP-MS and N-TIMS, respectively. Our procedure takes advantage of group separation of PGE and Re by cation exchange techniques and then complete removal of potential interfering elements such as Zr, Hf, Mo and W in the PGE-Re fractions by BPHA extraction chromatography. Both PGE-Re concentration and Os isotope data for four international reference materials determined with our method agree well with published data for these reference materials. However, it is evident that poor reproducibilities for Ru, Ir and Os concentrations in UB-N were due to the insufficient dissolution of PGE-bearing refractory phases rather than sample heterogeneity. Although PGE concentrations in TDB-1 are generally thought to be relatively homogeneous, Re-Os isotope data for this reference material showed that irreproducible PGE abundances are caused by real sample inhomogeneity and not erroneously produced by our analytical method. Large variations in the Pt data (RSD = 49%) contrast with reproducible Ru, Pd, Ir, Os and Re concentration data and

^{187}Os/^{188}Os ratios for BHVO-2. The poor Pt concentration reproducibility might reflect heterogeneous distribution of Pt-rich nuggets in BHVO-2. However, unlike BHVO-2 and TDB-1, PGE-Re and Os isotopes appear to be homogeneously distributed in WGB-1.

Acknowledgements

Note added by the Journal: The authorship of the version of record of this article was modified following Accepted Article publication (on 3 June 2013) with the agreement of the Joint Editor in Chief and all of the participating authors.

References

Becker H., Horan M.F., Walker R.J., Gao S., Lorand J.-P. and Rudnick R.L. (2006)
Highly siderophile element composition of the Earth's primitive upper mantle: Constraints from new data on peridotite massifs and xenoliths. Geochimica et Cosmochimica Acta, 70, 4528–4550.

Bell K. (1981)
A review of the geochronology of the Precambrian of Saskatchewan – Some clues to uranium mineralization. Mineralogical Magazine, 44, 371–378.

Birck J.L., Roy-Barman M. and Capmas F. (1997)
Re-Os isotopic measurements at the femtomole level in natural samples. Geostandards Newsletter: The Journal of Geostandards and Geoanalysis, 21, 19–27.

Cohen A.S. and Waters F.G. (1996)
Separation of osmium from geological materials by solvent extraction for analysis by thermal ionization mass spectrometry. Analytica Chimica Acta, 332, 269–275.

Creaser R.A., Papanastassiou D.A. and Wasserburg G.J. (1991)
Negative thermal ion mass spectrometry of osmium, rhenium and iridium. Geochimica et Cosmochimica Acta, 55, 397–401.

Dale C.W., Burton K.W., Greenwood R.C., Gannoun A., Wade J., Bernard J., Wood B.J. and Pearson D.J. (2012a)
Late accretion on the earliest planetesimals revealed by the highly siderophile elements. Science, 336, 72–75.

Dale C.W., Macpherson C.G., Pearson D.J., Hammond S.J. and Arculus R.J. (2012b)
Inter-element fractionation of highly siderophile elements in the Tonga Arc due to flux melting of a depleted source. Geochimica et Cosmochimica Acta, 89, 202–225.

Day J.M.D., Pearson D.G. and Taylor L.A. (2007)
Highly siderophile element constraints on the accretion and differentiation of the Earth-Moon system. Science, 315, 217–219.

Ely J.C., Neal C.R., O'Neill J.A. and Jain J.C. (1999)
Quantifying the platinum-group elements (PGEs) and gold in geological samples using cation exchange pretreatment and ultrasonic nebulization inductively coupled plasma-mass spectrometry (USN-ICP-MS). Chemical Geology, 157, 219–234.

Fischer-Gödde M., Becker H. and Wombacher F. (2011)
Rhodium, gold and other highly siderophile elements in orogenic peridotites and peridotite xenoliths. Chemical Geology, 280, 365–383.

Goguel R. (1992)
Group separation by solvent extraction from silicate rock matrix of Nb, Mo, Ta and W at low levels for ICP-MS. Fresenius' Journal of Analytical Chemistry, 344, 326–333.

Hirata T. (2000)
Development of a flushing spray chamber for inductively coupled plasma-mass spectrometry. Journal of Analytical Atomic Spectrometry, 15, 1447–1450.

Jarvis I., Totland M.M. and Jarvis K.E. (1997)
Determination of the platinum-group elements in geological materials by ICP-MS using microwave digestion, alkali fusion and cation-exchange chromatography. Chemical Geology, 143, 27–42.

Kato Y., Fujinaga K. and Suzuki K. (2005)
Major and trace element geochemistry and Os isotopic composition of metalliferous umbers from the Late Cretaceous Japanese accretionary complex. Geochemistry Geophysics Geosystems, 6, Q07004.

Li J., Zhong L.F., Tu X.L., Liang X.R. and Xu J.F. (2010a)
Determination of rhenium content in molybdenite by ICP-MS after separation of the major matrix by solvent extraction with N-benzoyl-N-phenylhydroxalamine. Talanta, 81, 954–958.

Li J., Liang X.R., Xu J.F., Suzuki K. and Dong Y.H. (2010b)
Simplified technique for the measurements of Re-Os isotope by multicollector inductively coupled plasma-mass spectrometry (MC-ICP-MS). Geochemical Journal, 44, 73–80.

references

Li J., Zhong L.F., Tu X.L., Hu G.Q., Sun Y.M., Liang X.R. and Xu J.F. (2011)
Platinum-group elements and Re-Os isotope analyses for geological samples using a single digestion procedure. Geochimica (Beijing), 40, 372–380.

McDonough W.F. and Sun S-s (1995)
The composition of the Earth. Chemical Geology, 120, 223–253.

Meisel T. and Moser J. (2004a)
Reference materials for geochemical PGE analysis: New analytical data for Ru, Rh, Pd, Os, Ir, Pt and Re by isotope dilution ICP-MS in 11 geological reference materials. Chemical Geology, 208, 319–338.

Meisel T. and Moser J. (2004b)
Platinum-group element and rhenium concentrations in low abundance reference materials. Geostandards and Geoanalytical Research, 28, 233–250.

Meisel T., Moser J., Fellner N., Wegscheider W. and Schoenberg R. (2001a)
Simplified method for the determination of Ru, Pd, Re, Os, Ir and Pt in chromitites and other geological materials by isotope dilution ICP-MS and acid digestion. The Analyst, 126, 322–328.

Meisel T., Moser J. and Wegscheider W. (2001b)
Recognizing heterogeneous distribution of platinum-group elements (PGE) in geological materials by means of the Re-Os isotope system. Fresenius' Journal of Analytical Chemistry, 370, 566–572.

Meisel T., Fellner N. and Moser J. (2003a)
A simple procedure for the determination of platinum-group elements and rhenium (Ru, Rh, Pd, R, Os, Ir and Pt) using ID-ICP-MS with an inexpensive on-line matrix separation in geological and environmental materials. Journal of Analytical Atomic Spectrometry, 18, 720–726.

Meisel T., Reisberg L., Moser J., Carignan J., Melcher F. and Brugmann G. (2003b)
Re-Os systematics of UB-N, a serpentinized peridotite reference material. Chemical Geology, 201, 161–179.

Morgan J.W. (1985)
Osmium isotope constraints on Earth's late accretionary history. Nature, 317, 703–705.

Nozaki T., Suzuki K., Ravizza G., Kimura J-I. and Chang Q. (2012)
A method for rapid determination of Re and Os isotope compositions using ID-MC-ICP-MS combined with the sparging method. Geostandards and Geoanalytical Research, 36, 131–148.

Pearson D.G. and Woodland S.J. (2000)
Solvent extraction/anion exchange separation and determination of PGE (Os, Ir, Pt, Pd, Ru) and Re-Os isotopes in geological samples by isotope dilution ICP-MS. Chemical Geology, 165, 57–107.

Pearson D.G., Parman S.W. and Nowell G.M. (2007)
A link between large mantle melting events and continent growth seen in osmium isotopes. Nature, 449, 202–205.

Peucker-Ehrenbrink B., Bach W., Hart S.R., Blusztajn J. and Abbruzzese T. (2003)
Rhenium-osmium isotope systematics and platinum-group element concentrations in oceanic crust from DSDP/ODP Sites 504 and 417/418. Geochemistry Geophysics Geosystems, 4, 1–28.

Plessen H. and Erzinger J. (1998)
Determination of the platinum-group elements and gold in twenty rock reference materials by inductively coupled plasma-mass spectrometry (ICP-MS) after pre-concentration by nickel sulfide fire-assay. Geostandards Newsletter: The Journal of Geostandards and Geoanalysis, 22, 187–194.

Puchtel I.S. and Humayun M. (2000)
Platinum-group elements in Kostomuksha komatiites and basalts: Implications for oceanic crust recycling and core-mantle interaction. Geochimica et Cosmochimica Acta, 64, 4227–4242.

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

Puchtel I.S., Walker R.J., James O.B. and Kring D.A. (2008)
Osmium isotope and highly siderophile element systematics of lunar impact melt rocks: Implications for the late accretion history of the Moon and Earth. Geochimica et Cosmochimica Acta, 72, 3022–3042.

Qi L. and Zhou M.F. (2008)
Platinum-group elemental and Sr-Nd-Os isotopic geochemistry of Permian Emeishan flood basalts in Guizhou Province, SW China. Chemical Geology, 248, 83–103.

Qi L., Zhou M.F. and Wang Y. (2004)
Determination of low concentrations of platinum group elements in geological samples by ID-ICP-MS. Journal of Analyitical Atomic Spectrometry, 15, 1335–1339.

Rehkämper M., Halliday A.N., Barfod D., Fitton J.G. and Dawson J.B. (1997)
Platinum-group element abundance patterns in different mantle environments. Science, 278, 1595–1598.

Rehkämper M., Halliday A.N. and Wentz R.F. (1998)
Low-blank digestion of geological samples for platinum-group element analysis using a modified Carius tube design. Fresenius' Journal of Analytical Chemistry, 361, 217–219.

references

Rosman K.J.R. and Taylor P.D.P. (1998)
Isotopic compositions of the elements 1997. Pure and Applied Chemistry, **70**, 217–238.

Savard D., Barnes S.-J. and Meisel T. (2010)
Comparison between nickel-sulfur fire assay Te co-precipitation and isotope dilution with high-pressure asher acid digestion for the determination of platinum-group elements, rhenium and gold. Geostandards and Geoanalytical Research, **34**, 281–291.

Schmidt G. and Snow J. (2002)
Os isotopes in mantle xenoliths from the Eifel volcanic field and the Vogelsberg (Germany): Age constraints on the lithospheric mantle. Contributions to Mineralogy and Petrology, **143**, 694–705.

Shinotsuka K. and Suzuki K. (2007)
Simultaneous determination of platinum-group elements and rhenium in rock samples using isotope dilution inductively coupled plasma-mass spectrometry after cation exchange separation followed by solvent extraction. Analytica Chimica Acta, **603**, 129–139.

Shirey S.B. and Walker R.J. (1995)
Carius tube digestion for low-blank rhenium-osmium analysis. Analytical Chemistry, **67**, 2136–2141.

Strelow F.W.E. and Victor A. (1991)
Improved separation of palladium from base metals by cation-exchange chromatography. Analytica Chimica Acta, **248**, 535–542.

Sun Y.L, Chu Z.Y., Sun M. and Xia X.P. (2009)
An improved Fe-Ni sulfide fire assay method for determination of Re, platinum group elements, and Os isotopic ratios by inductively coupled plasma- and negative thermal ionization-mass spectometry. Applied Spectroscopy, **63**, 1232–1237.

Suzuki K., Miyata Y. and Kanazawa N. (2004)
Precise Re isotope ratio measurements by negative thermal ion mass spectrometry (NTI-MS) using total evaporation technique. International Journal of Mass Spectrometry, **235**, 97–101.

Volkening J., Walczyk T. and Heumann K.G. (1991)
Osmium isotope ratio determinations by negative thermal ionization mass spectrometry. International Journal of Mass Spectrometry and Ion Processes, **105**, 147–159.

Yang X.J. and Pin C. (2002)
Determination of niobium, tantalum, zirconium and hafnium in geological materials by extraction chromatography and inductively coupled plasma-mass spectrometry. Analytica Chimica Acta, **458**, 375–386.