



Platinum stable isotope analysis of geological standard reference materials by double-spike MC-ICPMS



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ABSTRACT

We report a method for the chemical purification of Pt from geological materials by ion-exchange chromatography for subsequent Pt stable isotope analysis by multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS) using a ^{196}Pt – ^{198}Pt double-spike to correct for instrumental mass bias. Double-spiking of samples was carried out prior to digestion and chemical separation to correct for any mass-dependent fractionation that may occur due to incomplete recovery of Pt. Samples were digested using a NiS fire assay method, which pre-concentrates Pt into a metallic bead that is readily dissolved in acid in preparation for anion-exchange chemistry. Pt was recovered from anion-exchange resin in concentrated HNO_3 acid after elution of matrix elements, including the other platinum group elements (PGE), in dilute HCl and HNO_3 acids. The separation method has been calibrated using a precious metal standard solution doped with a range of synthetic matrices and results in Pt yields of $\geq 90\%$ with purity of $\geq 95\%$. Using this chemical separation technique, we have separated Pt from 11 international geological standard reference materials comprising of PGE ores, mantle rocks, igneous rocks and one sample from the Cretaceous–Paleogene boundary layer. Pt concentrations in these samples range from ca. 5 ng g^{-1} to $4 \mu\text{g g}^{-1}$. This analytical method has been shown to have an external reproducibility on $\delta^{198}\text{Pt}$ (permil difference in the $^{198}\text{Pt}/^{194}\text{Pt}$ ratio from the IRMM-010 standard) of ± 0.040 (2 sd) on Pt solution standards (Creech et al., 2013, *J. Anal. At. Spectrom.* 28, 853–865). The reproducibility in natural samples is evaluated by processing multiple replicates of four standard reference materials, and is conservatively taken to be ca. ± 0.088 (2 sd). Pt stable isotope data for the full set of reference materials have a range of $\delta^{198}\text{Pt}$ values with offsets of up to 0.4‰ from the IRMM-010 standard, which are readily resolved with this technique. These results demonstrate the potential of the Pt isotope system as a tracer in geochemical systems.

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1. Introduction

Platinum (Pt) has six naturally occurring isotopes (^{190}Pt , ^{192}Pt , ^{194}Pt , ^{195}Pt , ^{196}Pt and ^{198}Pt). Like all platinum group elements (PGE; Ru, Rh, Pd, Os, Ir and Pt), Pt is highly siderophile and prefers bonds with metal over silicon and oxygen and, as such, is concentrated in the cores of terrestrial planets. The PGE also show some chalcophile behaviour, and in the conditions found in the crust and mantle are strongly partitioned into sulphide minerals. Platinum can exist in a range of oxidation states, but in the Earth principally occurs as Pt^0 , Pt^{2+} and Pt^{4+} (Cotton and Wilkinson, 1966). The relatively large mass difference (2%) between the abundant heavy and light isotopes of Pt, coupled with its variable redox states in the Earth's core, mantle and surficial environments, and the large differences in Pt abundances that characterise Earth's major geochemical reservoirs suggest that Pt may exhibit significant stable isotope variations. However, to-date there have been no

published studies of Pt stable isotope variations in natural terrestrial samples.

We have developed an improved anion-exchange method for chemical separation of Pt from geological materials. Using this method, Pt has been separated from a range of international geological standard reference materials, and their Pt stable isotopic compositions were then determined using a recently developed method for precise Pt stable isotope measurement by double-spike (DS) multiple collector inductively coupled plasma mass spectrometry (MC-ICPMS) (Creech et al., 2013). These results reveal significant differences in Pt stable isotopic composition amongst this suite of samples and provide reference Pt stable isotope data for standards for use in future applications of this technique.

2. Samples

A suite of 11 international geological standard reference materials were selected based on availability and published Pt contents. The Pt abundances of these samples span practically the entire range found

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on Earth. A short description of each of the analysed materials is given here and summarised in Table 1.

The standard reference materials are considered in groups as follows:

- (a) Pt ore samples: SARM-76 is from the Merensky Reef Ore of the Bushveld Igneous Complex in South Africa, which contains most of the world's known reserves of PGE. The PGE are hosted in extensive sulphide layers within the unit, which have an emplacement age of ca. 2.06 Ga (Walraven et al., 1990). SARM-76 is distributed by MINTEK. PTA-1 is a platiniferous black sand from the Tulameen River area of British Columbia, Canada, which is described as being essentially a magnetite concentrate, containing an abundant Pt–Fe alloy (Faye and Sutarno, 1976). The Tulameen ultramafic–gabbro complex has an emplacement age of ca. 186 Ma (Findlay, 1969). The PTA-1 reference material is distributed by the CANMET Canadian Certified Reference Materials Project (CCRMP). WPR-1 is an altered ultramafic igneous rock from the Wellgreen Complex, Yukon, Canada, which is also distributed by CANMET-CCRMP. The Wellgreen Complex is part of the greater Quill Creek ultramafic complex, which has an emplacement age of 232 Ma (Marcantonio et al., 1994). Pt in WPR-1 is thought to be hosted in base metal sulphides (Barkov et al., 2002; Meisel and Moser, 2004), platinum group minerals (Barkov et al., 2002) and tellurides (CANMET-CCRMP reference certificate). The three Pt ore standards have Pt concentrations ranging from 285 to 3590 ng g⁻¹ (Table 1).
- (b) Mantle-derived samples: PCC-1 is a peridotite standard from California, USA, distributed by the US Geological Survey (USGS), although supplies of this material are now exhausted. JP-1 is a peridotite from the Horoman peridotite, Hokkaido Island, Japan. The petrogenesis of the Horoman peridotite is complicated, but it is considered to have been emplaced ca. 23 Ma (Takazawa et al., 1999) and to represent former sub-oceanic lithosphere (Takazawa et al., 1992, 1996, 2000). JP-1 is distributed by the Geological Society of Japan (GSJ). OKUM is an ultramafic komatiite distributed by Geosciences Laboratories, that was sampled from Serpentine Mountain, Ontario, Canada. This area is located at the western end of the Abitibi Greenstone Belt, and was emplaced into the crust ca. 2.7 Ga (Houlé et al., 2009). PGE in these rocks are found as Ni–Cu–PGE minerals (Houlé et al., 2009). Although OKUM is technically an igneous sample, komatiites are considered to be large degree partial melts of the underlying mantle (e.g. Nisbet and Walker, 1982) and their compositions are expected to reflect the mantle source. Platinum concentrations in the mantle-derived samples range from ca. 5–12 ng g⁻¹ (Table 1).
- (c) Igneous samples: SARM-6 is a dunite from an ultrabasic pipe in the Bushveld Complex, South Africa provided by MINTEK. As with SARM-76 described above, this unit was emplaced ca. 2.06 Ga, and PGE are hosted in sulphide minerals. LK-NIP is a

dolerite from the Nipigon Diabase, Ontario, Canada distributed by Geosciences Laboratories. The Nipigon diabase sills were intruded into the crust ca. 1100 Ma (Hart and MacDonald, 2007; Heaman et al., 2007). DNC-1 is a dolerite from North Carolina, USA, distributed by the USGS. BIR-1 is a tholeiitic basalt from a lava flow near Reykjavik, Iceland, distributed by the USGS. These igneous samples have Pt concentrations ranging from ca. 4 ng g⁻¹ in BIR-1 to 39 ng g⁻¹ in SARM-6 (Table 1).

- (d) Other samples: FC-1 was collected from the Fish Clay at Stevns Klint in Denmark. FC-1 was sampled from a sedimentary layer that is stratigraphically located at the Cretaceous–Paleogene boundary and has elevated levels of Ir, due to the putative meteorite impact at that time (Alvarez et al., 1980). The FC-1 standard is distributed by the University of Copenhagen, and has a Pt concentration of 38 ng g⁻¹ (Table 1).

3. Materials and methods

3.1. Reagents, standard solutions and spikes

Analytical reagent grade nitric (HNO₃) and hydrochloric (HCl) acids were purified by sub-boiling distillation in quartz or Teflon stills, respectively, prior to use in anion-exchange chemistry. Acid used in the digestion steps (including aqua regia) and all solutions for MC-ICPMS analysis were prepared from Optima™ grade HNO₃ and HCl acids, which were used as supplied without further purification. Acid dilutions and all water rinses were performed with ultrapure (>18 MΩ·cm) water.

In the initial stages of technique development, a mixed 'precious metals' standard from Alfa Aesar supplier (SpecPure plasma standard, 100 µg mL⁻¹ in 20% HCl, Lot # 012912A) was used, containing Ru, Rh, Pd, Re, Os, Ir, Pt and Au. For performing column calibrations, several synthetic rock mixtures were prepared in order to have compositions approximating those of a peridotite, chondrite, and iron meteorite (Table S1) by mixing single-element standard solutions and the precious metal standard solution at the appropriate concentration levels. Mixtures containing all of the elements present in the synthetic rock mixtures were also prepared from standard solutions at concentrations of 1 µg mL⁻¹ and 1 ng mL⁻¹ and used as a bracketing standards in ICP-MS measurements of ion-exchange fractions for the construction of elemental elution profiles.

The Pt isotope standard IRMM-010 was purchased from the Institute for Reference Materials and Measurements, Belgium. The supplied Pt wire segments were carefully weighed and then cleaned prior to digestion by sequentially rinsing in ultrapure water, analytical grade methanol and dilute (5%) HNO₃. The cleaned IRMM-010 was then digested in aqua regia (HCl:HNO₃ prepared in a volume ratio of 3:1) in a Savillex Teflon beaker. The IRMM-010 solution was then evaporated, converted to chloride in concentrated HCl, evaporated again, and finally redissolved in 20% HCl. From this, a 60 ng mL⁻¹ solution of

Table 1
Details of the standard reference materials analysed in this study.

Group	Provider	Standard	Lot/batch	Type	Locality	Pt conc. ^a (µg g ⁻¹)
Ore	CANMET-CCRMP	PTA-1		Platiniferous black sand	Tulameen River, British Columbia	3.05
	CANMET-CCRMP	WPR-1		Ultramafic igneous rock	Wellgreen complex, Yukon, Canada	0.285
	MINTEK	SARM-76		PGM ore	Merensky Reef, Bushveld Complex, South Africa	3.59
Mantle	Geosciences Lab.	OKUM		Ultramafic komatiite	Serpentine Mountain, Ontario, Canada	0.01144
	GSJ	JP-1	Split 3 pos 42	Peridotite	Horoman peridotite, Horoman, Hokkaido, Japan	0.0049
	USGS	PCC-1	Split 34 pos 3	Peridotite	East Austin Creek, Sonoma County, California, USA	0.008
Igneous	Geosciences Lab.	LK-NIP		Diabase	Nipigon diabase, Ontario, Canada	0.01343
	MINTEK	SARM-6		Dunite	Ultrabasic pipe, Bushveld Complex, South Africa	0.039
	USGS	BIR-1	Lot 0036	Tholeiitic basalt	Reykjavik, Iceland	0.0043
	USGS	DNC-1	Lot 0667	Dolerite	Braggtown Quarry, North Carolina	0.0368
Other	Univ. of Copenhagen	FC-1		Fish Clay	Stevns Klint, Denmark	0.038

^a Concentrations for standard reference materials were taken from the GeoRem database and references therein.

IRMM-010 in 0.5 M HCl was prepared and double-spiked for use as a bracketing standard for MC-ICPMS isotopic measurements (Creech et al., 2013).

The Pt DS used for the isotopic analyses was prepared using two single isotope spikes (^{196}Pt and ^{198}Pt) obtained from the Oak Ridge National Laboratory, USA. Full details of the design and calibration of the DS are given in Creech et al. (2013).

3.2. Laboratory environment

Sample digestions were carried out in an ultra-clean laboratory at Victoria University of Wellington. All Pt separation work was conducted in class 10 laminar flow hoods situated in a class 100 clean laboratory.

Savillex™ Teflon beakers were used for all sample digestions and collection of eluents from chemistry. Beakers were cleaned thoroughly between uses by the following process: pre-cleaning by refluxing with aqua regia overnight on a hotplate at 120 °C; batch cleaning in 6 M HCl (AR grade) in a large glass beaker overnight on a hotplate at 50 °C; batch cleaning in 7 M HNO₃ (AR grade) in a large glass beaker overnight on a hotplate at 50 °C; two periods of overnight refluxing with aqua regia, prepared from Optima™ grade HNO₃ and HCl acids, on a hotplate at 120 °C. Beakers were thoroughly rinsed with ultrapure water between each of these steps.

Crushing of samples or NiS beads was performed using an agate mortar and pestle, which was cleaned thoroughly between uses by rinsing with methanol and ultrapure water and by grinding pure quartz grains.

3.3. Sample digestion

Digestion of the standards was carried out using the NiS fire assay technique. This method is commonly used in PGE work, and involves melting the sample in the presence of Ni and S, which form a metallic NiS bead into which the PGE are sequestered. The NiS bead can then be physically removed from the silicate slag and readily digested in acid. By eliminating most of the rock matrix elements, this approach has the advantage of pre-concentrating the PGE, but can have relatively high blanks when compared with acid digestion techniques (Rehkämper and Halliday, 1997). Most NiS fire assay procedures use relatively large amounts of sample, which has been found to reduce the influence of 'nugget' effects and improve the external reproducibility of PGE concentration measurements. A number of procedures for NiS fire assay have been published, with subtle differences in flux amounts and fusion time (e.g. Rehkämper and Halliday, 1997; Ravizza and Pyle, 1997; Gros et al., 2002; Morcelli et al., 2004; Savard et al., 2010). The procedure used here largely follows Morcelli et al. (2004), although it includes the addition of silica as has been adopted in some other studies (e.g. Gros et al., 2002).

Powdered material of the terrestrial standards was weighed directly into porcelain crucibles (50 mL, medium wall, Lomb Scientific). The NiS fire assay charges typically comprised 15 g of sample. When less sample was used due to high Pt concentrations or limited availability of material, the sample weight was made up to 15 g using pure silica. Procedural blanks for the NiS fire assay technique were assessed by digesting 15 g of pure silica with no sample.

The samples in the porcelain crucibles were then thoroughly mixed with 10 g of sodium carbonate, 20 g of sodium tetraborate, 1 g of nickel powder and 0.75 g of sulphur. For samples that were spiked prior to NiS digestion, Pt DS was added to the mixture in the crucible from a solution of the ^{196}Pt – ^{198}Pt DS in the appropriate volume for a ratio of 55% Pt from DS and 45% natural Pt, and allowed to dry. Crucibles were then placed in a furnace and fused at 950 °C for 30 min, and at 1050 °C for a further 30 min (Morcelli et al., 2004). The crucibles were removed from the furnace and left to cool at room temperature. Once cooled, the crucibles were physically broken and NiS beads were carefully removed from the silicate slag. The NiS beads were then weighed and crushed into smaller

fragments in an agate mortar and then weighed again before being transferred to Savillex Teflon beakers for acid dissolution.

The NiS beads were dissolved in ca. 30 mL of concentrated HCl on a hotplate at 120 °C with lids off, and then left to evaporate. Once dry, another ca. 30 mL of concentrated HCl was added to the samples, and the beakers were again placed on a hotplate at 120 °C with their lids off for 2–3 h. The beakers were removed from the hotplate, and a volume of concentrated HNO₃ approximately one-third of that of the remaining HCl volume was added to produce aqua regia. The beakers were then closed and placed on a hotplate at 120 °C overnight, following which the samples were typically fully in solution.

The samples were then evaporated to dryness, taken up in ca. 5–10 mL of concentrated HCl to convert them to chloride form, evaporated to dryness again, and finally taken up in 10 mL of 0.5 M HCl in preparation for anion-exchange chemistry.

3.4. Anion-exchange chemistry

Chemical separation of the element of interest is desirable in order to increase analytical sensitivity and to reduce potential isobaric or molecular interferences or matrix effects during isotope analysis by MC-ICPMS. Ion-exchange chromatographic techniques have been widely employed for this purpose. Methods for the separation of PGEs from rocks have previously been developed (e.g., Rehkämper and Halliday, 1997; Pearson and Woodland, 2000). However, the focus of these methods has generally been the recovery of all the PGE for the determination of their concentrations. In this study, we developed a technique for the recovery and purification solely of Pt at a level suitable for precise determination of isotopic compositions by MC-ICPMS.

Prior to loading in columns, Bio-Rad® AG1-X8 anion exchange resin (100–200 mesh, chloride form) was sequentially cleaned by shaking in ultrapure water, 6 M HCl, ultrapure water, 4 M HNO₃ and then ultrapure water, with the liquid decanted off between each step (Rehkämper and Halliday, 1997). All ion-exchange separations were performed using Eichrom polypropylene columns with a 2 mL resin capacity and a 20 mL reservoir. Approximately 1 mL of fresh BioRad® AG1-X8 anion exchange resin was loaded as a slurry into the columns and allowed to gravity settle. The resin bed was cleaned prior to use with the following sequence of reagents: 20 mL of 0.8 M HNO₃, 10 mL of 11 M HCl, 25 mL of 13.5 M HNO₃ and 40 mL of 6 M HCl (for reversion to chloride form) (Rehkämper and Halliday, 1997).

Immediately prior to loading, columns were equilibrated using 40 mL of 0.5 M HCl. The elution sequence used is shown in Fig. 1. Samples were loaded onto the columns in 10 mL of 0.5 M HCl. Loading was followed by a 40 mL rinse with 0.5 M HCl, during which virtually all of the major cationic constituents of the sample and some of the weakly retained PGE (Rh, Ru and Ir) were eluted. This was followed by elution of 20 mL of 1 M HCl, which elutes any remaining weakly retained PGE. Following these HCl elutions, 20 mL of 0.8 M HNO₃ was added to elute transition metals such as Zn (Rehkämper and Halliday, 1997; Pearson and Woodland, 2000). This was followed by elution of 60 mL of 11 M HCl, which elutes Re, Pd and any remaining Ru from the resin. The Pt fraction was finally eluted with 40 mL of 13.5 M HNO₃. Pt cuts were collected in Savillex Teflon beakers and evaporated to dryness on a hotplate at 120 °C. During elution tests, cuts from every step were collected in 20 mL fractions, apart from the 0.5 M HCl wash which was collected in one 40 mL fraction.

To monitor procedural blanks, a blank sample solution was processed through anion-exchange chemistry with each batch of samples.

3.5. Column calibration by ICP-MS

Prior to analysis, dried fractions from the column calibration experiments were converted to chloride form by taking them up in concentrated HCl and evaporating before being redissolved in 5 mL of 0.5 M HCl and left on a hotplate for 2–3 h before analysis by ICP-MS. An

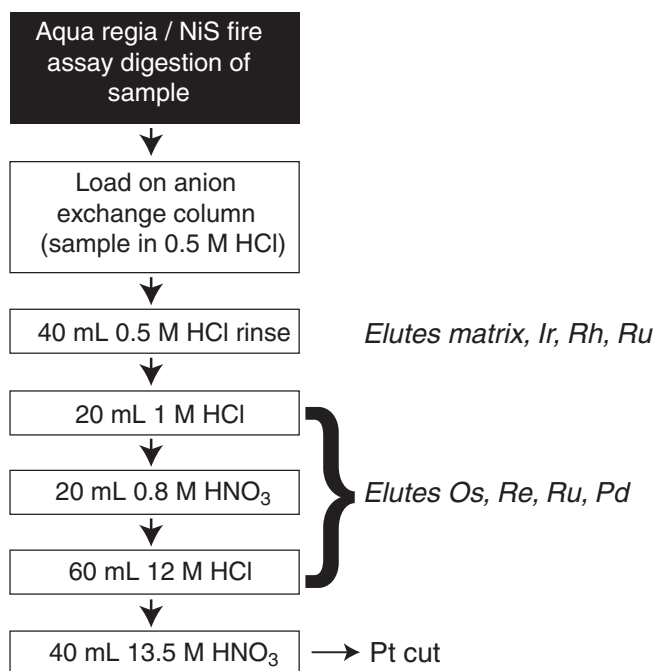


Fig. 1. Flow chart illustrating the Pt separation scheme.

Agilent 7500CS quadrupole ICP-MS with a standard cross-flow nebuliser was used to measure the column fractions. The following masses were monitored for column calibration experiments with the precious metal standard: ^{99}Ru , ^{103}Rh , ^{105}Pd , ^{185}Re , ^{189}Os , ^{191}Ir and ^{195}Pt . Analyses of the column calibration cuts were bracketed with analyses of a gravimetrically prepared solution of the same precious metal standard with a concentration of 1 ng mL^{-1} .

For column calibration experiments with synthetic rock matrices, the following masses were monitored: ^{23}Na , ^{25}Mg , ^{27}Al , ^{29}Si , ^{33}S , ^{43}Ca , ^{47}Ti , ^{52}Cr , ^{55}Mn , ^{57}Fe , ^{59}Co , ^{60}Ni , ^{63}Cu , ^{66}Zn , ^{71}Ga , ^{72}Ge , ^{75}As , ^{95}Mo , ^{99}Ru , ^{103}Rh , ^{105}Pd , ^{118}Sn , ^{121}Sb , ^{182}W , ^{185}Re , ^{189}Os , ^{191}Ir , ^{195}Pt and ^{197}Au . Analyses of the column calibration cuts were bracketed with standard solutions containing all of these elements ($1 \mu\text{g mL}^{-1}$ and 1 ng mL^{-1}) that were gravimetrically prepared from single element standards. Semi-quantitative concentrations of the relevant elements were calculated for each fraction relative to the measured signal intensities for the standard. Elution curves constructed with these data are estimated to be accurate to $\pm 5\%$.

3.6. Platinum stable isotope analysis by double-spike MC-ICPMS

A ^{196}Pt – ^{198}Pt DS was used to correct for instrumental mass fractionation during MC-ICPMS analysis. The development of the Pt DS and mass spectrometry protocols are described in detail by Creech et al. (2013).

Samples for isotopic analysis were either spiked before sample digestion or prior to ion-exchange chemistry. Samples that were spiked prior to ion-exchange chemistry were refluxed in aqua regia on a hotplate at 120°C overnight to ensure complete sample–spike equilibration. These sample–spike mixtures were subsequently evaporated to dryness, reconverted to chloride form by evaporating concentrated HCl, and finally redissolved in 10 mL of 0.5 M HCl for loading onto columns.

In order to destroy any potential organic interferences arising from resin that may have been stripped from the resin bed by the large volume of concentrated HNO_3 that was used to elute Pt, the Pt cuts were treated after chemistry by the following steps. Pt cuts were evaporated to dryness, refluxed in aqua regia on a hotplate overnight, evaporated to dryness again, and then refluxed overnight in a mixture of HNO_3 – H_2O_2 . The Pt cuts were then evaporated to dryness, reconverted to chloride

form by evaporating concentrated HCl, and finally redissolved in an appropriate volume of 0.5 M HCl resulting in a Pt solution concentration of approximately 60 ng mL^{-1} . Samples were refluxed on a hotplate for at least 2 to 3 h prior to analysis.

Pt stable isotope measurements were carried out using a Nu Plasma MC-ICPMS at Victoria University of Wellington, New Zealand. The Nu Plasma MC-ICPMS was operated in low-resolution mode, with a mass resolution of ~ 1840 ($M/\Delta M$; peak edge width from 5 to 95% full peak height). A Nu Instruments DSN-100 desolvation nebuliser system with an ESI PFA micro-flow nebuliser was used for Pt solution introduction to the mass spectrometer. Measurements were made on 0.5 M HCl solutions with ca. 60 ng mL^{-1} of natural Pt. The sample uptake rate was ca. 80 mL min^{-1} , and the sensitivity of the instrument was typically ca. 280 V ppm^{-1} total Pt under these conditions. Each analysis comprised $100 \times 8 \text{ s}$ integrations, corresponding to 13.3 min of data acquisition, and consumed ca. 80 ng of natural Pt. Baselines were obtained by measuring on-peak for $100 \times 8 \text{ s}$ integrations prior to each analysis. A washout time of ca. 30 min was applied between analyses and baseline measurements. Using this approach, background levels were typically $< 1 \text{ mV}$ on all Pt isotopes.

Data reduction was performed off-line using the freely available data reduction software Iolite, which runs within Igor Pro (Paton et al., 2011). The DS calculations were performed algebraically based on the equations presented in Rudge et al. (2009) using a new procedure incorporated within Iolite (Creech and Paul, submitted for publication). We report Pt stable isotope results in terms of $\delta^{198}\text{Pt}$, representing the permil deviation of the $^{198}\text{Pt}/^{194}\text{Pt}$ ratio in the sample from the same ratio for the IRMM-010 Pt isotope standard. This technique has been shown to have an external reproducibility on $\delta^{198}\text{Pt}$ measurements of Pt solution standards of ± 0.04 (i.e. $\pm 0.01 \text{ amu}^{-1}$; Creech et al., 2013).

4. Results and discussion

4.1. Chemical separation and recovery of Pt

Results of elution tests for the chemical separation of Pt are shown in Fig. 2. Despite undertaking these column calibration experiments on a wide range of synthetically prepared materials, there is little difference in the elution profiles of the matrix elements and PGE. In all of the elution tests, almost all of the matrix elements are entirely eluted from the column prior to Pt collection, passing through the column in the loading acid. The exceptions to this are Zn, which is eluted in 0.8 M HNO_3 , minor amounts of Si and Sn that were occasionally found in other cuts, and Au which was found to also be completely recovered in the 13.5 M HNO_3 cut.

Rh is only very weakly retained on the anion resin, and is almost entirely eluted in the sample loading solution, with any remaining Rh being eluted in the 0.5 M HCl wash. Ru and Ir are also relatively weakly retained on the column. Previous studies have used oxidants (e.g., bromine water, chlorine gas) to convert Ir to Ir(IV), which is more strongly retained on the resin, and can be subsequently eluted with the addition of a reducing agent. However, given that we did not use such a step, Ir is only weakly retained and is largely eluted during the 0.5 M HCl rinse after loading and, hence, is presumably mostly in the reduced state (i.e., Ir(III)). In some cases, traces of Ir were found to be present in the 0.8 M HNO_3 or 11 M HCl cuts and, thus, some Ir was likely present as Ir(IV). The same is also probably the case for Ru, which is mostly eluted during the post-loading wash, but also shows a second peak in the 11 M HCl cuts. During elution tests with the precious metal solution, 80–90% of the Os was eluted in 0.8 M HNO_3 . However, in all of the elution tests with a synthetic rock matrix, virtually no Os was present. Given that multiple evaporations of the solutions were conducted in the preparation of these samples and the highly volatile nature of Os, it is likely that Os was lost during those steps. Re was largely eluted in the first 20 mL of the 11 M HCl cut, with the remainder being eluted in the next 20 mL of 11 M HCl . Pd is less easily eluted than Re in 11 M HCl ,

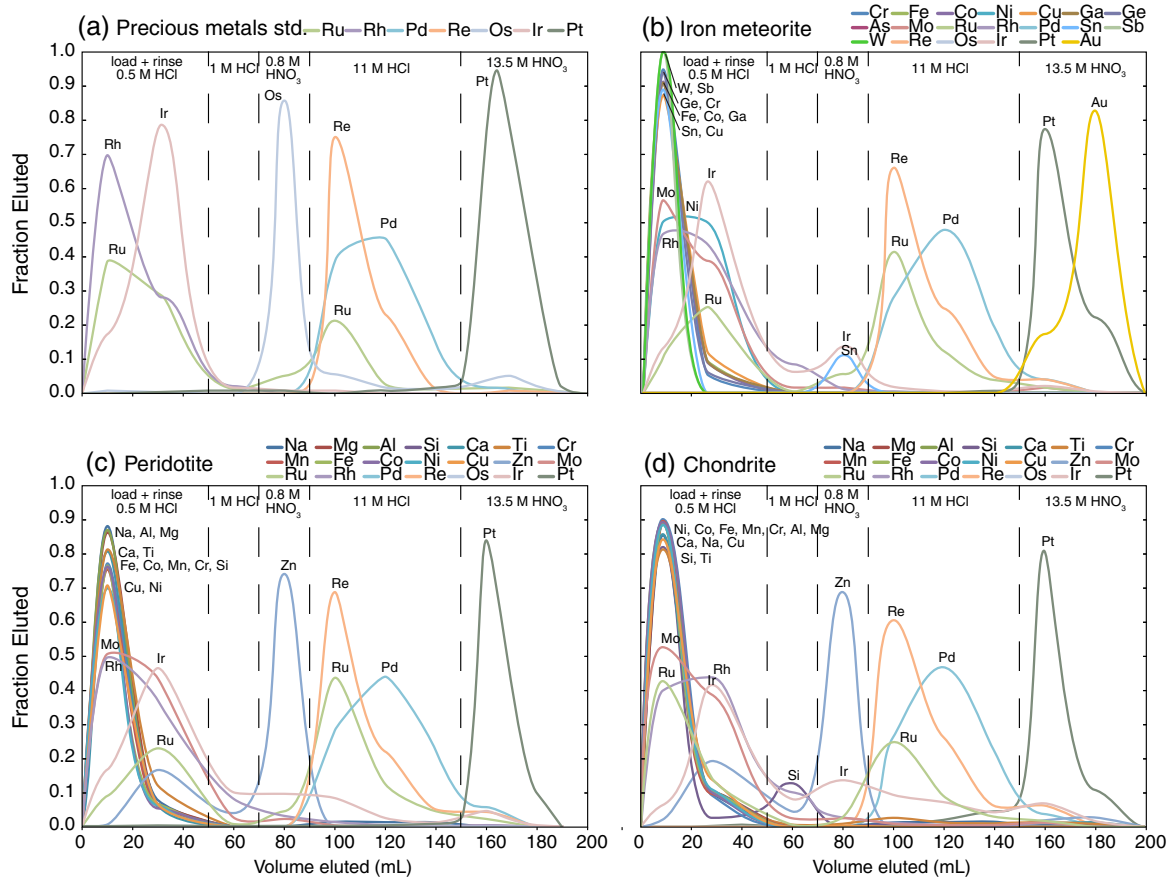


Fig. 2. Elution profiles for (a) precious metal standard solution, (b) synthetic iron meteorite, (c) synthetic peridotite, and (d) synthetic chondrite. In the synthetic rock solutions, the major cationic components are not retained on the column and are eluted with the sample loading solution. The PGE are eluted in a sequence of HCl and HNO₃ acids, and 90–95% of the Pt is collected in the 13.5 M HNO₃ cut.

with ca. 30% of the Pd being eluted in the first and last 20 mL volumes of 11 M HCl, and ca. 40% in the middle 20 mL volume of 11 M HCl.

Pt is finally eluted in 40 mL of 13.5 M HNO₃. At least 80% of Pt is eluted in the first 20 mL of 13.5 M HNO₃, but a further 20 mL of 13.5 M HNO₃ was eluted to ensure (near) complete recovery of Pt. At least 90–95% of Pt is recovered in the combined 40 mL of 13.5 M HNO₃. This level of recovery was deemed adequate given that isotopic samples were double-spiked prior to anion-exchange chemistry and, thus, incomplete recovery should not affect the measured isotopic compositions of samples. This was tested by processing a sample of IRMM-010 through the entire sample preparation procedure, whereby a NiS blank charge was prepared as described above and a double-spiked aliquot of IRMM-010 was added to it. The results of this test are discussed below. Minor amounts of the other PGE were also recovered in the Pt cut, but these were all <5% of the Pt concentration, and this level has been previously shown to be sufficient for accurate stable isotope determinations of Pt (Creech et al., 2013).

As a large fraction of Au was collected with Pt, and the effects of this on DS MC-ICPMS isotopic analysis of Pt were only explored up to 10% of the Pt concentration by Creech et al. (2013), an analytical test was carried out by doping IRMM-010 with Au at 50% of the Pt concentration. Au doping at 30 ng mL⁻¹ produced a signal of ca. 3 V on ¹⁹⁷Au, which is higher than was observed in any samples analysed in this study. Au doped Pt stable isotope analyses had a reproducibility on $\delta^{198}\text{Pt}$ identical to those of undoped IRMM-010 (ca. ± 0.042 ; 2 sd) and Pt stable isotope ratios identical to pure IRMM-010 (Table 2).

The total procedural blank of the analytical procedure was monitored by processing a blank with each batch of samples through anion-exchange chemistry, both with and without NiS fire assay. Anion-exchange column Pt blanks were typically ca. ≤ 0.1 ng. Combined

Pt blanks from NiS digestions and anion-exchange chemistry were typically ca. 0.5–2 ng. The importance of blanks at these levels for accurate isotopic measurements is discussed below.

4.2. Pt concentrations of standards

Pt concentrations of the standard reference materials were determined by performing isotope dilution calculations on double-spiked samples, treating ¹⁹⁸Pt as the spike isotope and ¹⁹⁴Pt as the unspiked isotope (although some ¹⁹⁴Pt is also present in the DS). The accuracy of the calculated sample concentrations potentially depends on when spiking was carried out (i.e., prior to or after NiS fire assay digestion) as spiking after digestion will only yield accurate concentrations if the NiS fire assay quantitatively recovers all the Pt. In samples that were double-spiked prior to NiS fire assay, concentrations determined by isotope dilution calculations were between 80 and 108% of reference Pt concentrations (Table 2). The sample of the komatiite standard OKUM that was double-spiked prior to NiS fire assay had a Pt concentration of 12.4 $\mu\text{g g}^{-1}$ (reference Pt = 11.44 $\mu\text{g g}^{-1}$), compared with 9.0 $\mu\text{g g}^{-1}$ when spiking took place after digestion. This is consistent with Pt concentrations determined from replicate WPR-1 digestions, where double-spiking took place after digestion, for which calculated Pt concentrations vary between ca. 80–100% of the reference value.

4.3. Platinum stable isotope results

4.3.1. Reproducibility of processed standards

The reproducibility of Pt stable isotopic measurements on the geological standards was estimated by measuring replicate

Table 2
Pt stable isotope compositions of terrestrial standard reference materials. Uncertainties given for individual digestions represent the weighted means of the number of analyses (n) of each digestion. Uncertainties for replicate digestions are given as the 2 sd of the mean of all digestions. An additional table including all of the individual analyses is available in the Supplementary information.

Group	Sample	Replicate	$\delta^{198}\text{Pt}$	n	Sample Pt (ng)	Pt conc. (ng g ⁻¹)	Ref. Pt conc. (ng g ⁻¹)	Meas./ref. conc.	DS before digestion? ^a			
Anal. tests	IRMM-010 Au Doped		-0.003 ± 0.042	3								
	IRMM-010 NiS proc.		-0.039 ± 0.060	7								
Ore	PTA-1	1	0.067 ± 0.028	6	2720	2719	3050	0.89	N			
		2	0.046 ± 0.015	9					Y			
		Average	0.057 ± 0.030	15								
Mantle	WPR-1	DS after chem.	1	-0.067 ± 0.016	6	417	239	285	0.84	N		
			2	-0.107 ± 0.013	6	439	251	285	0.88	N		
			5	-0.100 ± 0.019	4	384	218	285	0.77	N		
			6	-0.130 ± 0.016	4	420	239	285	0.84	N		
			7	-0.087 ± 0.020	4	432	246	285	0.86	N		
			average	-0.098 ± 0.047	24	240	285	0.84				
			DS before chem.	1	-0.075 ± 0.025	4	462	264	285	0.93	N	
				2	-0.086 ± 0.026	4	489	278	285	0.98	N	
				3	-0.116 ± 0.023	4	448	255	285	0.89	N	
				4	-0.025 ± 0.030	3	422	242	285	0.85	N	
		5		-0.028 ± 0.035	2	403	230	285	0.81	N		
		6		-0.036 ± 0.028	3	458	262	285	0.92	N		
		7		-0.065 ± 0.029	3	483	276	285	0.97	N		
				Average	-0.061 ± 0.067	23	258	285	0.91			
			Overall average		-0.077 ± 0.069	48						
		Mantle	SARM-76	OKUM	1	-0.052 ± 0.013	9	3955	3868	3590	1.08	Y
					2	-0.146 ± 0.030	3	157	10.4	11.44	0.91	Y
					2	-0.228 ± 0.034	2	149	9.8	11.44	0.86	Y
					3	-0.159 ± 0.054	2	154	10.2	11.44	0.89	Y
					Average	-0.178 ± 0.088	7	10.1	11.44	0.89		
JP-1	-0.335 ± 0.037				2	77	5.1	5	1.02	Y		
PCC-1	-0.324 ± 0.053				2	96	7.9	8	0.99	Y		
Igneous	SARM-6				1	-0.144 ± 0.017	6	588	39.2	39	1.00	Y
					2	-0.133 ± 0.017	6	551	36.2	39	0.93	Y
					Average	-0.139 ± 0.016	12	37.7	39	0.97		
Other	DNC-1	LK-NIP	FC-1	1	-0.050 ± 0.018	5	534	35.6	36.8	0.97	Y	
				2	-0.215 ± 0.028	2	186	12.3	13.43	0.92	Y	
				2	-0.020 ± 0.043	2	120	30.4	38	0.80	Y	

^a Indicates whether sample was double-spiked prior to sample digestion by NiS fire assay.

digestions of several standard reference materials. Seven replicate digestions of WPR-1 were split and processed twice, once with double-spiking prior to anion-exchange chemistry, and once with double-spiking after anion-exchange chemistry. In addition, the three standards OKUM, SARM-6 and PTA-1 were also digested 2–3 times. One digestion of PTA-1 was double-spiked before NiS digestion and the other was double-spiked prior to anion-exchange chemistry. All digestions of OKUM and SARM-6 were double-spiked prior to NiS digestion. Each processed digestion was typically analysed 3–6 times. Pt stable isotope results for the replicate digestions of standard reference materials are shown in Table 2 and Fig. 3.

Repeat digestions of PTA-1 and SARM-6 yielded uncertainties of ± 0.030 and ± 0.016 (2 sd of weighted means), respectively. Replicates of OKUM were less reproducible, with an uncertainty of ± 0.088 (2 sd of weighted means). WPR-1 replicates where double-spiking was carried out after anion exchange chemistry yielded a mean $\delta^{198}\text{Pt} = -0.098 \pm 0.047$ (2 sd of weighted means), whereas those spiked prior to anion exchange chemistry yielded a mean $\delta^{198}\text{Pt} = -0.061 \pm 0.067$ (2 sd of weighted means). These yield a combined average for WPR-1 of $\delta^{198}\text{Pt} = -0.077 \pm 0.069$ (2 sd). Additionally, the NiS-processed IRMM-010 sample (described in Section 4.1) yielded a mean $\delta^{198}\text{Pt}$ of -0.039 ± 0.060 (2 sd; Table 2; Fig. 4). The uncertainty demonstrated by these tests must be taken into account when interpreting data from single digestions of samples. Possible explanations for the poorer reproducibility of measurements of

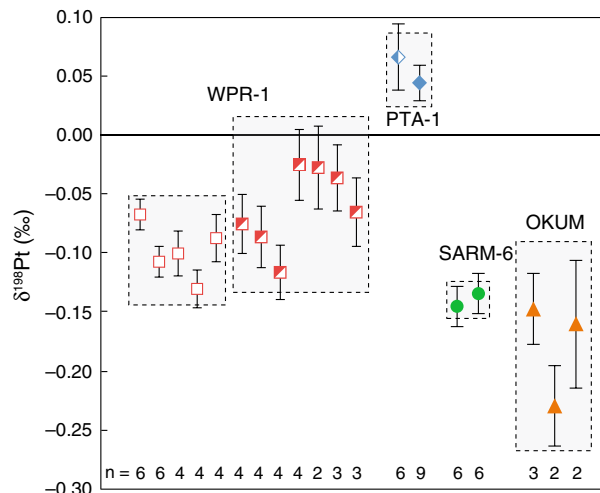


Fig. 3. Pt stable isotopic measurements of the standard reference materials WPR-1, PTA-1, SARM-6 and OKUM, for which replicate digestions were processed. Hollow symbols indicate that the sample was double-spiked after NiS digestion and anion-exchange chemistry, half-filled symbols indicate that the sample was double-spiked after NiS digestion but prior to anion-exchange chemistry, and filled symbols indicate that the sample was double-spiked prior to both NiS digestion and anion-exchange chemistry. Data points are error-weighted means of the number of analyses (n) indicated below each data point, with associated combined errors. Dashed lines indicate the 2 sd uncertainty from all of the replicates they enclose.

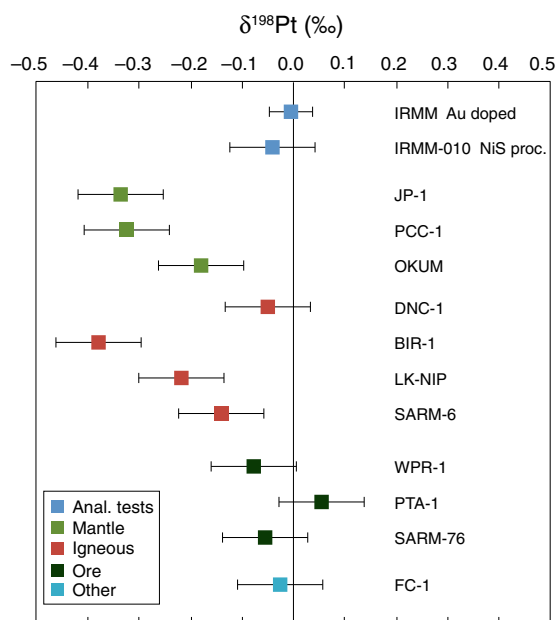


Fig. 4. Pt stable isotope variations in standard reference materials relative to IRMM-010. Error bars reflect the reproducibility as determined by the 2 sd of replicate digestions of OKUM of ± 0.088 (Table 2).

replicate digestions of WPR-1 and OKUM compared with that of Pt solution standards include:

- Anion exchange chemistry yields. WPR-1 replicates spiked before and after chemistry were spiked with identical amounts of DS. Isotope dilution concentration results for WPR-1 replicates spiked after anion exchange chemistry have ca. 10% lower apparent Pt concentrations than those spiked prior to chemistry, consistent with elution results shown in Section 4.1. The overlap in $\delta^{198}\text{Pt}$ results for replicates spiked before and after anion exchange chemistry suggests that incomplete recovery of Pt during anion-exchange chemistry does not isotopically fractionate Pt significantly at this level of recovery. Additionally, no correlation is observed between $\delta^{198}\text{Pt}$ and Pt recovery within WPR-1 replicates spiked after chemistry (Table 2). Thus, yields from anion exchange chemistry cannot explain the variations observed in the WPR-1 replicates.
- Incomplete sample-spike equilibration. Incomplete sample-spike equilibration could result in an apparent isotopic fractionation of a sample. Although all of the WPR-1 replicates were subjected to identical preparation that was intended to equilibrate the sample and DS, incomplete and inconsistent equilibration could explain some of the variability in the WPR-1 replicates, and potentially explain why the replicates double-spiked before anion-exchange chemistry show poorer reproducibility than those double-spiked after chemistry. However, samples double-spiked prior to digestion are considered to have fully equilibrated.
- NiS fire assay blanks. Pt blanks from the NiS fire assay technique were found to vary between ca. 0.5–2.0 ng. The influence of blank Pt is difficult to assess without knowing the isotopic composition of the blank, and depends also on the Pt content of the sample. Given that each digestion of WPR-1 involved processing of ca. 4000 ng of Pt it can be calculated that the stable Pt isotopic composition of the blank would need to have an implausibly high $\delta^{198}\text{Pt}$ of ca. +10 and be highly variable either in terms of this blank composition or content to account for the range of $\delta^{198}\text{Pt}$ values exhibited by the replicate digestions of WPR-1. Furthermore, the Pt concentrations obtained for our most Pt depleted samples agree well with published reference values for these standards.

- Spectral or non-spectral matrix effects from residual organics from anion exchange resin. Element doping tests have shown that minor amounts of the most likely contaminants from incomplete Pt separation should not affect isotopic measurements (Creech et al., 2013). As described above, Pt cuts were treated with aqua regia and $\text{HNO}_3\text{-H}_2\text{O}_2$ to attempt to destroy any organics stripped from the anion exchange resin. While this is considered to be effective, the presence of any residual organics may have variable spectral or non-spectral matrix effects that could explain the variations observed between replicates of WPR-1.
- True isotopic heterogeneity of the sample. This may be more apparent with OKUM than the other standards due to the lower Pt concentration in that standard. However, due to its lower concentration, each replicate of OKUM was only measured 2–3 times, which also affects the resulting uncertainty. Further work is required to establish the level of Pt isotopic heterogeneity within various types of samples. It is hoped that additional investigations utilising these methods will be forthcoming, which will help to resolve this question.

The relatively consistent results between replicate digestions of SARM-6 and PTA-1 suggest that reproducibility may be improved where samples are double-spiked prior to digestion (Fig. 3). However, for the data for natural samples presented in Fig. 4 we have conservatively imposed uncertainties of ± 0.088 (Table 2), as determined from replicate digestions of OKUM.

4.3.2. Pt stable isotope variations in terrestrial rock standards

The 11 standard reference materials analysed in this study showed Pt stable isotope variations that are readily resolvable by this technique (Fig. 4; Table 2). The Pt stable isotope composition of Earth's mantle as defined by mantle samples JP-1, PCC-1 and OKUM, is clearly distinct from those of the ultramafic ore deposits PTA-1 and SARM-76. The two peridotites (JP-1 and PCC-1) have identical Pt stable isotope compositions within analytical uncertainty ($\delta^{198}\text{Pt} = -0.335$ and -0.324 , respectively).

The ore materials, WPR-1, SARM-76 and PTA-1, have the heaviest Pt isotopic compositions, which are similar to the composition of the IRMM-010 standard (i.e. close to zero). The similarity between the ore materials and IRMM-010 may be consistent with the IRMM-010 Pt isotope standard having been ultimately derived from a Pt ore. The igneous group of reference materials generally have Pt stable isotopic compositions intermediate between the mantle and ores. Although the ores used in this study may have formed through different processes, the isotopic offset between igneous samples and ores suggests that there may be an isotopic fractionation associated with the removal of Pt from silicate magmas to form Pt ore deposits. The Icelandic basalt BIR-1, which is a mafic and isotopically depleted product of the Iceland plume, has the most extreme Pt stable isotopic composition of $\delta^{198}\text{Pt} = -0.377 \pm 0.051$. This composition is similar to that of the peridotite samples, which are considered to represent the upper mantle.

DNC-1 has the heaviest Pt stable isotopic composition of the igneous standard reference materials ($\delta^{198}\text{Pt} = -0.050$). DNC-1 is also characterised by an unusually high Pt concentration (38 ng g^{-1} ; Table 1) compared with other igneous samples. The isotopic similarity between DNC-1 and the ore samples coupled with its relative enrichment in Pt potentially indicates that either the source deposit of DNC-1 is associated with sulphide-enriched ultramafic deposits or that the DNC-1 standard was contaminated during crushing and preparation of the standard. Similar contamination during preparation and crushing of geological standard reference materials has been documented for other isotopic systems (e.g., Pb; Baker et al., 2004).

The reproducibility of Pt stable isotope data documented in the standard reference materials of which multiple digestions were made in this study, particularly SARM-6 and PTA-1, demonstrates that these could be

potentially useful as isotopic standards in future applications of Pt and other highly siderophile element stable isotope studies.

5. Conclusions

We have developed a chemical separation procedure for purification of Pt from geological and potentially from meteoritic samples for Pt stable isotopic analysis. We have shown:

1. Pt can be separated from various rock matrices with a recovery of 90–95% and with sufficient purity (>95%) for accurate Pt stable isotope determinations by double-spike MC-ICPMS.
2. While the current reproducibility of processed replicates of terrestrial rock standards (e.g., ca. ± 0.088 for OKUM) is poorer than for repeat measurements of Pt solution standards (ca. ± 0.040), this level of precision appears to be adequate to resolve variations between natural samples.
3. Pt stable isotopic analyses of 11 terrestrial standard reference materials show a readily resolvable range in $\delta^{198}\text{Pt}$, with offsets of up to ca. 0.4 for some standards.

These results demonstrate that the Pt stable isotope system holds considerable promise as a tracer in geochemical systems.

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.chemgeo.2013.11.009>.

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References

- Alvarez, L.W., Alvarez, W., Asaro, F., Michel, H.V., 1980. Extraterrestrial cause for the Cretaceous–Tertiary extinction. *Science* 208, 1095–1108. <http://dx.doi.org/10.1126/science.208.4448.1095>.
- Baker, J., Peate, D., Waight, T., Meyzen, C., 2004. Pb isotopic analysis of standards and samples using a ^{207}Pb – ^{204}Pb double spike and thallium to correct for mass bias with a double-focusing MC-ICP-MS. *Chem. Geol.* 211, 275–303. <http://dx.doi.org/10.1016/j.chemgeo.2004.06.030>.
- Barkov, A.Y., Lafamme, J.H.G., Cabri, L.J., Martin, R.F., 2002. Platinum-group minerals from the Wellgreen Ni–Cu–PGE deposit, Yukon, Canada. *Can. Mineral.* 40, 651–669. <http://dx.doi.org/10.2113/gscanmin.40.2.651>.
- Cotton, F.A., Wilkinson, G., 1966. *Advanced Inorganic Chemistry: A Comprehensive Text*. Interscience Publishers.
- Creech, J., Baker, J., Handler, M., Schiller, M., Bizzarro, M., 2013. Platinum stable isotope ratio measurements by double-spike multiple collector ICPMS. *J. Anal. At. Spectrom.* 28, 853–865. <http://dx.doi.org/10.1039/C3JA50022E>.
- Creech, J., Paul, B., 2013. *IsoSpike: improved double-spike deconvolution software*. *Geostand. Geoanal. Res.* (submitted for publication).
- Faye, G.H., Sutarno, R., 1976. Certified compositional reference materials for the earth sciences. *Can. Mineral.* 14, 164–171.
- Findlay, D.C., 1969. Origin of the Tulameen ultramafic–gabbro complex, southern British Columbia. *Can. J. Earth Sci.* 6, 399–425. <http://dx.doi.org/10.1139/e69-040>.
- Gros, M., Lorand, J., Luguét, A., 2002. Analysis of platinum group elements and gold in geological materials using NiS fire assay and Te coprecipitation; the NiS dissolution step revisited. *Chem. Geol.* 185, 179–190.
- Hart, T.R., MacDonald, C.A., 2007. Proterozoic and Archean geology of the Nipigon Embayment: implications for emplacement of the Mesoproterozoic Nipigon diabase sills and mafic to ultramafic intrusions. *Can. J. Earth Sci.* 44, 1021–1040. <http://dx.doi.org/10.1139/E07-026>.
- Heaman, L., Easton, R., Hart, T., Hollings, P., MacDonald, C., Smyk, M., 2007. Further refinement to the timing of Mesoproterozoic magmatism, Lake Nipigon region, Ontario. *Can. J. Earth Sci.* 44, 1055–1086. <http://dx.doi.org/10.1139/E06-117>.
- Houlé, M.G., Préfontaine, S., Fowler, A.D., Gibson, H.L., 2009. Endogenous growth in channelized komatiite lava flows: evidence from spinifex-textured sills at Pyke Hill and Serpentine Mountain, Western Abitibi Greenstone Belt, Northeastern Ontario, Canada. *Bull. Volcanol.* 71, 881–901. <http://dx.doi.org/10.1007/s00445-009-0273-y>.
- Marcantonio, F., Reisberg, L., Zindler, A., Wyman, D., Hulbert, L., 1994. An isotopic study of the Ni–Cu–PGE-rich Wellgreen intrusion of the Wrangellia Terrane: evidence for hydrothermal mobilization of rhenium and osmium. *Geochim. Cosmochim. Acta* 58, 1007–1018. [http://dx.doi.org/10.1016/0016-7037\(94\)90522-3](http://dx.doi.org/10.1016/0016-7037(94)90522-3).
- Meisel, T., Moser, J., 2004. 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. *Chem. Geol.* 208, 319–338. <http://dx.doi.org/10.1016/j.chemgeo.2004.04.019>.
- Morcelli, C.P.R., Figueiredo, A.M.G., Enzweiler, J., Sarkis, J.E.S., Jorge, A.P.S., Kakazu, M., 2004. Determination of Platinum-Group elements in geological reference materials by high resolution-ICP-MS after nickel sulfide fire-assay collection and Te coprecipitation. *Geostand. Geoanal. Res.* 28, 305–310. <http://dx.doi.org/10.1111/j.1751-908X.2004.tb00745.x>.
- Nisbet, E.G., Walker, D., 1982. Komatiites and the structure of the Archaean mantle. *Earth Planet. Sci. Lett.* 60, 105–113. [http://dx.doi.org/10.1016/0012-821X\(82\)90025-5](http://dx.doi.org/10.1016/0012-821X(82)90025-5).
- Paton, C., Hellstrom, J., Paul, B., Woodhead, J., Hergt, J., 2011. Iolite: freeware for the visualisation and processing of mass spectrometric data. *J. Anal. At. Spectrom.* 26, 2508–2518. <http://dx.doi.org/10.1039/c1ja10172b>.
- Pearson, D.G., Woodland, S.J., 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. *Chem. Geol.* 165, 87–107. [http://dx.doi.org/10.1016/S0009-2541\(99\)00161-8](http://dx.doi.org/10.1016/S0009-2541(99)00161-8).
- Ravizza, G., Pyle, D., 1997. PGE and Os isotopic analyses of single sample aliquots with NiS fire assay preconcentration. *Chem. Geol.* 141, 251–268.
- Rehkämper, M., Halliday, A.N., 1997. Development and application of new ion-exchange techniques for the separation of the platinum group and other siderophile elements from geological samples. *Talanta* 44, 663–672. [http://dx.doi.org/10.1016/S0039-9140\(96\)02100-5](http://dx.doi.org/10.1016/S0039-9140(96)02100-5).
- Rudge, J.F., Reynolds, B.C., Bourdon, B., 2009. The double spike toolbox. *Chem. Geol.* 265, 420–431. <http://dx.doi.org/10.1016/j.chemgeo.2009.05.010>.
- Savard, D., Barnes, S., Meisel, T., 2010. Comparison between nickel–sulfur fire assay Te coprecipitation and isotope dilution with high-pressure asher acid digestion for the determination of platinum-group elements, rhenium and gold. *Geostand. Geoanal. Res.* 34, 281–291. <http://dx.doi.org/10.1111/j.1751-908X.2010.00090.x>.
- Takazawa, E., Frey, F., Shimizu, N., Obata, M., 1996. Evolution of the Horoman Peridotite (Hokkaido, Japan): implications from pyroxene compositions. *Chem. Geol.* 134, 3–26. [http://dx.doi.org/10.1016/S0009-2541\(96\)00083-6](http://dx.doi.org/10.1016/S0009-2541(96)00083-6).
- Takazawa, E., Frey, F., Shimizu, N., Obata, M., 2000. Whole rock compositional variations in an upper mantle peridotite (Horoman, Hokkaido, Japan): are they consistent with a partial melting process? *Geochim. Cosmochim. Acta* 64, 695–716. [http://dx.doi.org/10.1016/S0016-7037\(99\)00346-4](http://dx.doi.org/10.1016/S0016-7037(99)00346-4).
- Takazawa, E., Frey, F.A., Shimizu, N., Obata, M., Bodinier, J.L., 1992. Geochemical evidence for melt migration and reaction in the upper mantle. *Nature* 359, 55–58. <http://dx.doi.org/10.1038/359055a0>.
- Takazawa, E., Frey, F.A., Shimizu, N., Saal, A., Obata, M., 1999. Polybaric petrogenesis of mafic layers in the Horoman Peridotite Complex, Japan. *J. Petrol.* 40, 1827–1851. <http://dx.doi.org/10.1093/ptro/40.12.1827>.
- Walraven, F., Armstrong, R., Kruger, F., 1990. A chronostratigraphic framework for the north-central Kaapvaal craton, the Bushveld Complex and the Vredefort structure. *Tectonophysics* 171, 23–48. [http://dx.doi.org/10.1016/0040-1951\(90\)90088-P](http://dx.doi.org/10.1016/0040-1951(90)90088-P).