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High-precision Determination of Gold Mass Fractions in Geological Reference Materials by Internal Standardisation

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Determination of gold abundances in natural rock is critical for applications, but very challenging. Here, we report a method for determining gold with a very low mass fraction (> 0.01 ng g^{-1}) in rocks. The method involves Carius tube digestion with reverse *aqua regia*, chromatographic separation to remove most of the sample matrix and measurement by high-sensitivity ICP-MS. The mono-isotopic element gold was quantified by external calibration using an internal standardisation of gold to platinum that was precisely determined by isotope dilution. The method is robust and the obtained results are indistinguishable (< 5–10%, 2*s*) from those independently obtained by a standard addition technique on the same solution. The results from reference materials TDB-1 and GPt-2 are consistent with the certified values and those determined by HF-*aqua regia* digestion, confirming the validity of the method. TDB-1 (*n* = 20), GPt-2 (*n* = 6), BHVO-2 (*n* = 9) and other mafic RMs are homogenous for gold (10–20%, 2*s*) at the 2 g test portion level; however, sample heterogeneity affects some RMs. Gold and platinum-group elements also display different extents of sample heterogeneity for different RMs. Given the homogeneity observed for TDB-1, GPt-2 and BHOV-2, they are recommended as well-suited RMs for inter-laboratory comparison studies of gold.

Keywords: gold, platinum-group elements, reference materials, internal standardisation, standard addition, sample heterogeneity.

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Gold, given its rarity and nobility, is one of the most desired commodities for humanity. Understanding gold origin and enrichment processes is of great importance for exploring gold deposits and requires the knowledge of gold mass fractions in various natural rocks. Silicate rocks in the Earth's mantle and crust commonly display very low gold abundances, ranging from sub-ng g^{-1} to a few ng g^{-1} (e.g., Terashima 1988, Fischer-Gödde *et al.* 2011, Pitcairn 2011, Saunders *et al.* 2018). Quantification of such low gold abundances is very challenging (Barefoot and Van Loon 1999, Pitcairn *et al.* 2006). For instance, isotope dilution-based methods produce high-precision data for low abundance platinum-group elements (PGEs); however, these approaches cannot be applied to mono-isotopic gold. Thus, robust analytical methods are important for the accurate determination of gold in geological samples.

Geological reference materials (RMs) with well-certified gold mass fractions are critical for evaluating the validity and robustness of analytical methods. However, only a limited number of reference materials have been certified for gold (e.g., TDB-1, WGB-1, OKUM). Although previous studies have reported gold mass fractions for many RMs (e.g., Terashima 1988, Terashima and Taniguchi 2000, Richardson and Burnham 2002, Maier *et al.* 2003, Savard *et al.* 2010, Jochum *et al.* 2016), the results often show variable ranges with large uncertainty, particularly for samples with low gold abundances, such as 0.2–3.5 ng g^{-1} for WGB-1

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(gabbro, certified at 2.9 ± 1.1 ng g^{-1}) and 3.9–7.1 ng g^{-1} for TDB-1 (diabase, certified at 6.3 ± 1.0 ng g^{-1}, see the GeoReM database and the compiled details in Table S1). The highly variable gold mass fractions could result from many factors, including incomplete sample digestion, low recovery during chemical purification, overestimation due to high procedural blanks or high detection limits of the instruments used, or sample heterogeneity.

Complete sample attack by fire assay, alkaline fusion or acid digestion using HF are the most desirable procedures for the dissolution of Au from geological materials. *Aqua regia* or reverse *aqua regia* (mixtures of concentrated HCl and HNO_3) is another widely used reagent to release gold from rocks, and is considered highly efficient. However, *aqua regia* only partially dissolves silicates and therefore may lead to incomplete extraction of gold from samples (Hall *et al.* 1989). The incomplete extraction by *aqua regia* digestion may depend on sample type and also experimental conditions; prolonged digestion at high temperature with low volume ratio of sample to digestion acid might overcome this issue (Hall *et al.* 1989).

Most analytical techniques for Au measurement in geological samples require a pre-treatment step to enrich and separate Au from matrix elements. Fire assay, solvent extraction and chemical purification are the commonly used means (Barefoot and Van Loon 1999), during which complete recovery is necessary for quantitative analysis of gold. However, low recovery often occurs, especially for samples with low Au mass fractions (Barefoot and Van Loon 1999). In addition to this, gold is unstable in some acids (e.g., HNO_3, very dilute HCl; Pitcairn *et al.* 2006), so that, improper treatment during sample preparation may cause Au loss thus underestimating the true abundance.

Overestimation of gold can also occur due to high procedural blanks, high detection limits of the instruments and/or potential oxide interference if inductively coupled plasma-mass spectrometry (ICP-MS) is employed. One of the most widely used pre-treatment methods is nickel sulfide fire assay (Young 1980, Barefoot and Van Loon 1999, Oguri *et al.* 1999, Gros *et al.* 2002), but the large quantities of reagents required often result in high and variable procedural blanks (i.e., a few ng; (Asif and Parry 1989, Oguri *et al.* 1999, Gros *et al.* 2002), a level sometimes higher than many natural rocks. ICP-MS can achieve lower detection limits relative to INAA, RNAA and GF-AAS (Barefoot and Van Loon 1999, Pitcairn *et al.* 2006), but Au may suffer from a potential oxide interference from $^{181}Ta^{16}O$ on ^{197}Au because of high Ta abundance in samples (e.g., 1 µg g^{-1} Ta vs. 1–2 ng g^{-1} Au in BHVO-2). Finally, sample heterogeneity (known as 'nugget effect' for PGEs; Meisel *et al.* 2004b, Meisel and Horan 2012) may play a critical role in the observed variation of gold mass fractions in RMs. Similarly, gold may be strongly affected if it is mostly hosted by accessory sulfide phases.

A simple way to quantify mono-isotopic gold is external calibration using an internal standardisation (IS) method (Fischer-Gödde *et al.* 2011), a technique previously employed by Meisel *et al.* (2003) for the determination of Rh, which is also mono-isotopic. PGEs with masses similar to Au, such as Ir and Pt, are used as the internal standardisation to calculate gold mass fractions, where PGEs in the same sample aliquot can be accurately determined by isotope dilution. Because the method is based on the intensity ratio of Au to PGEs rather than gold intensity (Fischer-Gödde *et al.* 2011), one of its great advantages is that it does not require complete recovery of gold during sample treatment after digestion except during chemical separation, because the Au/Ir or Au/Pt ratios remain unchanged even if a fraction of sample solution is lost during the transfer.

In this study, we modified the chromatographic separation procedure and the internal standardisation method described in Fischer-Gödde *et al.* (2011) for high-precision determination of gold with a very low mass fraction in natural rocks (> 0.01 ng g^{-1}). Sample digestion in borosilicate Carius tubes with reverse *aqua regia* and high-sensitivity ICP-MS achieved very low total procedural blanks (3 ± 3 pg) and low detection limits (< 0.8 pg ml^{-1}), respectively. The chromatographic separation led to complete recovery (> 99%) of both Au and PGEs, which is critical for the application of internal standardisation. An independent method of standard addition (SA) on the same sample solution was used to cross check data quality. Eight geological RMs were repeatedly measured, and the effect of sample heterogeneity on variations in gold mass fractions, as well as PGEs, was evaluated. These results were also compared with literature values obtained by different analytical methods and, if any, certified values and those from the HF-*aqua regia* digestion approach.

Experimental method

Geological reference materials

The geological RMs analysed in this study are ultramafic-mafic rocks (n = 7), and a sediment (n = 1): TDB-1 (diabase, CANMET, Ottawa, Canada), WGB-1 (gabbro, CANMET), UB-N (serpentinized peridotite, Centre de Recherches Petrographiques et Geochimiques (CRPG), Vandoeuvre-lès-Nancy Cedex, France), OKUM (komatiite,

Geosciences Laboratories, Sudbury, Canada), BHVO-2 (basalt, USGS), BCR-2 (basalt, USGS), JB-2 (basalt, Geological Survey of Japan) and GPt-2 (sediment, Institute of Geophysical and Geochemical Exploration, Beijing, China). The gold mass fractions in these RMs range from about 1 to 10 ng g^{-1}. Because natural rocks often contain low gold mass fractions of sub-ng g^{-1} to a few ng g^{-1}, RMs with higher gold mass fractions were not selected in this study.

Most of these RMs have been determined for PGE and Au by different methods (see Table S1 compiled from the GeoReM database). Some RMs display relatively homogeneous PGE mass fractions, for example, OKUM (Savard *et al.* 2010), but others, such as WGB-1, BCR-2 and BHVO-2, show more variability (Maier *et al.* 2003, Meisel and Moser 2004a, b). Gold and PGEs are strongly chalcophile elements, and it is unclear if gold shows a similar level of sample heterogeneity as PGEs. Thus, determining gold and PGE mass fraction data from the same sample digestion aliquot will help to understand this issue.

The selected ultramafic-mafic rocks include crystalline and extrusive rock types, in which gold is mainly hosted in sulfides or basaltic glasses, respectively. The variety of the investigated rock types is very useful in evaluating the effect of sample heterogeneity on gold mass fractions and how this is related to different rock types. Reverse *aqua regia* digestion used in this study only partly dissolves samples, and the extrusive samples and sediments could be important to evaluate the efficiency of *aqua regia* digestion for recovery of Au from silicate glass or phases. Some RMs such as TDB-1 and GPt-2 have been extensively analysed by different methods, including complete attack by HF-*aqua regia*, and certified values are available (e.g., Yan *et al.* 1998, Richardson and Burnham 2002, Savard *et al.* 2010, Pitcairn *et al.* 2015). These are useful in evaluating the validity of our methods.

Instrumentation and reagents

Because of low gold and PGE mass fractions in natural rocks, high-sensitivity instruments are important for precise determinations. In this study, a high-sensitivity sector field ICP-MS (Element XR, Thermo Fisher Scientific Inc., Waltham, MA, USA) at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan, was used. Reagent grade concentrated HCl and HNO_3 were purified twice by sub-boiling distillation in Savillex Teflon stills and then used for sample digestion, chemical separation and ICP-MS measurement. Water used to dilute acids and for chemical separation was all from 18.2 MΩ cm resistivity water (Milli-Q, Millipore Corporation, Molsheim, France). The borosilicate Carius tubes that were used (2 mm thick with volumes of about 50 ml) were pre-cleaned in sub-boiling 50 ml/100 ml *aqua regia* (48 h) and water. The cation exchange resin (Eichrom 50W-X8, 100–200 mesh) was also pre-cleaned in Milli-Q water, HCl and HNO_3 of different concentrations (1 and 6 mol l^{-1}, three times). Teflon beakers and tubes were used for sample solutions and, after use, sequentially cleaned with 50 ml/100 ml *aqua regia*, HNO_3, HCl and Milli-Q water on a hot plate overnight at 100 °C. The acetone reagent was analytical grade and used to prepare the mixture with HCl (0.5 mol l^{-1} HCl + 40 ml/100 ml acetone) for the exchange chromatography separation.

Aqua regia sample digestions

Acid digestion commonly can achieve very low procedural blanks. In this study, sample digestion by reverse *aqua regia* in Carius tubes was employed. Importantly, reverse *aqua regia* only partially dissolves silicates and as a consequence, this commonly leads to limited release of potentially interfering elements such as Ta (for Au), Hf, Zr and Mo (for PGEs). It is thus preferable if ICP-MS is employed for Au determination. After addition of a suitable amount of a mixed spike solution containing ^{191}Ir-^{194}Pt-^{99}Ru-^{105}Pd and a spike solution of ^{185}Re, 2 g powder test portions of each RM were digested by reverse *aqua regia* (5 ml of 14 mol l^{-1} HNO_3 and 2.5 ml of 9 mol l^{-1} HCl) in pre-cleaned Carius tubes at 240–270 °C over 4 days. Following this the samples were transferred to centrifuge tubes, and 6 mol l^{-1} HCl was used to rinse the Carius tubes, and combined with the sample solution. After centrifugation, the supernatant solution of samples without residues was transferred to weighed beakers, and 6 mol l^{-1} HCl was used to rinse the tubes and combined with the supernatant solution (Figure 1). These steps removed the residues and ensured complete recovery of Au and PGEs during transfer of sample solutions. Omitting the rinsing steps or rinsing by water may lead to an incomplete transfer of gold. This would be a problem for the standard addition method but not for internal standardisation because the latter is based on the intensity ratio of Au/Pt to calculate gold mass fractions (see below).

About one-quarter of the sample solution (equivalent to 0.5 g sample) was weighted precisely and converted to chloride form by twice repeated addition and evaporation of concentrated HNO_3 (14 mol l^{-1}) and HCl (9 mol l^{-1}). The samples were then dissolved in 10 ml of a mixture of 0.5 mol l^{-1} HCl-40 ml/100 ml acetone, ready for chemical separation. The procedure can be applied to obtain gold mass fractions of the same sample solution by both internal standardisation and standard addition methods. The steps

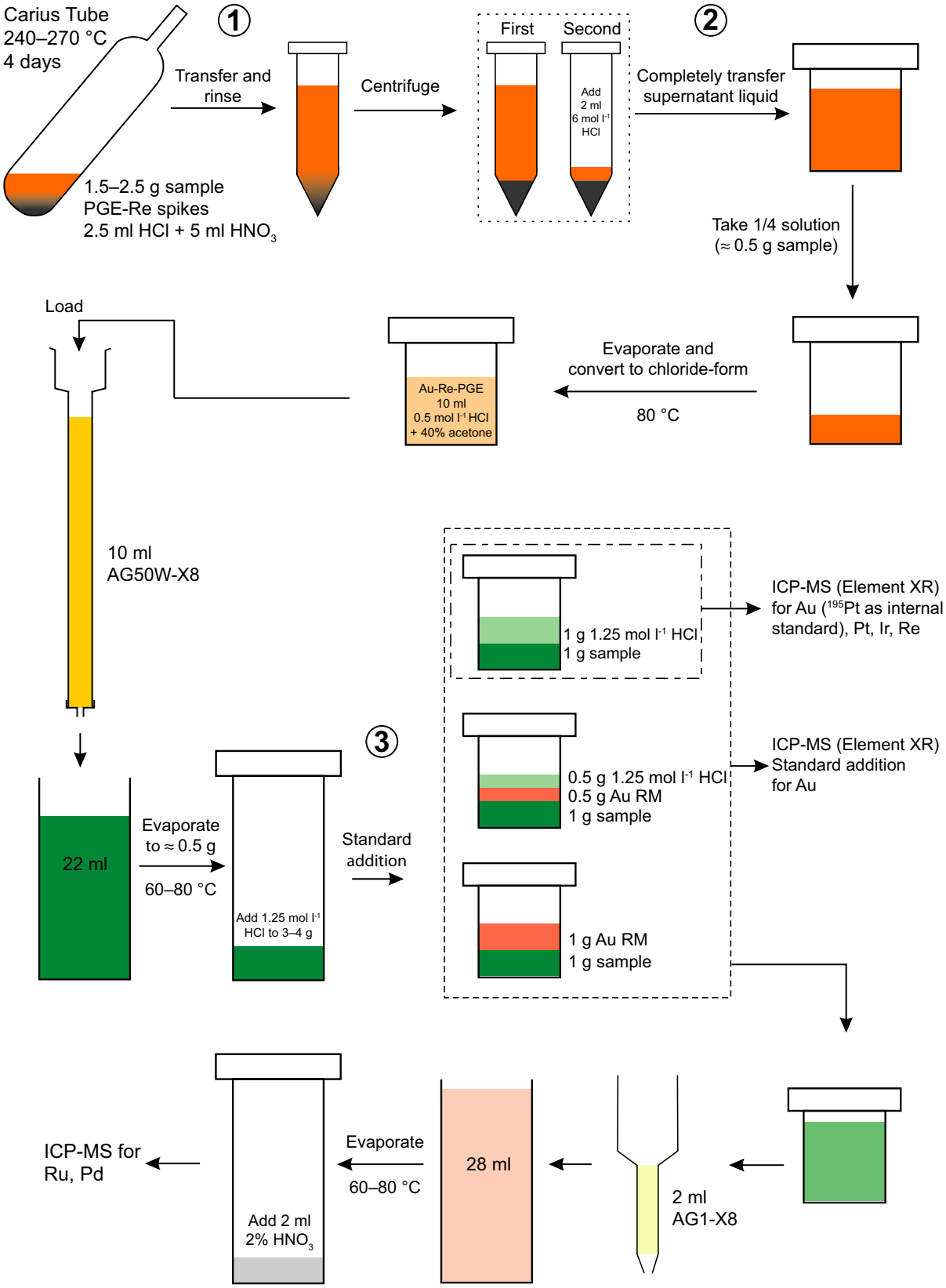

Figure 1. Schematic flow chart showing the procedure for the determination of Au mass fraction, as well as Re and PGEs in this study. Steps 1 and 2 represent rinsing of the Carius and centrifuge tubes by 6 mol l^{-1} to ensure for complete transfer of Au and PGEs to the Teflon beakers. Step 3 is the splitting of the sample solution into three aliquots and treating them for standard addition. The sample aliquot without the addition of Au standard solution was used to calculate the Au mass fraction by internal standardisation. Platinum, Ir and Re mass fractions can be obtained with Au, and the remaining solution was used to determine Ru and Pd mass fractions after the second cleanup (Table 1). [Colour figure can be viewed at wileyonlinelibrary.com]

can be greatly simplified if only internal standardisation is used for gold mass fractions.

Chemical separation

Chemical separation was modified from techniques described previously, and Au, Re and PGEs were separated from the matrix by cation exchange chromatography using 10 ml of pre-cleaned Eichrom 50W-X8 (100–200 mesh) resin (Figure 1; Fischer-Gödde *et al.* 2011). In the work of Fischer-Gödde *et al.* (2011), gold mass fractions were calculated by standardisation to the ^{193}Ir signal intensity. In this study, owing to the very low Ir mass fractions in basalts and crustal materials, Pt rather than Ir was employed for the internal standardisation. In this case, complete recovery must be achieved for Au and Pt in the same cut of collected eluent.

Elution curves were generated for TDB-1 and BHVO-2 (Figure 2). After loading the sample solution, an additional 24 ml 0.5 mol l^{-1} HCl – 40 ml/100 ml acetone was sequentially eluted (Table 1). Gold and PGEs formed complexes with Cl^- and, as anions, were not retained on the cation resin and were both collected. This led to separation from most of the matrix, which remained on the cation resin (Fischer-Gödde *et al.* 2011). The eluent curves show that for the 14 ml collected after the first 2 ml of 0.5 mol l^{-1} HCl – 40 ml/100 ml acetone yields reached > 99% for Pt and > 95% for Au, and very little Ta and Hf were in the eluted solution (Figure 2). In the study, 22 ml of 0.5 mol l^{-1} HCl – 40 ml/100 ml acetone (from 3 to 24 ml) was collected in Teflon beakers for the complete recovery of both Au and PGEs (> 99% yield, Table 1). The collected solution was evaporated to about 0.5 ml on hot plate at 60–80 °C, and about 2.5 ml of 1.25 mol l^{-1} HCl was added, ready for determination of Au, Re and PGEs.

The chromatographic separation removed most matrix elements, but minor matrices such as Cr (greenish in the eluent) sometimes remained present. The remaining Cr did result in interference on Au during ICP-MS measurement, but has the potential to cause a matrix effect because the Cr mass fraction is very high in ultramafic-mafic rocks (e.g., ~ 2400 µg g^{-1} Cr in UB-N and OKUM). To evaluate the potential effect of the minor matrices on the results obtained by the IS method, the standard addition method was used.

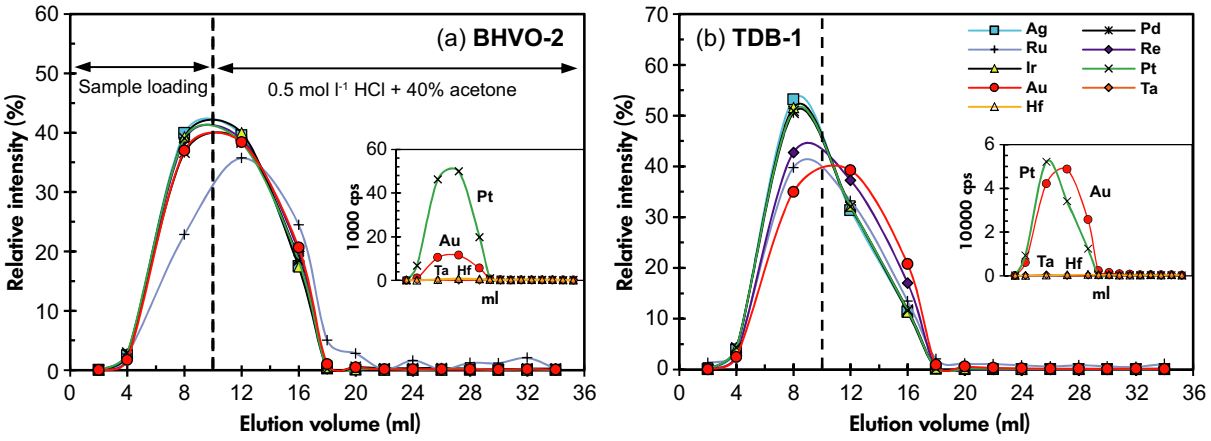

Figure 2. The elution curves of (a) BHVO-2 and (b) TDB-1 by cation exchange chromatography on 10 ml of Eichrom 50W-X8 (100–200 mesh) resin. Complete recovery (> 99%) of Au and Pt was obtained in 22-ml eluents of 0.5 mol l^{-1} HCl – 40 ml/100 ml acetone. Note that Ta and Hf intensities were very low in the eluent containing Au and PGEs. [Colour figure can be viewed at wileyonlinelibrary.com]

Table 1.
Summary of Au-Re-PGE separation chemistry

	Steps	Eluents	Volume (ml)	Comments
(1) Separate Au-Re-PGE from sample matrix				
10 ml AG50W-X8 (100–200 mesh)	Back wash	High-purity H_2O	10	
	Resin conditioning	0.5 mol l^{-1} HCl + 40% acetone	10 + 10	
	Sample loading	0.5 mol l^{-1} HCl + 40% acetone	2	Discarded
	Sample loading	0.5 mol l^{-1} HCl + 40% acetone	4 + 4	Collected
	Elution	0.5 mol l^{-1} HCl + 40% acetone	4 + 4+4 + 2	Collected
	Resin cleaning	6 mol l^{-1} HCl	25 + 25 + 25	Discarded
(2) Secondary purification of Ru-Pd (Ir-Pt-Re are also together)				
2 ml AG1-X8 (100–200 mesh)	Resin cleaning	14 mol l^{-1} HNO_3	12	
	Resin conditioning	4.5 mol l^{-1} HCl	2 + 2	
	Sample loading	4.5 mol l^{-1} HCl	2	Discarded
	Cleaning	4.5 mol l^{-1} HCl	2 + 2	Discarded
		0.05 mol l^{-1} HCl	5 + 5	Discarded
		0.7 mol l^{-1} HNO_3	5 + 5	Discarded
	PGE collection	14 mol l^{-1} HNO3	5 + 5 + 4	Collected
		12 mol l^{-1} HCl	5 + 5 + 4	Collected

The collected sample solution was evaporated to about 0.5 ml, and 1.25 mol l^{-1} HCl was added until the total solution of each sample reached about 3 g. The sample solution was quantitatively separated into three fractions, and a different amount of 1.25 mol l^{-1} HCl and/or gold standard solution with known concentration was added to two fractions (Figure 1). The SA method was used to calculate the gold mass fractions. The fraction without the addition of gold standard solution can be additionally used to obtain the Au the mass fraction via the IS method, as well as mass fractions of Pt, Ir and Re. In this study, we measured the collected sample solution by both IS and SA methods for gold mass fractions of most RMs.

After the determination of Au-Pt-Ir-Re, the remaining solutions were evaporated to near dryness and the residues were dissolved in 2 ml of 4.5 mol l^{-1} HCl. These solutions were then purified on 2 ml Eichrom AG1-X8 (100–200 mesh) resin for determination of Ru and Pd mass fractions, following modified procedures of Rehkämper and Halliday (1997) and Meisel *et al.* (2001). After the elution of 4 ml 4.5 mol l^{-1} HCl, 10 ml 0.05 mol l^{-1} HCl, 10 ml 0.7 mol l^{-1} HNO_3, Ru-Pd were collected in 14 ml concentrated HNO_3 and 14 ml of concentrated HCl (Table 1, note that Ir-Pt-Re were also together). This clean up removed the interferences such as Cr and Cd that affect Ru and Pd, respectively. Finally, these PGE-bearing fractions were evaporated to dryness and then diluted in 2 ml of 2% HNO_3. The Ru-Pd mass fractions were determined via isotope dilution by ICP-MS (see next section).

Mass spectrometry

All Au-Re-PGE were measured using a high-sensitivity Element XR sector field ICP-MS equipped with a quartz spray chamber, in low resolution mode. The measurements were performed in two parts: Au-Pt-Ir-Re for solution after cation resin separation and Ru-Pd after anion resin separation.

For the Au-Pt-Ir-Re fraction, a mixed standard solution with precisely known mass fractions (about 1 ng g^{-1} Au-Ir-Re and 2 ng g^{-1} Pt) for correction of instrumental mass bias was prepared in 1.25 mol l^{-1} HCl. Under routine measurement conditions, around 150000 cps were obtained for a 1 ng g^{-1} Au standard solution and about 100–150 cps for the 1.25 mol l^{-1} HCl acid background. During the measurements, the intensities of ^{197}Au, $^{194,195,196,198}Pt$, $^{191,193}Ir$, $^{185,187}Re$ and those of potential interferences such as ^{181}Ta, ^{178}Hf, ^{189}Os and ^{202}Hg were monitored. The intensity ratios of $^{197}Au/^{195}Pt$ in the bracketing standard solutions and samples were stable with RSD values of 1–3%, overall better than those for the intensities. The wash solution used between samples and standard solutions was 1.25 mol l^{-1} HCl, which can effectively remove Au from the system after each analysis (Pitcairn *et al.* 2006). In order to keep the background levels low and to minimise potential memory effects, a 4-min rinse with 1.25 mol l^{-1} HCl was performed after each sample and standard solution measurement.

Tantalum, Hf and Hg, if present in the sample solution, could affect the results for Au, Ir and Pt because they generate oxide interferences such as $^{181}Ta^{16}O$ on ^{197}Au, $^{177,178,179}Hf^{16}O$ on ^{193}Ir, ^{194}Pt and ^{195}Pt, and isobaric interferences ^{196}Hg on ^{196}Pt, and ^{198}Hg on ^{198}Pt. The oxide formation rate was monitored by Ce, Ta and Hf standard solutions. Generally, CeO/Ce was at a level of 0.03–0.05, TaO/Ta at 0.001–0.003, HfO/Hf at 0.001–0.004. Because *aqua regia* incompletely digested the silicate phases, only a small fraction of Ta and Hf was released to the sample solution. After chemical separation, the monitored intensity of ^{181}Ta, ^{178}Hf and ^{198}Hg was very low (e.g., $^{181}Ta/^{197}Au < 0.001$, $^{178}Hf/^{194}Pt < 0.01$, Figure 2) and the potential oxide interference of ^{181}TaO on ^{197}Au, $^{177,178,179}Hf^{16}O$ on ^{193}Ir, ^{194}Pt and ^{195}Pt was negligible.

After cation resin separation, the sample solution was quantitatively split into three aliquots. HCl (1.25 mol l^{-1}) and/or the Au standard solution in 1.25 mol l^{-1} HCl were added to the three aliquots for the standard addition method (see step 3 in Figure 1). All aliquots were added gravimetrically. The mass fraction of Au was calculated by the standard addition method (e.g., Saxberg and Kowalski 1979).

Diluting the sample solution or splitting it into a few fractions does not affect the application of the internal standardisation method because it is based on intensity ratios of Au/Pt rather than the intensity of Au. Gold mass fractions thus can also be calculated by the IS using a fraction of the sample solution without addition of the Au standard solution (Figure 1). The mass fractions of Pt were precisely determined by isotope dilution and calculated from ratios of $^{194}Pt/^{195}Pt$. Gold mass fractions were then calculated by standardisation of ^{197}Au to ^{195}Pt signal intensities, which was modified from Fischer-Gödde *et al.* (2011). The calculation formula is:

$$Au_{sample}[ng\ g^{-1}] = (Pt_{sample}[ng\ g^{-1}]/RF) \times (^{197}Au[cps]/^{195}Pt_{corrected}[cps]) \quad (1)$$

where Au_{sample} is the Au mass fraction of the sample, Pt_{sample} is the Pt mass fraction of the sample determined by isotope dilution. $^{197}Au[cps]$ represents signal intensity (in cps) obtained for the sample solution from ICP-MS analysis after subtraction of acid background, and $^{195}Pt_{corrected}[cps]$ is the signal intensity of the sample solution corrected from the contribution of the added spike and acid background. The instrumental response factor (RF), which represents the relative intensities of $^{197}Au/^{195}Pt$, was inferred from the analysis of the external bracketing Au-Pt standard solution with known concentrations:

$$RF = (^{197}Au[cps]/Au[ng\ g^{-1}])/(^{195}Pt[cps]/Pt[ng\ g^{-1}]) \quad (2)$$

where $^{197}Au[cps]$ and $^{195}Pt[cps]$ are intensity (cps) obtained from the Au-Pt standard solution, and Au[ng g^{-1}] and Ir[ng g^{-1}] are the known concentrations of the standard solution.

For the determination of Ru-Pd mass fractions, a mixed standard solution (1 ng g^{-1} Ir, 2 ng g^{-1} Pd) in 2% HNO_3 was prepared for calibration of instrumental mass bias and measured between samples. During the measurement, $^{99,100,101,102}Ru$, $^{105,106,108,110}Pd$ and isotopes of potential interferences such as ^{90}Zr, ^{95}Mo, ^{111}Cd were monitored. Most of the Zr, Mo and Cd had been removed during the anion resin separation, and thus did not affect the results because of very low intensity ratios i.e., $^{90}Zr/^{106}Pd$ (< 0.05), $^{95}Mo/^{108}Pd$ (< 0.1) and $^{111}Cd/^{106}Pd$ (< 0.02). Meanwhile, Ru and Pd mass fractions, which were calculated from $^{99}Ru/^{101}Ru$, $^{99}Ru/^{102}Ru$ or $^{105}Pd/^{106}Pd$, $^{105}Pd/^{108}Pd$ and $^{105}Pd/^{110}Pd$, respectively, were identical (RSD < 1%), implying negligible effects from interferences. The mass fractions of Re and PGEs reported in Table 3 were calculated from isotopic ratios $^{185}Re/^{187}Re$, $^{191}Ir/^{193}Ir$, $^{194}Pt/^{195}Pt$, $^{99}Ru/^{101}Ru$ and $^{105}Pd/^{106}Pd$, respectively.

Detection limits and total procedural blanks

Detection limits and total procedural blanks are important parameters in the high-precision determination of samples with low Au and PGE mass fractions. The detection limits of the instrument for Au, Re and PGEs were calculated as three times the standard deviation of the acid background. The results indicate very low detection limits for Au (e.g., < 0.8 pg ml^{-1}) and PGEs (Table 2), similar to those obtained at the Freie Universität Berlin (Fischer-Gödde *et al.* 2011, Wang *et al.* 2013).

The low total procedural blank (TPB) is also critical for reliable determination of Au, Re and PGE mass fractions. Sample digestion by purified reverse *aqua regia* in pre-cleaned Carius tubes and chemical separation via cation resin led to very low procedural blanks (Table 2). The mixture solution of 0.5 mol l^{-1} HCl + 40% acetone was measured, and its intensity for Au (178 cps) showed no difference from 1.25 mol l^{-1} HCl (168 cps), indicating a rather low Au blank level in the acetone. The procedural blanks of Re and PGE were determined by isotope dilution, Au from internal standardisation. The procedural blanks over a period of 2 years were Au = 3 ± 3 pg (n = 25, 1s), Pt = 5 ± 3 pg, Ir = 0.4 ± 0.6 pg, Re = 2 ± 1 pg, Ru = 19

Table 2.
Instrumental detection limits and total procedural blanks (TPB) in the study

Element	Au	Pt	Ir	Re	Ru	Pd
Detection limit of ICP-MS (pg ml^{-1})	0.8	0.5	0.3	0.2	3.5	1.0
TPB (pg)	3	5	0.4	2	19	13
1*s* (pg)	3	3	0.6	1	11	9
n	25	25	24	23	12	12
Procedural detection limit (3*s* of TPB, pg)	9	9	1.8	3	33	27

± 11 pg, Pd = 13 ± 9 pg (Figure 3). Occasionally, some erratic high blanks for Ir (7 pg) and Re (9 or 12 pg) were observed. These are higher than the most values of blanks and likely reflect contamination or problems during measurements at low intensities. However, the total procedural blanks were negligible (mostly < 0.5%) for the Au, Re and Pt mass fractions of the measured RMs in most cases. All results presented in Table 3 were subtracted by the mean values of the blanks.

Results and discussion

Comparison of the results of the SA and IS methods

The chromatographic separation removed most matrix, but in a few cases, minor amounts of matrix elements such as Cr remained in the eluted Au-Re-PGEs fractions. The SA method can eliminate the effect of matrix so that accurate gold mass fraction can be obtained. In this study, we compare the results obtained by both the SA and IS methods from the same purified sample solution. The results determined by the two methods agree within a few per cent for all RMs, although these RMs show different gold mass fractions (Figure 4a). Because the standard solution does not contain matrix, the minor difference may reflect the effect of remaining matrix on the response factor RF between sample and standard solutions. The difference between the SA and IS methods defines the analytical uncertainty in this study (< 5–10%, 2*s*).

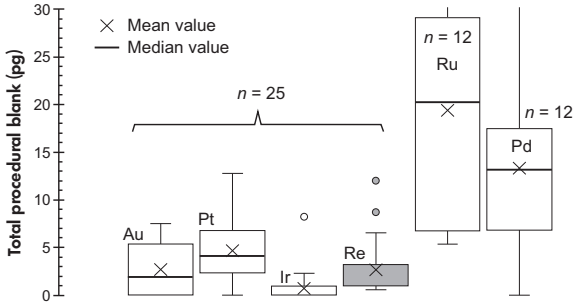

Figure 3. The total procedural blanks (TPB) of the methods used in the study.

The SA method requires the complete transfer of gold during sample treatment and column separation. The incomplete transfer of gold, if present, could result in under-determination of gold mass fractions by the SA methods (Figure 4b). The eluent curves ensured the complete recovery during chemical separation, but the loss of gold may occur during the transfer of digestion sample solution from the Carius tubes to beakers. For instance, the gold mass fractions of replicates of TDB-1 were 10–20% lower than those determined by the IS method on the same digestion solution if the Carius tubes and centrifuge tubes were not repeatedly rinsed (Figure 4b). Furthermore, using water to rinse sample containers did not yield effective recovery because gold tends to be unstable in water or dilute acids (Pitcairn *et al.* 2006). Therefore, 6 mol l^{-1} HCl was used to rinse and transfer digestion solutions in this study. This yielded systematically higher gold mass fractions by about 10–20% for the SA method, which are similar to those of the IS methods (Figure 4a). This observation highlights the importance of complete recovery during sample pretreatment for the SA method. Because repeated rinse with 6 mol l^{-1} HCl ensued complete recovery during sample transfer, the results from the standard addition thus represent the gold mass fractions of the RMs.

On the other hand, the IS method avoids the potential issue from incomplete recovery during sample transfer. The IS method only requires complete yield of both Au and Pt during column purification in our case. Incomplete recovery during sample pre-treatment, which was serious for the SA method, did not affect the results from the IS method because the intensity ratio of Au/Pt was used to calculate Au mass fractions. Diluting or splitting sample solution does not affect the mass fraction ratio of Au/Pt. The IS method thus greatly eliminates the potential problem of Au loss during sample pre-treatment, as shown by the similar results without

Table 3.
Measurement results for Au, Re, PGE contents (ng g^{-1}) in the reference materials

Sample	T (°C)	Mass (g)	Au (IS)	2*s*	Au (SA)	2*s*	Ir	2*s*	Pt	2*s*	Re	2*s*	Ru	2*s*	Pd	2*s*
TDB-1 (Diabase, CCRMP)																
1	270	1.9992	6.21	0.17	6.24	0.24	0.065	0.002	4.82	0.07	1.03	0.03	0.202	0.012	24.3	1.0
2	270	1.9991	5.85	0.23	5.97	0.28	0.068	0.002	4.89	0.16	1.07	0.02	0.223	0.012	21.8	1.8
3	270	2.0289	5.97	0.29	6.20	0.47	0.087	0.003	4.81	0.07						
4	270	2.0246	5.79	0.22	5.96	0.21	0.083	0.003	4.81	0.09						
5	250	2.0072	6.10	0.19	6.26	0.32	0.073	0.003	5.02	0.09	1.02	0.03				
6	250	2.0076	6.32	0.23	6.22	0.32	0.111	0.003	5.81	0.13	1.04	0.03				
7	250	2.0035	5.44	0.18	5.54	0.23	0.070	0.003	4.92	0.11	1.07	0.07				
8	240	1.9939	6.26	0.20	6.39	0.28	0.059	0.003	4.70	0.09	1.03	0.03				
9	240	2.0065	5.67	0.21	5.71	0.32	0.067	0.003	4.95	0.10	1.04	0.03				
10	240	2.0019	5.68	0.18	5.95	0.25	0.068	0.002	4.81	0.11	1.05	0.03				
11[a]	270	2.0111	7.01	0.27	7.30	0.36	0.095	0.003	5.70	0.16	1.01	0.03	0.244	0.012	23.4	1.3
11[b]	270	2.0111	6.90	0.15			0.094	0.002	5.74	0.06	1.04	0.02				
11[b#]	270	2.0111	6.85	0.20			0.094	0.004	5.73	0.11	1.04	0.02				
12[a]	270	2.0193	6.32	0.24	6.34	0.27	0.068	0.003	5.00	0.13	1.04	0.03	0.211	0.012	22.2	1.1
12[b]	270	2.0193	6.18	0.22			0.068	0.002	4.98	0.12	1.04	0.02				
13[*]	270	2.0025	6.36	0.19	*5.50*[*]	0.20	0.085	0.003	5.25	0.09	1.03	0.03	0.212	0.012	23.9	4.3
14[*]	270	2.0022	6.21	0.15	*5.03*[*]	0.07	0.082	0.002	5.26	0.13	1.06	0.02	0.219	0.012	22.0	0.7
15[*]	250	2.0015	6.10	0.24	*5.21*[*]	0.37	0.086	0.003	5.28	0.12	1.06	0.03	0.319	0.013	23.2	2.3
16[*]	270	2.0097	6.25	0.15	*5.71*[*]	0.22	0.082	0.002	5.17	0.13	1.05	0.02				
17	270	1.5342	5.68	0.17			0.072	0.005	5.19	0.10	1.06	0.03	0.214	0.016	23.5	0.8
18	250	2.0196	5.59	0.12			0.066	0.002	4.68	0.07	1.09	0.02	0.204	0.013	23.3	2.1
19	250	2.0030	6.50	0.18			0.062	0.002	4.68	0.08	1.05	0.02	0.234	0.013	22.9	2.3
20	240	2.0052	6.02	0.16			0.082	0.002	5.16	0.09	1.05	0.02				
Mean			6.1	0.7	6.2	0.9	0.077	0.025	5.05	0.63	1.05	0.04	0.228	0.069	23.0	1.6
Certified value			6.3	1.0			0.150		5.8	1.1			0.30		22.4	1.4
Meisel and Moser (2004a, *n* = 6)							0.075	0.020	5.01	0.36	0.794	0.048	0.179	0.010	24.30	3.79
BHVO-2 (Hawaiian basalt, USGS)																
1	270	2.0094	1.12	0.03	1.21	0.02	0.077	0.001	5.89	0.13	0.511	0.006	0.112	0.011	3.07	0.05
2	270	2.0006	1.30	0.05	1.22	0.07	0.073	0.003	5.62	0.14	0.524	0.014	0.118	0.012	2.93	0.09
3	270	1.9939	1.46	0.05	1.19	0.05	0.080	0.002	6.10	0.21	0.576	0.010	0.130	0.011	3.19	0.05
4	250	2.5010	1.13	0.04	1.22	0.07	0.063	0.002	10.67	0.28	0.532	0.025	0.150	0.010	3.67	0.15
5	250	2.0065	1.33	0.08	1.12	0.10	0.064	0.003	8.37	0.36	0.540	0.020	0.158	0.012	3.42	0.20
6[a]	270	2.5069	1.33	0.07	1.30	0.08	0.061	0.002	6.89	0.32	0.520	0.012	0.108	0.009	2.88	0.06
6[b]	270	2.5069	1.25	0.05			0.063	0.002	6.91	0.25	0.540	0.009				
7	270	2.0032	1.33	0.04			0.070	0.003	6.99	0.21	0.515	0.013	0.114	0.011	2.93	0.06
8	270	2.0007	1.19	0.04			0.061	0.002	6.14	0.14	0.537	0.015				
9	240	1.9882	1.44	0.05			0.073	0.002	7.74	0.20	0.516	0.009				
10	270	2.0560					0.069	0.003	8.12	0.27	0.536	0.014	0.108	0.011	3.07	0.05
11	270	1.9916					0.069	0.003	9.88	0.36	0.529	0.015	0.141	0.011	2.90	0.07
Mean			1.29	0.24	1.21	0.11	0.069	0.013	7.49	3.31	0.531	0.036	0.126	0.038	3.12	0.54
Constantin (2009 *n* = 4)			2.62	0.63												
Meisel and Moser (2004a)							0.058	0.029	10.10	9.90	0.543	0.045	0.129	0.111	2.94	0.08
OKUM (Komatiite, OGS)																
1	270	2.0464	0.82	0.00	0.80	0.02	0.952	0.009	11.6	0.2	0.560	0.007	4.72	0.06	12.1	0.3
2	270	2.0012	1.05	0.03	1.09	0.07	0.960	0.011	12.1	0.1	0.523	0.011	4.71	0.07	12.1	0.1
3	270	2.0230	0.76	0.03	0.84	0.08	0.988	0.011	12.0	0.3	0.541	0.019	4.79	0.07	12.0	0.2
4	270	1.9989	1.51	0.06	1.63	0.12	0.905	0.012	12.0	0.3	0.424	0.012	4.66	0.07	11.8	0.2
5	270	1.9983	1.03	0.05	1.02	0.05	0.968	0.013	12.3	0.4	0.587	0.021	4.82	0.06	12.0	0.3
6	250	2.0031	0.91	0.03	0.95	0.08	0.892	0.013	11.7	0.2	0.431	0.010	4.62	0.08	11.9	0.4
7[a]	240	1.9925	1.76	0.06	1.60	0.09	0.874	0.010	12.3	0.2	0.508	0.013				
7[b]	240	1.9925	1.67	0.05	1.90	0.10	0.883	0.012	12.4	0.2	0.515	0.011				
8	250	1.9664	0.88	0.04	0.77	0.08	0.835	0.013	11.5	0.2	0.408	0.009				
9	250	1.9985	0.86	0.04	0.69	0.06	0.843	0.012	11.6	0.2	0.494	0.011				
10	250	2.0002	1.49	0.07	1.41	0.16	1.012	0.019	12.1	0.2	0.453	0.023				
11	240	2.0043	1.24	0.05	1.29	0.10	0.815	0.012	11.6	0.2	0.512	0.014				

Table 3 (continued).
Measurement results for Au, Re, PGE contents (ng g^{-1}) in the reference materials

Sample	T (°C)	Mass (g)	Au (IS)	2*s*	Au (SA)	2*s*	Ir	2*s*	Pt	2*s*	Re	2*s*	Ru	2*s*	Pd	2*s*
12	240	2.0104	0.78	0.03	1.03	0.08	1.021	0.011	11.5	0.2	0.474	0.024				
13	270	1.9999	0.80	0.02			0.852	0.011	11.8	0.3	0.396	0.006	4.68	0.12	12.0	0.2
Mean			1.06	0.64	1.10	0.69	0.92	0.14	11.9	0.6	0.49	0.12	4.71	0.14	12.0	0.2
Certified value			1.49	0.16			0.99	0.07	11.0	0.6			4.25	0.30	11.7	0.5
Richardson and Burnham (2002, *n* = 6)			1.4	0.4			0.96	0.08	11.0	1.1			4.1	0.3	11.4	0.8
UB-N (Serpentinite, ANRT)																
1	270	2.0128	1.11	0.00	1.12	0.02	3.24	0.04	7.33	0.06	0.174	0.005	6.55	0.15	6.04	0.08
2	250	2.0090	1.10	0.05	1.15	0.06	3.11	0.24	7.18	0.26	0.201	0.007	6.32	0.33	6.14	0.40
3	250	2.0069	1.20	0.08	1.29	0.16	3.14	0.14	6.96	0.34	0.203	0.007	6.21	0.35	5.99	0.45
4	250	2.0000	1.30	0.08	1.16	0.10	3.43	0.16	6.86	0.29	0.176	0.006	6.97	0.44	5.93	0.38
5	250	2.0006	1.18	0.06	1.22	0.08	3.83	0.20	7.68	0.25	0.186	0.005	6.96	0.37	6.44	0.40
Mean			1.18	0.16	1.19	0.13	3.35	0.59	7.20	0.65	0.188	0.027	6.60	0.71	6.11	0.40
Fischer-Gödde *et al.* (2011, *n* =11)			1.49	0.52			3.16	0.44	7.31	0.94	0.188	0.048	6.43	0.76	5.85	0.40
WGB-1 (Gabbro, CCRMP)																
1	250	2.01653	1.40	0.05	1.42	0.09	0.194	0.005	4.81	0.11	1.18	0.04	0.169	0.012	17.1	1.7
2	240	2.02780	1.90	0.08	1.79	0.10	0.219	0.004	11.22	0.37	1.25	0.03				
3	270	2.03000	2.29	0.09	2.43	0.09	0.292	0.022	4.00	0.10						
4	250	1.99530	1.53	0.05			0.177	0.003	4.89	0.09	1.18	0.04				
5	240	2.00114	2.29	0.06			0.239	0.004	5.35	0.11	1.21	0.02				
6	250	1.99681	1.77	0.06			0.222	0.003	5.10	0.10	1.16	0.02				
7	240	2.00560	1.57	0.08			0.182	0.004	11.39	0.52	1.19	0.02				
8	240	2.00708	1.59	0.06			0.207	0.004	4.75	0.14	1.20	0.02				
9	270	2.07933					0.202	0.004	5.51	0.16	1.18	0.02	0.214	0.012	10.8	0.5
Mean			1.79	0.69	1.88	1.02	0.21	0.07	6.3	5.7	1.20	0.05	0.19	0.06	14.0	8.8
Certified value			2.9	1.1			0.33		6.1				0.3		13.9	2.1
Richardson & Burnham (2002, *n* = 9)			2.4	1.3			0.20	0.04	4.7	1.0			0.22	0.1	13.0	2.3
Maier *et al.* (2003, *n* = 5)			1.7	1.2			0.21	0.08	3.8	2.2					11	3.8
GPt-2 (sediment, IGGE)																
1	240	1.9805	10.22	0.35	9.83	0.47	0.034	0.002	1.84	0.03	0.580	0.012				
2	250	2.0082	10.31	0.31	8.83	0.32	0.048	0.002	1.85	0.03	0.596	0.012				
3	250	2.0093	10.39	0.38	9.17	0.39	0.048	0.002	1.83	0.03	0.601	0.014				
4	250	2.0115	10.66	0.35	9.42	0.35	0.050	0.002	1.91	0.03	0.607	0.013				
5	HF+AR	2.0008	9.70													
6	HF+AR	2.0082	9.69													
Mean	AR		10.40	0.38	9.31	0.85	0.045	0.015	1.86	0.07	0.596	0.023				
Mean	HF+AR		9.69	0.01												
Yan *et al.* (1998)			10	2			0.05		1.6	0.3						
Li *et al.* (2012)							0.054		1.205							
BCR-2 (Basalt, USGS)																
1	250	2.0154	0.83	0.04	0.79	0.06	0.008	0.002	1.97	0.03	12.1	0.2				
2	250	2.0032	0.82	0.05	0.72	0.05	0.006	0.002	0.76	0.01	12.1	0.2				
3	240	0.5207	0.87	0.09			0.007	0.006	4.83	0.09	11.8	0.5				
Mean	*n* = 3		0.84	0.05	0.75	0.11	0.007	0.002	2.52	4.18	12.0	0.3				
Constantin (2009)			1.32	0.19												
Chu *et al.* (2015)	*n* = 5						0.0055	0.0004	0.85	0.80	11.7	0.2				
JB-2 (Basalt, GSJ)																
1	250	1.5038	4.78	0.15	4.56	0.19	0.012	0.002	3.32	0.05	0.415	0.009				
2	250	1.4947	4.73	0.15	4.66	0.19	0.009	0.002	2.85	0.05	0.418	0.010				
Mean			4.76	0.07	4.61	0.13	0.011	0.005	3.08	0.66	0.416	0.004				
Constantin (2009)			6.33	0.7												
Imai *et al.* (1995, *n* = 10)			5.64	2.68					4		0.38					

The digestion was carried out in 4 days for RMs. a/b means re-measurement of the same digestion solution with independent chemical separation; b# means repeated measurement of the purified sample solution. AR, digested by *aqua regia*; HF + AR, digested by *aqua regia* after HF desilicification; IS, internal standardisation; SA, standard addition. Italic values with * mean no repeated rinse of the Carius tubes and centrifuge tubes during sample transfer.

and with a 6 mol l^{-1} HCl rinse (Figure 4b). Provided that the complete recovery of Au and Pt during column separation is obtained (Figure 2), the IS method can provide precise data for Au. The results from IS match well with those from standard addition (within 5–10%, Figure 4a), further indicating negligible fractionation of Au and Pt during sample treatment. However, the IS method does not require quantitative record after sample digestion and the procedure can be greatly simplified relative to the SA method. The IS method can also achieve better precision because the Au/Pt intensity ratio is less affected by the intensity drift during longer-term measurements as required for the SA method. Internal standardisation is thus is a simple and robust routine method for determination of Au with uncertainties of a few per cent. To check the repeatability of the methods, replicate analyses of the remaining digestion solutions of different RMs were conducted via repeated column purification and measurement by the IS method (n = 4, Table 3). The obtained results were identical within 5% (2s, Table 3), which is similar to or lower than the "external" analytical uncertainty defined by the difference between the SA and IS methods (< 5–10%, 2s).

Sample heterogeneity

Gold heterogeneity: Sample heterogeneity is critical for accurate Au and PGEs mass fraction determinations, especially for samples with low contents. Based on the results from the same methods, sample heterogeneity can be evaluated by replicate analyses of the RMs. The eight geological RMs were repeatedly analysed at the 2 g test portion level (Table 3, Figures 4–6).

Twenty replicates of TDB-1 were measured in this study, and the results range from 5.44 to 6.50 ng g^{-1} with one higher value of 7.01 ± 0.27 ng g^{-1}. Gold and/or PGE mass fractions of TDB-1 have been widely determined by different methods in different laboratories (Richardson and Burnham 2002, Savard *et al.* 2010, Maier *et al.* 2012, Goderis *et al.* 2013, Pitcairn *et al.* 2015). The previous results for Au display a larger range of 3.9–7.1 ng g^{-1} with a certified value of 6.3 ± 1.0 ng g^{-1} (2s, Figure 6a, Table S1). Given a few per cent analytical uncertainty in this study, the resolvable difference of the Au mass fractions should reflect to a certain extent the sample heterogeneity at the 2 g test portion level (Figure 4). However, the replicates of TDB-1 display a mean value of 6.1 ± 0.7 ng g^{-1} (2s, n = 20, Figures 5 and 6a), similar to the certified value 6.3 ± 1.0 ng g^{-1} (2s). Multiple analyses by NiS-FA and HF-acid digestion have also provided similar results, such as 6.2 ± 0.6 ng g^{-1} (2s, n = 20) (Richardson and Burnham 2002) and 6.3 ± 1.7 ng g^{-1} (2s, n = 21) (Pitcairn *et al.* 2015). These consistent results from different analytical methods indicate that TDB-1 is a reliable RMs for Au with a 10–20% uncertainty.

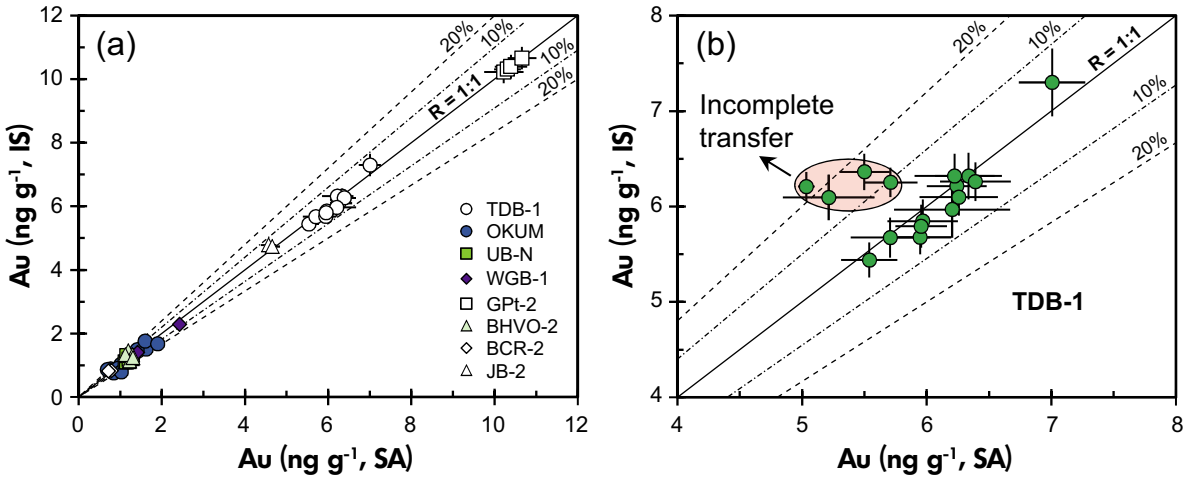

Figure 4. (a) Comparison of the results obtained by internal standardisation (IS) and standard addition (SA) methods on the same solutions of the RMs. The values are consistent within a few per cent uncertainties. (b) The results for TDB-1 show that without rinsing the Carius tubes and centrifuge tubes repeatedly with 6 mol l^{-1} HCl (steps 1 and 2 in Figure 1), the recovery of gold was significantly lower and resulted in 10–20% lower mass fractions for the standard addition method relative to the internal standardisation. This is because a minor fraction of gold remained in the residue. Gold could be completely extracted by repeated rinsing with 6 mol l^{-1} HCl, but not water. Note that a certain extent of sample heterogeneity is present for TDB-1 (b). [Colour figure can be viewed at wile yonlinelibrary.com]

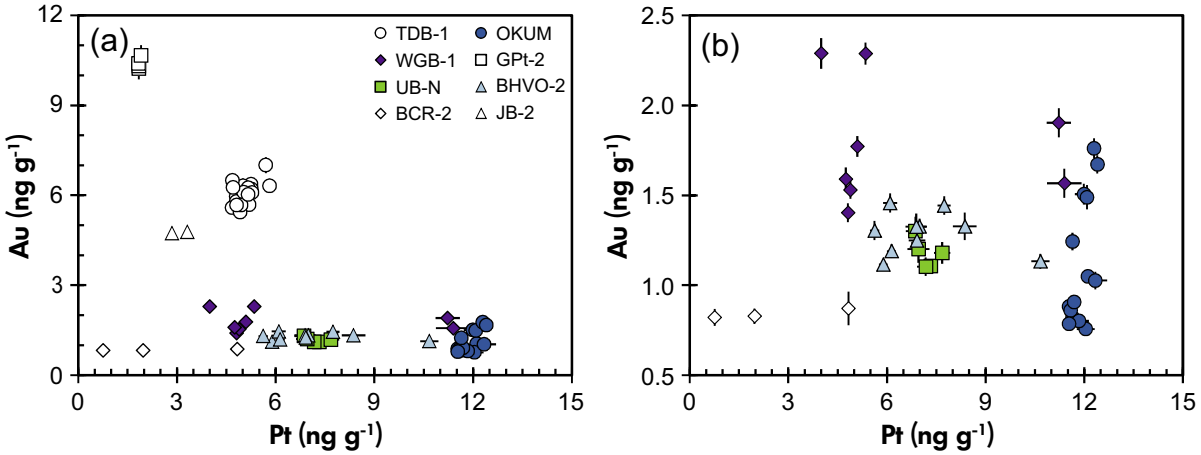

Figure 5. Different extents of sample heterogeneity for Au and PGEs (shown by Pt) in different RMs. GPt-2, TDB-1 and UB-N seem to show homogeneous Au and Pt mass fractions. BHVO-2 and BCR-2 show variable Pt mass fractions but relatively homogeneous Au mass fractions, whereas there were homogeneous Pt but variable Au mass fractions for OKUM. WGB-1 shows sample heterogeneity for both Au and PGEs. (b) is enlarged from (a) to show the RMs with low Au mass fractions. [Colour figure can be viewed at wileyonlinelibrary.com]

The basalts and sediment also seem to be relatively homogeneous for Au mass fractions (Figures 5 and 6b). Gold mass fractions of BHVO-2 ranged from 1.11 to 1.46 ng g^{-1} with a mean value of 1.29 ± 0.24 ng g^{-1} (2*s*, *n* = 9). The number of replicates for BCR-2 and JB-2 is smaller, but the data show that the mass fractions for these samples reproduce well within 5% (BCR-2: 0.82, 0.83, 0.87 ng g^{-1}; JB-2: 4.73 and 4.78 ng g^{-1}). The sediment GPt-2 has the highest Au mass fraction among the analysed RMs in this study, and it is rather homogeneous with a mean value of 10.4 ± 0.4 ng g^{-1} obtained from the IS method (2*s*, *n* = 4). This result is indistinguishable from the certified value of 10 ± 2 ng g^{-1} (2*s*; Yan *et al.* 1998).

The RMs WGB-1 and OKUM show resolvable extents of sample heterogeneity (Table 3). For WGB-1, Au determined in this study ranged from 1.40 to 2.29 ng g^{-1} (Figure 5) with a mean value of 1.79 ± 0.69 ng g^{-1} (2*s*, *n* = 8). Previous studies show a larger range (0.2 to 3.5 ng g^{-1}, Figure 6c). The certified value of 2.9 ± 1.1 ng g^{-1} also displays a significant uncertainty (38%, 2RSD). In this study, a range of 0.76 to 1.76 ng g^{-1} Au was obtained for OKUM (Figure 5 and 6c), with a mean value of 1.06 ± 0.64 ng g^{-1} (2*s*, *n* = 13). Repeated measurement of the same digestion solution of OKUM showed precise data with 5% uncertainty (2*s*, Table 3), indicating that the observed large variation of Au mass fractions for OKUM does not result from the analysis but reflects sample heterogeneity. Previous studies on OKUM also reported a large uncertainty of 30–80% 2 RSD, such as 1.4 ± 0.4 ng g^{-1} (2*s*, *n* = 6; Richardson and Burnham 2002) and 1.41 ± 1.14 ng g^{-1} (2*s*) (Savard *et al.* 2010). Based on the data of this study, the gold mass fraction of UB-N ranges from 1.10 to 1.30 ng g^{-1} (*n* = 5) and is homogeneous (Figures 5 and 6d). However, the values determined also by the IS method (Fischer-Gödde *et al.* 2011) displayed a certain range from 0.99 to 1.75 ng g^{-1} with a mean value of 1.49 ± 0.52 ng g^{-1} (2*s*, *n* = 11). Other previously reported values seem to show higher values (Figure 6d). We cannot rule out the possible effect of analytical uncertainty of previous studies, but these results indicate that sample heterogeneity is obvious for WGB-1, OKUM and probably UB-N.

Consequently, the effect of sample heterogeneity on gold mass fractions is variable for different RMs. Combining previous values and and those from this study, TDB-1, GPt-2, BHVO-2 and probably other basaltic samples are homogeneous within a typical uncertainty of 10–20% (2*s*) and therefore can be considered as suitable RMs for gold determination.

Different extents of heterogeneity for Au and PGEs: The reproducibility of PGE analysis is mainly compromised by sample heterogeneity (the 'nugget effect'). In most rocks, the PGEs and Re are strongly distributed in sulfides, selenides, tellurides, and Ru, Ir, Pt may form micro-PGM or alloys leading to sample heterogeneity (e.g., Luguet *et al.* 2004, Lorand *et al.* 2013, Lorand and Luguet 2016, Baumgartner *et al.* 2017). In this study, Au mass fractions were calculated using ^{195}Pt as internal standard. Therefore, it is necessary to evaluate the effect of PGE heterogeneity, especially for Pt, because it is used for the calculation of gold mass fractions.

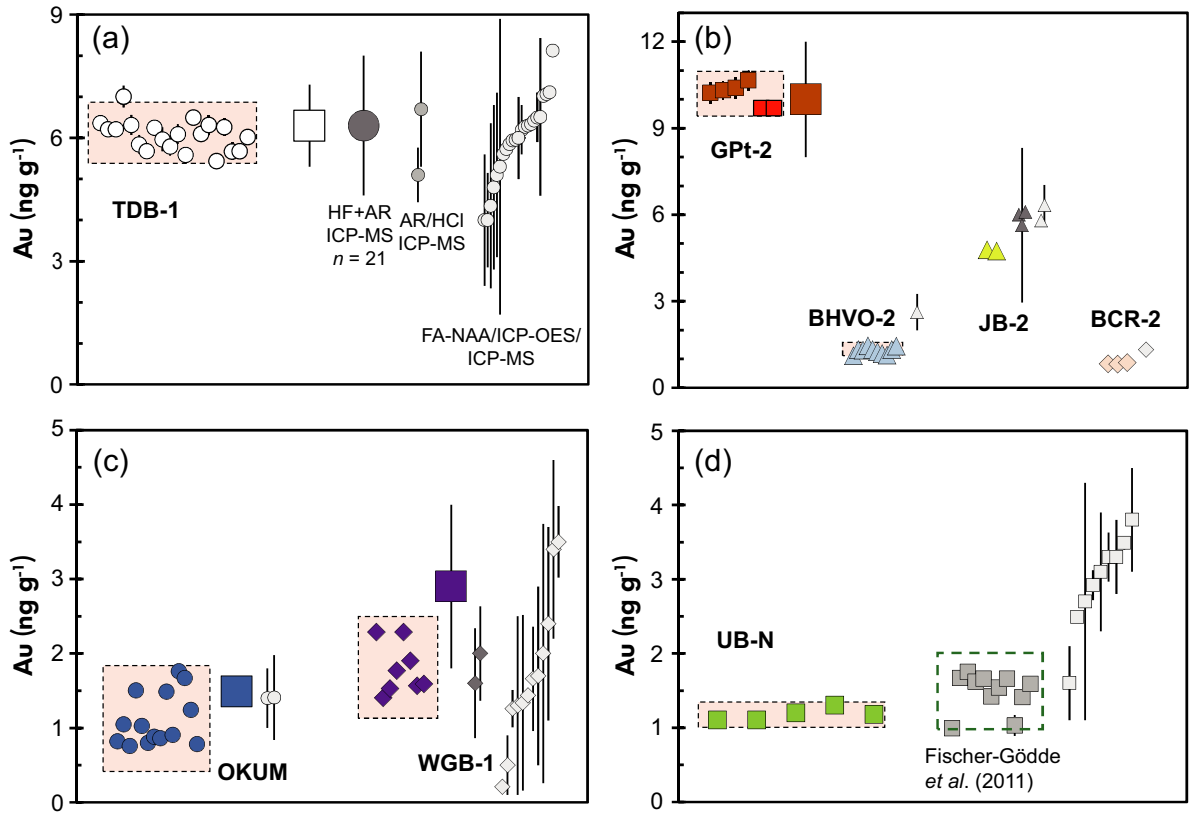

Figure 6. Gold mass fractions of TDB-1 (a), GPt-2, BHVO-2, JB-2 and BCR-2 (b), OKUM and WGB-1 (c), UB-N (d) obtained by internal standardisation (colour symbols), and comparison with literature data (grey symbols, but dark grey symbols for JB-2 and WGB-1 are compiled from the literature) and if any, certified values (large coloured squares). The light red rectangular area with dashed frame is the mean value with 2*s* of different RMs. TDB-1 displays a mean value indistinguishable with the certified value and that from HF-*aqua regia* digestion (*n* = 21; Pitcairn *et al.* 2015). The values of GPt-2 obtained from the internal standardisation (orange squares) and the HF-aqua digestion-GF-AAS (red squares) are similar and also consistent with the certified value (b). The literature values of UB-N and WGB-1 show large ranges (Table S1). Other RMs have not been often measured for gold, and the literature data are limited. See the Table S1 for the data sources compiled from GeoReM database.[Colour figure can be viewed at wileyonlinelibrary.com]

OKUM shows homogeneous PGE mass fractions (Richardson and Burnham 2002, Meisel *et al.* 2013), and our results for Re and PGEs at the 2 g test portion level are consistent with this conclusion (Figure 7 and Table S1). However, previous studies reported Au mass fractions of 1.4 ± 0.4 ng g^{-1} (Richardson and Burnham 2002) and 1.41 ± 1.14 ng g^{-1} (Savard *et al.* 2010). Our gold values vary from 0.8 to 1.8 ng g^{-1} (*n* = 13), indicating a certain degree of sample heterogeneity for gold mass fractions of OKUM. The Au and PGE mass fractions in this study were obtained from the same sample aliquots, confirming that sample heterogeneity is significant for Au but limited for PGEs.

Sample heterogeneity has been clearly demonstrated for PGEs in BHVO-2 (Meisel and Moser 2004a). Our measurement results also display variable values for Pt and other PGEs in BHVO-2 (Figure 5). In contrast, the gold mass fraction is very homogeneous with a mean value of 1.29 ± 0.24 ng g^{-1} (2*s*, *n* = 9). A similar observation also applies to BCR-2, whose Au mass fraction is homogenous whereas Pt is not (Figure 5). It should be noted that the gold mass fractions based on internal standardisation to Pt are similar and are also consistent with values from standard addition (Figure 4). The results suggest the validity of the IS method for Au, provided that the Pt mass fraction is precisely determined even if Pt is not homogeneous in the samples.

Gold and platinum-group elements are strongly chalcophile, and the nugget effect also often occurs for both Au and PGEs. For example, WGB-1 shows strong sample heterogeneity for both of Au and PGE mass fractions (Figure 5). Other samples such as OKUM show homogeneous PGE mass fractions but not for Au, whereas BHVO-2 and BCR-2 show homogeneous Au mass fractions but not for PGEs. Evidently, Au and PGEs display different extents of sample heterogeneity in different materials. The specific reasons for this are still not fully understood, but could be related to different behaviours or hosts for PGEs and Au. WGB-1 is a gabbro where sulfide minerals may be dominant. Therefore, its Au and PGEs have obvious heterogeneity at the 2-g test portion level, provided accessory sulfides are not homogeneously distributed. Basalts such as BHVO-2 display heterogeneity in PGEs but to a lesser extent for Au (This study, Meisel and Moser 2004a), and show homogeneous S, Se, Cu and Ag mass fractions even at the 0.2-g level (Wang *et al.* 2015). Such differences probably reflect their contrasting partition coefficients (*D*) between sulfide (alloy) and silicate melt, wherein a smaller *D* value results in greater homogeneity. Future work to obtain mass fractions of different chalcophile elements from the same sample portion could test this possibility. Based on available data and the extent of sample homogeneity (Figure 5), GPt-2 (sediment) and TDB-1 (diabase) seem to be the optimum RMs for both Au and PGEs.

The validity of *aqua regia* digestion for gold determination

The mixture of concentrated HCl and HNO_3 (*aqua regia* or reverse *aqua regia*) is widely used to digest geological silicate samples in high-pressure asher or Carius tubes for determination of PGE and Re mass fractions (e.g., Shinotsuka and Suzuki 2007, Fischer-Gödde *et al.* 2011,

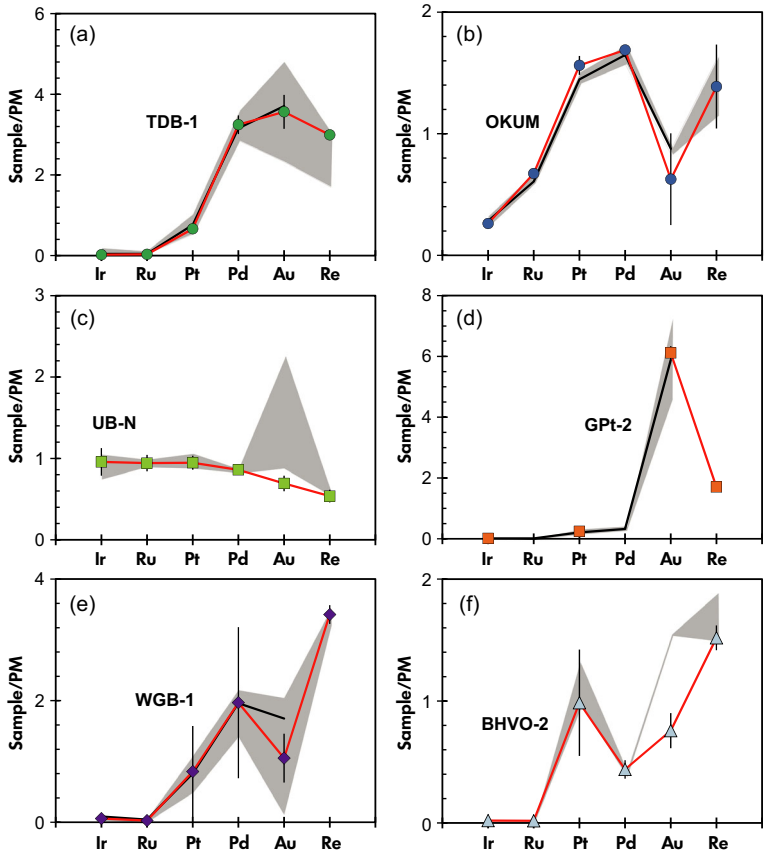

Figure 7. Primitive mantle (PM) normalised PGE-Au-Re patterns for TDB-1 (a), OKUM (b), UB-N (c), GPt-2 (d), WGB-1 (e), BHVO-2 (f). The mass fractions of PM are from Becker *et al.* (2006). The mean values of RMs in this study (red lines with various symbols) are compared with the certified values (black lines in a, b, d and e) and the range of previously published values (shaded areas). For GPt-2, the shaded area is the range of values published in Yan *et al.* (1998) and Li *et al.* (2012). See Table S1 for the data sources compiled from the GeoReM database. [Colour figure can be viewed at wileyonlinelibrary.com]

Ishikawa *et al.* 2014, Li *et al.* 2014, 2015a, Puchtel *et al.* 2014, Chu *et al.* 2015, Chen *et al.* 2016, Liu *et al.* 2016, Meisel and Horan 2016). We digested samples using reverse *aqua regia* in Carius tubes, and the results for Au, Re and PGEs are listed in Table 3 and Table S1. The mean values are shown in Figure 7 and are compared with certified and previously reported values. It has been well shown that PGE mass fractions in OKUM, TDB-1, UB-N and GPt-2 are homogenous, and our results are consistent with this (Figure 7).

However, *aqua regia* digestion only partially dissolves silicates and may lead to under-determination of Re by 10–20% (e.g., Dale *et al.* 2012, Ishikawa *et al.* 2014, Li *et al.* 2015b). The results would imply that sample digestion involving HF is necessary for accurate determination of Re. Similarly, *aqua regia* digestion in Carius tubes used in this study potentially results in incomplete extraction of gold from samples (Hall *et al.* 1989). Therefore, it is necessary to evaluate the validity of *aqua regia* digestion for gold determination in this study.

The incomplete extraction by *aqua regia* digestion may result from the experimental conditions, such as for Re (Ishikawa *et al.* 2014). Prolonged digestion (> 72 h) by *aqua regia* at high temperature (240 °C) can achieve Re mass fractions similar to those obtained by HF desilicification for TDB-1 (Ishikawa *et al.* 2014). It has also been suggested that prolonged digestion at high temperature with a low volume ratio of sample to digestion acid might overcome the issue for gold (Hall *et al.* 1989). In this study, the RMs were digested by reverse *aqua regia* in Carius tubes at 240–270 °C for 4 days. The results from different digestion temperatures were indistinguishable within uncertainty (Table 3), indicating that *aqua regia* (Carius tube) digestion at ≥ 240 °C for a 4-day duration is enough for efficient extraction of Au-Re-PGE with 2 g test portions (Figure 7).

The Au and Re mass fractions of TDB-1 have been certified, and the results obtained from HF-acid digestion are also available. Here, we compare our results for TDB-1 with these values (Figure 7 and Table S1). The Re mass fractions of TDB-1 replicates were very stable at 1.05 ± 0.04 ng g^{-1} (2*s*, *n* = 18) and identical with those obtained from HF-acid digestions (Dale *et al.* 2012, Ishikawa *et al.* 2014). Similarly, the replicates of TDB-1 display a mean value of 6.1 ± 0.7 ng g^{-1} gold (2*s*, *n* = 20), indistinguishable from the certified 6.3 ± 1.0 ng g^{-1} (2*s*) and the values obtained from nickel sulfide fire assay digestion (6.2 ± 0.6 ng g^{-1}, 2*s*, *n* = 20; Richardson and Burnham 2002). More importantly, our results are also consistent with those by HF-acid digestion (6.3 ± 1.7 ng g^{-1}, 2*s*, *n* = 21; Pitcairn *et al.* 2015). These results indicate that the experimental conditions in this study led to accurate values for Au, Re and PGE mass fractions, even if *aqua regia* did not completely digest the silicates.

The Au mass fraction of sediment GPt-2 (10.4 ± 0.4 ng g^{-1}, 2*s*, *n* = 4) determined using *aqua regia* digestion is also identical with the certified value (10 ± 2 ng g^{-1}, 2*s*), which was obtained by different analytical methods (Yan *et al.* 1998). Additionally, two Au values were obtained from HF-*aqua regia* digestion and determination by GF-AAS at Institute of Geology and Geophysics, China Academy of Sciences (Figure 6b). These independent results further confirm the validity of the reverse *aqua regia* digestion. TDB-1 is a diabase and GPt-2 is a sediment. Thus, even though using *aqua regia* for sample digestion will not achieve complete dissolution for these samples, the results indicate that reliable gold mass fractions were obtained. Therefore, sample digestion by reverse *aqua regia* in Carius tubes at ≥ 240 °C for 4 days is valid for determination of the mass fractions of Au, Re and PGEs.

We also attempted to digest TDB-1, BHVO-2 and BCR-2 by HF-*aqua regia* digestion (Table S2). The digestion solutions were also purified using the chemical separation and measured as the routine procedure. HF-*aqua regia* digestion decomposed silicate phases and thus led to very high Ta, Hf and other potential interferences in the digestion solution. After chromatographic separation, high intensities of Ta and particularly Hf still existed and caused serious oxide interferences on Au, Pt and Ir, respectively (Table S2). In this case, the Au, Pt and Ir mass fractions could not be accurately determined. For instance, the oxide interferences would lead to the deviation of Pt and Ir mass fractions from the certified values at variable degrees for different RMs. It would cause inaccurate Au mass fractions based on the internal standardisation method (Table S2). If the standard addition method was used, the high intensity of ^{181}Ta would overestimate gold mass fractions by 5–15% even after the correction of the effects of oxide interferences $^{181}Ta^{16}O$ on ^{197}Au (Table S2). The attempt suggests that the high Ta and Hf mass fractions must be removed for accurate determination of gold and PGE mass fractions if HF-acid digestion is used. In contrast, *aqua regia* digestion does not lead to such potential problems (Figure 2), which is clearly preferable for high-precision determination of gold

Conclusions

This study has described a high-precision and robust method, internal standardisation of gold to platinum that was precisely determined by isotope dilution, for determining gold with a very low mass fraction in natural rocks

(> 0.01 ng g^{-1}). Sample digestion in Carius tubes by reverse *aqua regia* and high-sensitivity ICP-MS led to very low total procedural blanks (3 ± 3 pg) and low detection limits (< 0.8 pg ml^{-1}). Chromatographic separation by cation resin removed most matrix. It also achieved complete recovery (> 99%) of gold and PGEs, which is a prerequisite for the internal standardisation method. The results obtained from the internal standardisation and standard addition methods on the same sample solution are consistent within a few per cent analytical uncertainty (< 5–10%, 2*s*). However, internal standardisation is much simpler, because it does not necessarily require the complete recovery of gold during sample pre-treatment except during chromatographic separation. Therefore, we recommend the internal standardisation method as a simple and robust tool to achieve high-quality measurement of gold mass fractions.

The sample digestion with reverse *aqua regia* in Carius tubes at ≥ 240 °C for 4 days yielded Au and Re mass fractions for TDB-1 and GPt-2 that are indistinguishable from certified values and those obtained by HF-*aqua regia* digestion. Reverse *aqua regia* is thus an efficient reagent for gold extraction during high-temperature digestion. Because *aqua regia* digestion only releases limited amounts of Ta and Hf, which could generate significant oxide interference on gold, it is preferable for gold determination by solution-based ICP-MS analysis. Sample heterogeneity is a key factor for variable gold mass fractions observed for some RMs at the 2 g test portion level, such as WGB-1 and OKUM. In contrast, TDB-1, GPt-2 and BHVO-2 exhibit homogeneous Au mass fractions within 10–20% (2*s*). Additionally, gold and PGEs display different extents of sample heterogeneity in different RMs. The results of this study show that TDB-1, GPt-2 and probably the basaltic RMs (e.g., BHVO-2, JB-2, BCR-2), owing to their homogeneous Au mass fractions, are excellent RMs for gold determinations and should be used for inter-laboratory comparison.

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Supporting information

The following supporting information may be found in the online version of this article:

Table S1. Comparison of the results of gold, Re, PGE contents (ng g^{-1}) in RMs from this study with literature data.

Table S2. The effects of oxide interferences on Au, Pt and Ir contents after HF-*aqua regia* digestion and chromatographic separation using cation resin.

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