Determination of Platinum-Group Elements in Geological Samples by Isotope Dilution-Inductively Coupled Plasma-Mass Spectrometry Combined with Sulfide Fire Assay Preconcentration

Minghao **Ren** (1, 2), Yali **Sun** (1, 3)*, Christina Yan **Wang** (4) and Shengling **Sun** (1)

(1) State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China
(2) University of Chinese Academy of Sciences, Beijing, China
(3) Key Laboratory of Continental Collision and Plateau Uplift, Institute of Tibetan Plateau Research, Chinese Academy of Sciences, Beijing, China
(4) Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China
* Corresponding author. e-mail: yalisun@itpcas.ac.cn

A method was developed for the determination of platinum-group elements (PGE) in geological samples by isotope dilution-inductively coupled plasma-mass spectrometry combined with sulfide fire assay preconcentration. Samples were fused and PGE analytes were concentrated in sulfide buttons. The buttons were dissolved using HCl leaving PGE analytes in insoluble residues, which were digested in HNO_3 and simultaneously processed for the distillation of Os. The remaining solutions were further prepared for the purification of Ru, Rh, Pd, Ir and Pt using a tandem assembly of cation and Ln resin columns. The eluents were directly analysed by membrane desolvation-ICP-MS. Ruthenium, Pd, Os, Ir and Pt were determined by isotope dilution, whereas Rh was determined by conventional reference material calibration combined with [193]Ir as the internal standard element. The method was validated using a series of PGE reference materials, and the measurement data were consistent with the recommended and the literature values. The measurement precision was better than 10% RSD. The procedural blanks were 0.121 ng for Ru, 0.204 for Rh, 0.960 ng for Pd, 0.111 ng for Os, 0.045 ng for Ir and 0.661 ng for Pt, and the limits of detection (3s) were 0.011 ng g^{-1} for Ru, 0.008 ng g^{-1} for Rh, 0.045 ng g^{-1} for Pd, 0.009 ng g^{-1} for Os, 0.006 ng g^{-1} for Ir and 0.016 ng g^{-1} for Pt when a test portion mass of 10 g was used. This indicates that the proposed method can be used for the determination of trace amounts of PGE in geological samples.

Keywords: platinum-group elements, isotope dilution, sulfide fire assay, geological samples.

Une méthode a été développée pour la détermination des éléments du groupe du platine (EGP) dans les échantillons géologiques en utilisant la dilution isotopique par spectrométrie de masse couplée à un plasma inductif, combinée avec la pré-concentration des sulfures par pyroanalyse. Les échantillons ont été fondus et les EGP à analyser ont été concentrés dans des boutons de sulfure. Ces derniers ont été dissous en utilisant HCl en laissant des résidus insolubles contenant les EGP à analyser. Les résidus ont été dissous dans HNO_3 et simultanément utilisés pour la distillation de l'Os. Les solutions résiduelles ont été ensuite préparées pour la purification de Ru, Rh, Pd, Ir t Pt en utilisant un assemblage en tandem de colonnes de résines cationiques et de résines Ln. Les éluants ont été directement analysés par ICP-MS avec une membrane de désolvatation. Ru, Pd, Os, Ir et Pt ont été déterminés par dilution isotopique tandis que Rh a été déterminé en utilisant une méthode conventionnelle de calibration avec matériel de référence associé à l'élément [193]Ir comme standard interne. La méthode a été validée en utilisant une série de matériaux de référence pour les EGP et les données mesurées sont conformes aux valeurs recommandées et de la littérature. La précision des mesures est supérieure à 10% RSD. Les blancs utilisés sont de 0,121 ng pour Ru, 0,204 pour Rh, 0.960 pour Pd, 0,111 pour Os, 0,045 pour Ir et 0,661 pour Pt et les limites de détection (3s) sont de 0,011 ng g^{-1} pour Ru, 0,008 ng g^{-1} pour Rh, 0,045 ng g^{-1} pour Pd, 0,009 ng g^{-1} pour Os, 0,006 ng g^{-1} pour Ir et 0,016 ng g^{-1} pour Pt lorsque une portion test d'une masse de 10 g a été utilisée. Ceci indique que la méthode proposée peut être utilisée pour la détermination des concentrations à l'état de traces des EGP dans les échantillons géologiques.

Platinum-group elements (PGE: Ru, Rh, Pd, Os, Ir and Pt) have highly compatible siderophile characteristics. Due to similarities and differences in chemical behaviour, the PGE are important geochemical tools for understanding fundamental aspects of the origin and evolution of the Earth, including planetary differentiation, core segregation, late accretion history and core–mantle exchange (Oguri *et al.* 1999, Pearson and Woodland 2000, Gros *et al.* 2002, Meisel and Moser 2004a, Savard *et al.* 2010, Li *et al.* 2012). It is therefore critical to quantify PGE contents in geological samples. In nature, however, abundances of PGE are extremely low and their distribution is heterogeneous (i.e., the 'nugget effect'; Juvonen *et al.* 2002). Therefore, PGE determination requires both instrumental measurements with sufficient sensitivity and decomposition techniques capable of dealing with large test portion sizes. Currently, the most promising instrumentation is inductively coupled plasma-mass spectrometry (ICP-MS), which is capable of simultaneous multi-element determination with very high sensitivity and excellent detection limits. As the first step, sample decomposition plays a crucial role, and here Carius tube digestion (Shirey and Walker 1995, Barefoot 1998, Rehkämper *et al.* 1998, Qi *et al.* 2004, 2011, 2013, Qi and Zhou 2008, Savard *et al.* 2010, Li *et al.* 2013) and sulfide fire assay fusion (Ravizza and Pyle 1997, Rehkämper and Halliday 1997, Barefoot 1998, Barefoot and Van Loon 1999, Oguri *et al.* 1999, Pearson and Woodland 2000, Gros *et al.* 2002, Savard *et al.* 2010, Li *et al.* 2012) are commonly used in PGE determination. Due to the lower procedural blanks involved, the former is very attractive; however, because of low PGE abundance and their heterogeneous distribution, larger test portion sizes are always required (Van Loon and Barefoot 1991, McDonald 1998, Pearson and Woodland 2000). Sulfide fire assay fusion, which can readily deal with test portion masses in the range 20–50 g, is more advantageous in this respect than Carius tube digestion, which is applicable to test portions of ~ 2 g. In addition to the problems inherent in PGE in unknown samples due to solution chemistry, Carius tube digestion does not decompose samples as effectively as sulfide fire assay fusion (Meisel *et al.* 2003, Savard *et al.* 2010). Despite the effective decomposition of large sample aliquots, minimising the nugget effect, sulfide fire assay still has disadvantages such as procedural blanks, as well as potential PGE loss during fusion, sulfide button crushing and HCl dissolution (Pearson and Woodland 2000, Gros *et al.*

2002). Therefore, efforts have been made to improve the technique over the past four decades (Robert *et al.* 1971, Hoffman *et al.* 1978, Jackson *et al.* 1990, Hall and Pelchat 1994, Sun *et al.* 1998, 2009, 2000, Sun and Sun 2005). To lower the procedural blanks, small quantities of nickel reagents were added at the preconcentration stage of PGE to a mini-bead (Asif and Parry 1989, Boisvert *et al.* 1991, Li 1995, Sun *et al.* 2000), and nickel reagents were purified by chemical methods (Sun *et al.* 1998, Lü *et al.* 2002). To reduce the PGE loss during HCl dissolution, Gros *et al.* (2002) conducted a semi-open dissolution using a flask equipped with a refluxing apparatus. To recover lost PGE analytes at the fusion/dissolution stages, slag refusion (Oguri *et al.* 1999) and Te coprecipitation (Sun *et al.* 1993, Gros *et al.* 2002) have been applied. However, these procedures are not only time-consuming but also may introduce contamination via reagents. To overcome the loss and cross-contamination of PGE arising from sulfide button crushing, carbonyl metal powder of both Ni and Fe (instead of Ni alone) was optimised for the preconcentration of PGE into a Fe-Ni sulfide button that can disintegrate to powder. As a result, mechanical crushing is avoided, as well as PGE loss (Sun and Sun 2005). Furthermore, the sulfide powder can be dissolved in HCl relatively quickly, further reducing PGE loss. Even with the help of the remaining residues it is not easy to minimise the loss of PGE. Moreover, the loss of soluble PGE analytes is difficult to evaluate due to their heterogeneity. In addition to PGE in residues, there are also chalcophile and siderophile elements (e.g., Cu and Mo derived from samples) due to the insolubility of their sulfides in HCl solutions. Such elements should occur in resulting solutions along with PGE. Moreover, Ni together with Fe as main constituents of sulfide buttons cannot be totally removed during the collection of the insoluble residues by filtration. These coexisting elements can lead to isobaric and polyatomic interferences with PGE during ICP-MS measurements, mainly related to Ru, Rh and Pd (Ravizza and Pyle 1997, Oguri *et al.* 1999, Sun *et al.* 2009).

To take advantage of the sulfide fire assay for the determination of PGE, an isotope dilution method was developed to tackle possible PGE loss during sample fusion and sulfide button dissolution. To prevent isobaric and polyatomic interferences, the chemical properties of PGE analytes and coexisting elements such as Fe, Ni, Cu, Cd and Mo were fully considered, and their separation prior to

solution analysis by ICP-MS was carried out using cation and Ln resins, the latter a specific extraction chromatographic resin applied to the purification of rare earth elements (Lehto and Hou 2010). Due to its high sensitivity and low oxide yield, the membrane desolvation introduction system has been widely used for subtrace analysis (Conver *et al.* 1997, Chung *et al.* 2009) and also extended to PGE determination in environmental samples (Köllensperger *et al.* 2000, Kanitsar *et al.* 2003). This study employed isotope dilution-ICP-MS combined with the membrane desolvation introduction technique, with the aim of making sulfide fire assay more practical for application to PGE reference materials.

Experimental

Instrumentation

The ICP-MS employed in this study was an X Series II (Thermo Fisher Scientific, Bremen, Germany) instrument, and the membrane desolvation device was an Aridus II (Cetac, USA), located at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. The membrane desolvation-ICP-MS was optimised using a multi-elemental tuning solution of 1 ng ml^{-1}, such that the sensitivity was over 250000 cps (counts per second) for ^{115}In. Under operating conditions, the sensitivity was at least five times of that using the routine solution introduction system and the oxide production yield was < 0.02% (see details in Table 1). For the determination of Ru, Rh, Pd, Ir and Pt, a 2 ng ml^{-1} calibration solution was measured for each element every five samples, and its function was both to standardise the ICP-MS for Rh determination and to obtain fractionation factors for correcting the measured ratios ^{99}Ru/^{101}Ru, ^{110}Pd/^{105}Pd, ^{193}Ir/^{191}Ir and ^{198}Pt/^{194}Pt, which were applied to the isotope dilution equation (see Equation 1) for their content calculation. A calibration solution with a concentration of 2 ng ml^{-1} was used for the membrane desolvation-ICP-MS system. For the determination of Os, a conventional solution system coupled with the same ICP-MS was used, and the determined isotopes were ^{185}Re, ^{187}Os, ^{188}Os, ^{190}Os and ^{192}Os, whereas ^{185}Re was selected for monitoring the interference of ^{187}Re on ^{187}Os. During the ICP-MS measurements for Os, a calibration solution (3 ng ml^{-1} in 0.15 mol l^{-1} HNO$_3$) was also measured every five samples to obtain the fractionation factor for the ^{190}Os/^{192}Os ratio. Using the same method, the measured ^{190}Os/^{192}Os ratios in unknown samples were corrected and then applied to the isotope dilution equation to calculate the Os content. For the PGE standard solutions, the measurement precision for the isotopic ratios was better than 0.5% RSD.

Table 1.
Instrumentation and operating conditions

ICP-MS (X series II, Thermo Fisher Scientific)		
Forward power	1300 W	
Reflected power	< 5 W	
Ar cooling gas flow rate	13 l min^{-1}	
Nebuliser pressure	1.5 bar	
Analyser pressure	3.2×10^{-7} mbar	
Expansion pressure	2.0 mbar	
Ni sampling cone orifice	1.0 mm	
Ni skimmer cone orifice	0.7 mm	
Acquisition mode	Peak jumping	
Channel dwell time per sweep	10 ms	
Channel per mass	3	
Channel spacing	0.02	
Sample introduction system	Membrane desolvation	Routine solution
Ar auxiliary gas flow rate	1.0 l min^{-1}	0.8 l min^{-1}
Ar nebuliser gas flow rate	0.80 l min^{-1}	0.75 l min^{-1}
Number of sweeps	200	500
Isotopes determined	^{99}Ru, ^{101}Ru, ^{103}Rh, ^{105}Pd, ^{106}Pd, ^{108}Pd, ^{110}Pd, ^{111}Cd, ^{191}Ir, ^{193}Ir, ^{194}Pt, ^{195}Pt, ^{198}Pt and ^{200}Hg	^{185}Re, ^{187}Os, ^{188}Os, ^{190}Os and ^{192}Os

Reagents and standard solutions

Water with a resistivity of 18.2 MΩ cm was prepared using a Milli-Q system (Millipore, Billerica, MA, USA) and used throughout for experimental preparation. Concentrated HNO$_3$, HCl and H$_2$O$_2$ of electronics industry grade were purchased from the Beijing Institute of Reagents. HNO$_3$ and HCl were purified using a DST-1000 sub-boiling distillation system (Savillex). Na$_2$B$_4$O$_7$ and S (analytical grade, Alfa Aesar), Na$_2$CO$_3$ (analytical grade, Tianjin Chemical Reagent Research Institute), Ni (carbonyl nickel, Inco, Canada) and Fe (carbonyl iron, Fluka) were also used.

A PGE standard stock solution of 100 μg ml^{-1} for each of Ru, Rh, Pd, Ir and Pt in 10% *m/v* HCl (AccuStandard Inc., New Haven, CT, USA) was used to prepare working standard solutions by stepwise dilution.

Spikes with the isotopes ^{99}Ru, ^{110}Pd, ^{193}Ir and ^{198}Pt (Cambridge Isotope Laboratories, Inc., Tewksbury, MA, USA) and ^{190}Os (Oak Ridge National Laboratory, Oak Ridge, TN, USA) were purchased as pure metal powder, and their isotopic abundances are listed in Table 2. Due to differing properties, these spikes were decomposed using different methods before they were turned into their individual stock solutions. The ^{110}Pd and ^{198}Pt spikes were directly dissolved with *aqua regia*, then evaporated and changed to 1.2 mol l^{-1} HCl stock solutions. The ^{190}Os spike was digested in a

Carius tube with concentrated HNO_3 following the method of Shirey and Walker (1995). After digestion, the solution with $Ce(SO_4)_2 \cdot 2H_2O$ was distilled for volatile OsO_4, which was simultaneously trapped in HBr solution. The HBr solution, which reduces Os to a non-volatile bromide species, was further evaporated and prepared to a 3 mol l^{-1} HCl stock solution. The ^{99}Ru and ^{193}Ir spikes were fused at 700 °C with Na_2O_2 in pyrographite crucibles produced by pyrolysis of highly pure methane under reducing conditions. The former melt dissolved with H_2O was turned into 2 mol l^{-1} H_2SO_4 and then distilled with $KMnO_4$ for volatile RuO_4 similar to the distillation of OsO_4 (Sun et al. 2001). At the same time, the volatile RuO_4 was absorbed with a 1.2 mol l^{-1} HCl solution. The latter melt was dissolved with H_2O, then concentrated and centrifuged to collect the IrO_2 precipitate. The precipitate was then dissolved with HCl (6 mol l^{-1}) and converted to a 1.2 mol l^{-1} HCl stock solution. Depending on the PGE chemical behaviour, three groups of spike working solutions were composed: ^{99}Ru-^{193}Ir, ^{110}Pd-^{198}Pt and ^{190}Os. A series of spike working solutions were diluted to 10 to 100 ng g^{-1} in 1.2 mol l^{-1} HCl. Based on the reverse isotope dilution method, the synthetic spike solutions were calibrated using the PGE standard solutions. For calibration of the ^{190}Os spike, appropriate amounts of the ^{190}Os solution were mixed with common Os RMs, which were diluted from its stock solution of 1000 µg ml^{-1} in 3 mol l^{-1} HCl by dissolution of $(NH_4)_2OsCl_6$ (Johnson Matthey

Chemicals, London, UK) in which the Os weight fraction was indistinguishable from the ideal value observed based on the thermogravimetric analysis of Markey et al. (2007). To reach Os isotopic equilibrium, the mixture was sealed in a Carius tube and then treated following the method described by Shirey and Walker (1995). After that, the mixture was distilled for Os as volatile OsO_4, which was trapped using H_2O (Sun et al. 2009). The H_2O solution was analysed for Os by ICP-MS.

Cation-exchange resin (AG 50W-X12, 200–400 mesh) and Ln resin (50–100 µm, Triskem International, France) were applied to separate interfering elements. These resins were soaked in water for 24 hr, and then 1 ml of each was packed into a mini-column (5 mm × 50 mm). The tandem assembly of the mini-columns is shown in Figure 1. Prior to use, the tandem columns were cleaned with 10 ml of 3.9 mol l^{-1} HNO_3 and 20 ml of water and then conditioned by 5 ml of HCl (0.24 mol l^{-1}).

Samples

In this study, a series of PGE reference materials were employed, which included CANMET-CCRMP WGB-1 (gabbro) and TDB-1 (basalt), as well as Chinese national reference materials GBW07289 (alluvial soil), GBW07290 (peridotite), GBW07291 (pyroxene peridotite), GBW07294

Table 2.
Isotopic abundances (%) of Ru, Pd, Os, Ir and Pt in nature and spikes as well as their relative atomic weight (A) and the atomic weight ratio of nature to spike

Ru isotopes		96	98	99	100	101	102	104	A
Abundance	Nature[a]	5.54	1.87	12.76	12.6	17.06	31.55	18.62	101.07
	Spike	0.16	0.19	96.4	1.4	0.74	0.78	0.55	99.30
Atomic weight ratio/k									1.0178
Pd isotopes		102	104	105	106	108	110		A
Abundance	Nature[a]	1.02	11.14	22.33	27.33	26.46	11.72		106.42
	Spike	0.04	0.13	0.39	0.47	1.52	97.46		109.92
Atomic weight ratio/k									0.9682
Os isotopes		184	186	187	188	189	190	192	A
Abundance	Nature[a]	0.02	1.59	1.96	13.24	16.15	26.26	40.78	190.23
	Spike	0.001	0.02	0.04	0.34	0.97	96.97	1.67	190.02
Atomic weight ratio/k									1.0011
Ir isotopes		191	193						A
Abundance	Nature[a]	37.3	62.7						192.22
	Spike	17.59	82.41						192.65
Atomic weight ratio/k									0.9977
Pt isotopes		190	192	194	195	196	198		A
Abundance	Nature[a]	0.01	0.79	32.97	33.83	25.24	7.16		195.08
	Spike	0.005	0.04	1.74	2.83	3.61	91.76		197.73
Atomic weight ratio/k									0.9866

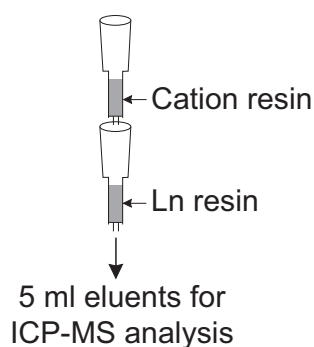[a] Natural isotopic abundances from the report of Berglund and Wieser (2011).

Figure 1. Schematic diagram showing the tandem assembly of two mini-columns packed with cation resin (above) and Ln resin (below) used in this study.

(synthetic material of soil and peridotite) and GBW07340 (synthetic soil).

Sample preparation

Each of the samples (10–20 g) was mixed with 30 g of $Na_2B_4O_7$, 10 g of Na_2CO_3, 2.5 g of Fe, 1 g of Ni and 1 g of S and transferred to fire clay crucibles. Appropriate amounts of ^{99}Ru-^{193}Ir, ^{110}Pd-^{198}Pt and ^{190}Os spike solutions were weighed to a tiny glass cup and evaporated to dryness at 120 °C on a hot plate. The contents were added to the mixture, which was covered with 5 g of $Na_2B_4O_7$ powder and fused at 1000 °C for 1.5 hr. Following the method of Sun *et al.* (2009), the crucible was broken and the resulting sulfide button was collected and placed in a 150 ml glass beaker containing 15 ml of H_2O. After it was disintegrated to powder, concentrated HCl (15 ml) was added. The mixture was heated to ~ 150 °C on a hot plate ensuring no violent reaction occurred, following which the temperature was increased. When the solution became clear, it was filtered to collect insoluble residue using a Millipore filter membrane (25 mm diameter, 0.25 μm pore size). The residue was transferred to a distillation apparatus with 3 ml HNO_3, then Os was distilled at 120 °C for 30 min, and the volatile OsO_4 was simultaneously absorbed with H_2O. The H_2O solution was directly analysed by ICP-MS for Os. After distillation, the remaining solution was concentrated to ~ 0.5 ml, then 0.5 ml of H_2O_2 was added, and this treatment was repeated three times to ensure effective digestion of the membrane constituents. Following this, 1 ml of HCl was added and the mixture was evaporated to near dryness. With an additional 1 ml of HCl, this step was repeated twice and then 2 ml of 0.24 mol l^{-1} HCl was added. This solution was loaded onto the tandem columns packed with cation and Ln resins (Figure 1). After loading,

the tandem columns were continuously washed using 3 ml of 0.24 mol l^{-1} HCl (3 × 1 ml). At this stage, the cation resin retained Fe, Ni, Cu, Zn and Cd, and the Ln resin retained Mo, whereas PGE analytes were not. All (5-ml) eluents passing through the columns were retained for the direct determination of Ru, Rh, Pd, Ir and Pt by membrane desolvation-ICP-MS.

Results and discussion

Removal of interfering elements and PGE recovery

As is well known in the sulfide fire assay method, the PGE analytes are preconcentrated in the sulfide phase, whereas the lithophile elements enter the slag phase, such as the major elements K, Na, Ca and Mg, and the trace elements Sr, Zr and Hf during sample fusion. As a result, simultaneous separation is achieved, and therefore, the PGE analytes can be expected to be free from both isobaric and polyatomic interferences arising from Sr, Zr and Hf during ICP-MS measurement (Ravizza and Pyle 1997, Barefoot 1998, Oguri *et al.* 1999). However, not only can chalcophile and siderophile elements occur in the sulfide phase, but some cannot be dissolved by HCl (i.e., Cu, Mo, Cd and Hg). As a result, they pass to resulting solutions and form polyatomic species or occur as isobaric ions during ICP-MS measurement (Ravizza and Pyle 1997). As shown in Table 3, isobaric interferences from sulfide fire assay fusion are similar to those from Carius tube digestion, whereas the polyatomic interferences are much simpler for the former than the latter. The reason is that base elements can react with argon/chloride/oxygen and form polyatomic species during ICP-MS analysis, leading to more complicated interferences on PGE analytes (Pearson and Woodland 2000, Meisel *et al.* 2003). Although the yield of the polyatomic species is very low, the interferences cannot be considered negligible because of the very low abundances of PGE in nature (Ravizza and Pyle 1997, Barefoot 1998, Oguri *et al.* 1999, Meisel *et al.* 2003). From sulfide fire assay fusion, some siderophile and chalcophile elements can occur in resulting solutions and produce both isobaric and polyatomic interferences on all isotopes of Ru, Rh and Pd (Table 3). As a result, such interferences can lead to a bias in the measured isotope ratio, leading to inaccurate PGE data. The isotope dilution method requires that the ratios of at least two isotopes are free from any significant interference.

As the chloride complex anion, the existing form of PGE in HCl media is different from interfering elements. With this consideration, cation-exchange resin was used for their separation as it can absorb the interfering elements but not the PGE analytes (Jarvis *et al.* 1997a, b,

Table 3.
Isobaric and polyatomic interferences arising from sulfide fire assay (FA) fusion as well as Carius tube (CT) digestion

	Isobaric		Polyatomic					
			-Ar⁺		**-Cl⁺**		**-O⁺**	
	FA	**CT**	**FA**	**CT**	**FA**	**CT**	**FA**	**CT**
^{96}Ru	^{96}Mo	^{96}Zr	^{56}Fe^{40}Ar		^{57}Fe^{35}Cl/^{59}Co^{37}Cl		–	–
^{98}Ru	^{98}Mo		^{58}Fe^{40}Ar/^{58}Ni^{40}Ar		^{63}Cu^{35}Cl/^{61}Ni^{37}Cl		–	–
^{99}Ru	–		^{59}Co^{40}Ar		^{64}Ni^{35}Cl/^{62}Ni^{37}Cl		–	–
^{100}Ru	^{100}Mo		^{60}Ni^{40}Ar		^{65}Cu^{35}Cl/^{63}Cu^{37}Cl		–	^{84}Sr^{16}O
^{101}Ru			^{61}Ni^{40}Ar		^{66}Zn^{35}Cl/^{64}Zn^{37}Cl		–	^{85}Sr^{16}O / ^{85}Rb^{16}O
^{102}Ru/^{102}Pd	–		^{62}Ni^{40}Ar		^{67}Zn^{35}Cl/^{65}Cu^{37}Cl		–	^{86}Sr^{16}O
^{103}Rh	–		^{63}Cu^{40}Ar		^{68}Zn^{35}Cl/^{66}Zn^{37}Cl		–	^{87}Sr^{16}O
^{104}Ru/^{104}Pd	–		^{64}Ni^{40}Ar/^{64}Zn^{40}Ar		^{69}Ga^{35}Cl/^{67}Zn^{37}Cl		–	^{88}Sr^{16}O
^{105}Pd	–		^{65}Cu^{40}Ar		^{70}Zn^{35}Cl/^{68}Zn^{37}Cl		–	^{89}Y^{16}O
^{106}Pd		^{106}Cd	^{66}Zn^{40}Ar		–	–	–	^{90}Zr^{16}O
^{108}Pd		^{108}Cd	^{68}Zn^{40}Ar		–	–	–	^{92}Zr^{16}O
^{110}Pd		^{110}Cd	^{70}Zn^{40}Ar		–	–	–	^{94}Zr^{16}O / ^{94}Mo^{16}O
^{190}Pt	–		–	^{150}Nd^{40}Ar / ^{150}Sm^{40}Ar	–	–	–	^{174}Yb^{16}O / ^{174}Hf^{16}O
^{191}Ir	–		–	^{151}Eu^{40}Ar	–	–	–	^{175}Lu^{16}O
^{192}Pt		^{182}W	–	^{152}Gd^{40}Ar / ^{152}Sm^{40}Ar	–	^{157}Gd^{35}Cl / ^{155}Gd^{37}Cl	–	^{176}Lu^{16}O / ^{176}Yb^{16}O
^{193}Ir	–		–	^{153}Eu^{40}Ar	–	^{158}Gd^{35}Cl / ^{158}Dy^{35}Cl / ^{156}Gd^{37}Cl / ^{156}Dy^{37}Cl	–	^{177}Hf^{16}O
^{194}Pt	–		–	^{154}Gd^{40}Ar / ^{154}Sm^{40}Ar	–	^{159}Tb^{35}Cl / ^{157}Gd^{37}Cl	–	^{178}Hf^{16}O
^{195}Pt	–		–	^{155}Gd^{40}Ar	–	^{160}Gd^{35}Cl / ^{158}Gd^{37}Cl / ^{158}Dy^{37}Cl	–	^{179}Hf^{16}O
^{196}Pt		^{196}Hg	–	^{156}Gd^{40}Ar / ^{156}Dy^{40}Ar	–	^{161}Dy^{35}Cl / ^{159}Tb^{37}Cl	–	^{180}Hf^{16}O
^{198}Pt		^{198}Hg	–	^{158}Gd^{40}Ar / ^{158}Dy^{40}Ar	–	^{163}Dy^{35}Cl / ^{161}Dy^{37}Cl	–	^{182}W^{16}O

Oguri et al. 1999, Pearson and Woodland 2000, Meisel et al. 2003). However, Mo exists as MoO_4^{2-} and cannot be removed by the cation resin. In nature, the abundance of Mo is much higher than that of PGE, so Mo can be expected to appear in resultant PGE solutions as a major coexisting element. In order to determine PGE with higher sensitivity by membrane desolvation-ICP-MS, Mo must be separated prior to analysis of the resulting solutions.

Firstly, the solutions containing 10 μg of Mo and 50 ng of PGE as well as Hg in 0.12 mol l^{-1}, 0.24 mol l^{-1} and 0.6 mol l^{-1} of HCl, respectively, were loaded onto the Ln resin columns, then the columns were washed continually, and every 2 ml of the eluent was collected until a total of 10 ml was obtained. The eluent was analysed and the recovery of Mo was 0.78% in 0.12 mol l^{-1} HCl, 1.09% in 0.24 mol l^{-1} HCl and 2.00% in 0.6 mol l^{-1} HCl, whereas the recovery of PGE and Hg was over 99% (Table 4). These results imply an effective separation of PGE and Mo was achieved using Ln resin in 0.12–0.6 mol l^{-1} HCl media.

The HCl medium for Mo separation was also carried out for the cation resin to absorb the interfering elements Fe, Cu, Ni, Cd and Hg. With 250 μg for Cu, Fe and Ni and 50 ng for Cd, Hg and PGE analytes, the 0.12, 0.24 and 0.6 mol l^{-1} HCl solutions were loaded onto the cation columns. The eluents were analysed, and results showed an effective separation of PGE with Fe, Cu, Ni, Zn and Cd could be achieved in the 0.12–0.24 mol l^{-1} HCl solution.

Based on the above experimental parameters, a 0.24 mol l^{-1} HCl solution was chosen, which was then prepared with 50 ng of PGE and Hg for loading to the tandem columns (Figure 1). Every 2 ml quantity of eluent

Table 4.
Recovery (%) of PGE, Mo and Hg in HCl solution passing through Ln resin in sequence

HCl	Eluents	Mo	Ru	Rh	Pd	Ir	Pt	Hg
0.12 mol l^{-1}	1	0.19	74.7	73.0	72.3	74.2	72.8	24.7
	2	0.15	25.8	24.6	26.0	25.4	27.1	67.2
	3	0.14	1.16	1.10	1.88	1.15	1.22	8.44
	4	0.15	0.09	0.09	0.66	0.11	0.12	1.40
	5	0.15	0.02	0.02	0.41	0.04	0.04	0.48
	Total	0.78	101.7	98.8	101.3	100.9	101.3	102.2
0.24 mol l^{-1}	1	0.26	74.8	73.3	71.8	75.9	74.2	36.9
	2	0.22	26.0	25.0	26.8	25.4	27.6	61.7
	3	0.20	0.71	0.69	1.75	0.73	0.81	4.88
	4	0.21	0.03	0.03	0.65	0.05	0.05	0.77
	5	0.20	0.01	0.01	0.41	0.02	0.02	0.40
	Total	1.09	101.5	99.1	101.4	102.1	102.1	104.6
0.60 mol l^{-1}	1	0.36	73.9	72.2	72.0	72.1	71.6	51.8
	2	0.40	27.0	25.7	27.5	25.0	27.7	47.1
	3	0.41	0.73	0.69	1.68	0.73	0.82	3.05
	4	0.42	0.04	0.05	0.64	0.09	0.06	0.65
	5	0.41	0.03	0.03	0.47	0.06	0.03	0.28
	Total	2.00	101.7	98.7	102.3	98.0	100.2	102.9

was collected in sequence and analysed. As shown in Figure 2, more than 95% of PGE analytes and more than 90% of Hg passed through the tandem columns in a 4 ml of 0.24 mol l^{-1} HCl solution. In this study, 5 ml of eluent was collected and directly analysed by membrane desolvation-ICP-MS. Despite an ineffective separation of PGE and Hg, the interference of ^{198}Hg on ^{198}Pt cannot be considered important due to very low partition coefficient of Hg in sulfide buttons (Ravizza and Pyle 1997). In this study, ^{200}Hg was monitored during ICP-MS measurements, and the interference of ^{198}Hg on ^{198}Pt could be easily corrected according to their natural abundances, that is 9.97% for ^{198}Hg and 23.10% for ^{200}Hg. For the resulting solutions of all the reference materials, the highest and lowest intensity counts of ^{200}Hg were 7 and 272 cps, and accordingly, counts of ^{198}Hg are 3 cps and 118 cps for GBW07291 and GBW07294, respectively, further confirming the interference of ^{198}Hg on ^{198}Pt was limited.

As this study was particularly concerned with the measured isotope ratios of PGE analytes, the unspiked experimental solutions, which are PGE standard solutions containing the interfering elements Mo, Cu, Fe, Ni, Cd and Hg, were also examined for the target isotope ratios. However, due to the existence of a matrix, the unspiked experimental solutions were not suitable for the membrane desolvation introduction system, so they were examined after their separation by cation and Ln resins in a 0.24 mol l^{-1} HCl solution. The measured ratios were compared with those of the PGE reference materials (Table 5), and significant differences could not be observed even for ^{99}Ru/^{101}Ru and ^{105}Pd/^{110}Pd, which are very sensitive to polyatomic interference (Table 3). This examination further confirmed the interfering elements could be successfully separated using the proposed method with the cation and Ln resins.
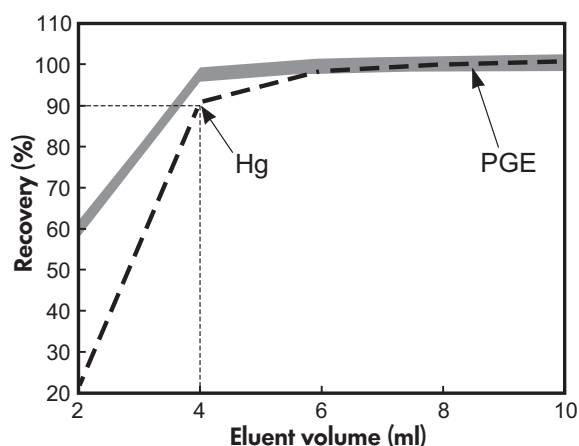

Figure 2. Recovery of PGE and Hg in the eluent relative to the amount of 50 ng analytes added to a 0.24 mol l^{-1} HCl solution passing through the tandem columns of cation and Ln resins (in the 5 ml of eluent, the recovery of PGE dropped to 98.2–100.2% along with 94.5% Hg).

Mass fractionation of ICP-MS and its correction

Mass fractionation, as a typical characteristic of mass spectrometry instrumentation, can make the measured

Table 5.
Comparison of the measured isotope ratios with the natural ratios

Date (month/date/year)	$^{99}Ru/^{101}Ru$	$^{105}Pd/^{110}Pd$	$^{191}Ir/^{193}Ir$	$^{194}Pt/^{198}Pt$
28/02/2014	0.7168 ± 0.0014	1.579 ± 0.006	0.5883 ± 0.0023	4.464 ± 0.020
28/02/2014[a]	0.7173 ± 0.0018	1.576 ± 0.008	0.5879 ± 0.0021	4.457 ± 0.019
15/01/2014	0.7183 ± 0.0030	1.550 ± 0.007	0.5858 ± 0.0025	4.567 ± 0.024
07/01/2014	0.7290 ± 0.0029	1.549 ± 0.007	0.5871 ± 0.0021	4.609 ± 0.023
30/12/2013	0.7267 ± 0.0029	1.623 ± 0.007	0.5891 ± 0.0028	4.580 ± 0.012
06/12/2013	0.7167 ± 0.0031	1.551 ± 0.001	0.5828 ± 0.0023	4.566 ± 0.021
19/11/2013	0.7207 ± 0.0028	1.543 ± 0.007	0.5915 ± 0.0029	4.505 ± 0.021
08/11/2013	0.7222 ± 0.0024	1.620 ± 0.002	0.5932 ± 0.0020	4.464 ± 0.020
28/10/2013	0.7219 ± 0.0023	1.594 ± 0.007	0.5919 ± 0.0022	4.544 ± 0.021
28/10/2013[a]	0.7221 ± 0.0037	1.589 ± 0.007	0.5921 ± 0.0017	4.538 ± 0.014
18/10/2013	0.7187 ± 0.0031	1.682 ± 0.007	0.5871 ± 0.0019	4.526 ± 0.022
12/10/2013	0.7161 ± 0.0021	1.652 ± 0.006	0.5861 ± 0.0023	4.444 ± 0.001
29/09/2013	0.7138 ± 0.0008	1.577 ± 0.004	0.5875 ± 0.0027	4.505 ± 0.001
Mean	0.7200	1.584	0.5885	4.520
s	0.0043	0.043	0.003	0.053
Natural[b]	0.7470	1.905	0.5950	4.566
Fractionation/amu	-0.018	-0.033	-0.006	-0.002
Fractionation factor	0.9638	0.8315	0.9891	0.9899

[a] Measured ratios of the unsipked experimental solutions after separation of interference elements using cation and Ln resins.
[b] Natural ratios derived from natural isotope abundances of Berglund and Wieser (2011).

ratios different from the true values. For the desolvation-ICP-MS measurements, the isotope fractionation of Ru, Pd, Ir and Pt analytes was evaluated using the 2 ng ml^{-1} of PGE standard solution, in which the isotopes were measured without interference. To observe the mass fractionation, the uncorrected ratios of target isotopes used for isotope dilution equations are presented in Table 5. Over a period of 5 months, the ratio data varied as follows: 0.7138–0.7290 for $^{99}Ru/^{101}Ru$, 1.543–1.682 for $^{105}Pd/^{110}Pd$, 0.5828–0.5932 for $^{191}Ir/^{193}Ir$ and 4.444–4.609 for $^{194}Pt/^{198}Pt$. Compared with their true values derived from natural isotope abundances (Berglund and Wieser 2011), the largest fractionation was observed for the ratio of $^{105}Pd/^{110}Pd$, which is attributable to the largest mass difference between ^{105}Pd and ^{110}Pd. According to the difference between the measured and true ratios, the fractionation of a mass unit, that is fractionation/amu, was -33‰ for $^{105}Pd/^{110}Pd$, -18‰ for $^{99}Ru/^{101}Ru$, -6‰ for $^{191}Ir/^{193}Ir$ and -2‰ for $^{194}Pt/^{198}Pt$, indicating that the lower atomic number isotopes of Ru and Pd have much larger fractionation/amu than the higher atomic number isotopes of Ir and Pt, consistent with the mass fractionation pattern. At the same scale, the largest fractionation/amu was found for the isotopes of Pd. A similar phenomenon was reported by Ravizza and Pyle (1997). Lacking a reasonable explanation, the main cause is probably related to the properties of Pd itself. Due to the difference between the measured and true ratios, the mass fractionation was corrected through a fractionation factor derived from analyses of the calibrator

standard solution, that is the measured ratios divided by their true values.

In this study, the measured ratios for resulting solutions were corrected and were then applied to the isotope dilution equation for calculation of the PGE mass in unknown samples:

$$^{A}M_u = k \times {}^{A}M_s \times \frac{^{E}A_s - {}^{R}A_s \times R}{^{R}A_n \times R - {}^{E}A_n} \quad (1)$$

where $^{A}M_u$ is the mass of analyte in the unknown sample; k is a constant of the element's relative atomic weight in the unknown sample to the spike; $^{A}M_s$ is the mass of the spike added to the unknown sample; $^{E}A_s$ and $^{R}A_s$ are the abundances of the enriched and the reference isotopes in the spike; accordingly, $^{E}A_n$ and $^{R}A_n$ are their abundances in nature; and R is the corrected ratio of the enriched to reference isotopes. In this study, the isotope ratio R was $^{99}Ru/^{101}Ru$ for Ru, $^{110}Pd/^{105}Pd$ for Pd, $^{193}Ir/^{191}Ir$ for Ir and $^{198}Pt/^{194}Pt$ for Pt.

For Os, its measured $^{190}Os/^{192}Os$ ratio was also corrected in the same way prior to calculation of its content in unknown samples. Due to the radiogenic characteristics of ^{187}Os caused by β^{-} decay of ^{187}Re, radiogenic ^{187}Os was also considered. By monitoring the $^{187}Os/^{188}Os$ ratio during Os measurements, it can be assessed whether or not radiogenic ^{187}Os is negligible. For the reference material TDB-1, the measured $^{187}Os/^{188}Os$ ratio was up

to 0.797–1.197, consistent with the ratio range of 0.7542–1.0477 measured by precise negative-thermal ionisation mass spectrometry (Li *et al.* 2013). Therefore, radiogenic ^{187}Os can be considered significant relative to the common Os content in TDB-1. In this case, total ^{187}Os can be derived according to the measured ratio of ^{187}Os/^{188}Os, as the common Os content and the addition of the ^{190}Os spike are known. By subtracting the ^{187}Os fraction of both common Os and ^{190}Os spike from the total ^{187}Os, the radiogenic ^{187}Os can be obtained. In TDB-1, the radiogenic part of ^{187}Os was taken into account and was < 10% of the total Os (Table 8). For unknown samples, the level of radiogenic ^{187}Os contents is closely dependent upon the contents of Re and their geological age but it generally can be considered negligible due to its parent ^{187}Re with very low abundances and very long half-life.

Determination of Rh

Among the PGE, only Rh is mono-isotopic and cannot be determined by isotope dilution. During chemical preparation, however, Rh coexists with Ru, Pd, Ir and Pt and occurs in resulting solutions. For the determination of Ru, Pd, Ir and Pt by isotope dilution, appropriate amounts of ^{99}Ru, ^{110}Pd, ^{193}Ir and ^{198}Pt spikes are added to the samples before preparation, and they are also captured in the sulfide phase during sample fusion. As the added amounts of these spikes are known, the quantity of individual isotopes can be derived according to their abundances. As proposed by Meisel *et al.* (2003), the enriched isotopes of the added spikes were employed as the internal standard for Rh determination following cation separation. For complicated chemical preparations, however, similarity of behaviour is required between Rh and the internal standard. For example, similar recoveries were found for Rh and Pt during Te coprecipitation by Qi *et al.* (2004), so the enriched isotope of ^{194}Pt was chosen as the internal standard for the determination of Rh. In this study, it was also attempted to determine Rh using the enriched isotopes as the internal standard, which included the total mass of the isotope from the spike and the unknown sample. The concentration of Rh in resulting solutions was derived from Equation (2):

$$^{Rh}C_r = {}^{Rh}C_{std} \times \frac{^{103}I_r}{^{103}I_{std}} \times \frac{^{IS}I_{std}}{^{IS}I_r} \times \frac{^{IS}C_r}{^{IS}C_{std}} \qquad (2)$$

where $^{Rh}C_r$ and $^{Rh}C_{std}$ are the concentrations of Rh, and $^{103}I_r$ and $^{103}I_{std}$ are the intensity counts of ^{103}Rh in the resulting and standard solutions, respectively. Accordingly, $^{IS}I_r$ and $^{IS}I_{std}$ are the internal standard counts, and $^{IS}C_r$ and $^{IS}C_{std}$ are the internal standard concentrations in the resulting and standard solutions.

For known amounts of PGE spikes, the highest percentages added to unknown samples are the enriched isotopes of ^{99}Ru, ^{110}Pd, ^{193}Ir and ^{198}Pt. Taking ^{193}Ir as an example, the total mass of ^{193}Ir in the resulting solution is equal to the following:

$$^{193}M_r = {}^{193}M_u + {}^{193}M_s \qquad (3)$$

where $^{193}M_r$, $^{193}M_u$ and $^{193}M_s$ are the masses of ^{193}Ir in the resulting solution, in the unknown sample and in the spike, respectively. The latter two items can be derived according to the relative abundances of ^{193}Ir in nature and in the ^{193}Ir spike, that is 0.627 and 0.8241 (see Table 2), and the formulae are as follows:

$$^{193}M_u = 0.627 \times {}^{Ir}M_u \qquad (4)$$

$$^{193}M_s = 0.8241 \times {}^{Ir}M_s \qquad (5)$$

In the resulting solution with a certain volume *V*, the concentration of ^{193}Ir ($^{193}C_r$) is equal to the following:

$$^{193}C_r = \frac{0.627 \times {}^{Ir}M_u + 0.8241 \times {}^{Ir}M_s}{V} \qquad (6)$$

By combining Equation 3 and 6, the content of Rh ($^{Rh193}C_u$) in the unknown sample (*W*) can be derived as follows:

$$\begin{aligned} ^{Rh193}C_u = & \frac{^{Rh}C_{std}}{W} \times \frac{^{103}I_r}{^{103}I_{std}} \times \frac{^{193}I_{std}}{^{193}I_r} \\ & \times \frac{0.627 \times {}^{Ir}M_u + 0.8241 \times {}^{Ir}M_s}{^{193}C_{std}} \end{aligned} \qquad (7)$$

Using this method, the enriched isotopes ^{99}Ru, ^{110}Pd and ^{198}Pt were also used as internal standards, and the contents of Rh were obtained (Table 6) for the reference materials TDB-1 and WGB-1. The precision (RSD) of the Rh data derived from the internal standard ^{193}Ir was 4.0% for TDB-1 and 5.5% for WGB-1, whereas other data sets had larger variations and revealed that ^{99}Ru, ^{110}Pd and ^{198}Pt cannot be considered satisfactory as internal standard elements. The results regarding ^{193}Ir as the internal standard (Table 6) were compared with the provisional and information values, and they have significant differences. As PGE reference materials, however, TDB-1 and WGB-1 have been investigated using different approaches (Qi *et al.* 2004, Savard *et al.* 2010) and the values are also presented in Table 6. This comparison shows our Rh data are consistent with the literature values. Despite using the same concepts for Rh determination related to the enriched isotopes of PGE spikes as internal standards (Meisel *et al.* 2003, Qi *et al.* 2004), the

Table 6.
Rh results (ng g^{-1}) for TDB-1 and WGB-1 using ^{99}Ru, ^{110}Pd, ^{193}Ir and ^{198}Pt as internal standard elements (IS)

	IS-^{133}Cs	IS-^{99}Ru	IS-^{110}Pd	IS-^{193}Ir	IS-^{198}Pt
TDB-1	0.369	0.762	0.665	0.440	0.538
	0.341	0.516	1.350	0.397	0.767
	0.323	0.481	0.556	0.405	0.542
	0.312	0.463	1.195	0.399	1.387
	0.356	0.655	0.608	0.399	0.443
	0.334	0.464	0.699	0.414	1.042
Mean	0.339	0.557	0.845	0.409	0.787
% RSD^a	6.1	22.2	40.0	4.0	46.4
Information value	0.7				
Literature	0.35^b, 0.47^c				
WGB-1	0.174	0.250	0.345	0.195	0.419
	0.141	0.209	0.293	0.172	0.199
	0.163	0.243	0.357	0.201	0.331
	0.150	0.201	0.254	0.184	0.199
	0.145	0.224	0.275	0.188	0.371
	0.135	0.221	0.288	0.183	0.313
Mean	0.151	0.225	0.302	0.188	0.305
% RSD^a	9.7	8.3	13.4	5.5	29.4
Provisional value	0.32 ± 0.21				
Literature	0.19^b, 0.21^c				

^{a} % RSD = Per cent relative standard deviation.
^{b} Qi *et al.* (2004).
^{c} Savard *et al.* (2010).

chemical preparation was different, so the selected internal standards were also probably different. For example, Qi *et al.* (2004) and our study selected ^{194}Pt and ^{193}Ir, respectively. The former was based on the similar recovery of Rh and Pt found for Te coprecipitation; both working standard solutions and unknown samples were treated with the same addition of a ^{194}Pt spike and then prepared using the same procedure. Only the enriched isotope of ^{194}Pt was deduced as the internal standard for Rh determination. In this study, there were no spikes involved in the working standard solutions, and Rh was determined using the enriched isotope of ^{193}Ir as the internal standard, which included two parts of ^{193}Ir from both spikes and unknown samples. Although different chemical processes were employed, our data of Rh are consistent with the literature values. For the same reference materials, TDB-1 and WGB-1, Rh was also determined using a conventional internal standard (^{133}Cs), which was added to the resulting solution at the last stage. As shown in Table 6, the precision was 6.1% for TDB-1 and 9.7% for WGB-1, slightly greater than that using ^{193}Ir as the internal standard. The Rh data related to ^{133}Cs were compared with those related to ^{193}Ir, and the former was slightly lower than the latter. This comparison indicates ^{193}Ir can perform better than ^{133}Cs due to the coexistence of Ir and Rh throughout the whole procedure. Therefore, ^{193}Ir was chosen as internal standard for the determination of Rh in this study.

Uncertainty of PGE measurement results

Uncertainty budgets were estimated by Moser *et al.* (2003a) and revealed that analyte heterogeneity is the major contribution, whereas the isotopic ratio measurement is always the second largest contribution to the combined uncertainty of PGE mass fractions. If no consideration of the heterogeneity is made, the ratio measurement would become a major source of the uncertainty in PGE results. In practical analysis, this is influenced by factors such as dead time, background, spectral interference and mass discrimination. Besides the effect of the ratio measurement on the resulting uncertainty, the effect of the isotope ratio magnitude itself is also relevant for trace determination of PGE. According to error propagation, the relative uncertainty in the mass fraction can be derived as follows:

$$\left[\frac{d^A M_u}{^A M_u}\right]^2 = \left[\frac{(^R A_s \times {^E A_n} - {^E A_s} \times {^R A_n}) \times R}{(^R A_n \times R - {^E A_n})(^E A_s - {^R A_s} \times R)}\right]^2 \times \left[\frac{dR}{R}\right]^2$$
(8)

This equation shows that uncertainty depends on either the ratio measurement uncertainty (*dR*) or the isotope ratio magnitude (*R*).

Based on the specifics of our procedure and the constant detector settings of the ICP-MS, the effects of spectral

interference and dead time can be considered insignificant. Here, only the effect of the ratio magnitude on the PGE results was evaluated using the reference material GBW07291 in which there are higher PGE contents and the contribution of procedural blanks can be considered insignificant. Let

$$\left[\frac{(^{R}A_{s} \times {^{E}A_{n}} - {^{E}A_{s}} \times {^{R}A_{n}}) \times R}{(^{R}A_{n} \times R - {^{E}A_{n}})(^{E}A_{s} - {^{R}A_{s}} \times R)}\right]^{2} = P \qquad (9)$$

Here the uncertainty dependence on the ratio R can be clearly presented based on a P-R diagram (Figure 3).

Among the minimal P values related to the optimum isotope dilution ratios, the largest was shown for Ir (Figure 3), the reason being that the [193]Ir spike, instead of the ideal [191]Ir spike, was employed. The largest uncertainty in the PGE results was also observed for Ir from a single preparation of the reference material

GBW07291 (Table 7), further confirming the effect of larger P values. As proposed by Meisel et al. (2001), this comparison also indicates that both an ideal spike and its appropriate addition to unknown samples are important in order to produce a reasonable isotope dilution ratio and to minimise the total uncertainty of the concentration determination.

PGE blanks and detection limits

Because of the strong effect of reagents and chemical preparation on procedural blanks, much attention was paid to the clay crucibles eroded during the sulfide fire assay fusion. At a temperature of 1000 °C, sample-free runs were performed using fusion times of 1, 1.5 and 2 hr. Despite the severe erosion observed for the clay crucibles with longer fusion times, the procedural blanks were not significantly different, implying the effect of the eroded crucibles is very limited. The procedural blanks obtained for a 1.5 hr fusion
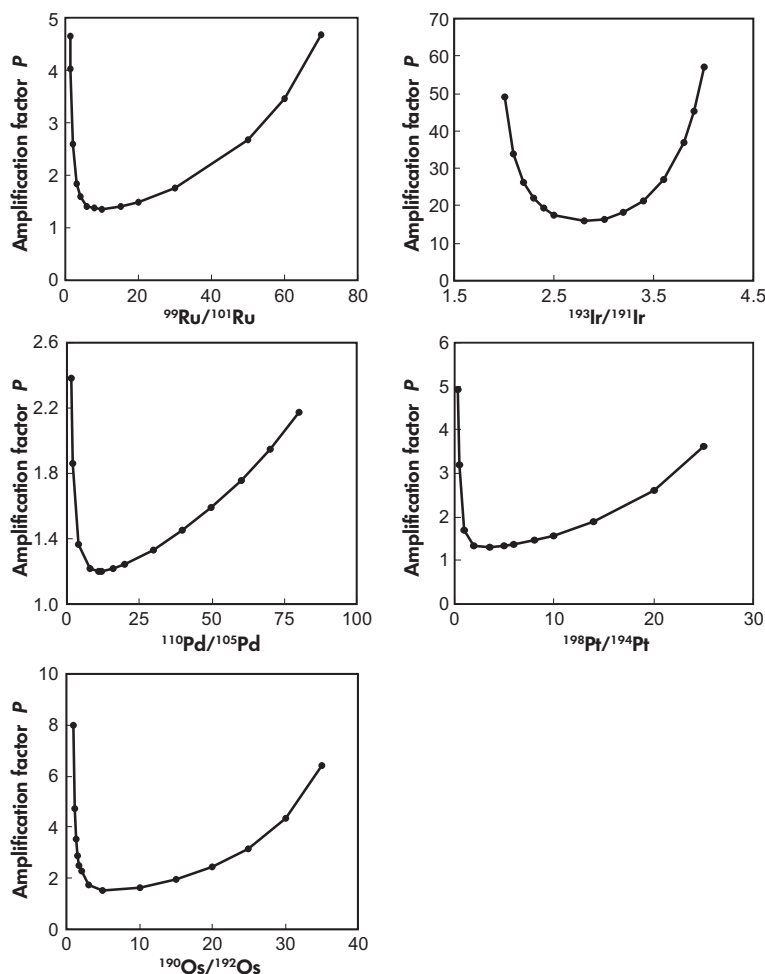

Figure 3. The dependence of the amplification factor (P) on isotope dilution ratio (R).

Table 7.
Measured isotope ratios, *P* values and relative uncertainties in ratio measurements and PGE contents for the reference material GBW07291

Element	Content (ng g^{-1})	dC/C (%)	*P* value	dR/R (%)	Isotope ratio
Ru	1.652	0.61	1.40	0.51	15.28
	1.726	0.54	1.39	0.46	14.70
	1.676	0.61	1.39	0.50	14.70
	1.799	0.59	1.39	0.50	14.17
	1.827	0.64	1.38	0.54	14.00
Pd	82.4	0.36	1.24	0.32	6.467
	84.2	0.56	1.25	0.50	6.336
	81.0	0.39	1.24	0.34	6.423
	86.4	0.45	1.25	0.40	6.191
	88.7	0.25	1.25	0.22	6.047
Os	2.212	1.12	6.99	0.42	1.040
	2.379	0.89	7.65	0.32	1.012
	2.59	0.69	8.52	0.24	0.982
	2.261	0.66	7.18	0.25	1.031
	2.754	0.92	9.23	0.30	0.962
Ir	7.275	2.03	18.39	0.47	2.447
	7.496	2.07	18.70	0.48	2.429
	7.149	1.87	18.29	0.44	2.453
	7.89	1.71	19.27	0.39	2.399
	8.068	1.82	19.52	0.41	2.387
Pt	51.8	0.80	1.31	0.70	4.529
	60.7	0.98	1.30	0.86	3.940
	53.1	0.94	1.31	0.82	4.433
	59.2	0.88	1.30	0.77	4.031
	60.4	0.40	1.30	0.35	3.960

were 0.121 ± 0.037 ng for Ru, 0.204 ± 0.025 ng for Rh, 0.960 ± 0.149 ng for Pd, 0.111 ± 0.029 ng for Os, 0.045 ± 0.020 ng for Ir and 0.661 ± 0.054 ng for Pt. Based on the 3*s* criterion, the following limits of detection (LOD) were obtained for a 10 g test portion: 0.011 ng g^{-1} for Ru, 0.008 ng g^{-1} for Rh, 0.045 ng g^{-1} for Pd, 0.009 ng g^{-1} for Os, 0.006 ng g^{-1} for Ir and 0.016 ng g^{-1} for Pt. According to the relation,

$$\text{corrected mass } (m_c) = \text{measured mass } (m_m)\text{- blank contribution } (m_b) \tag{10}$$

the resultant uncertainty ($\sqrt{u_m^2 + u_b^2}$) can be derived for the analysis of unknown samples. At very low content levels, the resultant uncertainty would be considered equivalent to the blank uncertainty, simplified to $\sqrt{2}u_b$. For test portions of 20 g, the relative uncertainties were 26–5.2, 18–3.5, 20–4.1 and 14–2.8% RSD for Ru, Rh, Os and Ir, respectively, at content levels of 0.01–0.05 ng g^{-1}, whereas they were 10–2.1 and 3.8–0.8% RSD for Pd and Pt at content levels of 0.1–0.5 ng g^{-1}. This assessment shows the effect of the procedural blanks was up to 26% for Ru at a content level of 0.01 ng g^{-1}.

This level of the procedural blanks was compared with that of Sun *et al.* (2009), who also employed the sulfide fire assay method for PGE preconcentration, and it is higher. This can be attributed to the extra reagents Na_2CO_3 and H_2O_2 applied, and the extra chemical purification performed using cation–Ln resin. By normalising to one gram of sample, the procedural blanks were compared with those from conventional sulfide fire assay (Jackson *et al.* 1990, Gros *et al.* 2002) and improved Carius tube digestion (Qi *et al.* 2013); they were found to be at the same levels as those of the former but higher than those of the latter. Despite the significant contribution of the procedural blanks to lower PGE contents, sulfide fire assay is still an attractive technique for the determination of trace levels of PGE in geological materials because it can readily decompose bulk test portions of 20–50 g, and even up to the 500 g required for the accurate measurement of Os (Ireland *et al.* 2011). With such test portion sizes, the nugget effect may be expected to be overcome and PGE data to be more reasonable.

Analysis of reference materials

To validate the applicability and suitability of the proposed method, several PGE reference materials were prepared and analysed. As shown in Table 8, the results are generally in agreement with the certified values within the 95% confidence interval except for Ir and Pt in GBW07291 and for Ru, Rh and Ir in WGB-1 and TDB-1. In GBW07291,

Table 8.
Analytical results (ng g^{-1}) of PGE analytes in reference materials

		Ru	Rh	Pd	Os	Ir	Pt
GBW07289	1	0.077	0.059	2.09	0.060	0.032	1.59
20 g, n = 5	2	0.063	0.060	2.40	0.060	0.028	1.49
	3	0.076	0.061	1.96	0.052	0.032	1.50
	4	0.064	0.054	2.38	0.067	0.031	1.30
	5	0.062	0.067	2.40	0.058	0.024	1.71
	Found ± s	0.068 ± 0.007	0.060 ± 0.005	2.25 ± 0.21	0.059 ± 0.005	0.029 ± 0.003	1.52 ± 0.15
	Recommended	0.10[a]	0.095 ± 0.012	2.3 ± 0.2	0.06 ± 0.01	0.05 ± 0.01	1.6 ± 0.3
GBW07290	Found ± s	13.3 ± 1.2	1.15 ± 0.11	5.22 ± 0.51	9.65 ± 0.43	5.52 ± 0.53	6.76 ± 0.62
10 g, n = 10	Recommended	14.8 ± 2.7	1.3 ± 0.3	4.6 ± 0.6	9.6 ± 2.0	4.3 ± 0.5	6.4 ± 0.9
GBW07291	Found ± s	1.74 ± 0.07	4.31 ± 0.22	84.5 ± 3.1	2.44 ± 0.23	7.58 ± 0.39	57.0 ± 4.3
10 g, n = 5	Recommended	2.5 ± 0.2	4.3 ± 0.8	60 ± 9	2.4 ± 0.6	4.7 ± 1.1	58 ± 5
	Literature[b]	3.85	6.65	92.5	2.35	7.9	64
GBW07294	Found ± s	0.56 ± 0.03	0.98 ± 0.03	18.7 ± 1.0	0.50 ± 0.02	1.34 ± 0.11	16.1 ± 1.1
10 g, n = 6	Recommended	0.66 ± 0.20	1.1 ± 0.2	15.2 ± 2.3	0.64 ± 0.14	1.24 ± 0.3	14.7 ± 2.5
GBW07340	Found ± s	0.44 ± 0.04	0.062 ± 0.005	0.64 ± 0.06	0.24 ± 0.02	0.15 ± 0.01	0.67 ± 0.05
20 g, n = 6	Literature[d]	0.43 ± 0.16	0.066 ± 0.008	0.66 ± 0.08	0.25 ± 0.04	0.16 ± 0.03	0.66 ± 0.08
WGB-1	Found ± s	0.131 ± 0.014	0.188 ± 0.010	15.0 ± 1.4	0.658 ± 0.130	0.191 ± 0.043	4.73 ± 0.87
10 g, n = 6	Recommended	0.3[c]	0.32 ± 0.21[c]	13.9 ± 2.1		0.33 ± 0.17[c]	6.1 ± 1.6
	Literature[e]	0.182 ± 0.015	0.207 ± 0.025	12.4 ± 0.4	0.544 ± 0.158	0.199 ± 0.011	4.71 ± 0.29
TDB-1	Found ± s	0.206 ± 0.004	0.409 ± 0.016	26.8 ± 1.2	0.157 ± 0.017[f]	0.057 ± 0.012	4.38 ± 0.16
10 g, n = 6	Recommended	0.3[a]	0.7[c]	22.4 ± 1.4		0.15[c]	5.8 ± 1.1
	Literature[e]	0.253 ± 0.018	0.466 ± 0.004	22.82 ± 0.8	0.159 ± 0.027	0.084 ± 0.02	4.64 ± 0.31

[a] Information values.

[b] Mean values derived from the PGE analyses of two sulfide buttons from Jorge *et al.* (1998).

[c] Provisional values.

[d] Gu *et al.* (2007).

[e] Savard *et al.* (2010).

[f] The content of Os with inclusion of 0.015 ng g^{-1} radiogenic ^{187}Os.

the data for Pd and Ir were 84.5 ng g^{-1} and 7.58 ng g^{-1}, respectively, much higher than their recommended values of 60 ng g^{-1} and 4.7 ng g^{-1}. Considering the reasonable precision of 5.3% for Pd and 7.2% for Ir, the larger difference cannot be explained by their heterogeneity. In addition, the data for Rh related to ^{193}Ir as the internal standard are comparable to its recommended value. Another influence from the procedural blank of Ir (0.05 ng) was also considered, but its contribution to the relatively high content of Ir cannot be expected to be significant even for the 1 g test portion size of GBW07291. Therefore, the results of Ir as well as Pd are considered reasonable. Compared with the literature values of 92.5 ng g^{-1} for Pd and 7.9 ng g^{-1} for Ir reported by Jorge *et al.* (1998), our data for Pd and Ir are consistent. For WGB-1 and TDB-1, the measurement data for Pd and Pt were consistent with their recommended values, whereas the values for Ru, Rh and Ir were much lower than their provisional or information values (Table 8). However, they agree well with the data reported by Meisel and Moser (2004b), Qi *et al.* (2004) and Savard *et al.* (2010), who employed different methods for sample decomposition. The results for reference materials GBW07290 and WGB-1 showed some differences compared with those of Sun *et al.*

(2009). Despite a PGE preconcentration with the same sulfide fire assay, the subsequent chemical procedures differed. Prior to ICP-MS analysis in this study, the resulting solutions were further purified by cation and Ln resins, whereas they were not in the study of Sun *et al.* (2009). As a result, the potential interferences on Ru, Rh and Pd would be expected to be different, and this may have led to the contrasting results.

Using the measured results for the RMs, the precision was evaluated for the proposed method. For the reference material GBW07289, RSDs were > 10% for Rh and Os, probably attributable to the higher contribution of the procedural blanks. For other reference materials, their data precision was better than 10%, except for Os, Ir and Pt in WGB-1 and TDB-1. The data for Ir were variable, up to 22.5% RSD for WGB-1 and 19.3% RSD for TDB-1. Despite the poor reproducibility, Ir was used as the internal standard in the determination of Rh, and reasonable Rh results were obtained – 5.5% RSD for WGB-1 and 4.0% RSD for TDB-1 (Table 6). Both precise and accurate Rh data seem to illustrate the heterogeneity of Ir in reference materials WGB-1 and TDB-1. The contribution of proce-
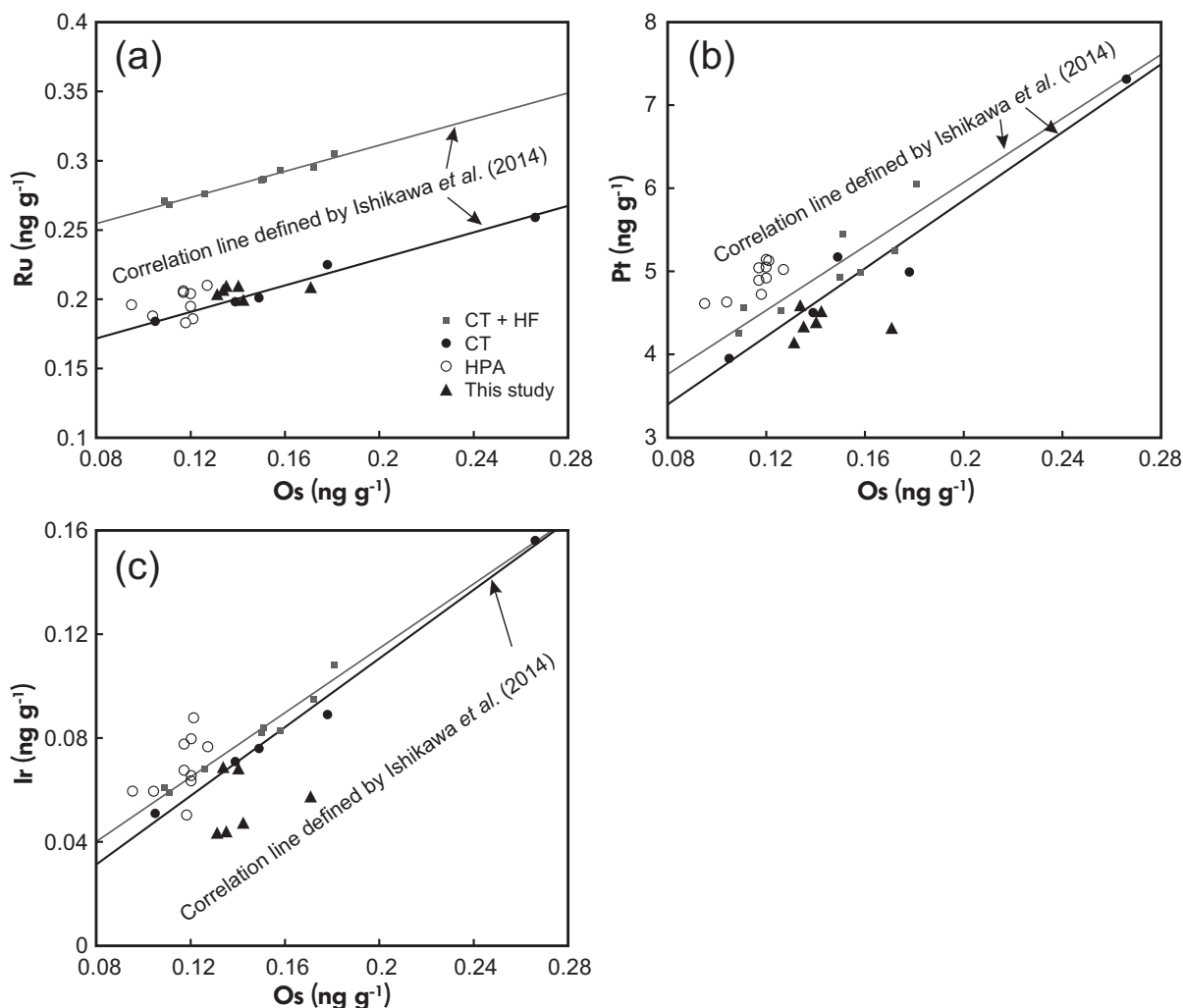
Figure 4. The contents of Ru versus Os (a), Pt versus Os (b) and Ir versus Os (c) in the reference material TDB-1 decomposed by different methods (CT stands for traditional Carius tube digestion, CT+HF for Carius tube digestion combined with HF desilicification and HPA for high-pressure asher).

dural blanks to the lower contents of Ru, Rh, Os and Ir is not expected to be over 10%. Recent investigations of Carius tube (CT) digestion combined with HF desilicification (Ishikawa *et al.* 2014) found PGE data of poor reproducibility for the material TDB-1. Our data as well as data from high-pressure asher (HPA) digestion (Meisel and Moser 2004b, Dale *et al.* 2009, 2012, Ishikawa *et al.* 2014) were compared with the correlation line defined by Ishikawa *et al.* (2014). Figure 4a (Ru *versus* Os) shows that they plot around the data line for traditional CT and basically parallel to the data line for CT+HF desilicification. However, the same phenomenon was not observed for both Pt versus Os (Figure 4b) and Ir *versus* Os (Figure 4c). As proposed by Ishikawa *et al.* (2014), this is attributable to the existence of minor minerals rich in Os, Ir, Ru and Pt in the reference material TDB-1. Due to such minerals, poor

reproducibility for PGE data would probably be expected even using sulfide fire assay fusion with test portions > 10 g. For example, data for Ir in TDB-1 were up to 24% RSD (Savard *et al.* 2010). It is therefore likely that the heterogeneity of PGE analytes in the reference materials analysed in this study is the principal reason for the large variation in the data. To overcome this problem, larger test portion masses should be used in conjunction with the proposed method for PGE preconcentration.

Summary

In this study, isotope dilution-ICP-MS in combination with sulfide fire assay preconcentration was applied to geological samples for the determination of platinum-group elements. Related to the fire assay technique,

possible interference on PGE analytes was fully considered and it was successfully eliminated using tandem columns of cation and Ln resins in 0.24 mol l^{-1} HCl solutions. As a result, PGE analytes in the resulting solution could be directly analysed by membrane desolvation-ICP-MS, increasing their detection sensitivity by at least five times. Using sulfide fire assay preconcentration coupled with ID-ICP-MS, precise and accurate PGE data at very low levels were obtained for a series of geological reference materials.

Acknowledgements

References

Asif M. and Parry S.J. (1989)
Elimination of reagent blank problems in the fire-assay pre-concentration of the platinum-group elements and gold with a nickel sulphide bead of less than one gram mass. Analyst, 114, 1057–1059.

Barefoot R. (1998)
Determination of the precious metals in geological materials by inductively coupled plasma-mass spectrometry. Journal of Analytical Atomic Spectrometry, 13, 1077–1084.

Barefoot R. and Van Loon J. (1999)
Recent advances in the determination of the platinum-group elements and gold. Talanta, 49, 1–14.

Berglund M. and Wieser M.E. (2011)
Isotopic compositions of the elements 2009 (IUPAC Technical Report). Pure and Applied Chemistry, 83, 397–410.

Boisvert R., Bergeron M. and Turcotte J. (1991)
Re-examination of the determination of palladium, platinum and rhodium in rocks by nickel sulphide fire assay followed by graphite furnace atomic absorption measurements. Analytica Chimica Acta, 246, 365–373.

Chung C.H., Brenner I. and You C.F. (2009)
Comparison of microconcentric and membrane-desolvation sample introduction systems for determination of low

rare earth element concentrations in surface and subsurface waters using sector field inductively coupled plasma-mass spectrometry. Spectrochimica Acta Part B, 64, 849–856.

Conver T.S., Yang J. and Koropchak J.A. (1997)
New developments in thermospray sample introduction for atomic spectrometry. Spectrochimica Acta Part B, 52, 1087–1104.

Dale C.W., Burton K.W., Pearson D.G., Gannoun A., Alard O., Argles T.W. and Parkinson I.J. (2009)
Highly siderophile element behaviour accompanying subduction of oceanic crust: Whole rock and mineral-scale insights from a high-pressure terrain. Geochimica et Cosmochimica Acta, 73, 1394–1416.

Dale C.W., Macpherson C.G., Pearson D.G., Hammond S.J. and Arculus R.J. (2012)
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.

Gros M., Lorand J.P. and Luguet A. (2002)
Analysis of platinum-group elements and gold in geological materials using NiS fire assay and Te coprecipitation: The NiS dissolution step revisited. Chemical Geology, 185, 179–190.

Gu T., Shi C., Pu W., Yan W., Liu M. and Yan M. (2007)
New progress on certified reference materials for platinum-group elements: IGGE GPt-8, GPt-9 and GPt-10. Geostandards and Geoanalytical Research, 31, 125–132.

Hall G. and Pelchat J. (1994)
Analysis of geological materials for gold, platinum and palladium at low ppb levels by fire assay-ICP mass spectrometry. Chemical Geology, 115, 61–72.

Hoffman E., Naldrett A., Van Loon J., Hancock R. and Manson A. (1978)
The determination of all the platinum-group elements and gold in rocks and ore by neutron activation analysis after preconcentration by a nickel sulphide fire-assay technique on large samples. Analytica Chimica Acta, 102, 157–166.

Ireland T., Walker R. and Brandon A. (2011)
^{186}Os–^{187}Os systematics of Hawaiian picrites revisited: New insights into Os isotopic variations in ocean island basalts. Geochimica et Cosmochimica Acta, 75, 4456–4475.

Ishikawa A., Senda R., Suzuki K., Dale C.W. and Meisel T. (2014)
Re-evaluating digestion methods for highly siderophile element and ^{187}Os isotope analysis: Evidence from geological reference materials. Chemical Geology, 384, 27–46.

references

Jackson S., Fryer B., Gosse W., Healey D., Longerich H. and Strong D. (1990)
Determination of the precious metals in geological materials by inductively coupled plasma-mass spectrometry (ICP-MS) with nickel sulphide fire-assay collection and tellurium coprecipitation. Chemical Geology, 83, 119–132.

Jarvis I., Totland M.M. and Jarvis K.E. (1997a)
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.

Jarvis I., Totland M.M. and Jarvis K.E. (1997b)
Assessment of Dowex 1-X8-based anion-exchange procedures for the separation and determination of ruthenium, rhodium, palladium, iridium, platinum and gold in geological samples by inductively coupled plasma-mass spectrometry. Analyst, 122, 19–26.

Jorge A.P.d.S., Enzweiler J., Shibuya E.K., Sarkis J.E. and Figueiredo A.M.G. (1998)
Platinum-group elements and gold determination in NiS fire assay buttons by UV laser ablation ICP-MS. Geostandards Newsletter: The Journal of Geostandards and Geoanalysis, 22, 47–55.

Juvonen R., Lakomaa T. and Soikkeli L. (2002)
Determination of gold and the platinum-group elements in geological samples by ICP-MS after nickel sulphide fire assay: Difficulties encountered with different types of geological samples. Talanta, 58, 595–603.

Kanitsar K., Koellensperger G., Hann S., Limbeck A., Puxbaum H. and Stingeder G. (2003)
Determination of Pt, Pd and Rh by inductively coupled plasma sector field mass spectrometry (ICP-SFMS) in size-classified urban aerosol samples. Journal of Analytical Atomic Spectrometry, 18, 239–246.

Köllensperger G., Hann S. and Stingeder G. (2000)
Determination of Rh, Pd and Pt in environmental silica containing matrices: Capabilities and limitations of ICP-SFMS. Journal of Analytical Atomic Spectrometry, 15, 1553–1557.

Lehto J. and Hou X. (2010)
Chemistry and analysis of radionuclides: Laboratory techniques and methodology. Wiley (Weinheim), 408pp.

Li X.L. (1995)
Neutron activation analysis for platinum-group elements in geological materials. Nuclear Technique, 18, 20–23.

Li Y.Q., Li Z.L., Sun Y.L., Santosh M., Langmuir C.H., Chen H.L., Yang S.F., Chen Z.X. and Yu X. (2012)
Platinum-group elements and geochemical characteristics of the Permian continental flood basalts in the Tarim Basin, northwest China: Implications for the evolution of the Tarim Large Igneous Province. Chemical Geology, 328, 278–289.

Li J., Jiang X.Y., Xu J.F., Zhong L.F., Wang X.C., Wang G.Q. and Zhao P.P. (2013)
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. Geostandards and Geoanalytical Research, 38, 37–50.

Lü C.F., He H.L., Zhou Z.R., Zhi X.X., Li B. and Zhang Q. (2002)
Determination of platinum-group elements and gold in geochemical exploration samples by nickel sulfide fire assay-ICP-MS, II. Reduction of reagent blank. Rock and Mineral Analysis, 21, 7–11.

Markey R., Stein H.J., Hannah J.L., Zimmerman A., Selby D. and Creaser R.A. (2007)
Standardizing Re-Os geochronology: A new molybdenite reference material (Henderson, USA) and the stoichiometry of Os salts. Chemical Geology, 244, 74–87.

McDonald I. (1998)
The need for a common framework for collection and interpretation of data in platinum-group element geochemistry. Geostandards Newsletter: The Journal of Geostandards and Geoanalysis, 22, 85–91.

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. (2001)
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. Analyst, 126, 322–328.

Meisel T., Fellner N. and Moser J. (2003)
A simple procedure for the determination of platinum-group elements and rhenium (Ru, Rh, Pd, Re, 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.

Moser J., Wegscheider W., Meisel T. and Fellner N. (2003a)
An uncertainty budget for trace analysis by isotope-dilution ICP-MS with proper consideration of correlation. Analytical and Bioanalytical Chemistry, 377, 97–110.

Oguri K., Shimoda G. and Tatsumi Y. (1999)
Quantitative determination of gold and the platinum-group elements in geological samples using improved NiS fire-assay and tellurium coprecipitation with inductively coupled plasma-mass spectrometry (ICP-MS). Chemical Geology, 157, 189–197.

Pearson D. and Woodland S. (2000)
Solvent extraction/anion exchange separation and determination of PGEs (Os, Ir, Pt, Pd, Ru) and Re–Os isotopes in geological samples by isotope dilution ICP-MS. Chemical Geology, 165, 87–107.

Qi L. and Zhou M.F. (2008)
Determination of platinum-group elements in OPY-1: Comparison of results using different digestion techniques. Geostandards and Geoanalytical Research, 32, 377–387.

references

Qi L., Zhou M.-F. and Wang C.Y. (2004)
Determination of low concentrations of platinum-group elements in geological samples by ID-ICP-MS. Journal of Analytical Atomic Spectrometry, 19, 1335–1339.

Qi L., Gao J., Huang X., Hu J., Zhou M.F. and Zhong H. (2011)
An improved digestion technique for determination of platinum-group elements in geological samples. Journal of Analytical Atomic Spectrometry, 26, 1900–1904.

Qi L., Gao J.F., Zhou M.F. and Hu J. (2013)
The design of re-usable Carius tubes for the determination of rhenium, osmium and platinum-group elements in geological samples. Geostandards and Geoanalytical Research, 37, 345–351.

Ravizza G. and Pyle D. (1997)
PGE and Os isotopic analyses of single sample aliquots with NiS fire assay preconcentration. Chemical Geology, 141, 251–268.

Rehkämper M. and Halliday A. (1997)
Development and application of new iondashexchange techniques for the separation of the platinum-group and other siderophile elements from geological samples. Talanta, 44, 663–672.

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.

Robert R., Palmer R. and van Wyk E. (1971).
Concentration of the noble metals by a fire-assay technique using nickel sulphide as the collector. National Institute for Metallurgy (Johannesburg), Report No. 1371.

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.

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

Sun Y. and Sun M. (2005)
Nickel sulfide fire assay improved for pre-concentration of platinum-group elements in geological samples: A practical means of ultra-trace analysis combined with inductively coupled plasma-mass spectrometry. Analyst, 130, 664–669.

Sun M., Jain J., Zhou M. and Kerrich R. (1993)
A procedural modification for enhanced recovery of precious metals (Au, PGE) following nickel sulphide fire assay and tellurium coprecipitation: Applications for analysis of geological samples by inductively coupled plasma-mass spectrometry. Canadian Journal of Applied Spectroscopy, 38, 103–108.

Sun Y., Guan X. and Du A. (1998)
Determination of platinum-group elements by inductively coupled plasma-mass spectrometry combined with nickel sulfide fire assay and tellurium coprecipitation. Spectrochimica Acta Part B, 53, 1463–1467.

Sun Y., Sun M. and Gong A. (2000)
Pre-concentration of platinum group elements with about 2.5 g nickel sulfide button. Chinese Journal of Analytical Chemistry, 28, 1010–1012.

Sun Y., Zhou M.-F. and Sun M. (2001)
Routine Os analysis by isotope dilution-inductively coupled plasma-mass spectrometry: OsO_4 in water solution gives high sensitivity. Journal of Analytical Atomic Spectrometry, 16, 345–349.

Sun Y., Chu Z., Sun M. and Xia X. (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 spectrometry. Applied Spectroscopy, 63, 1232–1237.

Van Loon J.C. and Barefoot R. (1991)
Determination of the precious metals: Selected instrumental methods. Wiley (Chichester), 76pp.