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Platinum stable isotope ratio measurements by double-spike multiple collector ICPMS†

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We present a new technique for the precise determination of platinum (Pt) stable isotope ratios by multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS) using two different Pt double-spikes (^{192}Pt–^{198}Pt and ^{196}Pt–^{198}Pt). Results are expressed relative to the IRMM-010 Pt isotope standard as the parts per million difference in ^{198}Pt/^{194}PtPt ratios (μ^{198}Pt). Repeated measurements of the IRMM-010 Pt standard in two different laboratories, consuming *ca.* 40–85 ng of Pt, show that a long-term external reproducibility for μ^{192}Pt of ≤40 ppm (2 sd; equivalent to ≤10 ppm u^{-1}, where u is the unified atomic mass unit) can be obtained on Pt stable isotope ratios with either double-spike. Elemental doping tests reveal that double-spike corrected Pt stable isotope ratios are insensitive to the presence of relatively high (up to 10%) levels of matrix elements, although the ^{192}Pt–^{198}Pt double-spike is affected by an isobaric interference on ^{192}Pt from ^{192}Os. The ^{196}Pt–^{198}Pt double-spike does not use ^{192}Pt in the double-spike inversion and is unaffected by Os contamination, and is our recommended double-spike for use with natural samples. As part of this study, we re-determined the natural Pt isotopic composition of IRMM-010 by MC-ICPMS using external element (Pb) doping to correct for instrumental mass bias and have identified relative Pt isotope differences of up to 10% from the reference values for this standard. The new isotopic composition of the IRMM-010 standard (^{190}Pt = 0.01289%, ^{192}Pt = 0.7938%, ^{194}Pt = 32.81%, ^{195}Pt = 33.79%, ^{196}Pt = 25.29% and ^{198}Pt = 7.308%) results in a redefined Pt atomic weight of 195.08395 ± 0.00068. Using our technique we have measured small, reproducible and statistically significant offsets in Pt stable isotope ratios between different Pt element standards and the IRMM-010 standard, which potentially indicates that natural Pt stable isotope fractionations exist that are larger than the reproducibility of our technique.

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1 Introduction

A wide range of novel, non-traditional, stable isotope systems have recently been developed, largely as a result of the advent of multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS). These stable isotope systems are providing valuable new insights in the earth, environmental and planetary sciences.[1–7] The platinum (Pt) stable isotope system represents a potentially powerful, but as yet unexplored, addition to this new suite of stable isotope systems. Platinum is a highly siderophile transition metal with six naturally occurring isotopes—^{190}Pt, ^{192}Pt, ^{194}Pt, ^{195}Pt, ^{196}Pt and ^{198}Pt—with relative abundances of ~0.01%, 0.78%, 32.86%, 33.78%, 25.21% and 7.36%, respectively.[8] Only ^{190}Pt is radioactive ($t_{1/2} \sim 10^{11}$ years), and despite its long half-life, is the basis of the ^{190}Pt–^{186}Os decay system that has been used to infer interactions between Earth's core and mantle.[9] Platinum can exist in a range of oxidation states, but principally occurs as Pt^0, Pt^{2+} and Pt^{4+}.[10] Unlike most previously studied non-traditional stable isotope systems, Pt is not utilised by any known essential biological mechanisms. However, 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 environment, means that it has potential to exhibit significant stable isotope variations in Earth materials. The bulk of Earth's Pt budget is thought to reside in the core as evidenced by the relative depletion of Pt and other highly siderophile elements in Earth's upper mantle relative to chondritic meteorites.[11] Typical Pt concentrations in mantle rocks are *ca.* 1–100 ng g^{-1} as compared with 1–10 μg g^{-1} in chondrites, iron meteorites and, presumably, Earth's core. As a result, the relative distributions of elements such as Pt between these different reservoirs are important in constraining models of planetary differentiation.[11,12] Enrichments in Pt relative to the other platinum group elements (PGE; Rh, Ru, Pd, Os and Ir) have also been observed in authigenic marine sediments such as ferromanganese crusts

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and nodules.[13–16] This Pt enrichment may be related to its variable oxidation states.[13,17] As such, Pt stable isotopes hold considerable promise for use as an isotopic tracer for redox in surficial and marine environments and for processes relating to planetary accretion and differentiation.

In addition to being a potentially valuable geochemical tracer, Pt has a wide range of uses, including industrial, medical and scientific, where other potential applications for a Pt stable isotope tracer may be found. Various Pt compounds are used in medicine and, in particular, several different Pt complexes (cisplatin, carboplatin and oxaliplatin) are used in chemotherapy drugs.[18–21] Platinum has applications in various manufacturing processes, usually as a catalyst, and is widely used in the automotive industry in catalytic converters.[22,23] Given its use in automotive catalytic converters, Pt is also used for environmental monitoring of vehicle emissions by measuring Pt concentrations in roadside soils.[24,25]

Despite the potential range of uses for Pt stable isotopes, previous isotopic studies of Pt have been extremely limited. White *et al.* (1956)[26] measured the isotopic composition of Pt using a double focusing mass spectrometer with a thermal ionisation source (Table 1). This Pt isotopic composition was used in IUPAC reports of elemental isotopic compositions and atomic weights until 1995, when a revised isotopic composition determined by Taylor *et al.* (1994) using gas source mass spectrometry and electron impact ionisation of gaseous $Pt(PF_3)_4$ was adopted[27,28] (Table 1). In the late 1990s, two studies documented procedures for measurement of Pt isotopes by negative thermal ionisation mass spectrometry (N-TIMS).[29,30] One of the groups subsequently developed a Pt isotope reference material (IRMM-010) for the *Institute for Reference Materials and Measurements*, for which certified values were determined using quadrupole ICPMS[31] (Table 1). Later studies of IRMM-010 have been limited to its use in testing the analytical performance of axial inductively coupled plasma time-of-flight mass spectrometer instruments.[32,33] Two recently published studies used internally normalised Pt isotope ratios as a dosimeter for neutron capture in iron meteorites.[34,35] However, to-date there has been no investigation of the Pt stable isotopic system.

Herein, we describe a method for highly precise determination of Pt stable isotope ratios using ^{192}Pt–^{198}Pt and ^{196}Pt–^{198}Pt double-spikes (DS) to correct for instrumental mass bias. We show that this approach is capable of measuring Pt stable isotopes on *ca.* 40–85 ng of natural Pt with an external reproducibility of $\leq\pm10$ ppm u^{-1} (2 sd; u is the unified atomic mass unit), and identify measurable Pt stable isotope variations amongst commercially available Pt standards. Moreover, during the course of this work, we identified that the previously adopted abundances of some Pt isotopes are in relative terms up to 10% inaccurate and, as such, we present a revised schedule of the isotopic abundances and atomic weight of Pt.

2 Double-spike methodology

The DS technique has been extensively used in highly precise Pb isotope analysis, and has also been applied to a wide range of other isotope systems, including S, Ca, Cr, Zn, Fe, Mo, Cd, Ba and Os, by both MC-ICPMS and TIMS analysis.[36–49] The fundamentals of the DS approach for isotopic analysis have been well documented,[50–56] and mathematical solutions have been developed utilising both algebraic[56,57] and geometric[45,49,54,55,58] approaches. Here we use the algebraic method of Rudge *et al.* (2009).[56]

Table 1 Isotopic composition (in %) of natural platinum, Oak Ridge isotopic spikes and prepared double-spikes[a]

Material [ref.]	^{190}Pt	^{192}Pt	^{194}Pt	^{195}Pt	^{196}Pt	^{198}Pt
Natural Pt [8]	0.012	0.782	32.864	33.776	25.210	7.356
Oak Ridge ^{192}Pt spike [56]	0.01	56.93	26.34	11.12	4.77	0.83
Oak Ridge ^{196}Pt spike [56]	0.98	0.98	0.62	1.54	95.6	0.28
Oak Ridge ^{198}Pt spike [56]	0.05	0.05	0.83	1.23	2.23	95.61
Optimal ^{192}Pt–^{198}Pt DS [56]	0.03	22.18	10.75	5.08	3.22	58.74
Optimal ^{196}Pt–^{198}Pt DS [56]	0.31	0.31	0.77	1.31	28.1	69.2
^{192}Pt spike [this study]	0.0056	57.17	26.13	11.08	4.75	0.87
^{196}Pt spike [this study]	0.0002	0.01	1.47	3.58	94.47	0.47
^{198}Pt spike [this study]	0.0003	0.03	1.74	2.80	3.70	91.74
^{192}Pt–^{198}Pt DS [this study]	0.0028	26.21	12.88	6.58	4.17	50.16
^{196}Pt–^{198}Pt DS [this study]	0.0003	0.03	1.68	2.97	23.47	71.85

Year	Method [ref.]	^{190}Pt	^{192}Pt	^{194}Pt	^{195}Pt	^{196}Pt	^{198}Pt	Atomic wt
1947	Unpublished[b] [26]	0.09	0.78	32.8	33.7	25.4	7.23	195.079[c]
1956	Single collector TIMS [26]	0.0127(5)	0.78(10)	32.9(1)	33.8(1)	25.2(1)	7.19(4)	195.079[c]
1984	Compiled [59]	0.01(1)	0.79(50)	32.9(5)	33.8(1)	25.3(5)	7.2(2)	195.080
1996	Gas Source MS [28]	0.013634(68)	0.782659(35)	32.967(77)	33.831557(42)	25.24166(36)	7.16349(42)	195.078[d]
2002	MC-ICPMS [65]	0.01292(2)	0.80168	32.93367	33.79892	25.21481	7.240	
2002	Quadrupole ICPMS [31]	0.01172(58)	0.7819(80)	32.864(140)	33.776(79)	25.210(11)	7.356(43)	195.0844(58)
This study[e]	MC-ICPMS [this study]	0.01289(6)	0.79376(42)	32.8078	33.7871(40)	25.290(10)	7.308(11)	195.08395(68)

[a] Uncertainties on last digits are given in parentheses. [b] Inghram *et al.* (1947) unpublished data given in White *et al.*[26] [c] Atomic weight from De Bievre *et al.*[59] [d] Atomic weight from Rosman and Taylor.[60] [e] Mean of NZ and DK isotope ratios with uncertainties based on variance between NZ and DK measurements.

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The DS method is commonly accepted as the most rigorous method available for correcting for instrumental mass fractionation as it has several advantages over other methods such as standard–sample bracketing, which are: (1) for stable isotope systems where mass-dependent fractionation is being studied, DS-corrected isotope ratios can be obtained from a single analysis;[56] (2) the DS can potentially correct for any mass-dependent effects to the sample after addition of the DS, such as isotopic fractionations that might occur as a result of incomplete yields during chemical separation of the element from natural samples;[56,57] (3) the DS method has been shown to be less sensitive to the presence of minor amounts of remaining matrix elements than sample–standard bracketing methods.[41]

2.1 Pt double-spike design

With five stable isotopes and one with an extremely long half-life (^{190}Pt, $t_{1/2} \sim 10^{11}$ years), Pt is ideally suited to the DS approach. Error propagation in DS calculations needs to be minimised by selection of an optimal spike composition and sample–spike mixtures. A database of theoretically ideal spike compositions and spike/sample ratios for all elements with four or more naturally occurring isotopes was presented by Rudge *et al.*,[56] which includes optimal DS compositions based on available spikes from the Oak Ridge National Laboratory, USA. Two platinum DS were prepared as part of this study, as described below.

2.1.1 ^{192}Pt–^{198}Pt double-spike. The ^{192}Pt–^{198}Pt DS comprises a mixture of 38.9% ^{192}Pt and 61.1% ^{198}Pt spikes. This DS combination has one of the smallest error propagations predicted by the *double-spike toolbox* of Rudge *et al.*[56] (*ca.* 32 ppm u^{-1}, 1 sd). The ^{192}Pt–^{198}Pt DS inversion was performed using ^{192}Pt, ^{194}Pt, ^{196}Pt and ^{198}Pt. Given that the spiked isotopes ^{192}Pt and ^{198}Pt have relatively low natural abundances (0.78% and 7.36%, respectively;[8]) and the two unspiked isotopes in the inversion (^{194}Pt and ^{196}Pt) have high natural abundances, this DS permits precise isotopic determinations over a wide range of sample/spike ratios. The use of this DS is, however, complicated by a potentially large direct isobaric interference from Os on ^{192}Pt and the fact that, in some natural materials that might be targets for Pt stable isotope analysis, Pt and Os are both of similar abundance (*e.g.* chondritic and iron meteorites, Earth's mantle). ^{190}Pt and ^{192}Pt isotopes have isobars with abundant isotopes of osmium (^{190}Os and ^{192}Os with relative abundances of 26.2% and 40.8%, respectively). Thus, the presence of even small amounts of Os in a sample can significantly affect the Pt signal on those masses, producing inaccurate ^{192}Pt–^{198}Pt DS corrected ratios.

2.1.2 ^{196}Pt–^{198}Pt double-spike. The ^{196}Pt–^{198}Pt DS comprises a mixture of 27.7% ^{196}Pt and 72.3% ^{198}Pt spikes. The hypothetical error propagation on the ^{196}Pt–^{198}Pt DS is slightly larger than that of the ^{192}Pt–^{198}Pt DS (*ca.* 40 ppm u^{-1}; 1 sd). However, as alluded to above, the ^{196}Pt–^{198}Pt DS has some potential advantages over the ^{192}Pt–^{198}Pt DS in that the ^{196}Pt–^{198}Pt double-spike inversion is performed on masses ^{194}PtPt, ^{195}Pt, ^{196}Pt and ^{198}Pt, and this DS should thus be unaffected by the presence of Os.

3 Materials and methods

3.1 Chemicals and standard solutions

Optima™ grade nitric (HNO_3) and hydrochloric (HCl) acids were used as supplied without further purification. Acid dilutions were performed with ultrapure (>18 MΩ cm) water. All sample handling and preparation was performed in a class-100 ultra-clean laboratory at Victoria University of Wellington.

The Pt isotope standard IRMM-010 was purchased from the Institute for Reference Materials and Measurements, Belgium.[31] The standard was supplied in the form of Pt wire segments, which were cleaned prior to digestion by sequentially rinsing in ultrapure water, analytical grade methanol and dilute (5%) HNO_3. The IRMM-010 material was carefully weighed, and then digested in aqua regia (HCl : HNO_3 prepared in a volume ratio of 3 : 1) in a Savillex™ teflon beaker. The IRMM-010 Pt solution was dried down, refluxed with concentrated HNO_3, evaporated to dryness, and finally redissolved in 7 M HNO_3. At the time this standard was prepared, sample introduction was carried out in HNO_3. This was later changed to HCl, therefore a portion of this standard was converted to chloride form and stored in 20% HCl.

Two commercially available Pt ICPMS standards were used in this study: J. T. Baker 1000 μg mL^{-1} Pt ICP std in 20% HCl (Lot# H44N77), and SPEX CertiPrep 1000 μg mL^{-1} Pt ICP standard in 10% HCl from Fisher Scientific (Lot# 15-181PT; hereafter referred to as the Baker and Spex standards, respectively). Additionally, a piece of Pt metal ribbon used for TIMS filaments was obtained and digested for use as an in-house standard (hereafter referred to as the Ribbon standard). The Pt Ribbon standard was pre-cleaned and digested in the same manner as described above for IRMM-010. The digested filament was evaporated to dryness several times in concentrated HCl, and finally redissolved in 20% HCl.

3.2 Preparation of platinum double-spikes

Three single Pt isotope spikes (^{192}Pt, ^{196}Pt and ^{198}Pt) were obtained from the Oak Ridge National Laboratory, USA (Batch numbers 186140, 235601 and 235701, respectively). Reference Pt isotopic compositions for each isotopic spike are shown in Table 1 as well as the measured compositions obtained in this study. The ^{192}Pt spike was supplied as a segment of Pt metal ribbon, and the ^{196}Pt and ^{198}Pt spikes were provided as very fine-grained metallic powders. The ^{192}Pt spike ribbon was sequentially cleaned prior to digestion by rinsing with ultrapure water, analytical grade methanol and dilute (5%) HNO_3. Each spike was digested independently with aqua regia in Savillex™ teflon beakers. Once the spike material had been digested, the spike solutions were repeatedly evaporated to dryness in concentrated HCl, and finally redissolved in 20% HCl.

Aliquots of each single spike solution were taken to determine their concentrations (and isotopic compositions). These were measured by MC-ICPMS using a standard bracketing approach with the IRMM-010 standard. The two DS were then prepared by mixing the appropriate two spikes in the proportions calculated for optimal ^{192}Pt–^{198}Pt and ^{196}Pt–^{198}Pt DS mixtures as given by Rudge *et al.*[56] Each DS mixture was then

evaporated to dryness, taken up in a small volume of concentrated HCl, evaporated to dryness again, and finally taken up in 6 M HCl. Accurate isotopic determination by the DS technique requires calibration of the DS composition. The method for calibration of the DS prepared here and the accuracy of the calibrations are described below.

Platinum standards were spiked immediately prior to MC-ICPMS measurement in proportions close to that for optimal spiking as given in Rudge *et al.*[56] Reference Pt isotopic compositions for each isotopic spike and DS are shown in Table 1 along with the compositions measured by MC-ICPMS for the spikes and DS used in this study.

3.3 Mass spectrometry

Platinum isotope measurements were performed using MC-ICPMS instruments in two different laboratories. Most analyses were carried out with a Nu Plasma HR MC-ICPMS (Nu Instruments) at Victoria University of Wellington, New Zealand. Repeated measurements of selected standards were also undertaken with a ThermoFisher Neptune MC-ICPMS located at the Centre for Star and Planet Formation, Natural History Museum of Denmark, University of Copenhagen, Denmark. Data from these two laboratories are annotated as being from NZ or DK in the following text, tables and figures. Measurement conditions were kept as similar as possible between the instruments. Typical operating conditions and measurement parameters are summarised in Table 2, and collector configurations for both instruments are given in Table S1.† Both instruments were operated in low-resolution mode. Samples were introduced to both instruments in 0.5 M HCl, as HCl was found to result in better washouts over HNO_3.

3.3.1 Nu Plasma MC-ICPMS (NZ). The Nu Plasma MC-ICPMS was operated in low-resolution mode, with a mass resolution of ~1840 ($M/\Delta M$; peak edge width from 5–95% 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 typically made on 0.5 M HCl solutions with 75 or 60 ng mL^{-1} (for the ^{192}Pt–^{198}Pt or ^{196}Pt–^{198}Pt DS, respectively) of natural Pt, with an almost equivalent contribution from DS Pt. The sample uptake rate was *ca.* 80 μL min^{-1}, and the sensitivity of the instrument was typically *ca.* 280 V ppm^{-1} total Pt under these conditions. Peak centering was performed at the start of each session and checked at the end of the session. Each individual analysis comprised 100 × 8 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 × 8 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 mV on all Pt isotopes.

3.3.2 Thermo Neptune plus MC-ICPMS (DK). The Neptune MC-ICPMS was operated in low-resolution mode, with a mass resolution of ~1600 ($M/\Delta M$ as defined by the peak edge width from 5–95% full peak height). An ESI Apex IR desolvating nebuliser sample introduction system was used without nitrogen input and with an Actively Cooled Membrane (ACM) add-on module for additional membrane desolvation. The sample uptake rate was *ca.* 30 μL min^{-1}, and the sensitivity of the instrument under these conditions was typically ~100 V ppm^{-1} total Pt. Solutions were prepared with a natural Pt concentration of 100 ng mL^{-1} and an almost equivalent additional Pt contribution from DS. Peak centering was performed at the start of each analysis, and each analysis comprised 100 × 8.4 s integrations. Each analysis corresponded to 14 min of data acquisition and consumed *ca.* 40 ng of natural Pt. Baselines were obtained by on-peak measurements for 100 × 8.4 s integrations

Table 2 Instrumental operating and measurement conditions

		Nu Plasma (NZ)	Neptune (DK)
Instrument operating conditions			
RF power		1300 W	1200 W
Plasma gas flow rate		14 L min^{-1}	15 L min^{-1}
Interface cones	Sampler	Nickel	Jet cone
	Skimmer	High-sensitivity nickel	X-cone
Source slit width		0.3 mm	0.25 mm
Acceleration voltage		6 kV	10 kV
Instrument resolution		~1840	~1600
Mass analyser pressure		5–10 × 10^{-9} mbar	*ca.* 8 × 10^{-9} mbar
Detector		12 Faraday detectors; all Pt channels using 10^{11}Ω resistors	9 Faraday detectors; all Pt channels using 10^{11}Ω resistors
Sample introduction system		Nu Instruments DSN-100	ESI Apex IR w/ACM
Sample uptake rate		~80 μL min^{-1}	~30 μL min^{-1}
Measurement parameters			
Solution concentration		60–75 ppb	100 ppb
Typical sensitivity		~280 V ppm^{-1} total Pt[a]	~100 V ppm^{-1} total Pt[a]
Sample measurement time		100 × 8 s integrations	100 × 8.4 s integrations
Washout time		30 min	30 min
Background measurement time		100 × 8 s integrations	100 × 8.4 s integrations

[a] At specified uptake rate and concentration.

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prior to and following each analysis. A washout time of 30 min was used between sample analyses and baseline measurements. Using this approach, background levels were typically <1 mV for all Pt isotopes.

3.4 Interference correction

Isobaric interferences on Pt exist from Os (masses 190 and 192) and Hg (masses 196 and 198). These overlapping masses, as well as most relevant molecular species, have mass differences that are too small to be resolved at the mass resolving capability of the MC-ICPMS instruments used in this study (Table S1†). Contributions from Os and Hg were monitored using interference-free masses ^{188}Os and ^{200}Hg. Due to its extremely volatile nature, interferences from Hg in natural samples are unlikely to be significant. However, due to the high relative abundances of ^{190}Os and ^{192}Os (26.4% and 41%, respectively), Pt isotope analyses at these masses are likely to be severely impacted by the presence of even small amounts of Os. In all of the undoped analyses presented here, signals on monitored Os and Hg masses were negligible (*i.e.* <15 μV). An interference correction procedure for Os based on ref. 61 was tested. The interference-free ^{189}Os/^{188}Os ratio (1.21967 (ref. 62)) was used to calculate the Os mass bias, which was then used to calculate the Os interference corrections at masses 190 and 192 from the ^{188}Os signal intensity.

In all of the undoped analyses presented here, signals on monitored Os and Hg masses were indistinguishable from the baseline noise.

3.5 Data reduction

All data reduction was conducted off-line using Iolite, a freely available data reduction package that runs within the Igor Pro software from Wavemetrics.[63] An add-on has been developed for processing DS data within Iolite (Creech and Paul, in prep.), which can be adapted for any DS system. This procedure will be made freely available for download from the Iolite website (http://www.iolite.org.au). The DS calculations are performed algebraically using the equations of Rudge *et al.*[56]

3.6 Reporting of platinum stable isotope data

In non-traditional stable isotope systems, particularly in the intermediate- to heavy-mass range, it is conventional to report isotopic compositions as a ratio of a heavy over a light isotope for a given element (*e.g.* ^{44}Ca/^{40}Ca), as is the case for traditional stable isotope systems.[64] We report results here using that approach. Given that the abundances of the two lightest Pt isotopes (^{190}Pt and ^{192}Pt) are very small, we use ^{194}Pt as the denominator isotope. Typically, in stable isotope studies, the highest mass isotope of a reasonably high abundance would be chosen for the numerator isotope. Therefore, we report Pt stable isotopes in terms of ^{198}Pt/^{194}Pt ratios. Given that mass-dependent natural stable isotope fractionations in Pt isotopes might be expected to be relatively small (*i.e.* parts-per-million), we have adopted a μ notation representing the parts per million deviation of the ^{198}Pt/^{194}Pt ratio from the same ratio for the IRMM-010 Pt isotope standard. Isotopic compositions are thus reported as μ^{198}Pt:

$$\mu^{198}\mathrm{Pt} = \left[\frac{\dfrac{^{198}\mathrm{Pt}}{^{194}\mathrm{Pt}_{\mathrm{sample}}}}{\dfrac{^{198}\mathrm{Pt}}{^{194}\mathrm{Pt}_{\mathrm{IRMM\text{-}010}}}} - 1\right] \times 10^6$$

Assuming fractionation occurs through a mass-dependent process, stable isotope fractionations may also be expressed in terms of the relative difference per unified atomic mass unit (*i.e.* ppm u^{-1}).

3.7 Analytical tests

We conducted the following tests to demonstrate the veracity of our technique: (1) mixtures of the IRMM-010 and both DS were measured over a range of different mixing proportions to test the accuracy of the DS calibrations; (2) replicate DS measurements of the IRMM-010 standard were made over many months to assess both the within-session and long-term reproducibility of the technique; (3) a range of element doping tests were conducted to test the sensitivity of the technique to the presence of contaminants (particularly Os) that may be present, for example, following chemical separation of Pt from natural samples; (4) the potential effects arising from imperfect peak positioning or lower ion beam intensities were examined by analysis off the peak centre and in low Pt concentration solutions; (5) Pt stable isotope compositions of three different Pt standards were measured to investigate whether any variability in Pt stable isotope compositions exists.

4 Results and discussion

4.1 Platinum isotopic composition of the IRMM-010 standard

The currently accepted reference Pt isotope composition for IRMM-010 was determined using partially calibrated analyses by quadrupole ICPMS in 2002.[31] However, Pt isotope ratios reported by Morgan *et al.*[65] measured by MC-ICPMS show significant differences in isotopic composition for some Pt isotopes as compared with those of ref. 31. During this study, it was found that no DS calibration would yield consistent DS-corrected isotope ratios using the natural Pt isotopic composition reported by ref. 31, suggesting that the reference values for IRMM-010 may be inaccurate. Therefore, we elected to remeasure the isotopic composition of IRMM-010 by MC-ICPMS. Platinum isotope measurements of IRMM-010 were carried out using external normalisation to the Pb isotope standard SRM981. Lead was selected for performing the mass bias correction as it is the closest element in mass to Pt that does not have any overlapping isobaric interferences on Pt, and Pb isotopic reference standards with well constrained isotope ratios are available. Solutions of IRMM-010 were doped with the Pb isotope standard SRM981 at *ca.* 10% of the Pt concentration and an internal mass bias correction was performed using a ^{208}Pb/^{206}Pb ratio of 2.16775.[38] This ^{208}Pb/^{206}Pb ratio for SRM981 was determined using the Pb DS approach referenced to a ^{208}Pb/^{206}Pb ratio of 1.00016 for the Pb isotope standard SRM982. The mass-bias-corrected ^{207}Pb/^{206}Pb ratio (^{207}Pb/^{206}Pb$_{\mathrm{FC}}$) was also measured and

compared with the reference value of 0.91489.[38] The following factors must be taken into account when considering the accuracy of this approach to determining Pt isotope ratios:

(1) The potential presence of Pt oxide and nitride interferences on Pb isotopes (Table S1†), which must either be insignificant or corrected for. To account for these potential interferences, measurements of Pb-doped Pt standards were bracketed with analyses of an undoped Pt standard solution with an identical Pt concentration, and the signals observed in the undoped Pt standard at the Pb masses were subtracted from Pb doped analyses. The contributions on Pb masses from interferences were *ca.* 1 mV for undoped 150 ppb IRMM-010 solutions, compared with signals of 2–5 V in Pb doped analyses.

(2) That the relative mass bias behaviour of Pb and Pt are similar. Although the mass bias behaviour is unlikely to be identical for Pt and Pb, this assumption is still sufficient to explore and further refine the Pt isotopic composition of IRMM-010 given that the studies of ref. 31 and 65 yield differences of 1–10% in most Pt isotopic ratios.

(3) The accuracy of the Pb-corrected Pt isotope ratios are dependent on the reference values for the Pb isotope standard SRM981 and, in turn, SRM982 which are considered to be accurate to ±0.036%.[66]

Pb-corrected Pt isotope ratio measurements using the approach described above are shown in Table 3. For all these measurements, $^{207}Pb/^{206}Pb_{FC}$ ratios were within *ca.* 65 ppm of the SRM981 reference value. Measured Pt isotope ratios are shown in Fig. 1 normalised to the reference composition from Wolff Briche *et al.*[31] The most significant offsets in our data from the values of ref. 31 are for the minor isotope ratios $^{190}Pt/^{194}Pt$ and $^{192}Pt/^{194}Pt$, which show differences of *ca.* 10% and 1.7%, respectively. Corrected Pt isotope ratios are in good agreement between the two instruments used in this study, with relative differences of 0.02–0.2%. For all ratios, measured IRMM-010 Pt isotopic compositions from the two instruments in this study are in significantly better agreement with one another and with those of ref. 65 than they are with those of ref. 31. We have thus adopted the mean of the ratios from NZ and DK in this study as the composition of the IRMM-010 standard.

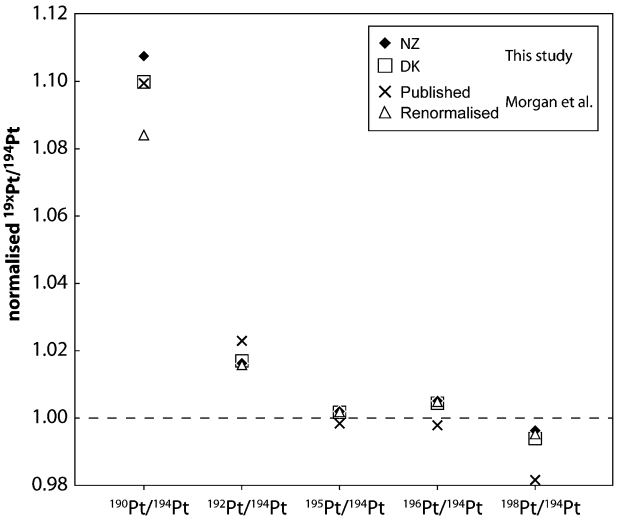

Fig. 1 Natural Pt isotopic composition from Morgan *et al.*[65] and Pb-mass-bias-corrected MC-ICPMS analysis of the IRMM-010 standard in NZ and DK from this study normalised to the reference composition of Wolff Briche *et al.*[31] Morgan *et al.* data represent published data internally normalised using $^{194}Pt/^{195}Pt$ = 0.9744 (crosses), and the same data renormalised to $^{194}Pt/^{195}Pt$ = 0.9710 as determined for natural Pt in this study (triangles).

The analytical uncertainties associated with the Pb-corrected Pt isotope ratios are relatively small compared with the differences from the reference composition.[31] Estimated combined uncertainties were calculated for corrected ratios according to the uncertainty propagation law.[67,68] However, the propagated uncertainties are significantly smaller than the variance between NZ and DK Pt isotope measurements. We have therefore conservatively adopted the 2 sd of the combined NZ and DK values as the uncertainty in the mean of the natural Pt isotope ratios.

Table 3 Natural Pt isotope ratios measured for IRMM-010 obtained by Pb doping, and DS Pt isotope compositions measured by Pb doping and standard bracketing[a]

	$^{190}Pt/^{194}Pt$	$^{192}Pt/^{194}Pt$	$^{195}Pt/^{194}Pt$	$^{196}Pt/^{194}Pt$	$^{198}Pt/^{194}Pt$	$^{207}Pb/^{206}Pb_{FC}$	$\delta^{207}Pb/^{206}Pb$ (‰)
Natural Pt							
Wolff Briche *et al.*	0.0003561	0.023798	1.02800	0.76719	0.22386		
Morgan *et al.*	0.0003921	0.024342	1.02627	0.76562	0.21978		
NZ	0.00039435(6)	0.024185(5)	1.02997(1)	0.77116(12)	0.22302(6)	0.91486(1)	−0.036(12)
DK	0.00039162(3)	0.024204(2)	1.02973(2)	0.77056(2)	0.22250(1)	0.91495(1)	0.063(8)
NZ + DK	0.0003930(39)	0.024194(26)	1.02985(35)	0.77086(85)	0.22276(74)	0.91490(13)	
^{192}Pt–^{198}Pt DS							
Pb doped NZ	0.00022(18)	2.03213(21)	0.510597(44)	0.32432(5)	3.9034(9)	0.91486(3)	−0.038(32)
Pb doped DK	0.000211(4)	2.03446(5)	0.510553(9)	0.32407(1)	3.8971(2)	0.91493(3)	0.047(37)
NZ + DK	0.000215(13)	2.0333(33)	0.510575(62)	0.32420(35)	3.9002(89)	0.91489(11)	
^{196}Pt–^{198}Pt DS							
Std bracketing	0.000161(23)	0.01633(21)	1.76510(93)	13.955(15)	42.732(48)		
Pb doping	0.000195(22)	0.01595(71)	1.76551(58)	13.960(9)	42.736(31)	0.914858(34)	−0.035(37)
Average NZ	0.000178(48)	0.01614(54)	1.76530(58)	13.957(8)	42.734(6)		

[a] Uncertainties on last digits are given in parentheses and are based on 2 sd of NZ and DK measurements (natural and ^{192}Pt–^{198}Pt DS) or 2 sd of results from different methods (^{196}Pt–^{198}Pt DS).

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Although the Pt isotope ratios measured in NZ and DK exhibit a closer agreement with one another than those of ref. 31, differences between the ratios measured in NZ and DK exceed the internal precision of the isotope ratio measurements by a factor of *ca.* 2–8. The differences are greatest for the ratio involving the minor ^{190}Pt isotope and for ratios where the relative mass difference between the numerator and denominator isotope is highest (*i.e.*, ^{198}Pt/^{194}Pt). The cause of this discrepancy is not entirely clear. The abundance sensitivity of both of the mass spectrometers used in this study is sufficiently low that tails from abundant Pt isotopes onto less abundant Pt isotopes cannot readily explain the difference. Similarly, the opposite offsets observed for ^{198}Pt/^{194}Pt and ^{192}Pt/^{194}Pt between the two laboratories cannot be attributed to contamination or memory from use of the ^{192}Pt–^{198}Pt DS (the natural measurements were made prior to development of the ^{196}Pt–^{198}Pt DS). The difference in measured ^{190}Pt/^{194}Pt (0.7%) obtained in the two laboratories is most likely a result of the very small ion beam size of the ^{190}Pt isotope (*ca.* 3 mV). The differences in the other Pt isotope ratios appear to broadly correspond to a mass fractionation relationship as the two sets of ratios lie within 40–180 ppm of a mass fractionation line that passes through the mean composition of both sets of data, implying that subtle differences in the relative mass bias of Pt and Pb characterised the two mass spectrometers used in this study.

Relative Pt isotope abundances were calculated from the mean NZ–DK Pt isotope ratios in Table 3. Uncertainties in the abundances were calculated by partitioning ratio uncertainties between the numerator and denominator isotope following an error propagation law and using measured ion beam intensities.[68] Given that the IRMM-010 Pt isotope standard is accepted as a reference for the natural composition of Pt,[8] the new composition for IRMM-010 presented here should also be representative of natural Pt. Our Pt isotopic composition is compared with previously published values for the natural composition of Pt in Table 1.

We have also recalculated the atomic weight of Pt from the new IRMM-010 isotopic composition presented here using the isotopic masses of ref. 69. We obtain an atomic weight for Pt of 195.08395 ± 0.00068. Despite the significant differences in the Pt isotopic composition reported in this study and ref. 31, this new atomic weight is very similar to the value of 195.0844 ± 0.0058 from ref. 31, although the uncertainty of our new value is significantly smaller than previous estimates (Table 1).

4.2 Calibration of the platinum double-spikes

Accurate isotopic determination by the DS technique requires calibration of the DS composition. Several approaches for calibrating the DS are possible. Here, we determined the compositions of the two DS in two ways: (1) externally normalised by doping with Pb in the same way as described above for the natural Pt isotopic composition of IRMM-010; and (2) external standard–spike bracketing *versus* IRMM-010. Isotopic abundances for both of the Pt DS used in this study are shown in Table 1 and expressed as ratios in Table 3. The calibrated DS compositions are not identical to the optimal DS from Rudge *et al.* (2009), which is due to subtle differences in the pure spike compositions from those used in the DS toolbox (Table 1).

4.2.1 ^{192}Pt–^{198}Pt double-spike. In the case of the ^{192}Pt–^{198}Pt DS, Pt-based oxide and nitride interferences on Pb isotopes were more significant than for IRMM-010 due to the higher abundance of ^{192}Pt. Potential levels of interferences on Pb isotopes were monitored in undoped Pt DS solutions with identical Pt concentrations to the SRM981–Pt DS mixture and were subtracted from Pb-doped analyses. Pb-doped measurements of the ^{192}Pt–^{198}Pt DS were repeated in NZ and DK. Pb-corrected ^{207}Pb/^{206}Pb$_{FC}$ ratios in both NZ and DK measurements were within *ca.* 50 ppm of the reference value for SRM981. Pt isotopic compositions of this DS measured in NZ and DK are in good agreement, and yielded mean ratios of ^{192}Pt/^{194}Pt = 2.0333 ± 0.0033, ^{196}Pt/^{194}Pt = 0.32420 ± 0.00035 and ^{198}Pt/^{194}Pt = 3.9002 ± 0.0089 for the three ratios used in the DS calculations, where the uncertainties represent the 2 sd of the NZ and DK isotope measurements (Table 3).

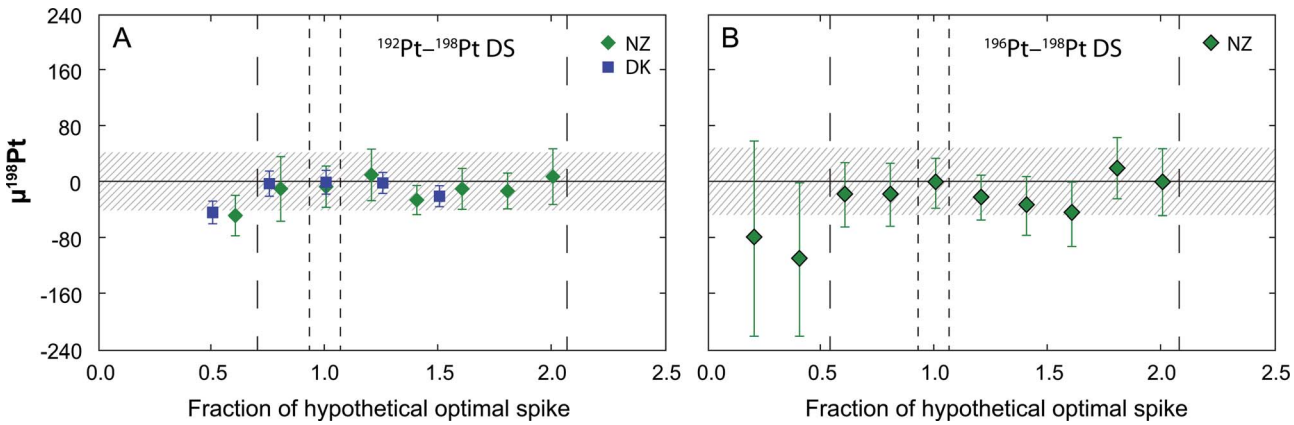

Fig. 2 Plot of μ^{198}Pt for a range of sample–spike mixtures expressed as a proportion of the hypothetical optimal sample–spike mixture. (A) Results for the ^{192}Pt–^{198}Pt double-spike from both NZ and DK. (B) Results for the ^{196}Pt–^{198}Pt double-spike from NZ only. These results demonstrate that DS-corrected stable Pt isotope ratios are relatively insensitive to the sample–spike ratio. Coarse-dashed vertical lines represent the minimum range over which the calibration appears to be accurate. Fine-dashed vertical lines represent the approximate range of sample–spike mixtures used in acquiring the data presented elsewhere in this paper.

4.2.2 ^{196}Pt–^{198}Pt double-spike. The ^{196}Pt–^{198}Pt DS composition was determined by both Pb doping and IRMM-010 standard-spike bracketing, although these measurements were only carried out in NZ. Both sets of results are very consistent, with compositions agreeing to within 0.04%. The Pt isotope ratios obtained for the ^{196}Pt–^{198}Pt DS were Pt/Pt = 1.76530 ± 0.00058, ^{196}Pt/Pt = 13.957 ± 0.008 and ^{198}Pt/Pt = 42.734 ± 0.006, where the uncertainties represent the 2 sd of the ratios obtained by the two different methods.

4.2.3 Accuracy of the double-spike calibrations. The accuracy of the DS calibrations was tested by measuring DS–IRMM-010 mixtures in different proportions. DS-corrected results for 8–10 calibration mixtures for both DS, where the mixtures were varied from 0.2–2.0 times the approximate 'optimal' sample–spike ratio are shown in Fig. 2. Varying the sample/spike ratios from ~0.6 to 2.0 times the optimal sample–spike proportion for either DS has no influence on the accuracy of the DS correction, indicating that the two DS have been well calibrated and that a relatively wide window is acceptable for measuring sample–DS mixtures without significant degradation of the results.

4.3 Internal precision and external reproducibility of double-spike-corrected platinum stable isotope ratios

Internal precision on DS-corrected Pt isotope ratios varied slightly from session-to-session depending on the stability of the sample introduction systems. However, typical internal (2 se) precision on μ^{198}Pt was *ca.* ±30 ppm and ±16 ppm for NZ and DK analyses, respectively. The improved internal precision

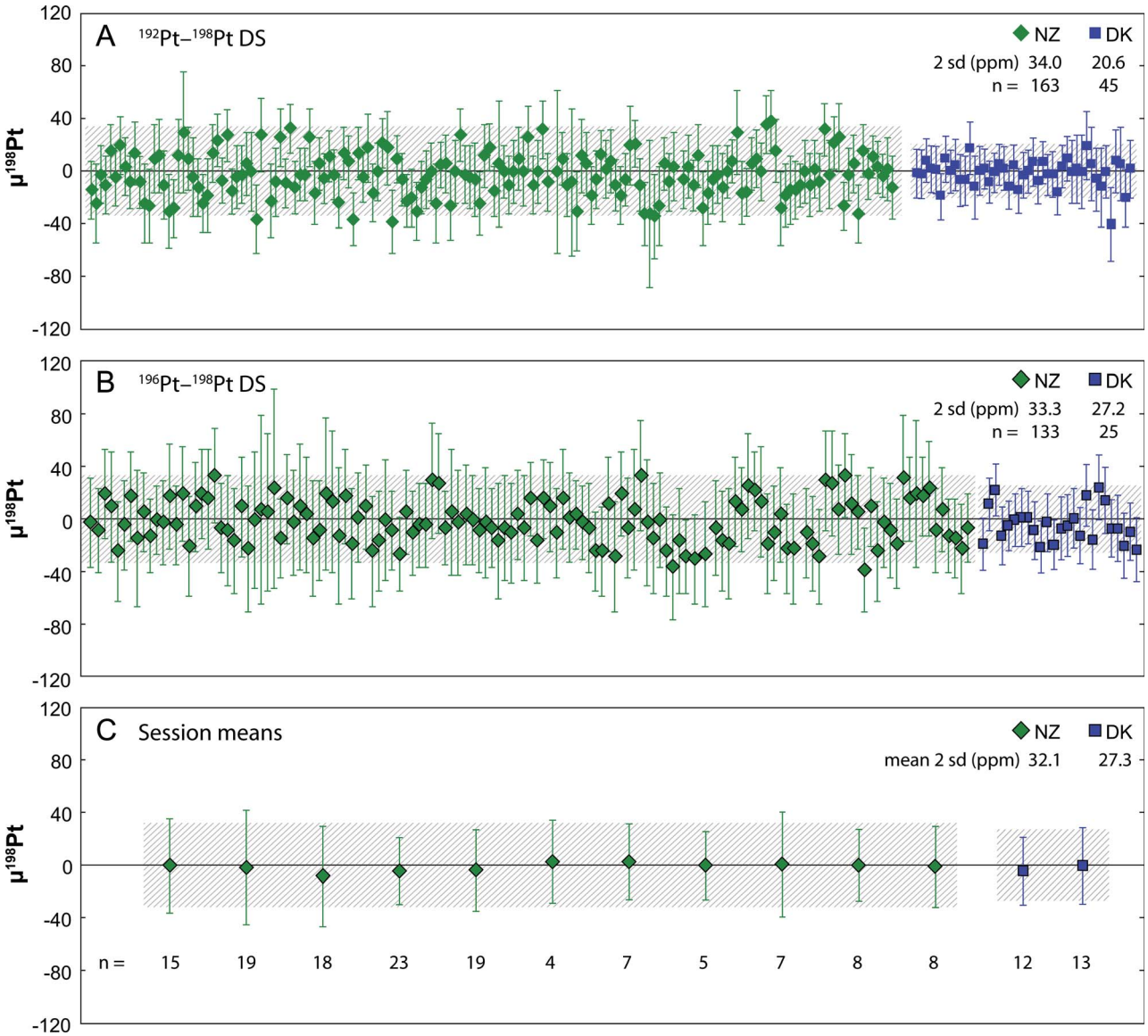

Fig. 3 Reproducibility of double-spiked MC-ICPMS stable Pt isotope measurements from analytical sessions over a period of several months. The first two panels show all analyses from sessions using the ^{192}Pt–^{198}Pt (A) and ^{196}Pt–^{198}Pt (B) double-spikes, and error bars representing the 2 se error for each analysis. Hatched fields represent the ±2 sd of all analyses. The bottom panel (C) shows the mean and 2 sd (error bars) for each analytical session for ^{196}Pt–^{198}Pt DS data, which is our preferred double-spike. The number of analyses in each session is shown. Hatched fields represent the combined ±2 sd of all sessions from each laboratory.

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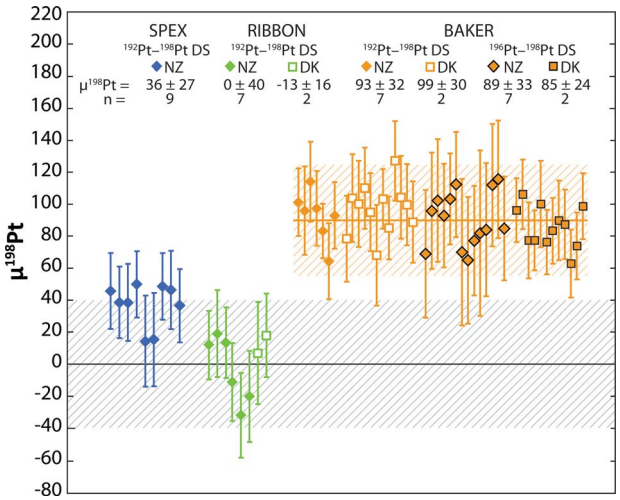

Fig. 4 Measurements of μ^{198}Pt in the additional Pt standards described in the text. The Ribbon standard is compositionally identical to the IRMM-010 standard. The Spex standard shows a potential offset from the IRMM-010 composition, although the offset is approximately equal to the reproducibility of the technique. However, the Baker standard show a clear offset from the IRMM-010 standard of 89 ± 33 ppm that is reproducible between laboratories and using both types of DS. Grey hatched area represents the reproducibility of the technique. Orange horizontal line and hatched area represent the mean and 2 sd, respectively, of all analyses of the Baker standard.

in DK compared with NZ mainly reflects the greater stability of the Apex sample introduction system.

DS-corrected Pt isotope results for IRMM-010 from a number of analytical sessions in both NZ and DK and using both DS are shown in Fig. 3. The external reproducibilities using the two DS are very similar. Within measurement sessions that are typically 1–2 days in length, DS-corrected IRMM-010 measurements have external reproducibilities (2 sd) on μ^{198}Pt of *ca.* ±35 ppm for NZ analyses and *ca.* ±25 ppm for DK analyses. External reproducibility over a large number of sessions is similar to reproducibility attained in a single session (Fig. 3.).

Small offsets (*ca.* 30–50 ppm) were sometimes observed between absolute DS-corrected Pt isotope ratios from different sessions. These offsets might possibly be related to small changes in the abundance sensitivity of the MC-ICPMS, drifts in the relative gains of the Faraday collectors, or a variable component of non-exponential mass bias that is not readily corrected for by the DS method. To account for these variations, we combined the DS correction method with a standard–sample bracketing approach, whereby analyses of the double-spiked standard are repeated throughout the session and alternated with "unknown" analyses. The analyses of "unknowns" are then normalised to the mean value of the bracketing standards. The long-term external reproducibility of these corrected ratios is approximately the same as the within-session reproducibility. The external reproducibility of our technique suggests that mass-dependent Pt stable isotope fractionations >10 ppm u^{-1} should be resolvable by this technique. This external reproducibility is comparable to those recently achieved for other non-traditional stable isotope systems such as Mg, Fe and Cd.[7,70,71]

4.3.1 Platinum stable isotope variations in standards. Repeated DS-corrected Pt stable isotope measurements were made of three different Pt element standards (Baker, Ribbon and Spex; Table 3; Fig. 4). ^{192}Pt–^{198}Pt DS-corrected measurements were made of all three standards in both NZ and DK.

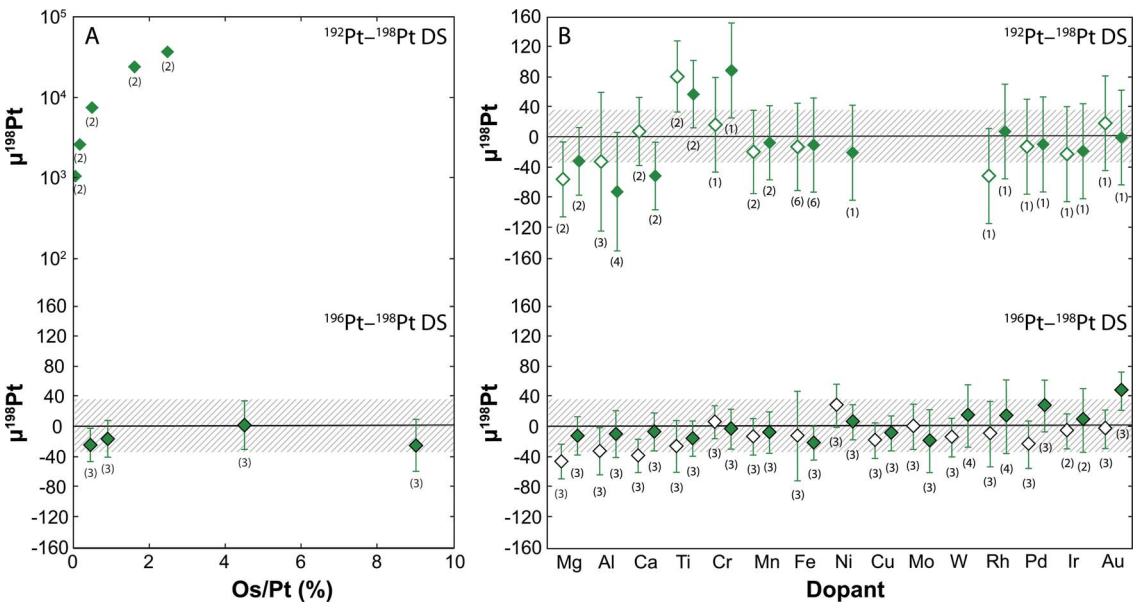

Fig. 5 Results of doped IRMM-010 standard measurements with both double-spikes from NZ. (A) Results of doping tests with a range of Os concentrations up to 10% of the Pt concentration of the standard. The ^{192}Pt–^{198}Pt DS-corrected μ^{198}Pt data are sensitive to very small amounts of Os contamination (note: data shown have no Os correction applied). However, the ^{196}Pt–^{198}Pt DS corrected μ^{198}Pt appears to be unaffected at the Os doping levels tested here. Hatched areas represent the 2 sd reproducibility of undoped measurements (not shown for the ^{192}Pt–^{198}Pt DS). (B) Results of doping tests with a range of common rock forming elements and siderophile elements for both double-spikes. Solutions of IRMM-010 were doped at 5% and 10% of the Pt concentration, represented by hollow and filled symbols, respectively. Hatched areas represent the 2 sd reproducibility of undoped measurements for each DS.

Measurements using the ^{196}Pt–^{198}Pt DS were only repeated in both laboratories for the Baker standard. The Spex standard may show a subtle variation from the IRMM-010 standard, however, both Spex and Ribbon are within error of the IRMM-010 composition. The Baker standard shows the largest offset in μ^{198}Pt of *ca.* 89 ± 33 ppm from IRMM-010, which was reproducibly observed between different analytical sessions in both NZ and DK and using both DS. The Baker standard thus represents a useful secondary standard with a known offset from IRMM-010 to monitor the quality of Pt isotope data within each analytical session. Moreover, these stable Pt isotopic differences between the IRMM-010 and Baker standards suggest that stable isotopic fractionations characterise terrestrial Pt, although it is currently unclear if this is due to variations in the natural Pt source material or those induced during preparation of the Pt metal used to make these standards.

4.4 Analytical tests

4.4.1 Spectral matrix effects. Due to the high relative abundances of Os and Os (26.4% and 41%, respectively), Pt isotope analyses at these masses are likely to be severely impacted by the presence of even small amounts of Os, particularly where one of these two Pt isotopes would be used in the DS calculations. In order to constrain the potential effects of Os isobaric interferences, such as those that might result from imperfect chemical separation of Pt from Os in natural samples, Os doping tests were carried out on DS–IRMM-010 mixtures using both the ^{192}Pt–^{198}Pt DS and ^{196}Pt–^{198}Pt DS (Fig. 5A). Os doping levels ranged from 0.1–10% of the Pt concentration. The ^{196}Pt–^{198}Pt spike does not use ^{192}Pt in the DS calculations, and is unaffected by the presence of Os even at the highest doping levels. However, DS-corrected Pt isotope data using the ^{192}Pt–^{198}Pt DS are highly sensitive to the presence of small amounts of Os. At Os/Pt ratios >0.1%, DS corrected μ^{198}Pt analyses are inaccurate by >1000 ppm. The VUW Nu Plasma collector configuration does not allow for Os/Os to be measured in the same cycle as Pt isotopes, so this approach to calculating Os corrections on ^{190}Pt and ^{192}Pt was tested by measuring Os/Os in a second cycle to determine the Os mass bias, and using Os signal measured in the same cycle as Pt to calculate the magnitude of the corrections. While the Os correction was somewhat effective, it was found to be not sufficiently reliable to enable accurate isotope determinations using the ^{192}Pt–^{198}Pt DS in standards even with only very minor amounts of Os contamination (*i.e.* Os/Pt < 0.1%).

The influence of Os in ^{192}Pt–^{198}Pt DS Pt stable isotope measurements may limit the application of this DS to natural samples where Os and Pt may have broadly similar concentrations. Whilst chemical separation techniques can be used to quantitatively separate Os from Pt, and the presence of Os can at least be monitored using non-overlapping masses (*e.g.*, Os), it is difficult to rigorously correct for the presence of even minor amounts of Os. As such, the ^{196}Pt–^{198}Pt DS is our preferred Pt DS for use with terrestrial samples. Furthermore, a recent study has shown that, due to their relatively large thermal neutron capture cross sections, Pt isotope compositions can be significantly altered by neutron capture in iron meteorites with long cosmic ray exposure ages.[34] These effects are significantly larger for ^{192}Pt than ^{196}Pt. Therefore, the ^{196}Pt–^{198}Pt DS is also our preferred DS for use with extraterrestrial samples.

4.4.2 Non-spectral matrix effects. Non-spectral matrix effects from elements that have no direct isobaric interferences with the element of interest can arise from a range of possible factors and can have an influence on instrumental mass bias.[57] In order to investigate potential non-spectral matrix effects, a range of elemental doping tests were performed whereby solutions of optimally double-spiked IRMM-010 were doped at levels of 5–10% of the Pt concentration, including a range of common rock-forming elements (Mg, Al, Ca, Ti, Cr, Mn, Fe, Ni and Cu) as well some siderophile elements (Mo, W, Rh, Pd, Ir and Au). The

Table 4 Results of elemental doping tests to assess potential matrix effects. Optimally spiked IRMM-010 samples were doped with a range of elements[a]

		^{192}Pt–^{198}Pt DS			^{196}Pt–^{198}Pt DS		
Dopant	Doping level	μ^{198}Pt	2 sd	*n*	μ^{198}Pt	2 sd	*n*
Undoped		0.0	63	39	0.0	43.0	49
Mg	5%	−54.5	38.4	2	−45.0	23.0	3
	10%	−30.5	31.9	2	−11.0	25.2	3
Al	5%	−31.0	86.5	3	−31.3	31.3	3
	10%	−70.8	72.1	4	−8.7	30.9	3
Ca	5%	9.0	32.6	2	−37.3	22.3	3
	10%	−50.0	31.8	2	−5.7	24.9	3
Ti	5%	82.0	35.1	2	−25.0	34.2	3
	10%	58.5	31.6	2	−14.7	23.0	3
Cr	5%	18.0	*63.0*	1	7.0	21.6	3
	10%	90.0	*63.0*	1	−2.0	26.4	3
Mn	5%	−18.0	45.3	2	−12.3	24.0	3
	10%	−6.0	38.0	2	−6.7	27.4	3
Fe	5%	−11.3	48.6	6	−11.3	59.2	3
	10%	−8.8	53.9	6	−20.7	22.4	3
Ni	5%				29.0	28.4	3
	10%	−19.0	*63.0*	1	7.0	23.2	3
Cu	5%				−17.3	23.4	3
	10%				−7.7	23.0	3
Mo	5%				1.0	29.9	3
	10%				−18.0	41.5	3
W	5%				−13.3	25.4	3
	10%				15.3	41.0	4
Rh	5%	−50.0	*63.0*	1	−8.7	43.3	3
	10%	9.0	*63.0*	1	14.5	48.8	4
Pd	5%	−11.0	*63.0*	1	−22.7	31.3	3
	10%	−8.0	*63.0*	1	28.0	34.5	3
Ir	5%	−21.0	*63.0*	1	−5.0	23.1	2
	10%	−17.0	*63.0*	1	9.5	42.0	2
Au	5%	20.0	*63.0*	1	−2.3	25.5	3
	10%	1.0	*63.0*	1	48.0	25.5	3
	0.1%	−2.0	135.8	2			
	0.2%	15.0	65.1	2			
	0.5%	117.0	45.3	2	−23.3	22.1	3
Os	0.9%	584.0	11.3	2	−15.3	24.2	3
	1.8%	1063.0		1			
	4.5%	3022.5	58.0	2	2.7	32.0	3
	9.0%				−24.0	34.2	3

[a] Uncertainties are propagated 2 sd errors. Italicised 2 sd values are where only one analysis was made and the session 2 sd is taken as the uncertainty. No Os interference correction for ^{192}Pt–^{198}Pt DS data was applied.

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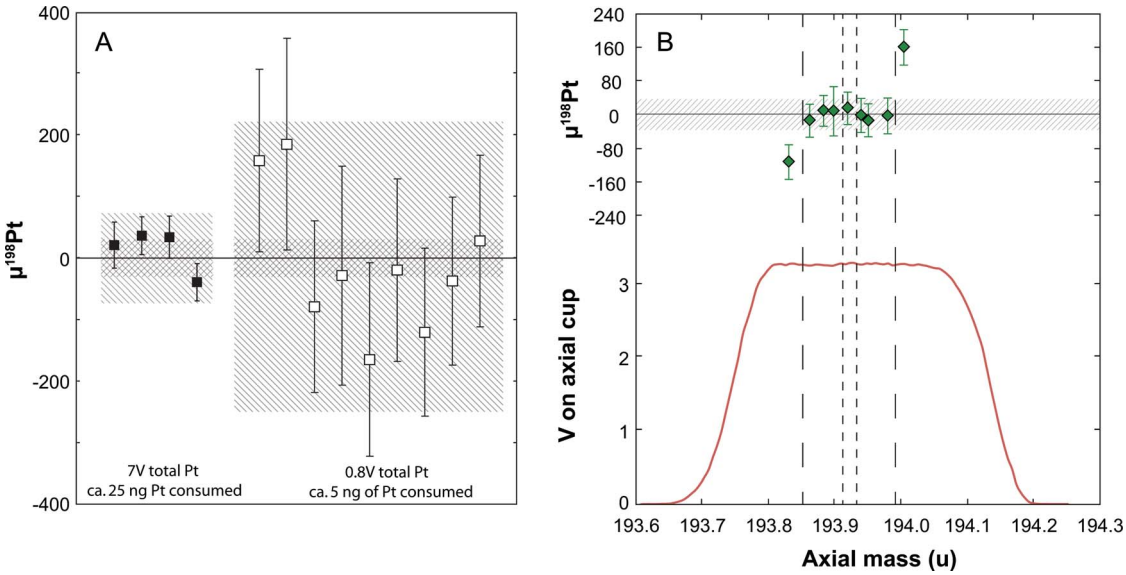

Fig. 6 (A) Repeat measurements of IRMM-010 with the ^{192}Pt–^{198}Pt DS at 7 V (filled symbols) and ^{196}Pt–^{198}Pt DS at 0.8 V total signal on Pt (usually 24 V at typical measurement concentration). Internal and external precision are concomitantly larger (*ca.* 35 ppm and 73 ppm, respectively, for 7 V signal, and *ca.* 150 ppm and 240 ppm, respectively, for 0.8 V signal). Hatched area represents the 2 sd error for each group of samples. Cross-hatched areas represent the reproducibility of the technique using typical measurement concentrations. (B) Peak scan from the Nu Plasma MC-ICPMS in low resolution, with measurements of μ^{198}Pt for IRMM-010 using the ^{196}Pt–^{198}Pt DS superimposed at their respective analysis peak positions (expressed in unified atomic mass units, u). The coarse dashed vertical lines represent the range over which the peak position had no effect. The fine dashed vertical lines represent the range of axial masses of normal measurements in this study. The hatched area represents the reproducibility of the technique.

results of these tests are shown in Fig. 5B. The ^{192}Pt–^{198}Pt DS-corrected data for IRMM-010 doped with this range of elements at levels of 5–10% are largely within analytical uncertainty of undoped IRMM-010, although Ti, Cr and Al may have a moderate (*ca.* <100 ppm) effect on the accuracy of Pt stable isotope measurements using the ^{192}Pt–^{198}Pt double-spike (Table 4; Fig. 5b). Element-doped IRMM-010 measured using the ^{196}Pt–^{198}Pt DS yielded Pt stable isotope ratios that were almost all within analytical precision of undoped IRMM-010. However, IRMM-010 doped with Au yielded a mean μ^{198}Pt of 48.0 ± 27.5 ppm, which might reflect a small hydride interference (AuH) on ^{198}Pt.

These elemental-doping tests show that for most elements tested, impurities of up to 10% of the Pt concentration do not significantly compromise the accuracy of the DS-corrected Pt isotope ratios. These results provide some constraints on the efficiency of chemical separation procedures that will be required to separate sufficiently pure Pt from natural samples for accurate Pt stable isotope analysis.

4.4.3 Effect of Pt signal intensity. To test the influence of signal intensity on DS-corrected Pt stable isotope measurements, DS–IRMM-010 mixtures were measured at *ca.* 30% and 3% of the typical Pt concentration analysed in this study (*i.e.* 7 V and 0.8 V total Pt signal compared with 24 V at the typical Pt concentration; Fig. 6A). At 7 V total Pt signal, the DS-corrected Pt stable isotope ratios were within error of those measured at optimal intensities, although the internal precision and external reproducibility were slightly higher (*ca.* 35 ppm and 70 ppm, respectively). At 0.8 V total Pt signal, the internal precision and external reproducibility were much larger (*ca.* 150 ppm and 240 ppm, respectively). These data show that it will be possible to measure the Pt stable isotopic composition (μ^{198}Pt) of natural samples to ±70 ppm on sample of 25 ng of Pt, and to ±240 ppm on a sample of 5 ng of Pt.

4.4.4 Effect of peak position. When operated in low-resolution mode, the Nu Plasma MC-ICPMS produces flat-topped peaks that are *ca.* 0.39 u wide (full width at half maximum) for Pt masses. We tested the potential effects on Pt stable isotope ratio measurements that might result from imperfect alignment of the Pt isotope peaks, peak centering, and peak flatness by measuring DS-corrected Pt isotope ratios on IRMM-010 in different peak measurement positions. Analyses were made by manually setting the axial mass to a range of positions up to 0.1 amu either side of the peak centre and performing analyses of IRMM-010 using the ^{196}Pt–^{198}Pt DS. These tests showed that DS-corrected Pt isotope ratios were within analytical precision of those at the peak centre even when positioned up to *ca.* ±0.075 u (*ca.* ±25% of the plateau width) from the peak centre (Fig. 6B). This range is significantly broader than any peak drift that is likely to occur during an analytical session and, thus, subtle changes in peak position are unlikely to have any effect on the accuracy of our measurements.

5 Conclusions

We have established a DS method for the precise measurement of Pt stable isotopes by MC-ICPMS using both ^{192}Pt–^{198}Pt and ^{196}Pt–^{198}Pt double-spikes. The latter spike is preferable for application to natural terrestrial and extraterrestrial samples as it is (relatively) insensitive to the presence of minor amounts of

Os and any cosmogenic effects that can affect Pt isotopes in meteorite samples with long cosmic ray exposure ages.[34,35] Repeated measurements of Pt standards show that an external precision of *ca.* ±10 ppm u^{-1} is routinely achievable using this technique, even in the presence of significant amounts of matrix elements. One of the analysed Pt standards clearly shows an offset from the IRMM-010 Pt isotope standard that suggest terrestrial stable Pt isotope variations exist that exceed our analytical uncertainty.

While Pt stable isotope variations in nature might be expect to be small, this new isotopic tracer may hold considerable promise for use in a range of areas, including; (1) provenancing of global Pt sources and precious metal archeological artefacts; (2) understanding the global Pt geochemical cycle and, in particular, using redox-controlled Pt stable isotope variations in marine authigenic sediments to trace and understand past changes in ocean and atmospheric chemistry; (3) metal–silicate and liquid–solid metal fractionation associated with the differentiation of asteroids and terrestrial planets in the young Solar System.

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