

Analysis of platinum group elements and gold in geological materials using NiS fire assay and Te coprecipitation; the NiS dissolution step revisited

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Abstract

The NiS fire assay–Te coprecipitation separation procedure for inductively coupled plasma mass spectrometry (ICP-MS) analyses of platinum-group elements (PGE) in silicate rocks has been revisited with the aim of reducing volatile PGE losses (Os, Pd). The NiS bead was dissolved in 20.2% HCl, in an open system allowing H₂S to escape without loss of HCl. Yield, accuracy and reproducibility were tested by replicate analyses of a CANMET reference material (UMT1), a mantle lherzolite (FON B 93), prepared as in-house standard, and abyssal harzburgites, analysed as unknowns. The yields as estimated from UMT1 range from 97% (Ir) to 93–94% (Rh, Pt, Pd) and 91% (Au). The Os value (7.13 ± 1.4 ppb) is equal within 1 sigma level, to the CANMET provisional value. The mean Os content of FON B 93 (3.42 ppb) fits the Os concentration inferred for the terrestrial mantle very well, as does the Os/Ir ratio (1.053 vs. 1.063) while Pd concentrations are increased by 18% compared to previous analyses after open-beaker dissolution steps. The abyssal harzburgites also yield consistent Os contents (3.28 ± 0.19 ppb) and a perfectly chondritic Os/Ir ratio (1.07). Thus modified, the NiS fire-assay method allows Os to be nearly completely recovered, while greatly reducing the volatility of Pd. Moreover, the PGE analyses of coarse-grained rocks are highly reproducible (1% for Rh, Pt, Pd; 4% for Ir, 5% for Ru, 6% for Au), if performed from large-sized powder aliquots. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Platinum-group elements (PGE; Os, Ir, Ru, Rh, Pt, Pd) and gold, a coherent group of highly siderophile elements, are powerful tools for understanding several fundamental aspects of the origin and evolution of the

Earth including core-segregation, late-accretion history and core–mantle exchange (Pattou et al., 1996; Snow and Schmidt, 1998; Brandon et al., 1998). Despite their very low concentrations, PGE are excellent tracers of petrogenetic processes such as adiabatic partial melting, melt–rock reactions and melt entrapment features that occur in the Earth's mantle (Lorand et al., 1993, 1999; Rehkämper et al., 1999; Luguët et al., 2001). The improvements of multi-elementary analytical techniques such as inductively coupled plasma mass spectrometry (ICP-MS) have made the

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determination of PGE concentrations possible down to ppt levels. However, PGE analyses of solid samples require a dissolution of the samples and a separation procedure to reduce as much as possible isobaric interferences with major and minor elements during ICP-MS analyses.

Various procedures for PGE analyses have been published over the past 10 years. They can be grouped into three different categories: (a) NiS fire assay coupled with a Te coprecipitation of the PGE and Au (e.g. Jackson et al., 1990; Sun et al., 1993; Oguri et al., 1999) and its variants using direct in situ laser ablation analysis of the NiS bead (Jarvis et al., 1995); (b) the fusion of powdered samples with oxidised fluxes (Na_2O_2) after a preliminary acid attack, separation of silica and Te coprecipitation (Enzweiler and Potts, 1995) with several variants using Se in addition to Te (e.g. Gueddari et al., 1996) or a microwave digestion step (Jarvis et al., 1997); (c) acid dissolution (aqua regia) in sealed tubes (Carius tubes) and separation of the PGE by anion exchange columns (Rehkämper et al., 1998) with variants including a solvent extraction step for separating Os from the PGE (Pearson and Woodland, 2000). Strengths and weaknesses of each method have been thoroughly discussed in several papers (Enzweiler and Potts, 1995; McDonald, 1998; Pearson and Woodland, 2000) and will not be addressed in detail in the present paper. Methods b and c have in common very low blank levels which make the determination of picograms/gram PGE in basalts possible. Conversely, alkali fusion methods currently dissolve 1 g of sample and the Carius tube digestion techniques 1–5 g (Rehkämper et al., 1998). Small-sized powder aliquots may decrease external reproducibility, especially for coarse-grained rocks where PGE are concentrated into discrete microphases (Hall and Pelchat, 1994; McDonald, 1998; Pearson and Woodland, 2000).

The NiS fire assay separation procedure for ICP-MS analyses also has its own limitations that may include (1) high blanks values, which can sometimes reach levels of hundreds of picograms/gram for several elements (Ru, Pt, Pd) and Au (c.f. Pattou et al., 1996; Rehkämper and Halliday, 1997); (2) Os losses as OsO_4 and (3) volatility of some PGE (e.g. Pd) as chlorides or Cl-bearing complexes during the dissolution of the NiS bead into HCl; (4) poor recovery (<90%) of some elements, indicating insufficient collection into the

NiS bead and/or incomplete separation by the Te coprecipitation. However, the NiS fire assay has as main advantage to allow a very efficient chemical decomposition of silicates and chromite from large-sized powder samples (usually 15–20 g) as well as dissolution of all PGE minerals (Tredoux et al., 1989). Such large powder aliquots considerably improve external reproducibility in reducing the nugget effect.

Since the Jackson et al. (1990) original design, attempts to improve the NiS fire assay–Te coprecipitation method include the use of NiS microbeads (1 vs. 7 g) to reduce reagent blanks (Oguri et al., 1999) and dissolution of the bead in Savillex[®] closed beakers to prevent losses of volatile PGE, coupled with centrifugation of the Te precipitate for a more efficient recovery (Sun et al., 1993). Although improving the recovery of Os compared to the Jackson et al. open-beaker dissolution technique, the Sun et al. (1993) closed-beaker technique suffers from several drawbacks: it often yields incomplete dissolution of the NiS bead and, in some cases, H_2S is not efficiently separated from HCl, which may decrease the amount of the Te precipitate formed during the Te-coprecipitation step. Also separation of the Te precipitate by centrifugation, as recommended by Sun et al. (1993), is often made difficult due to Te particles adhering inside Savillex[®] beakers. Ravizza and Pyle (1997) developed a method combining a chemical separation into NiS microbeads and the very precise isotope-dilution technique (ID) for analysis. ID has the advantage that once equilibration of the tracer and the sample has occurred, subsequent PGE losses have no effect on the calculated concentrations. Furthermore, this technique allows very precise concentration determinations. On the other hand, tracer-sample equilibration can sometimes be incomplete, for example, during the formation of the NiS bead in the NiS procedure. In addition, mono-isotopic elements (Rh, Au) cannot be determined by ID. More recently, Oguri et al. (1999) developed a double fusion technique that generates 1 g NiS beads (under reducing conditions) and coupled this with a double coprecipitation stage to improve recoveries. The reducing conditions are maintained in the oven by introducing two carbon crucibles along with the sample to be fire assayed. While certainly improving the collection for some PGE (Pt, Au), this method multiplies the handling steps, thus increasing the potential for contamination. Moreover, it does not

allow Os to be completely recovered as the NiS bead is dissolved in an open beaker. Here we present a semi-open NiS dissolution system that prevents volatile PGE losses. Thus modified, the NiS fire assay–Te coprecipitation method allows all the PGE (Os included) and Au to be recovered with good yields from silicate rocks down to concentration levels of a few tens of picograms/gram, while generating acceptable blank levels for a large variety of mafic and ultramafic rocks.

2. Experimental

2.1. Sample preparation

As shown by Pearson and Woodland (2000), external reproducibility of PGE analyses in geological materials critically depends on both sample size and powder grain size. Thus, all our analyses were performed on 15 g powder aliquots, ground to $< 160 \mu\text{m}$ in an agate mortar periodically cleaned from contaminations by powdering pure quartz.

2.2. NiS fire assay

The NiS beads were prepared according to a slightly modified version of the Jackson et al. (1990) method, that is, 20 g di-lithium tetraborate, 10 g sodium carbonate, 5 g Ni, 3 g SiO_2 and 2.5 g S. Reagent grades and suppliers are listed in Table 1. SiO_2 was increased to 8 g for procedural blanks. Di-lithium tetraborate was preferred to borax, because of its greater smelting properties. The amount of S was lowered to 2.5 g (instead of 3 g) to avoid formation of NiS_2 . Nickel disulfide is poorly soluble in hot hydrochloric acid (Pascal, 1963) while it is easily soluble in aqua regia. If present before the Te coprecipitation stage, NiS_2 will be filtered off along with Te precipitate. Once dissolved by aqua regia and transferred into ICP-torch, it will produce polyatomic $^{64}\text{Ni};^{37}\text{Cl}^+$ and $^{61}\text{Ni};^{40}\text{Ar}^+$ ions that strongly interfere on ^{101}Ru counts (Jackson et al., 1990). By decreasing the S/Ni ratio to 0.5, the NiS button is composed of $\text{Ni}_{1-x}\text{S}_x$ (X-ray data and electron microprobe analyses; Pattou, 1995) and the high-temperature polymorph of heazlewoodite ($\text{Ni}_{3 \pm x}\text{S}_2$; Craig and Scott, 1976) both theoretically soluble in hot hydrochloric acid (Pascal, 1963). This

change in the S/Ni ratio considerably reduces the formation of insoluble nickel sulfides but does not alter the efficiency of PGE collection into the bead (c.f. Mackovicky and Karup-Moller, 1993).

Before fusion, fire-assay reagents and sample powder are intimately mixed using 50 ml absolute ethanol which enhances the mixing. The resulting slurry is then progressively evaporated to dryness on a hot plate with continuous stirring. Once evaporated to dryness, the resulting powder is transferred into porcelain crucibles, covered with a lid. The crucibles are placed in a cold muffle furnace (THERMOLYNE[®] Type 47900). Heating is then switched on (setpoint temperature: 1000 °C). A series of quench tests was done to determine the adequate heating time. These tests showed that, after about 1 h, the NiS droplets disseminated throughout the borosilicate slag are collected into a single button at the bottom of the crucible, thus considerably limiting exchange with the borosilicate slags. A heating time of 1 h 30 min was therefore chosen. Once cooled, the NiS button, weighing 7.2–7.5 g on average, is crushed into small chips in an agate mortar ($< 1 \text{ mm}$ in diameter).

2.3. Dissolution of the NiS button

Dissolution of nickel sulfide within hydrochloric acid produces both gaseous hydrogen sulfide and nickel chlorides according to a chemical equilibrium. Concentrated hydrochloric acid (12 M) such as usually used in previous procedures (e.g. Jackson et al., 1990; Sun et al., 1993; Oguri et al., 1999) starts boiling at 50 °C. In open-beaker dissolution procedures, the dissolution step on a hot plate at 150 °C, a temperature necessary to completely dissolve a 7-g NiS button in a reasonable time, results in significant losses of HCl (up to 25% of the initial volume, from our own experience). During this step, volatile PGE can also escape; this is the case for Ru and Pd which form volatile chlorides at low temperature (Wood, 1987; Sassani and Shock, 1998). Dissolution in screw-capped Savilex[®] Teflon beakers could theoretically solve this problem (e.g. Sun et al., 1993). However, hydrogen sulfide is partly soluble within HCl, leading to incomplete outgassing in closed-beaker procedures and a slow down of the dissolution of the NiS. Moreover, trapped H_2S produces unidentified Te–S compounds during the Te coprecipitation step.

Table 1

Reagent grades used for preparation and dissolution of the NiS button

Nickel	Carbonyl Ni powder, 99.8% Ni, GOODFELLOW [®] Cambridge
Sulfur	Sublimated sulfur, MERCK
Di-lithium tetraborate	Anhydrous granular, GR for analysis, MERCK
Sodium carbonate	Anhydrous granular, GR for analysis, MERCK
Silica	Silicon dioxide floated powder, highly dispersed, high purity (food grade), MERCK
Hydrochloric acid	Hydrochloric acid 37% (max 0.000005% Hg) GR, MERCK
Nitric acid	Nitric acid 65%, GR, MERCK
Deionized water	purified by Milli-Q purifier (18 M Ω), MILLIPORE
Ethanol absolute	Ethanol absolute (99.5 % vol. min.) PROLABO
Stannous chloride	For one sample, 3.3 g of SnCl ₂ ·2H ₂ O from MERCK [Tin (II) chloride dihydrate, GR for analysis, max 0.000001% Hg] is dissolved in 4.5 ml of HCl 37% at 30 °C max and diluted to 15 ml with deionized water. This solution must be prepared weekly.
Te acid solution	2000 ppm in HCl 10%,—Made by dissolving 2 g of tellurium lumps (CERAC, 99.9999% Te) in aqua regia (9 ml hydrochloric acid 37% HCl + 3 ml nitric acid 65% HNO ₃) at low temperature (50 °C max). After complete dissolution, the solution is evaporated near to dryness. Then two successive evaporations to dryness are made with 10 ml concentrated HCl. The resulting compound is dissolved again in HCl and diluted to 1000 ml with HCl 10%. Stable for 1 year.

These compounds, easily evident by the brown, turbid aspect of the solution, drastically lower the efficiency of the PGE collection by the tellurium precipitate.

For all the reasons discussed above, we opted for a semi-open dissolution procedure combining the advantages of open-beaker dissolution (i.e. complete H₂S outgassing) and closed-beaker dissolution (keeping HCl losses and thus losses of volatile PGE chlorides to minimum values). This was achieved by fitting an Erlenmeyer flask (250 ml) with a refluxing system (referred to as an “adiabatic column”) consisting of a 35-cm-long (effective length) homemade glass column (Fig. 1A). This column has a double-sided jacket; the inner walls of the jacket were first silver plated to improve thermal insulation, and then vacuum sealed. The efficient part of the column is formed by nine 30-mm conventional bowls (Fig. 1B). The column is connected to a cryostat (HETO[®] CBN 8-30) that maintains the bowls at constant temperature (0 °C) by glycol–water circulation. To further reduce HCl loss, we chose the HCl grade corresponding to the maximum boiling temperature in the H₂O–HCl system (20.2% \approx 6.1 M HCl).

The Erlenmeyer flask containing 150 g of 20.2% HCl and the NiS chips is put on a hot plate and capped by the adiabatic column (Fig. 1A). The hot plate is heated in steps at 150 °C for 1 h, 200 °C for 1 h and finally maintained at 275 °C for 4.5 h; this last temperature maintains the acid solution to its boiling

point (110 °C) in our equipment. The NiS button is totally dissolved at the end of the second step. During the third step, the solution boils gently, which ensures complete degassing of H₂S. After this step, the hydrochloric acid solution is perfectly limpid. The HCl losses (ΔM) were systematically estimated as $M1 - M2$ [where $M1 = 150.0$ g (hydrochloric acid) + 5.0 g Ni and $M2 =$ mass of solution after NiS dissolution]. ΔM values, as calculated from 65 dissolution runs, are highly reproducible (0.30 ± 0.15 wt.%) and negligible, especially compared to those of open-beaker dissolution procedures. They show that HCl is efficiently recycled into the Erlenmeyer flask by our refluxing system.

2.4. Te coprecipitation

The Te coprecipitation procedure is similar to that described by Jackson et al. (1990) except that we added 7 ml of telluric acid (instead of 3.5 ml) to improve the recovery of the HSE. The effect of acidity on the recovery of PGE was determined through a series of Te coprecipitation tests on synthetic solutions. The optimum grade was found to be 14%, in agreement with previous determinations (e.g. Oguri et al., 1999). In practice, once the HCl solution is cooled to room temperature, 7 ml of Te solution is added. The solution remains perfectly limpid, a feature that indicates the lack of any Te–Se compounds.

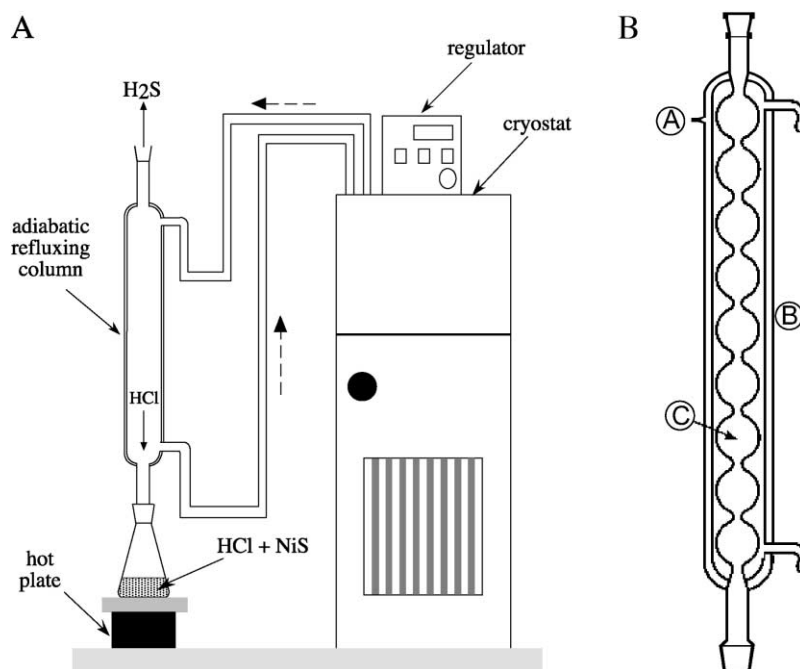


Fig. 1. (A) Apparatus for the dissolution of the NiS button. The dashed arrows indicate how the cooling liquid circulates. (B) Details of the adiabatic column: (A) vacuum sealing of the jacket; (B) double-sided, silver-plated jacket; (C) spherical bowls (30 mm diameter).

Twenty-three milliliters of deionized water is then added through the column, both to adjust the acidity to its optimal value and to recover the last acid droplets still adhering inside the column. After a short agitation, 12 ml SnCl_2 solution is added dropwise, very slowly for the first drops, while smoothly stirring the solution. The fine, black Te precipitate obtained is then coagulated by heating the solution on a hot plate at 150 °C during 25 min and then at 350 °C for about 5–10 min. Heating is stopped when the solution starts boiling.

2.5. Recovery of the Te precipitate and preparation of final solution

The Jackson et al. (1990) procedure for recovering the Te precipitate was kept unmodified apart from the temperature controlling digestion of the Te precipitate, which is maintained below 55 °C to avoid OsO_4 losses. Briefly, once cooled to room temperature, the solution is filtered with a MILLIPORE apparatus supplied with a cellulose ester membrane (HAWP

0.45 mm, MILLIPORE). The cellulose ester membrane coated with the thin Te precipitate is rinsed several times with HCl 10%. Then it is transferred into a spherical flask (25 ml) maintained at 10–15 °C. Five milliliters nitric acid (65% HNO_3) and, at least 30 min later, 5 ml hydrochloric acid (37% HCl) are added into the spherical flask through the open end of the test tube that capped the spherical flask. The latter is firmly sealed with a double thickness of Parafilm immediately after addition of hydrochloric acid to prevent any loss of volatile PGE (especially Os) during digestion of the membrane. As it is composed of saturated hydrocarbons, Parafilm is inert with respect to OsO_4 . To ensure a complete dissolution of this filter paper, the spherical flask is heated three times in a water bath, each heating being separated by at least 3 h. The cellulose ester membrane is totally digested within about 24 h. From our own experience, any residual organic matter does not harm the elemental mass spectra.

At least 3 h after the last heating, the solution is then transferred into glass bottles and diluted to 100 g

with ultrapure water, which is also used to rinse both the test tube and the spherical flask.

3. Mass spectrometry

The six PGE (Os, Ir, Ru, Rh, Pt, Pd) and gold were determined with ICP-MS (FISONS VG 353 Plasma-Quad PQplus) using the University of Montpellier II-MNHN facility operating with external calibration standards. All the ICP-MS measurements were carried out in the peak-jumping mode, and each element was counted three times for 30 s after 150 s rinsing and 45 s uptake. Each sample was analysed twice, with a 30-min rinsing period between each analytical run. The results reported in this paper always correspond to the average of these two runs. Uncertainties based on counting statistics were generally below 1%.

A complete set of ICP-MS glassware (nebuliser and torch) was reserved for analysis of highly siderophile elements at ultratrace concentration levels. This glassware was thoroughly washed with hot aqua regia after 50 analyses and instrumental backgrounds were checked twice a day by analysing diluted acid (HCl 0.6 M + HNO₃ 0.8 M). Instrumental backgrounds compiled over a period of 2.5 years range between 30 and 60 cps (corresponding to 2–5 pg/g for each PGE) and were subtracted from calculated concentrations of the analysed samples. Before starting any PGE analytical session, Ni sampling cones were cleaned with an abrasive paste. Details of the instrument operating parameters and isotopes analysed for each element are given in Table 2.

Sample concentrations were obtained by comparing their intensities with the standard calibration curve calculated from “external standards” of varying concentrations. The external standard solutions were prepared from SPEX multi-element PGE solutions (10 mg/ml each in 20% HCl in water) diluted to concentration of 5 and 10 ppb. Regression lines defined by these two concentrations systematically went through the origin for the seven elements analysed.

Isotopes ¹¹¹Cd and ²⁰³Tl, respectively close to the light (Ru, Rh and Pd) and heavy (Os, Ir, Pt and Au) PGE, were used as internal standards to correct for instrument drift and matrix suppression effects. They were prepared from SPEX stock solutions (1000 mg/

Table 2

ICP-MS operating conditions

Inductively coupled plasma (W)

Forward power: 1350

Reflected power: <5

Argon gas flows (l/min)

Outer gas: 14

Auxiliary gas: 0.9

Nebulizer gas: 0.85

Cones

Sampling cone: Ni, 1 mm

Skimmer cone: Ni, 0.7 mm

Sampling uptake rate (ml/min): 0.7

Typical ion lens settings (V)

Extraction: 1.6

Collector: 8.2

Lens 1: 8.0

Lens 2: 5.4

Lens 3: 5.5

Lens 4: 3.9

Data acquisition parameters

Acquisition mode: Pulse counting

Run numbers: 3

Acquisition time: 30 s

Counting time per element: 2 s/peak

Wash time: 150 s

Measured ion (isotopic abundance %)

¹⁸⁹Os (16.1)

¹⁹³Ir (62.7)

¹⁰¹Ru (17.07)

¹⁰³Rh (100)

¹⁹⁵Pt (33.8)

¹⁰⁵Pd (22.23)

¹⁹⁷Au (100)

Internal standard

¹¹¹Cd

²⁰³Tl

ml in HNO₃ 2%) diluted to 20 ppb in the solution to be analysed.

4. Results and discussion

4.1. Blanks

Procedural blanks for 15 g sample aliquots were determined from four replicate analyses of NiS-fire

assay charges prepared with the same proportions of reagents but containing 8 g of silica instead of sample powder. All the glassware (Erlenmeyer, refluxing silica glass column) was thoroughly washed into hot aqua regia before processing the charges for procedural blanks. Blank data for Os and Rh are at the ppt level, whereas Ir blanks are 5–10 times higher. For all three elements, the blanks are reproducible and our mean values are in the lower part of the range (Ir, Rh) or even better (Os) than literature data generated by the NiS fire assay–Te coprecipitation procedure (Table 3). For Os, the blank was systematically determined after prolonged rinsing (1 h), or just after thorough aqua-regia cleaning of the ICP glassware to avoid memory effects. Comparative data are few and sometimes unreliable as the open-beaker NiS dissolution procedure previously used was not able to completely retain this element. Our Os blank value closely matches that of Pearson and Woodland (2000) obtained by Carius tube dissolution. However, the latter was obtained using 2 g sample aliquots only. As repeatedly argued in recent analytical papers (see Pearson and Woodland, 2000), the NiS–Te coprecipitation procedure generates higher blanks for Ru, Pt, Pd and Au, at several tens to hundreds of picograms/gram. Our values for these four elements lie at the

lowermost end of the published values, or are considerably better (Table 3). The improvement of Au blank data may be partly explained by the repeated cleaning of all the glassware with hot aqua regia. For Ru, it cannot be ascertained that our Ru blank values reflect actual purity of the reagents or small isobaric interferences on ^{101}Ru polyatomic ions from $^{61}\text{Ni}^{40}\text{Ar}^+$ and $^{64}\text{Ni}^{37}\text{Cl}^+$. Even if all the NiS particles are dissolved into HCl, infinitesimal amounts of Ni are expected to be transferred from the HCl solution to the Te microprecipitate and can potentially create isobaric interferences on all the Ru isotopic masses during ICP-MS analyses using argon plasma and chlorhydric solutions. Our much lower Ru blank data compared to previously published values suggest that our semi-open dissolution technique certainly lowers such interferences to minimal values. Unlike Ru, the elements Pt, Pd and Au are free from memory effects or isobaric interferences and their blank values likely result from contamination of reagents (Ni, Te). Nickel is generally considered to be the most likely contaminant as it is used in very large amounts (5 g) and could be contaminated by Pt, Pd and Au. The six different batches of Ni powders analysed in the course of this study effectively revealed Pt (51 pg/g), Pd (103 pg/g) and Au (122 pg/g) and no detectable amounts of

Table 3
Procedural blanks

	Sample aliquot (g)	NiS button weight (g)	SnCl ₂ (ml)	Os (ppb)	Ir (ppb)	Ru (ppb)	Rh (ppb)	Pt (ppb)	Pd (ppb)	Au (ppb)
<i>NiS fire assay and Te coprecipitation</i>										
This study	15	≈ 7–8	12	0.007 <i>0.003</i>	0.04 <i>0.01</i>	0.14 <i>0.01</i>	0.005 <i>0.002</i>	0.10 <i>0.03</i>	0.08 <i>0.02</i>	0.57 <i>0.11</i>
Jackson et al. (1990)	15	≈ 7–8	12	0.01 <i>0.09</i>	0.04 <i>0.03</i>	0.4 <i>0.1</i>	0.001 <i>0.046</i>	0.09 <i>0.10</i>	0.12 <i>0.11</i>	0.51 <i>0.56</i>
Sun et al. (1993)	15	≈ 7–8	12	0.06 <i>0.02</i>	2.0 <i>0.6</i>	0.5 <i>0.15</i>	0.5 <i>0.15</i>	2.0 <i>0.6</i>	3.0 <i>0.9</i>	10 <i>3</i>
Pattou et al. (1996)	15	≈ 7–8	12	n.a. <i>n.a.</i>	0.04 <i>0.01</i>	0.78 <i>0.07</i>	0.009 <i>0.003</i>	0.15 <i>0.03</i>	0.12 <i>0.03</i>	0.7 <i>0.1</i>
Oguri et al. (1999)	20	≈ 1	4	n.a. <i>n.a.</i>	0.08 <i>< 0.001</i>	4.4 <i>0.007</i>	0.06 <i>0.001</i>	0.84 <i>0.004</i>	0.07 <i>0.003</i>	3.2 <i>0.013</i>
<i>Carius tube digestion and ion exchange separation</i>										
Rehkämper et al. (1998)				n.a.	<0.001	0.003	n.a.	0.007	0.003	n.a.
Pearson and Woodland (2000)				0.001–0.007	<0.001	<0.010	n.a.	0.010–0.025	0.010	n.a.

Blank values for Carius tube digestion and ion exchange separation method are given in nanograms per gram of sample. *n*: Number of analyses, n.a.: not analysed.

Os, Ir and Rh (<1 pg/g). It is worth noting that, although using significantly smaller NiS beads (1.2 vs. 7.3 g), the Oguri et al. (1999) technique generates much higher blanks for Pt. This would suggest that Ni is not the sole potential contaminant in the NiS fire assay separation procedure. Other contamination could come from SnCl₂.

4.2. PGE and Au analysis of geological materials

Reference material UMT1 (CANMET), repeatedly analysed for the past 3 years, was the standard used to develop this procedural modification of the NiS dissolution step and to monitor yield, accuracy and reproducibility. Pearson and Woodland (2000) pointed out that evaluation of a technique solely by comparison with “reference material rocks” is not necessarily the optimal method of evaluating a given analytical technique. For this reason, we also analysed a mantle lherzolite (FON B 93) prepared as an in-house standard in our institute (Pattou et al., 1996). The reproducibility of our method was also evaluated by analysing abyssal peridotites as unknowns. Abyssal peridotites contain PGE in the nanogram/gram concentration range. We selected three samples collected by submersible along the Kane fracture Zone (MARK area, 20–24°N, Mid-Atlantic Ridge). Samples from the same area have previously been analysed for PGE by various techniques—ICPMS after Carius tube digestion and anion exchange columns (Rehkämper et al., 1999)—INAA after NiS fire assay preconcentration (Snow and Schmidt, 1998).

4.2.1. UMT1

UMT1 is a standard created by homogenization of 772 kg of ultramafic mine tailings from the Giant Mascot Mines in British Columbia. Its Os, Ir, Ru and Rh concentrations are at the nanogram/gram level, while Pt concentrations range up to 129 ng/g. The results from seven replicate analyses are in good agreement with certified values (Table 4). Recovery proportions calculated from the mean of the seven analyses range from 97% (Ir) to 93–94% (Rh, Pt, Pd), 91% (Au) and 90% (Os). All PGE ratios are within 5% of the CANMET certified values. Only Ru was not satisfactorily recovered (83%); however, the same is also true for the other UMT1 analyses compiled in Table 4, which may lead to question the validity of the

CANMET «certified» value. The replicate analyses of mantle peridotites discussed below argue against systematic loss of Ru in our separation procedure. On average, our new NiS dissolution procedure yields better recovery (Ir: +24%; Os: +80%, all other PGE and Au: +11 to +17%) compared to previous analyses using the Jackson et al. (1990) NiS dissolution procedure. Our data compare well with the Oguri et al. (1999) analyses, suggesting that their double fusion and double Te coprecipitation stages have little influence on the PGE recovery, except perhaps for Pt and Au which are slightly higher. However, definitive conclusions are precluded because the Oguri et al. (1999) values are overestimated relative to certified values and their mean Pt value is less reproducible than ours.

Another important point is that our method allows Os to be almost completely recovered. Our mean value (7.13 ± 1.4 ppb) is similar, at the 1 sigma level, to the CANMET provisional value and to other, more recent determinations using different analytical techniques (Snow and Schmidt, 1998; Table 4). Sun et al. (1993) suggested that Os escapes as OsO₄ during dissolution of the filter paper containing the Te precipitate in aqua regia. As this step was not significantly modified from the Jackson et al. (1990) original procedure used by Pattou (1995) and Pattou et al. (1996), we have to conclude that it is our modification of the NiS dissolution stage that really improved the recovery of Os. At this stage, dissolution of the NiS bead liberates excess H₂S and generates a reducing medium preventing the formation of volatile osmium tetroxide (Wood, 1987). By limiting the HCl losses to near 0%, our refluxing apparatus apparently also reduces the volatility of any chlorine-bearing Os compound to near zero.

Another strength of our procedural improvement lies in its external reproducibility. The latter, expressed as percentage deviation from the mean (1 sigma/mean), is excellent (1% for Rh, Pt, Pd to 4% for Ir, 5% for Ru, 6% for Au) and generally two to seven times better than previously published values generated by the NiS fire assay and Te coprecipitation techniques (Table 4). Such improvements most probably result mainly from the strongly homogenizing effect of using 15 g powder aliquots. This effect can be evaluated by comparing our data with the Oguri et al. (1999) analyses performed on 5 g powder aliquots.

Table 4
Replicate analyses of UMT1

	Os (ppb)	Ir (ppb)	Ru (ppb)	Rh (ppb)	Pt (ppb)	Pd (ppb)	Au (ppb)
CANMET certified values (2 σ)	8 ^P	8.8 ^c 0.2	10.9 ^c 1.5	9.5 ^c 1.1	129 ^c 4	106 ^c 3	48 ^c 2
This study							
Average ($n=7$)	7.13	8.5	8.9	8.9	120.5	99	43.5
Standard deviation (1σ)	1.4	0.33	0.45	0.11	1.13	1.56	2.6
Batch #1	9.85 8.23	8.2 8.0	8.5 8.7	8.75 8.75	121 120.4	99.4 100	41.2 41.1
Batch #2							
Average ($n=5$)	6.37	8.73	9.1	8.97	120.4	99.2	44.5
Standard deviation (1σ)	0.28	0.16	0.48	0.05	1.41	1.78	2.45
Pattou (1995) ($n=3$)	1.5	6.6	7.6	8.0	99.9	88.0	37.1
Standard deviation (1σ)	0.6	0.6	0.1	0.4	14.9	4.8	3.0
Oguri et al. (1999) ($n=5$)	n.a.	10	8.7	8.8	132	95.6	50.5
Standard deviation (1σ)	n.a.	0.79	0.76	0.35	9.0	3.7	1.8
Snow and Schmidt (1998)	6 7.23	7.31 7.82	8.2 9.6	7.57 9.87	n.a. n.a.	98 93	27 32.6

p: provisional, c: certified, n : number of analyses, n.a.: not analysed.

However, the size of powder aliquots is not the sole factor as Pattou (1995) also used 15 g powder aliquots but found less reproducible results. The improvement also likely results from the semi-open NiS dissolution procedure that (1) ensured a constant acidity, a key parameter for the Te coprecipitation step and (2) reduced volatile PGE losses. Only Os data remain less reproducible (20%). In fact, UMT1 was analysed from two different bottles (Table 4). Although each bottle was thoroughly mixed before use, two powder aliquots from one bottle (batch 1) yielded Os contents clustering around the CANMET provisional value (8.2–9.85 ppb) while a second batch of 5 powder aliquots from another bottle (batch 2) yielded lower, but highly reproducible Os contents (6.37 ± 0.28 ppb). Systematic Os losses during processing of batch 2 analyses are highly unlikely as they would not produce such reproducible values. Slight variations in the Os content are more likely. It is worth pointing out that the Os value provided by CANMET is only provisional and could be slightly refined in the near future. Moreover, slight differences also appear in other elements, especially Ir and Au: when calculated from the batch 2 analyses, the recovery percentages

for these two elements increase to 99% and 93%, respectively, and our values fit the certified values very well at the 1 sigma level. Such variations corroborate the Pearson and Woodland (2000) remark that evaluation of accuracy and precision of a given analytical technique from “reference material rocks” may be biased by subtle variations between powder packages.

4.2.2. In-house standard FON B 93

FON B 93 is a sulfide-rich (S = 230 ppm), fertile mantle lherzolite ($Al_2O_3 = 3.23$ wt.%) from the Fontête Rouge orogenic massif (Eastern Pyrenées, France). It is characterized by homogeneous PGE concentrations close to McDonough and Sun (1995) primitive mantle estimates except for Pd (Pattou et al., 1996). Analyses of separated sulfides, completed by in situ laser ablation ICP-MS analyses (Pattou et al., 1996; Alard et al., 2000) demonstrated that most PGE in Pyrenean orogenic lherzolites are 100% hosted in the 0.1 wt.% disseminated base metal sulfides (pentlandite) apart from Pt, which probably occurs as discrete Pt-rich phases and Au, concentrated in subordinate Cu sulfides (chalcopyrite) (c.f. Lorand et al., 1999).

Five different powder aliquots of FON B 93 of 15 g each were analysed (Table 5). The mean Os value (3.42 ppb) fits the Os concentration inferred for the primitive mantle very well, as does the Os/Ir ratio (1.053 vs. 1.063; see McDonough and Sun, 1995). It is also similar within error (1 sigma) to the Reisberg and Lorand (1995) TIMS data (3.42 ± 0.25 vs. 3.81 ± 0.3 ppb). All of these results strengthen our conclusion that Os is nearly completely recovered by our modified NiS fire assay procedure. The contents of Ir, Ru, Rh and Pt are higher by 5–10% compared to the Pattou et al. (1996) average, while Pd and Au are increased by 18% and 50%, respectively. However, apart from Pd, both data sets overlap at the 1 sigma level. The Pd data are highly reproducible (RSD=3%) and distinctly offset from the Pattou et al. (1996) value at the 1 sigma confidence. Such a difference is likely significant and may be attributed to our semi-open dissolution procedure that prevents escape of Pd as volatile chlorides during dissolution of the NiS bead into HCl.

The external reproducibility determined from FON B 93 is nearly as good as that determined for UMT1 and improved by factors of 1.5 (Ir, Ru and Pd) to 3 (Rh, Pt, Au) compared to the Pattou et al. (1996) analyses. Moreover, osmium data are quite reproducible. These observations reinforce the conclusion drawn from UMT1, that is, the NiS fire assay method can achieve excellent reproducibility in PGE analysis of coarse-grained rocks if performed on large-sized powder aliquots and if the NiS bead is dissolved in a semi-open system preventing losses of volatile PGE. The excellent reproducibility of Pt data (RSD=3%) shows that our procedure can overcome nugget effects

inherent to elements occurring as discrete PGE microphases, provided that these microphases are physically associated with base metal sulfides. On the other hand, the Au analyses are less reproducible (14%) than the PGE analyses. This reflects the partitioning of Au into chalcopyrite, which is 10 times less abundant than pentlandite and by far less homogeneously distributed on the hand sample scale (Lorand, 1989).

4.2.3. Abyssal peridotites

The three abyssal peridotites analysed as unknowns yield results remarkably consistent with the few high-quality analyses available for these rocks (Snow and Schmidt, 1998; Rehkämper et al., 1999). Except for Pd, our mean composition lies within the 10% error interval of primitive mantle estimates. This is especially true for Os (3.28 ± 0.19 ppb). Furthermore, the Os/Ir ratio (1.07) is perfectly chondritic, as assumed for the terrestrial mantle. The agreement between our average Os content and the Snow and Schmidt value is impressive. This is also the case for Pd which varies by only 6% between the three mean values compiled in Table 6. Our samples display the characteristic Pd excess relative to primitive mantle estimates that was discussed by Snow and Schmidt (1998) and Rehkämper et al. (1999) for MARK abyssal peridotites. The agreement for the other PGE is less good but all three data sets overlap at the 1 sigma level, except for Pt which is distinctly higher in the Snow and Schmidt (1998) average (Table 6). Such variations may reflect within-sample and between-sample heterogeneities beyond the scope of the present paper. One may simply note that, apart from Pd, standard deviations (1 sigma)

Table 5
Replicate analyses of FON B 93

	Os (ppb)	Ir (ppb)	Ru (ppb)	Rh (ppb)	Pt (ppb)	Pd (ppb)	Au (ppb)
This study ($n=5$)							
Average	3.42	3.25	6.2	1.16	6.7	6.4	1.5
Standard deviation (1σ)	0.25	0.1	0.34	0.04	0.2	0.2	0.21
Reisberg and Lorand (1995) ^a	3.81						
Standard deviation (1σ)	0.25						
Pattou et al. (1996) ($n=11$)	n.d.	2.92	5.9	1.05	6.2	5.4	1.0
Standard deviation (1σ)	n.d.	0.1	0.4	0.1	0.5	0.3	0.3

n : Number of analyses, n.d.: not determined.

^a TIMS data.

Table 6
HSE analyses of abyssal harzburgites

	Os (ppb)	Ir (ppb)	Ru (ppb)	Rh (ppb)	Pt (ppb)	Pd (ppb)
This study						
KN 19-2 B	3.47	3.16	6.1	1.22	8.5	7.8
KN 3-4	3.02	2.95	5.4	1.11	7.9	6.9
KN 3-3	3.34	3.06	5.3	1.11	6.2	5.3
Average	3.28	3.06	5.6	1.15	7.5	6.7
Standard deviation (1σ)	0.19	0.09	0.36	0.05	0.97	1.03
Snow and Schmidt (1998) ($n=3$) ^a	3.22	3.35	6.31	1.32	10.73	6.58
Standard deviation (1σ)	0.12	0.08	0.39	0.14	0.65	0.05
Rehkämper et al. (1999) ($n=4$) ^b		3.77	7.10		8.30	6.99
Standard deviation (1σ)		1.20	1.43		2.18	1.20

n : Number of analyses. Only the analyses with Pd/Ir > 1 were selected for comparison.

^a INAA after NiS fire assay preconcentration.

^b ICP-MS after Carius tube digestion and ion-exchange separation.

of our analyses compare well with those calculated from the Snow and Schmidt (1998) data set. On the other hand, they are generally smaller than those calculated from the Rehkämper et al. (1999) database. Once again, such differences may testify to the strength of large-sized powder aliquots in homogenizing PGE abundances compared to the few grams of sample analysed in the Carius tube digestion–ID ICP-MS techniques.

5. Conclusions

Our semi-open dissolution system allows efficient separation of HCl (99.7% recycled into the Erlenmeyer) and H₂S (completely outgassed) during the NiS dissolution step. Thus modified, the NiS fire assay method allows Os to be almost completely recovered, while greatly reducing the volatility losses of Pd.

With our modifications, the NiS fire assay and Te coprecipitation technique remains a valuable PGE separation procedure for mantle rocks (and other coarse-grained mafic and ultramafic rocks) where all the PGE (including Os) and Au are in the nanogram/gram concentration range. Compared with current technologies, its strengths are (1) it is a relatively simple method, with a limited number of procedural steps—two samples can easily be processed per day; (2) PGE analyses of coarse-grained rocks are highly reproducible if performed from large-sized powder aliquots.

Good blank data can be achieved for analysis of mantle rocks and certain coarse-grained basic rocks. However, this technique could also be applied to most basalts, and also sediments and soils if the main reagents (Ni, SnCl₂) were chemically purified.

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References

- Alard, O., Griffin, W.L., Lorand, J.P., Jackson, S., O'Reilly, S.R., 2000. Non-chondritic distribution of highly siderophile elements in mantle sulphides. *Nature* 407, 891–894.
- Brandon, A.D., Walker, R.J., Morgan, J.W., Norman, M.D., Pritchard, H.M., 1998. Coupled ¹⁸⁶Os and ¹⁸⁷Os evidence for core–mantle interaction. *Science* 280, 1570–1573.
- Craig, J.R., Scott, S.D., 1976. Sulfide phase equilibria. In: Ribbee, P.H. (Ed.), *Sulfide Mineralogy, Reviews in Mineralogy*. Mineralogical Society of America, Washington, DC, pp. CS-1–CS-104, Chap. 5.

- Enzweiler, J., Potts, P.J., 1995. Determination of platinum, palladium, ruthenium and iridium in geological samples by isotope dilution inductively coupled plasma mass spectrometry using a sodium peroxide fusion and tellurium coprecipitation. *Analyst* 120, 1391–1396.
- Gueddari, K., Piboule, M., Amossé, J., 1996. Differentiation of platinum-group elements (PGE) and of gold during partial melting of peridotites in the lherzolitite massifs of the Bético–Rifean range (Ronda and Beni Bousera). *Chem. Geol.* 134, 181–197.
- Hall, G.E.M., Pelchat, J.C., 1994. Analysis of geological materials for gold, platinum and palladium at low ppb levels by fire-assay-ICP mass spectrometry. *Chem. Geol.* 115, 61–72.
- Jackson, S.E., Fryer, B.J., Gosse, W.D., Healey, C.H., Longerich, P., Strong, D.F., 1990. Determination of the precious metals in the geological materials by inductively coupled plasma-mass spectrometry (ICP-MS) with nickel-sulfide fire-assay collection and tellurium coprecipitation. *Chem. Geol.* 83, 119–132.
- Jarvis, K.E., Williams, J.G., Parry, S.J., Bertalan, E., 1995. Quantitative determination of the platinum group elements and gold using fire assay with laser-ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). *Chem. Geol.* 124, 37–46.
- Jarvis, I., Totland, M.M., Jarvis, K.E., 1997. Determination of the platinum group elements in geological materials by ICP-MS using microwave digestion, alkali fusion and cation-exchange chromatography. *Chem. Geol.* 143, 27–42.
- Lorand, J.P., 1989. Abundance and distribution of Cu–Fe–Ni sulphides, sulphur, copper and platinum group elements in orogenic-type spinel peridotites of Ariège (Northeastern Pyrenees, France). *Earth Planet. Sci. Lett.* 93, 50–64.
- Lorand, J.P., Keays, R.R., Bodinier, J.L., 1993. Copper- and noble metal enrichment across the asthenosphere–lithosphere mantle diapirs: the Lanzo lherzolite massif. *J. Petrol.* 34, 1111–1140.
- Lorand, J.P., Pattou, L., Gros, M., 1999. Fractionation of platinum group element in the upper mantle: a detailed study in Pyrenean orogenic lherzolites. *J. Petrol.* 40, 957–981.
- Luguet, A., Alard, O., Lorand, J.-P., Pearson, N.G., Ryan, C., O'Reilly, S.Y., 2001. Laser-ablation microprobe (LAM)-ICPMS unravels the highly siderophile elements geochemistry of the oceanic mantle. *Earth Planet. Sci. Lett.* 189, 285–294.
- Mackovicky, E., Karup-Moller, S., 1993. The system Pd–Fe–S at 900°, 725°, 550° and 400 °C. *Econ. Geol.* 88, 1269–1278.
- McDonald, I., 1998. The need for a common framework for collection and interpretation of data in platinum group element geochemistry. *Geostand. Newsl.* 22, 85–91.
- McDonough, W.F., Sun, S.S., 1995. The chemical composition of the Earth. *Chem. Geol.* 120, 223–253.
- Oguri, K., Shimoda, G., Tatsumi, Y., 1999. Quantitative determination of gold and platinum-group elements in geological samples using improved NiS fire-assay and tellurium coprecipitation with inductively coupled plasma-mass spectrometry (ICP-MS). *Chem. Geol.* 157, 189–197.
- Pascal, 1963. In: Masson, (Ed.), *Nouveau traité de chimie minérale*, tome XVII, 2nd fascicule, Masson et Cie editeurs Paris, 896 pp.
- Pattou, L., 1995. Abondance des éléments fortement sidérophiles et chalcophiles dans le manteau terrestre: une analyse ICP-MS des éléments du groupe du platine et de l'or dans les massifs lherzolitiques Pyrénéens. PhD thesis, Univ. Paris VII-MNHN, 281 pp. (unpublished).
- Pattou, L., Lorand, J.P., Gros, M., 1996. Non-chondritic platinum group element ratios in the Earth's mantle. *Nature* 379, 712–715.
- Pearson, D.G., Woodland, S.J., 2000. Solvent extraction/anion exchange separation and determination of PGEs (Os, Ir, Pt, Pd, Ru) and Re–Os isotopes in geological samples by isotope dilution ICP-MS. *Chem. Geol.* 165, 87–107.
- Ravizza, G., Pyle, D., 1997. PGE and Os isotopic analyses of single sample aliquots with NiS fire assay preconcentration. *Chem. Geol.* 141, 251–2682.
- Rehkämper, M., Halliday, A.N., 1997. Development and application of new iron-exchange techniques for the separation of the platinum group and other siderophile elements from geological samples. *Talanta* 44, 663–672.
- Rehkämper, M., Halliday, A.N., Wentz, R.F., 1998. Low-blank digestion of geological samples for platinum-group element analysis using a modified carius tube design. *Fresenius' J. Anal. Chem.* 361, 217–229.
- Rehkämper, M., Halliday, A.N., Alt, J., Fitton, J.G., Zipfel, J., Takazawa, E., 1999. Non-chondritic platinum-group element ratios in oceanic mantle lithosphere: petrogenetic signature of melt percolation? *Earth Planet. Sci. Lett.* 172, 65–81.
- Reisberg, L., Lorand, J.P., 1995. Longevity of sub-continental mantle lithosphere from osmium isotope systematics in orogenic peridotite massifs. *Nature* 376, 159–162.
- Sassani, D.C., Shock, E.L., 1998. Solubility and transport of platinum-group elements in supercritical fluids: summary and estimates of thermodynamic properties for ruthenium, rhodium, palladium and platinum solids, aqueous ions and complexes to 1000 °C and 5 kbar. *Geochim. Cosmochim. Acta* 62, 2643–2671.
- Snow, J.E., Schmidt, G., 1998. Constraints on Earth accretion deduced from noble metals in the oceanic mantle. *Nature* 391, 166–169.
- Sun, M., Jain, J., Zhou, M.F., Kerrich, R., 1993. A procedural modification for enhanced recovery of precious metals (Au, PGE) following nickel sulfide assay and tellurium coprecipitation; applications for analyses of geological samples by inductively coupled plasma mass spectrometry. *Can. J. Appl. Spectrosc.* 38, 103–108.
- Tredoux, M., DeWit, M.J., Hart, R.J., Armstrong, R.A., Lindsay, N.M., Sellschop, J.P.F., 1989. Evidence of deep mantle origin in an archaic nickel–iron–platinum occurrence. *J. Geophys. Res.* 94, 795–813.
- Wood, S.A., 1987. Thermodynamic calculations of the volatility of the platinum-group elements (PGE): the PGE content of fluids at magmatic temperatures. *Geochim. Cosmochim. Acta* 51, 3041–3050.