Determination of PGE Concentration(s) and Re-Os Isotope(s) using ID-ICP-MS and N-TIMS from a Single Digestion after Two-Stage Column Separation

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Abstract

We report an improved procedure for determination of platinum group elements (PGE) and Re concentrations, and Os isotopes on a single sample aliquot by isotope dilution (ID) using inductively coupled plasma-mass spectrometry (ICP-MS) and negative thermal ionization mass spectrometry (N-TIMS), respectively. A two-stage column method is used to purify PGE-Re from their sample matrix and interfering elements (e.g., Mo, Zr and Hf) after Os has been separated by CCl_4 solvent extraction. The first column separation step uses 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 is used to separate PGE-Re from the remaining interfering elements, which all remain strongly absorbed to the resin. We used this method to determine PGE-Re concentrations and Os isotope ratios for 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.

Introduction

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 process 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 inter-element 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., Volkening *et al*. 1991, Creaser *et al*. 1991, Shirey and Walker 1995, Pearson and Woodland 2000, Meisel *et al*. 2001a, Meisel *et al*. 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 allows separation of PGE and Re from the same sample aliquot for 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 PGE-Re 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 potentially 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 as 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 determination of PGE-Re concentrations and Os isotope ratios on the same sample digestion by isotope dilution-inductively coupled plasma-mass spectrometry (ID-ICP-MS) and negative thermal ionization 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 is used to separate and purify the PGE-Re. Given that PGE and Re have no affinity for cation exchange and BPHA extraction resins, only matrix elements and interfering elements are removed from the samples. Therefore, apart from volatile Os and mono-isotopic Rh, all the PGE and Re can be simultaneously measured by ID-ICP-MS. Prior to PGE separation, Os is 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 analyzing international reference materials of ultramafic to mafic composition with a wide range of PGE concentrations.

Experimental

Preparation of reagents and materials

Four geochemical reference materials of different lithologies and PGE concentrations were analyzed 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, USA). Before sub-boiling distillation of

HNO_3, the HNO_3 was heated to 350 ℃ and purged with clean air for *ca*. 2 hours 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., Germany) was used in the chemistry without further purification. An oxidizing solution $Cr^{VI}O_3$-H_2SO_4 was prepared by dissolving 8 g of $Cr^{VI}O_3$ (Alfa Aesar, Puratronic) in 92 g of 6 mol L^{-1} H_2SO_4 (ACS grade Fisher Scientific). This solution has an extremely high Os content and requires purification prior to use, which involves heating to *ca*. 100 ℃ 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-71m chromatographic grade resin (Rohm and Hass company, 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 ℃) 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, USA) in *aqua regia*. The *aqua regia* spike solutions were evaporated and re-dissolved 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, USA) were also used as required throughout this study.

We used Carius tubes that are conventional borosilicate glass tubes similar to those described by Shirey and Walker. (1995). The tubes have an inner volume of *ca*. 76 mL (220×250 mm). The tubes were pre-cleaned with 50% v/v *aqua regia* and heated to

300 ℃ for 6 h. After rinsing with Milli-Q water, the tubes were dried. All the labware that the samples were exposed to is 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 ℃. This step helps to further clean the PFA and ensures that the vials do not contribute Os blank during separation and microdistillation. Finally, all the labware was rinsed with Milli-Q water and air-dried.

Chemical separation

A schematic flow diagram of the method for determination of PGE–Re concentrations and Os isotope ratios is shown in Figure 1. Approximately 1–2 g of powder were digested and equilibrated with ^{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 ℃ for 24 h. 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 re-dissolved in 10 mL of 0.5 mol L^{-1} HCl and loaded onto the cation exchange columns (Bio-Rad, AG50W-X8, 200–400 mesh, Glass Econo-Column, 15×250 mm). 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 (Bio-Rad, Poly-Prep column, 8×40 mm).

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 hotplate and then diluted with 3 mL of 2% HNO_3. This resultant solution was ready for Pt, Pd, Ir, Ru and Re analysis by ID-ICP-MS.

Measurements

Os isotope measurements by N-TIMS: Os isotope ratios were determined with a Thermo-Finnigan Triton TIMS operated in the negative ion mode (NTIMS). This instrument is equipped with nine Faraday collectors and a secondary electron multiplier (SEM). The ion optics used for the Os isotope measurements in this study is a system dedicated to negative ion Os isotope analyses, and has 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) that had previously been outgassed in air for 3 minutes at *ca*. 4 A. Rhenium and Os blanks of the filaments are 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 $Ba(NO_3)2$ (10,000 ppm; Claritas, SPEX) (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^{-7} mbar. Osmium isotope ratios were determined by peak jumping on masses 235, 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 Xseries-2) was used for isotope dilution analysis of Pt, Pd, Ir, Ru and Re. A standard low-volume quartz impact bead spray chamber with a Peltier cooled (3 ℃) and a 0.4 mL min^{-1} borosilicate nebulizer (MicroMist GE) was used in the determinations. Ion lens settings, nebulizer gas flow rate, and torch position were optimized daily using a 10 ppb 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. We did not use a peristaltic pump, as free aspiration of the nebulizer 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 9 times.

All parts of the sample introduction system, such as the nebulizer, 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 were routinely < 5 cps. An instrumental mass bias correction was carried out by the standard-sample bracketing method using a 2 ppb synthetic of PGE-Re standard solution during the determination of PGE-Re concentrations. Measured PGE–Re isotopic ratios for the sample-spike mixtures were corrected using normalizing factors calculated from the average measured ratios on the bracketed standards as compared with the “true” IUPAC ratios (Rosman and Taylor 1998). Variations in these correction factors was 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 spread sheet.

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 optimize the chemical separation parameters in each stage of column purification. The solution was treated as the same procedure 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., Shinotsuka and Suzuki 2007, Ely *et al*. 1999, Strelow and Victor 1991). 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 elutant, > 95% of the PGE–Re were recovered in 30 mL of HCl, whereas when 0.1 mol L^{-1} HCl was used as the elutant, 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 elutant (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 with the other PGE. Therefore, in 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 minimize the volume of elutant 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., Shinotsuka and Suzuki

2007, Ely *et al*. 1999, Jarvis *et al*. 1997). 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 Figure 3B, respectively. As expected, all the interfering elements are strongly absorbed on the resin, whereas the PGE-Re are 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 has 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 elutants were measured by ICP–MS and compared with those in the loading solutions prior to column chemistry (Table 3). In all cases, from an HCl molarity of 0.5 to 3 mol L^{-1}, levels of the interfering elements were reduced to < 1%, and the PGE were quantitatively recovered in 2 mL of elutant. However, some retention of Re on the columns was observed and a greater volume of elutant (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 20 times in succession without any appreciable loss in the sorption efficiency.

Procedural blanks

In contrast to other chemical separation procedures for PGE–Re purification, our method only requires use of concentrated acids for the digestion step and subsequently only uses dilute HCl for the chemical separation. As such, the procedural blanks are 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, labware 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 10–25 pg. We followed this cleaning method, Pt blanks during the course of this study varied from 25 to 40 pg, with 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 Re blank was still higher and was not suitable for accurate determination of

Re-Os isotope for some low Re content samples (i.e., peridotite and lunar basalt)

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

We used the proposed method to determine the PGE-Re concentrations and Os isotope ratios of the geochemical reference materials of UB-N, TDB-1, WGB-1 and BHVO-2 (Table 4). The CI chondrite-normalized PGE-Re patterns for these reference materials were plotted in Fig. 4. Meisel and Moser (2004a) demonstrated that UB-N is the best reference rock standard 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 standard for evaluating our procedures. It should be noted that Meisel and Moser (2004a) concluded that 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 a 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 ℃. Ratios of Os/Ir and Pt/Ir obtained at a temperature of 240 ℃ were higher than those at 270 ℃. 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 minimize incomplete sample digestions. ^{187}Os/^{188}Os ratios measured for UB-N are reproducible to better than 0.2%, and our mean ^{187}Os/^{188}Os ratio is only 0.7% lower (0.1278 ± 2 vs. 0.1270 ± 3) (2SE) than that reported by Meisel *et al*. (2003b), and is in excellent agreement with more recent studies of this standard (0.1272 ± 4) (2SE) (Fischer-Godde *et al*. 2011).

Although previous studies have shown that that PGE concentrations in TDB-1 seems to be rather homogeneous in previous studies (Shinotsuka and Suzuki 2007, Meisel and Moser 2004a), we observed poorer reproducibilities for Ir–Os concentrations and ^{187}Os/^{188}Os ratios in TDB-1. Our results for this standard 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 versus 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 trendon 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 is 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 is 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 are lower than the ID-ICP-MS data reported by Meisel and Moser (2004b) and Shinotsuka and Suzuki (2007). Given the large variablility 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 is 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 conctrations obtained for WGB-1 agreed well with published data for this standard 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 is significantly more radiogenic (0.1858 vs. 0.1582) than N-TIMS data reported by Schmidt *et al.* (2002), but is 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 reproduces well (RSD = 3.4%) and indicates that Re is relatively homogeneously distributed in WGB-1.

Conclusions

We have developed a simple and effective procedure for the determination of PGE-Re 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 standards determined with our method agree well with published data for these standards. 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 standard show 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%) in 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.

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Table and figure captions

Table 1. Sumary of PGE-Re separation chemistry.

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

Table 3. The 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. The concentrations of the synthetic PGE-Re standard solution (10 ng g^{-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.

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) with literature data..

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

Figure 2. Elution profiles of PGE-Re (cumulative % recovery) during cation exchange separation using different molarity of HCl: (A) 0.5 mol L^{-1} HCl; (B) 0.1 mol L^{-1} HCl. 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 (10 ng g^{-1}) and potential interfering elements (10 μg g^{-1} of Zr, Mo, Hf and W) standard solution was used.

Figure 4. CI chondrite-normalized PGE-Re patterns for reference materials UB-N, TDB-1, BHVO-2 and WGB-1. The concentrations of CI chondrites are from McDonugh and Sun (1995). The reference field (shadow) was from the previously published values in Table 4.

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 versus ^{187}Os/^{188}Os.

Figure 6. Replicate analyses of Re-Os isotope data for TDB-1 showing an isochronous relationship that yields a meaningful geological age.

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 H_2O	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 15mm wide and 250 mm long for cation column and 8 mm wide and 20 mm long for BPHA column.

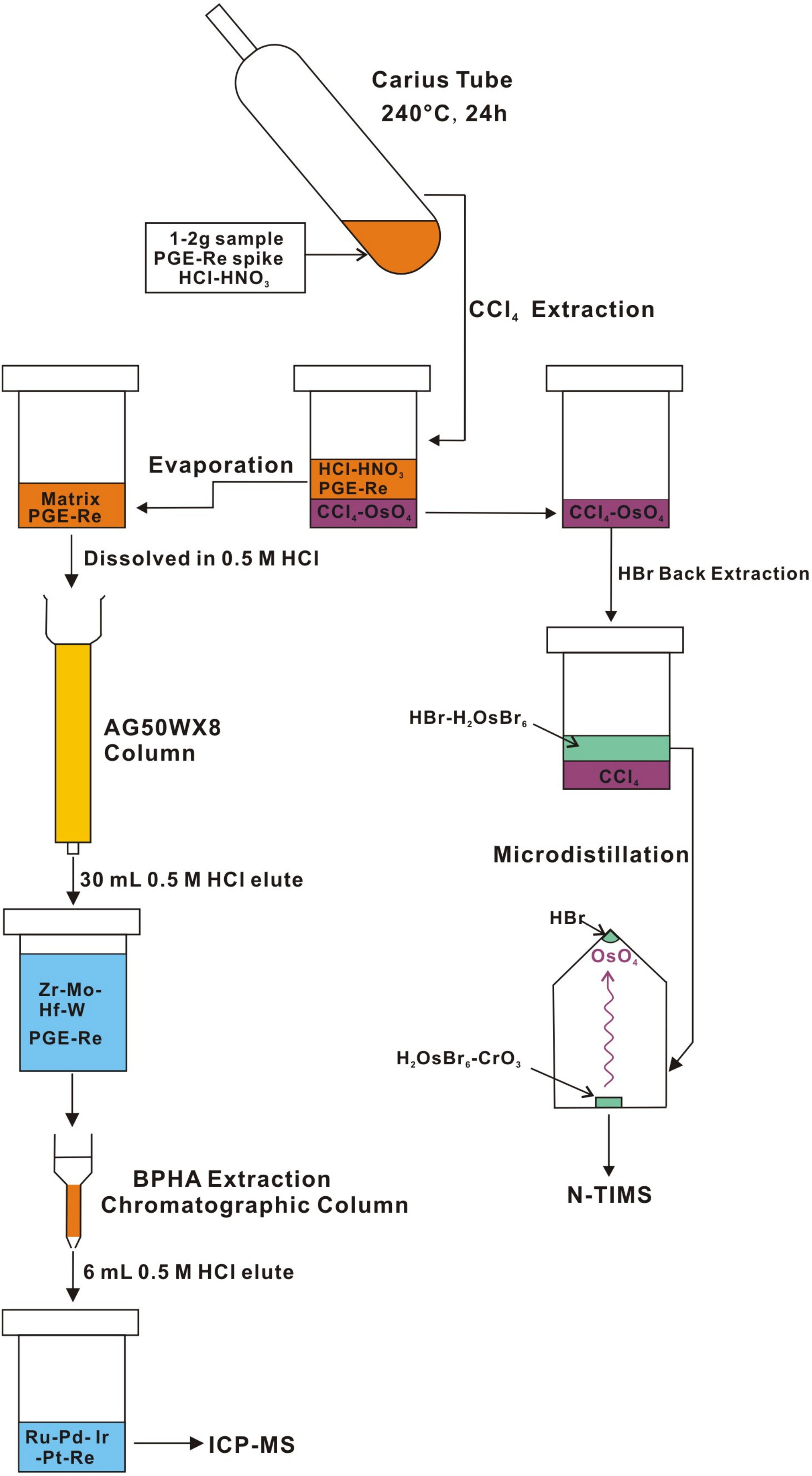
Monitored isotopes	**Spike composition (%)**	**Interferenc**	
		Isobaric	**Polyatomic**
$^{90}Zr^+$			
$^{95}Mo^+$			
$^{99}Ru^+$	97.69		
$^{100}Ru^+$	0.74		
$^{101}Ru^+$	0.48		
$^{105}Pd^+$	98.4		$^{89}Y^{16}O^+$
$^{106}Pd^+$	1.5	$^{106}Cd^+$	$^{90}Zr^{16}O^+$
$^{108}Pd^+$	1.31	$^{108}Cd^+$	$^{92}Zr^{16}O^+$,$^{92}Mo^{16}O^+$
$^{111}Cd^+$			$^{95}Mo^{16}O^+$
$^{178}Hf^+$			
$^{185}Re^+$	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		$^{179}Hf^{16}O^+$
$^{200}Hg^+$			

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

Run No	Digestion	Ru	Pd	Re	Os	Ir	Pt	^{187}Os/^{188} Os	2σ	^{187}Re/^{188}Os	2σ	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 et al. 2003b, 2004a	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)**	**0.1540**	**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
WGB-1(Gabbro, CCRMP)													
1		0.128	15.81	1.10	0.386	0.198	4.09	0.1880	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)	0.1870	0.0120				
Schmidt and Snow, 2002	NiS-FA				0.430(4.7)			0.1582	0.0002				
Total proceure blanks (in pg, n=4)													
Median Value		**7.0**	**7.6**	**8.1**	**0.19**	**3.5**	**32**	**0.34**					

[a] Digestion temperature on 240℃. [b] Digestion temperature on 270℃. [c] Relative standard deviations (1σ, %) are shown in parentheses. Errors of Re-Os isotope quoted at 2σ_{mean}.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Evaporation
$HCl-HNO_3$
PGE-Re
CCl_4-OsO_4
Matrix
PGE-Re
CCl_4-OsO_4
Dissolved in 0.5 M HCl
HBr Back Extraction
AG50WX8
Column
$HBr-H_2OsBr_6$
CCl_4
Microdistillation
30 mL 0.5 M HCl elute
Zr-Mo-
Hf-W
PGE-Re
HBr
OsO_4
$H_2OsBr_6-CrO_3$
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Chromatographic Column
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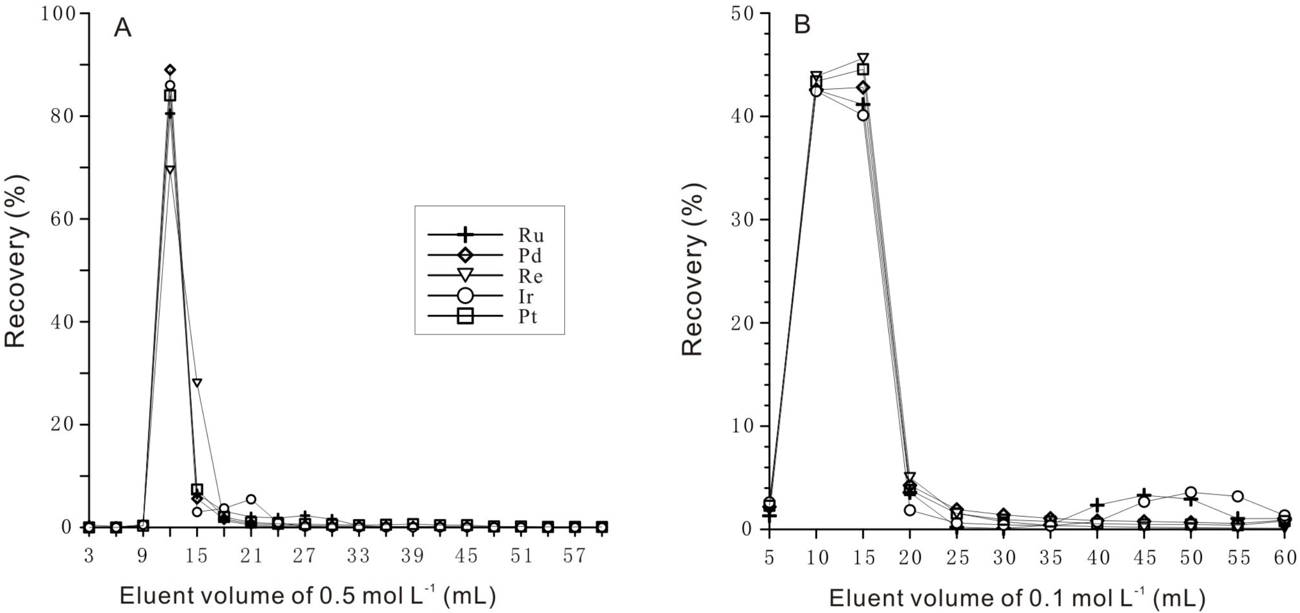
-Pt-Re
ICP-MS


A
B
Recovery (%)
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Eluent volume of 0.1 mol L^{-1} (mL)
0
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3
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15
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39
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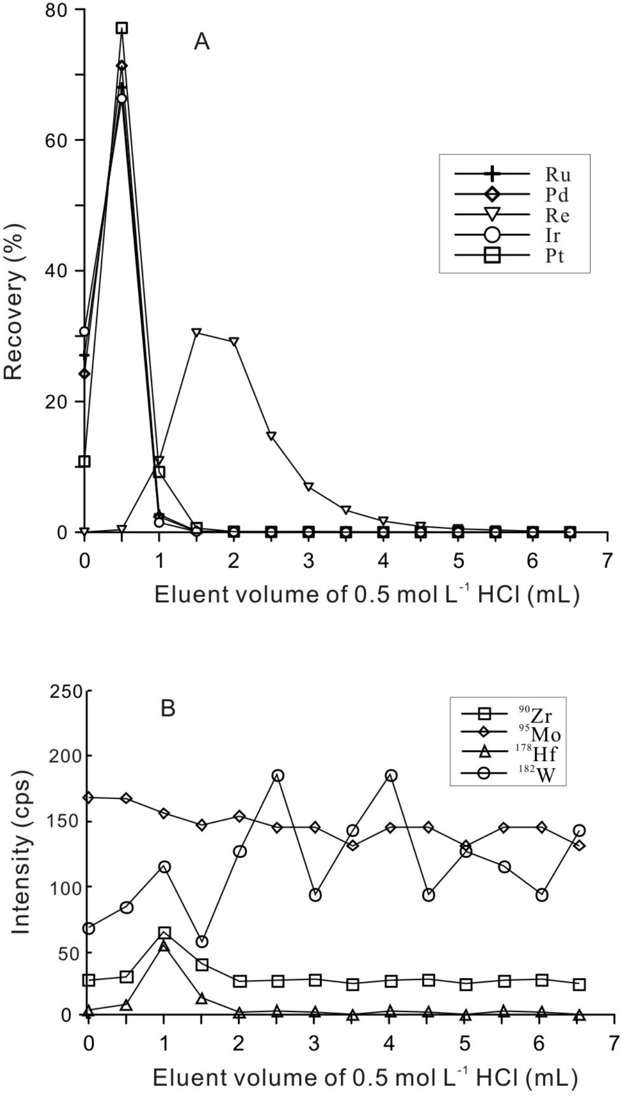
A
Recovery (%)
80
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7
Eluent volume of 0.5 mol L^{-1} HCl (mL)
B
Intensity (cps)
250
200
150
100
50
0
^{90}Zr
^{95}Mo
^{178}Hf
^{182}W
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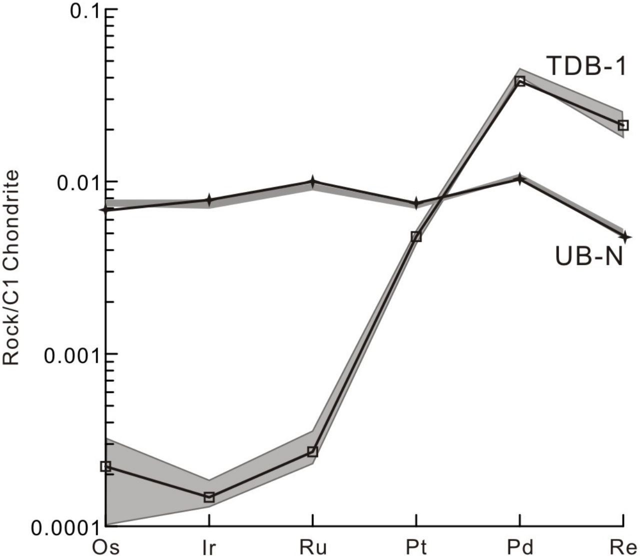
Eluent volume of 0.5 mol L^{-1} HCl (mL)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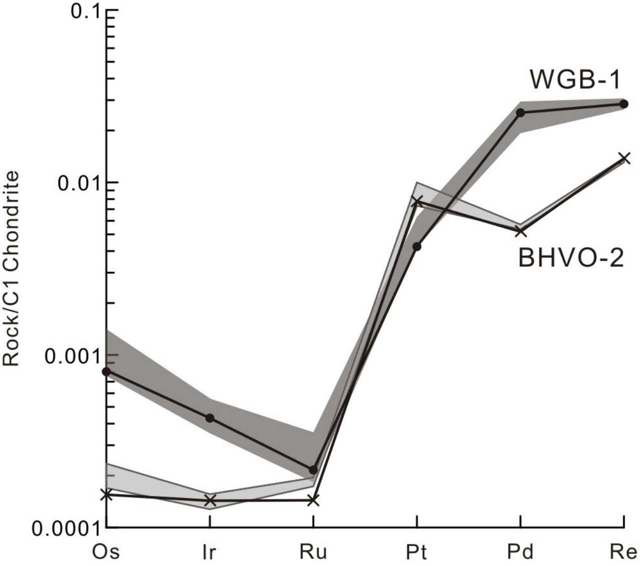
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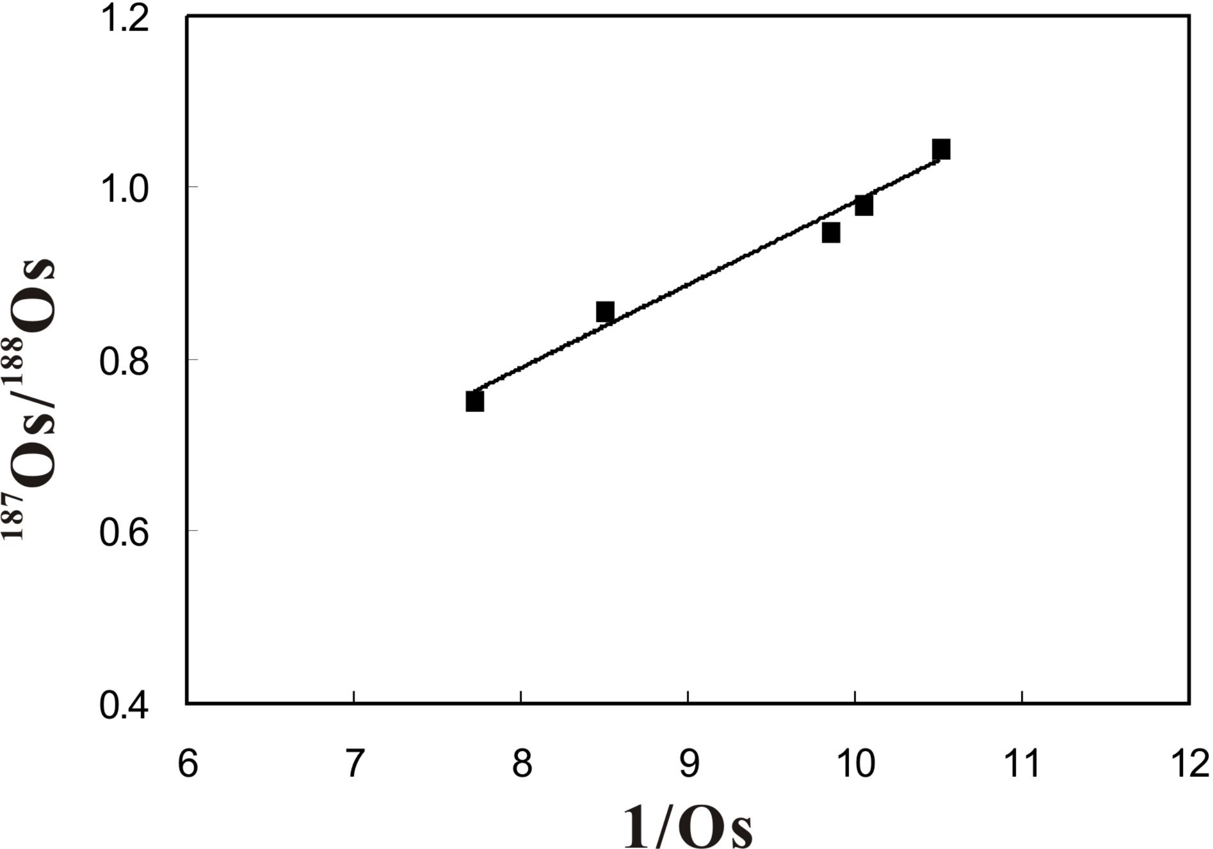
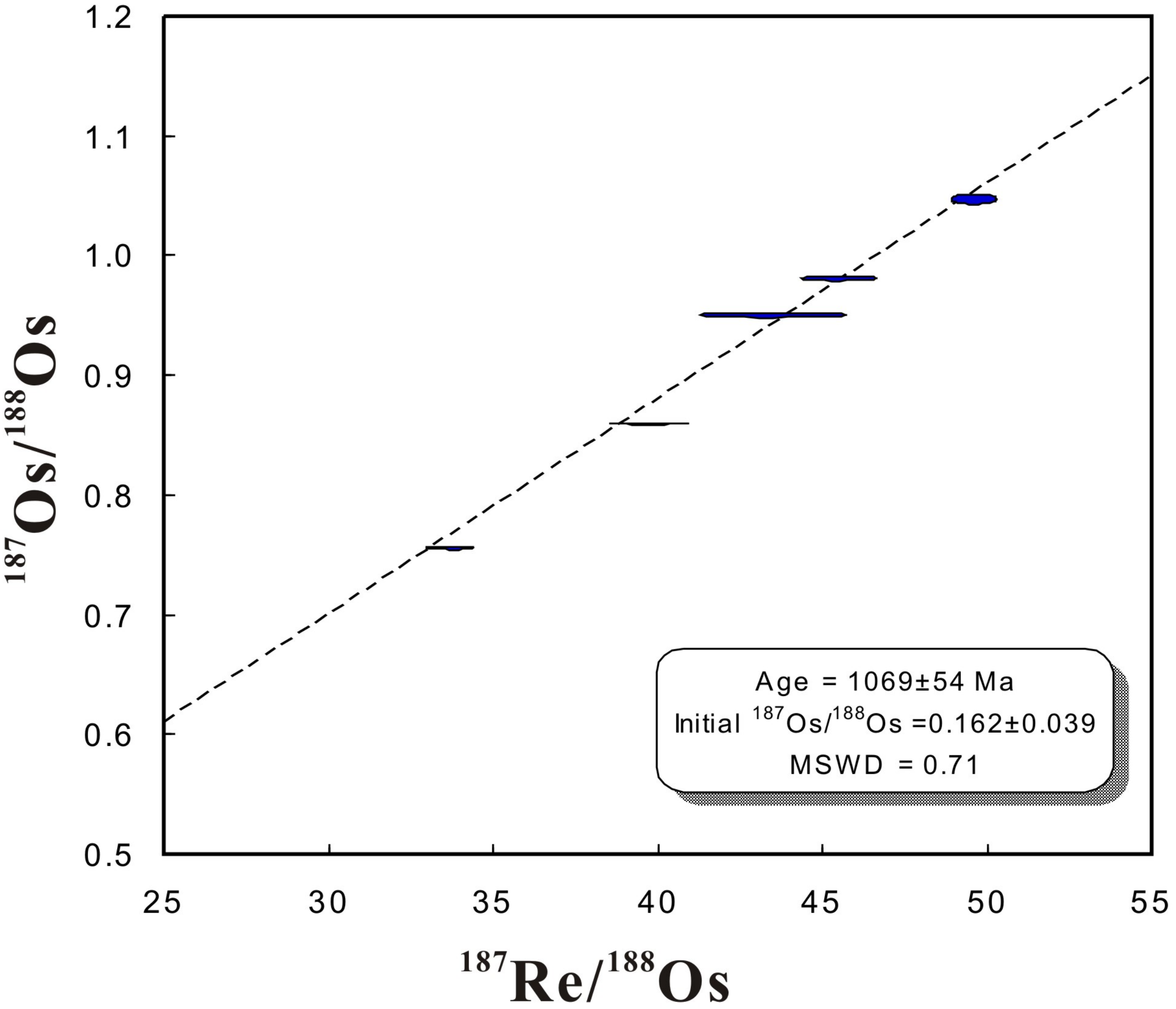
Rock/C1 Chondrite
WGB-1
BHVO-2
Os
Ir
Ru
Pt
Pd
Re


1.2
1.0
0.8
0.6
0.4
6
7
8
9
10
11
12
$^{187}Os/^{188}Os$
1/Os



1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
25
30
35
40
45
50
55
^{187}Os/^{188}Os
^{187}Re/^{188}Os
Age = 1069±54 Ma
Initial ^{187}Os/^{188}Os =0.162±0.039
MSWD = 0.71