

Determination of Platinum-Group Elements in OPY-1: Comparison of Results using Different Digestion Techniques

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A new proficiency testing sample, OPY-1 (ultramafic rock), the basis of the twentieth international proficiency test of analytical geochemistry laboratories (GeoPT 20), was recently prepared by the International Association of Geoanalysts (IAG). This paper reports analytical data for Os, Ir, Ru, Rh, Pt and Pd with different digestion techniques, including an improved Carius tube, Carius tube combined with HF dissolution and alkaline fusion. About 4–15% of the PGEs are in the silicate phase, which cannot be leached by *aqua regia* even when digested at 300 °C with the Carius tube technique. Both the Carius tube technique combined with HF dissolution and alkaline fusion can obtain reliable data. The results demonstrated that OPY-1 is sufficiently homogeneous at a 2 g test portion level to be suitable as a reference material for method validation. The procedure for sealing the Carius tube was simplified and the recommended digestion procedures are provided.

Keywords: OPY-1, GeoPT 20, PGE, ICP-MS, Carius tube.

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L'échantillon OPY-1 (roche ultrabasique) a été préparé par l'Association Internationale des Géoanalystes (IAG) et est le vingtième échantillon, récemment distribué dans le cadre du test international de compétence destiné aux laboratoires de géochimie analytique (GeoPT 20). On présente ici les données obtenues pour Os, Ir, Ru, Rh, Pt et Pd à partir de différentes techniques de mise en solution, dont celle du tube de Carius amélioré, du tube de Carius combiné à une dissolution par HF et du tube de Carius combiné à une fusion alcaline. Entre 4 et 15% des PGE sont contenus dans la phase silicatée qui ne peut pas être lessivée par l'eau régale même dans un tube de Carius chauffé à 300 °C. Les deux techniques avec tube de Carius combiné soit à une dissolution par HF soit à une fusion alcaline permettent d'obtenir des résultats fiables. Ces résultats ont démontré que OPY-1 est suffisamment homogène sur un aliquote de 2 g pour servir de matériau de référence dans le cadre de validation de méthodes. La procédure de fermeture du tube de Carius a été simplifiée et les protocoles d'attaque améliorés.

Mots-clés : OPY-1, GeoPT 20, PGE, ICP-MS, tube de Carius.

Platinum-group elements (PGEs) are important for understanding petrogenetic processes involving igneous rocks and evolution of the Earth, e.g., core segregation, as well as core-mantle and mantle-crust interaction (Aulbach *et al.* 2004, Pearson *et al.* 2004). The determination of PGEs in geological materials is difficult because of their low abundance, heterogeneous distributions and the complexity of sample preparation. Methods for dissolving geological samples include nickel sulfide (NiS) fire assay (Zhou *et al.* 2001,

Gros *et al.* 2002, Juvonen *et al.* 2002, Sun and Sun 2005), acid attack combined with Na₂O₂ fusion (Yi and Masuda 1996, Qi *et al.* 2003, 2004), *aqua regia* dissolution in a sealed Carius tube, and a high pressure ashler (HPA-S) (Shirey and Walker 1995, Cohen and Waters 1996, Rehkämper *et al.* 1998, Pearson and Woodland 2000, Brauns 2001, Meisel *et al.* 2001, 2003a, 2003b, 2004, Pretorius *et al.* 2003). Among these methods, the NiS fire assay technique utilises relatively large amounts of sample, such that the nugget

effect of sample heterogeneity is largely reduced, but the procedural blanks for PGEs are relatively high (Sun and Sun 2005). Techniques combining the acid attack with Na₂O₂ fusion have lower procedural blanks (< 0.1 ng g⁻¹) (Qi *et al.* 2004), but Os can not be measured because of the loss of the volatile Os tetraoxide, OsO₄.

Because samples are dissolved with *aqua regia* in a sealed glass tube under high temperatures (220–240 °C for Carius tube, 300 °C for HPA-S), the Carius tube and HPA-S techniques have the lowest procedural blanks amongst all the techniques and all the PGEs are in their highest oxidation state with complete equilibration between spikes and samples. However, silicate phases can only be totally dissolved by HF, and these phases may host a small portion of the PGEs that cannot be leached by *aqua regia*. Previous studies did not deal with the PGEs in the silicate portion.

The alkali fusion technique can rapidly and effectively dissolve almost all kinds of geological samples using glassy carbon crucibles (Enzweiler *et al.* 1995, Dai *et al.* 2001), zirconium crucibles (Enzweiler and Potts 1995, Yi and Masuda 1996) or corundum crucibles (Jin and Zhu 2000, Qi *et al.* 2003), but the silicate colloid, a by-product of the sample preparation, is difficult to remove when the sample mass is more than 5 g.

OPY-1 is a new proficiency testing reference material recently prepared by the IAG. The assigned values for major and trace elements were reported by Webb *et al.* (2007), but not for PGEs. In this paper, we measure the PGE contents and evaluate the homogeneity of this sample. The sample preparation techniques included an improved Carius tube method, the Carius tube method combined with HF dissolution and the alkaline fusion method. In particular, our modified procedure of dissolving the silicate phase with HF and HCl combining with the Carius tube dissolution was designed to ensure that all the PGEs are leached from the sample. Because OPY-1 was found to be very homogeneous and has relatively high Os, Ir and Ru, we also dissolved a 2 g sample by alkali fusion in order to compare the results with those from the Carius tube technique.

Experimental

Instrumentation

The instrument used for analysis in this study was an ELAN DRC-e ICP-MS at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry,

Chinese Academy of Sciences, Guiyang. Background counts for 2% v/v HNO₃ solutions were normally < 5 cps (counts per second) for PGEs. Relative standard deviations of 10 ng ml⁻¹ PGE standard solution were typically less than 2% for raw counts. Throughout this study, sample solutions were introduced using self-aspiration (about 17 cm for the introduction tube) to reduce memory effects. The sensitivity of the instrument was adjusted to more than 45000 cps for 1 ng ml⁻¹ of ¹¹⁵In, in order to achieve the desired detection limits. The instrument settings are outlined in Table 1.

Table 1.
Instrumental operating parameters

Parameter	Value
RF power	1100 W
Plasma gas	15 l min ⁻¹
Auxillary gas	1.20 l min ⁻¹
Nebuliser gas	0.79 l min ⁻¹
Sweeps	20
Readings	1
Replicates	3
Scan mode	Peak hopping
Dwell time per AMU	50 ms
Sampling cone (Ni)	1 mm
Skimmer cone (Ni)	0.8 mm

Reagents and solutions

Hydrofluoric acid, HCl and HNO₃ were purified by sub-boiling distillation. Water was obtained from an 18 MΩ cm grade Millipore purification system. Spike solutions with enriched stable isotopes, ¹⁹⁰Os, ¹⁹³Ir, ¹⁰¹Ru, ¹⁰⁵Pd and ¹⁹⁴Pt were prepared from pure metals (US Services Inc., Oxbow, N.J.) and then diluted to 100 ng g⁻¹ in 10% v/v HCl solution. The isotopic abundances of the spike are listed in Table 2. An ICP multi-element standard solution of 100 μg ml⁻¹ Ir, Ru, Rh, Pt, Pd and Au (AccuStandard, USA) was used and diluted as needed for spike calibration and external calibration for the mono-isotopic element Rh. The ¹⁹⁰Os spike for alkaline fusion was converted to 10% ammonia solution to avoid any possible loss during evaporation.

The Te solution (2 mg ml⁻¹) was prepared by dissolving 0.5 g of TeO₂ in 10 ml of concentrated HCl, and diluted to 200 ml with distilled water. The SnCl₂ solution (20% w/v) was prepared by dissolving 50 g of SnCl₂ in 250 ml of 6 mol l⁻¹ HCl. The Te-coprecipitation method was used to purify this solution from PGEs (Qi *et al.* 2003). Analytical reagent-grade Na₂O₂ and 30 ml corundum crucibles were used for the alkaline fusion.

Table 2.
Isotopic abundances of the spike

Isotope	Abundance (%)	Isotope	Abundance (%)
¹⁹⁵ Pt	3.78	¹⁰¹ Ru	96.03
¹⁹⁴ Pt	95.06	¹⁹¹ Ir	0.67
¹⁰⁶ Pd	2.35	¹⁹³ Ir	99.33
¹⁰⁵ Pd	96.58	¹⁹⁰ Os	91.95
⁹⁹ Ru	0.24	¹⁹² Os	4.27

Laboratory ware

The Carius tubes used in this study were conventional borosilicate glass tubes similar to those described by Shirey and Walker (1995), and had a length of 215 mm (the main body) with a 20 mm inner diameter and a 25 mm outer diameter. They had an inner volume of about 75 ml. The tubes were pre-cleaned with 60% v/v *aqua regia* and heated to 80 °C for 5 hours. After rinsing with water, the tubes were annealed at 560 °C for 8 hours to avoid possible cracking.

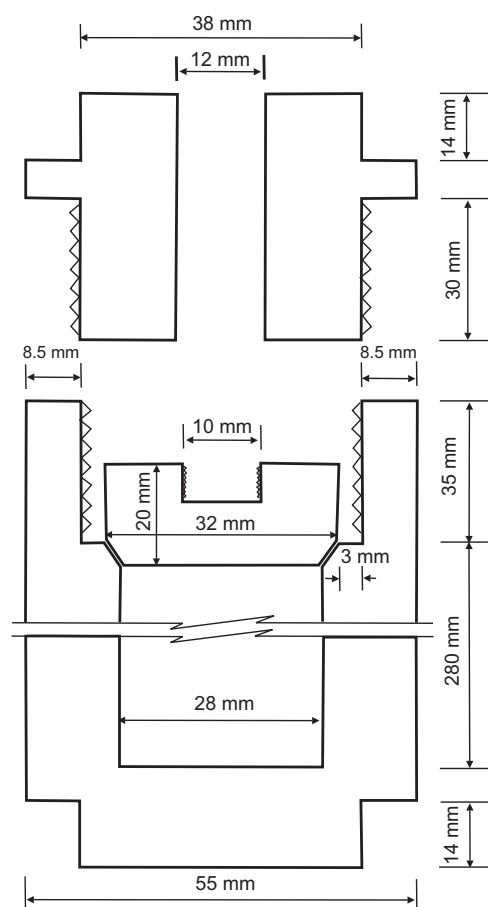


Figure 1. A sketch diagram showing the design of the stainless steel high pressure autoclave.

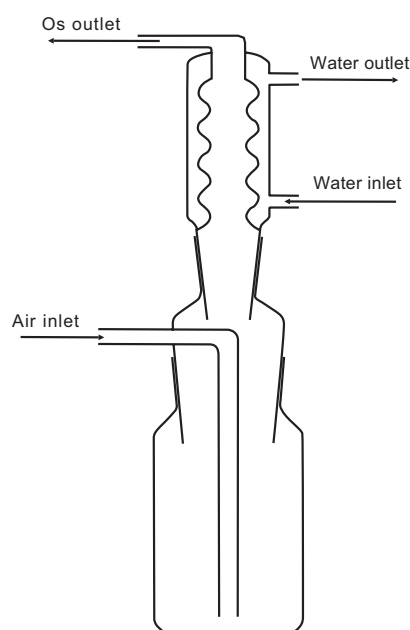


Figure 2. A sketch diagram showing the Os distillation system.

A custom-made, high-pressure steel autoclave with an inner volume of 172 ml was used to prevent explosion of the Carius tube (Figure 1). A custom-made distillation system (Figure 2) was used to distil Os from the matrix. Prior to the experiment, all parts were cleaned with hot *aqua regia*, then rinsed with water, and heated to 300 °C to reduce memory effects.

Mass spectrometry

The mass bias effects of Os and other PGEs were externally monitored using 10 ng ml⁻¹ of a natural standard solution determined during the course of the measurement. The mass bias factors were calculated using the measured values and isotopic reference values described in IUPAC (1991) following the exponential fractionation law as described by Schoenberg *et al.* (2000).

Analytical procedures

Improved Carius tube technique (Method 1)

Two grams of powdered sample were accurately weighed and placed in a Carius tube. Appropriate amounts of the enriched isotope spike solution containing ¹⁹³Ir, ¹⁰¹Ru, ¹⁹⁴Pt and ¹⁰⁵Pd were accurately weighed and added to each sample. The Carius tubes were cooled in an ice-water bath and 5 ml of 10 mol l⁻¹

HCl and 10 ml of 16 mol l⁻¹ HNO₃ were added to the Carius tube. A small glass tube (inner size: 3 mm x 25 mm) containing an ¹⁹⁰Os spike was accurately weighed and added to the Carius tube which was then sealed. The sealed Carius tube was placed in a stainless steel high-pressure autoclave, which was then filled with 55 ml of water. The autoclave was sealed and heated to 300 °C in an electric oven for 12 hours. After slowly cooling in air to room temperature, the autoclave was opened and the Carius tube was further cooled in a refrigerator for 2 hours. The Carius tube was then opened in order to transfer the contents into a 50 ml centrifuge tube (make up to 35 ml) which was centrifuged at 2200 rpm for 5 minutes.

The solution was decanted to a distillation system (Figure 2), leaving the solid portion behind and the solution was heated to boiling. The acid steam was cooled using a cooling water system and the OsO₄ vapour was trapped with 5 ml of 5% v/v HCl solution cooled in an ice-water bath. About 95% of the Os was trapped after a 90 minute distillation. This solution was used for measuring Os concentration by ID-ICP-MS.

After the distillation, the residual solution was transferred to a 125 ml Savillex Teflon beaker and evaporated to dryness. Following this, residual HNO₃ was removed from the sample by drying down twice with 6 ml of concentrated HCl. The residue was dissolved with 50 ml of 3 mol l⁻¹ HCl and then transferred to a 50 ml tube and centrifuged at 2200 rpm for 5 minutes. The upper solution was used to preconcentrate PGEs by Te-coprecipitation. After dissolving the Te-precipitate by *aqua regia*, the solution was evaporated to near dryness and dissolved with 0.5 ml of *aqua regia* and then diluted to 10 ml. The solution was passed through a mixed ion exchange column that contained a Dowex 50 WX 8 cation exchange resin and a P507 extraction chromatograph resin to remove the main interfering elements, including Cu, Ni, Zr and Hf (Qi *et al.* 2004). The eluted solution was collected in the original beaker and evaporated on a hot plate to about 3 ml for ICP-MS measurement. Platinum, Pd, Ru and Ir were measured by isotope dilution, whilst ¹⁹⁴Pt was used as the internal standard to calculate the abundance of the mono-isotope element, Rh (Qi *et al.* 2004).

The silicate residue from the original Carius tube digestion was washed with 2 mol l⁻¹ HCl six times to ensure total separation of the PGEs that were leached by *aqua regia* in the Carius tube. The residue was then dissolved by HF and HCl and transferred to a

Carius tube again for digestion. The PGEs were then pre-concentrated following the procedure described above to investigate PGEs in the silicate phase after Carius tube digestion.

Improved Carius tube technique combined with HF dissolution (Method 2)

The sample digestion steps before opening the Carius tube are same as described above. The contents of the Carius tube were transferred into a 50 ml centrifuge tube, which was centrifuged at 2200 rpm for 6 minutes. The upper part of the solution was transferred to the distillation system (Figure 2) and cooled in a refrigerator. The residue was rinsed five times with 5 ml of 1 mol l⁻¹ HCl to completely remove *aqua regia* and this wash was combined with the solution in the distillation system. HF (10 ml) was added to dissolve completely the residue, and was evaporated to dryness. Residual HF was removed from the sample by drying down twice with 3 ml of concentrated HCl. The residue was dissolved with 6 mol l⁻¹ HCl and the solution was added to the distillation system for Os distillation. The following steps for PGEs separation are as described above (Method 1).

Alkaline fusion (Method 3)

Two grams of powdered sample were accurately weighed and placed in a 30 ml corundum crucible. An appropriate amount of enriched isotope spike solution containing ¹⁹³Ir, ¹⁰¹Ru, ¹⁹⁴Pt and ¹⁰⁵Pd was added drop wise to each sample to avoid the solution contacting the crucible wall (the crucible may absorb the spike solution and it is then difficult to leach the spike out), and the crucible was evaporated to dryness on a hot plate. After cooling down, an ¹⁹⁰Os spike solution was added and evaporated as describe for the previous spike solution. The sample was crushed with a glass rod and mixed with 8 g of Na₂O₂. The crucible was then transferred into a cold furnace. The temperature of the furnace was slowly increased to 720 °C for 20 minutes. After cooling, the crucible was placed in a 150 ml beaker, and the fusion cake was dissolved with 30 ml of de-ionised water. The crucible was then removed from the beaker and rinsed with HCl. Concentrated HCl was added until the hydroxide precipitate was dissolved. This solution was transferred to the distillation system and 15 ml of *aqua regia* were added for Os distillation. After distillation, the solution was evaporated to dryness, dissolved with 40 ml of 2 mol l⁻¹ HCl and filtered to remove the silicate. The

filtered solution was used to separate PGE by Te-coprecipitation as described above (Method 1).

technique is still suitable for routine PGE analysis for ultramafic rocks.

Results and discussion

Procedural blank and detection limits

The total procedural reagent blank was prepared following the same techniques described above. The average compositions of five total procedural reagent blanks for the Carius tube technique combined with HF dissolution and alkaline fusion are shown in Table 3. The blank levels ranged from 0.0012 ng (Os) to 0.036 ng (Pd) for the Carius tube technique combined with HF dissolution and 0.034 ng (Os) to 0.46 ng (Pt) for alkaline fusion. The detection limit (ng g⁻¹) was calculated as three times the standard deviation of five individual procedural reagent blanks (ng), divided by the sample mass (2 g). The detection limits ranged from 0.0003 ng g⁻¹ (Os) to 0.006 ng g⁻¹ (Pd) for the Carius tube technique combined with HF dissolution and 0.007 ng g⁻¹ (Ir) to 0.098 ng g⁻¹ (Pt) for alkaline fusion (Table 3). The Carius tube technique had a blank level and detection limit almost the same as the Carius tube combined with HF dissolution technique. The results for the three methods described above were calculated by subtracting the relevant procedural blank.

As Na₂O₂ cannot be purified, the blank levels for alkaline fusion are higher than those for the Carius tube technique. However, ultramafic rocks have relatively high Os, Ir and Ru so that the procedural blanks are less than 6% of the total value for OPY-1. Thus, this

Addition of Os spike

In order to avoid possible loss of Os, Shirey and Walker (1995) froze the Carius tube in an ethanol-dry ice slush before sealing. In the current study, we placed the solution with the Os spike into a small glass tube (inner size, 3 mm x 25 mm) and then added it to the Carius tube, which was pre-cooled in an ice-water bath. Because of the small diameter of the tube (3 mm), the *aqua regia* did not enter the tube and loss of the Os spike was avoided. Thus, any possible loss of Os is from the sample. To determine if Os could be leached out of OPY-1 by *aqua regia* in our technique, *aqua regia* (10 ml) was added to 1 g of sample under an ice-water bath for 1 hour. After centrifuging, the upper portion of the solution was distilled and measured by ICP-MS. The Os intensity was almost the same as the blank, indicating a negligible loss of Os, which could be ignored. This demonstrates that an ice-water bath can be used to prevent the loss of Os in the spike and sample during sealing of the Carius tube. The ice-water bath is easier to use than the ethanol-dry ice slush. When the Carius tube was heated to high temperature, the Os spike in the small glass tube evaporated out and was fully equilibrated with the sample.

For alkaline fusion, the Os spike solution must be evaporated to dryness before digestion with Na₂O₂. Thus, the Os spike was prepared using a 10% v/v ammonia solution because Os may be lost from the

Table 3.
Blank level (ng) and detection limits (DL, ng g⁻¹)

Elements	Blank-1	Blank-2	Blank-3	Blank-4	Blank-5	Average (ng)	DL (3s)
Carius tube combined with HF dissolution							
Os	0.0012	0.0011	0.0009	0.0015	0.0013	0.0012	0.0003
Ir	0.008	0.010	0.011	0.009	0.007	0.009	0.0024
Ru	0.006	0.005	0.009	0.007	0.010	0.007	0.003
Rh	0.011	0.008	0.009	0.007	0.008	0.009	0.002
Pt	0.025	0.023	0.019	0.018	0.024	0.022	0.005
Pd	0.033	0.036	0.04	0.031	0.039	0.036	0.006
Alkaline fusion							
Os	0.023	0.040	0.035	0.031	0.042	0.034	0.011
Ir	0.036	0.032	0.045	0.035	0.038	0.037	0.007
Ru	0.051	0.041	0.058	0.049	0.045	0.049	0.010
Rh	0.046	0.034	0.036	0.041	0.045	0.040	0.008
Pt	0.45	0.48	0.55	0.371	0.44	0.46	0.098
Pd	0.25	0.22	0.21	0.26	0.23	0.23	0.031

acid solution during evaporation. In addition, the total volume for Os spike was reduced to 0.1 ml to avoid the solution contacting the crucible wall, which may absorb the spike solution.

Improved Carius tube technique

The Carius tube technique and HPA-S are often used for digesting refractory PGE minerals in geological samples and for Re-Os isotopic determinations (Shirey and Walker 1995, Cohen and Waters 1996, Rehkämper *et al.* 1998, Pearson and Woodland 2000, Brauns 2001, Meisel *et al.* 2001, 2003a, 2003b, 2004, Pretorius *et al.* 2003). This technique has the possible hazard of explosion at high temperature. In our improved Carius tube technique, a stainless steel high-pressure autoclave was used and filled with water before being sealed (Figure 1). The external pressure produced by the water when heated balanced the internal pressure of the Carius tube. This improved technique protected the Carius tube from explosion. Thus, the Carius tube could be heated to relatively high temperatures (300 °C) for more effective sample leaching and digestion.

Although explosions of the Carius tube can be prevented, some leakage of acid can occur if the tube is cracked due to incomplete annealing during sealing of the tube or the presence of sulfide or carbonate in the sample. Reaction between acids and stainless steel can produce high pressures in the autoclave. Thus, to avoid problems during the opening of the autoclave, the screw top of the autoclave was loosened gently, and the copper stopper was loosened through a 12 cm diameter hole in the top of the autoclave. After this, the autoclave could be completely opened (Figure 1). No cracks were produced in the

Carius tube when heating ultramafic rocks in the autoclave as long as the tube was well annealed. Our 172 ml autoclave filled with 160 ml water could reach temperatures of 400 °C, making it safe to heat the autoclave to 300 °C. Compared to the traditional Carius tube digestion technique, this improved technique is effective and safe.

Effectiveness of the Carius tube technique

Ultramafic rocks contain abundant refractory minerals (e.g., chromite) which host most of the PGEs in the sample. It has been demonstrated that chromite can be completely dissolved by *aqua regia* or concentrated sulfuric acid in a Carius tube (Pearson and Woodland 2000, Puchtel and Humayun 2001, Buchl *et al.* 2004), but the silicates cannot be dissolved. Although the effectiveness in quantitative extraction of PGEs from silicate rocks by using the Carius tube method and high-pressure asher (HPA-S) has been documented by previous workers (Shirey and Walker 1995, Cohen and Waters 1996, Pearson and Woodland 2000, Meisel and Moser 2004), no studies have been carried out to determine if any of the PGEs are hosted in the silicate phase.

In this study, the residue was washed with 2 mol l⁻¹ HCl six times to ensure total separation of the PGEs, which were leached by *aqua regia* in the Carius tube at 300 °C. The silicate residue was spiked and dissolved with HF and HCl in a Savillex Teflon beaker and then transferred to a Carius tube for further digestion. PGEs were separated and measured by ID-ICP-MS using the procedure described above. The results demonstrated that about 4-15% of the PGEs are hosted in the silicate phase (Table 4).

Table 4.
Analytical results (ng g⁻¹) of residue (R) and Carius tube (CT) methods for OPY-1

Sample No.	R*	CT**	R	CT	R	CT	R	CT	R	CT	Total
	1	1	2	2	3	3	4	4	Average ± s	Average ± s	
Sample mass (g)	2	2	2	2	2	2	2	2			
Os	0.023	0.67	0.027	0.58	0.029	0.61	0.024	0.59	0.026 ± 0.003	0.61 ± 0.04	0.64 ± 0.04
Ir	0.17	0.87	0.16	0.88	0.15	0.89	0.14	0.86	0.16 ± 0.01	0.88 ± 0.01	1.04 ± 0.02
Ru	0.22	4.48	0.25	4.57	0.18	4.55	0.23	4.59	0.22 ± 0.03	4.56 ± 0.05	4.78 ± 0.06
Rh	0.19	1.11	0.24	1.37	0.19	1.34	0.25	1.22	0.22 ± 0.03	1.26 ± 0.12	1.48 ± 0.13
Pt	1.43	11.1	1.48	11.0	1.60	10.9	1.66	11.0	1.54 ± 0.11	11.0 ± 0.1	12.5 ± 0.1
Pd	0.79	11.5	0.85	11.0	0.75	11.0	0.93	10.8	0.83 ± 0.08	11.1 ± 0.3	11.9 ± 0.3

* R = Residue. ** CT = Carius tube. s Standard deviation.

Meisel *et al.* (2003b) report that the well-established Carius tube acid digestion technique fails to completely digest all Os-bearing mineral phases. Becker *et al.* (2006) suggest that samples must be ground as finely as possible (< 10 μm) for successful digestion. They also report that even at 345 °C, clinopyroxene appears undigested, and orthopyroxene may only be partially digested by the Carius tube technique. Because the precise mineralogy of the geological samples may not be known, it is important to completely dissolve the sample, so as not to lose any of the PGEs.

Rehkämper *et al.* (1998) used HF to remove silica before Carius tube digestion. Because Ca and Mg were not removed, a large amount of fluoride precipitate results, which is difficult to remove and will erode the glass ware of the Os distillation system. Furthermore, transferring the residue to a Carius tube is difficult. To dissolve the sample completely, reduce the fluoride and eliminate the need to transfer the residue to a Carius tube, we used HF and HCl to dissolve completely the silicate residue after Carius tube digestion as describe above. Because most of the Ca and Mg were dissolved and separated during the Carius tube digestion, this modified procedure can significantly reduce the fluoride residue, totally dissolve the sample and avoid any loss of Os.

Comparison of values obtained using different digestion techniques

The analytical results using the Carius tube method and the composition of the relevant residue are listed in Table 4. The total values are the average values from the Carius tube method combined with average residue

values. In Table 5 we compare the measured PGE values of OPY-1 obtained using the Carius tube method combined with HF dissolution and the alkaline fusion technique. Table 5 also presents our analytical results using the Carius tube method combined with HF dissolution for the CCRMP (Canadian Certified Reference Material Project) reference material, WPR-1, and compares them to the certified values for this reference material from Govindaraju (1994). As seen in Table 5, our results for WPR-1 agree closely with the reference values, confirming the validity of this technique.

The values obtained for OPY-1 using the Carius tube method (Table 4) are slightly lower than those obtained using the Carius tube method with HF dissolution technique (Table 5), but when the residue values in Table 4 are added to the measured values (the total values in Table 4), the results are nearly identical (Figure 3). In Table 5 and Figure 3, it can also be seen that the values obtained using alkaline fusion are close to those obtained using the Carius tube method with HF dissolution technique.

Table 6 compares the results of twelve independent preparations of OPY-1 using all three techniques with information values from four international laboratories (Webb *et al.* 2007). Our average results (n = 12, except Os) were higher than the Carius tube technique and the four international laboratories (Table 6 and Figure 4), but the results for Ir, Ru, Rh, Pt and Pd for the Carius tube technique are in fairly good agreement with those from laboratories U36, U40 and U65 except that our Os value is somewhat lower than those reported by laboratories U36 ad U40 (Table 6 and Figure 4), although we do not know what techniques were used by each external laboratory. The Ru value

Table 5.
Analytical results (ng g⁻¹) for Carius tube combined with HF and fusion techniques for OPY-1 and for WPR-1 (with certified values)

Sample No.	Carius tube combined with HF						Alkaline fusion				
	OPY-1					Average ± s	WPR-1		OPY-1		
	1	2	3	4	5		N = 3	Certified*	1	2	3
Sample mass (g)	2	2	4	4	4	3		2	2	2	
Os	0.64	0.74	0.63	0.61	0.66	0.66 ± 0.04		0.71	0.69	0.66	0.69 ± 0.03
Ir	1.08	1.04	1.01	1.05	1.09	1.05 ± 0.03		1.17	1.09	1.12	1.13 ± 0.04
Ru	5.03	5.09	4.82	4.83	4.68	4.89 ± 0.14		5.09	5.13	4.88	5.03 ± 0.13
Rh	1.74	1.65	1.53	1.50	1.29	1.54 ± 0.14		1.58	1.63	1.55	1.59 ± 0.04
Pt	13.2	13.0	12.3	13.1	13.0	12.9 ± 0.29		12.9	13.5	13.3	13.2 ± 0.31
Pd	12.1	12.3	12.1	12.2	12.3	12.2 ± 0.1		12.4	12.9	12.2	12.5 ± 0.36

s Standard deviation. * Govindaraju (1994).

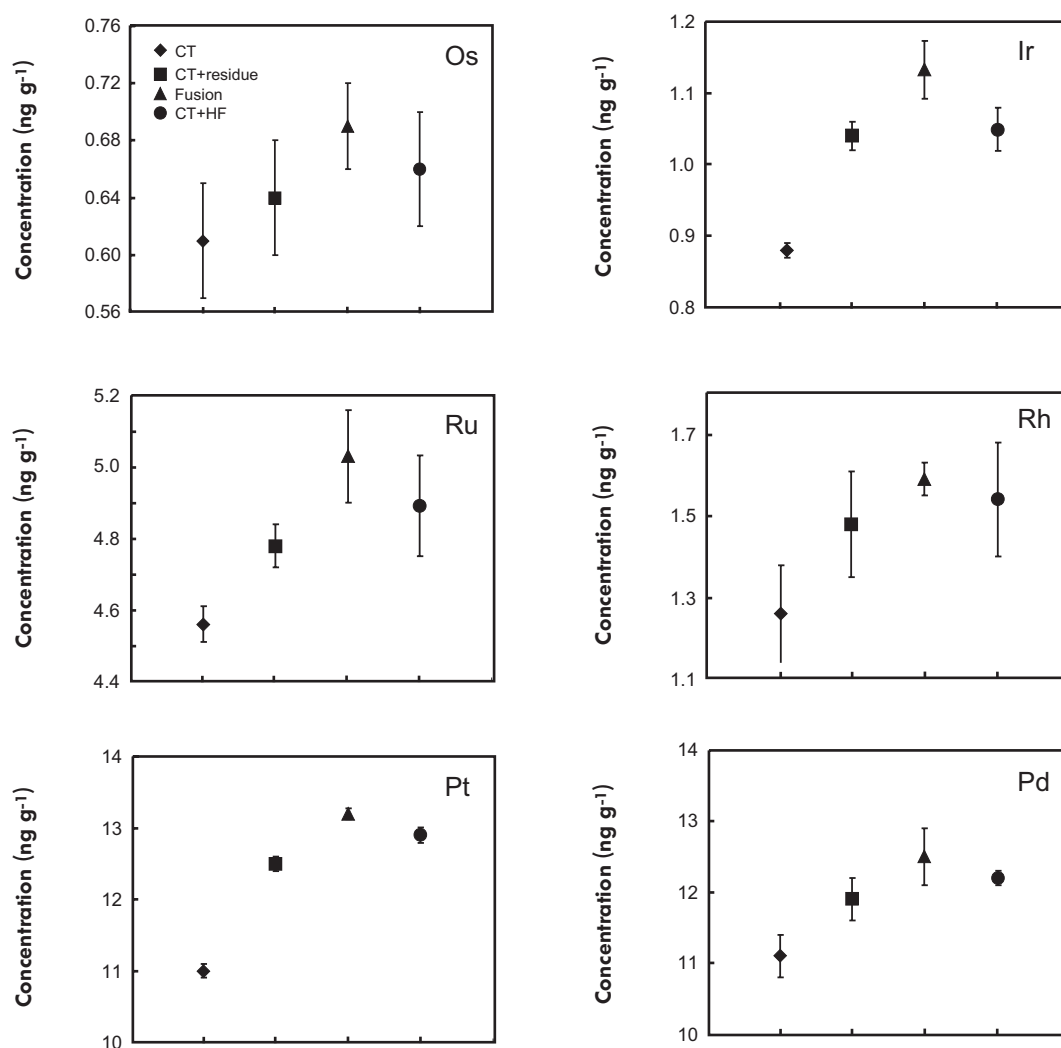


Figure 3. Comparison of results for OPY-1 for Carius tube, Carius tube + residue, Carius tube combined with HF dissolution and alkaline fusion methods.

Table 6.

Comparison the results (ng g⁻¹) of OPY-1 with information values from four laboratories

	Average ± s** (n = 12) This work	% RSD	Carius tube This work	Information value			
				U36*	U40*	U48*	U65*
Os	0.66 ± 0.04	6.5	0.61	1.01	0.79	-	-
Ir	1.06 ± 0.05	4.5	0.88	0.94	0.95	-	0.97
Ru	4.89 ± 0.16	3.3	4.56	3.78	4.17	-	4.54
Rh	1.53 ± 0.13	8.6	1.26	1.25	1.35	-	1.46
Pt	12.9 ± 0.4	2.9	11.0	10	10.16	5.6	11.36
Pd	12.2 ± 0.3	2.6	11.1	10	10.85	11.2	11.74

s Standard deviation.

* Is the Lab code of GeoPT-20 (Webb *et al.* 2007).

** Results of Carius tube + residue, Carius tube combined with HF dissolution and alkaline fusion.

produced by laboratory U36 is notably lower than the values produced by us and by the other two laboratories. All the values yield smooth primitive mantle-normalised patterns (Figure 5).

The evidence discussed above indicates that a small proportion of PGEs are hosted in the silicate phases in OPY-1. Thus, complete dissolution is needed for ultramafic rocks.

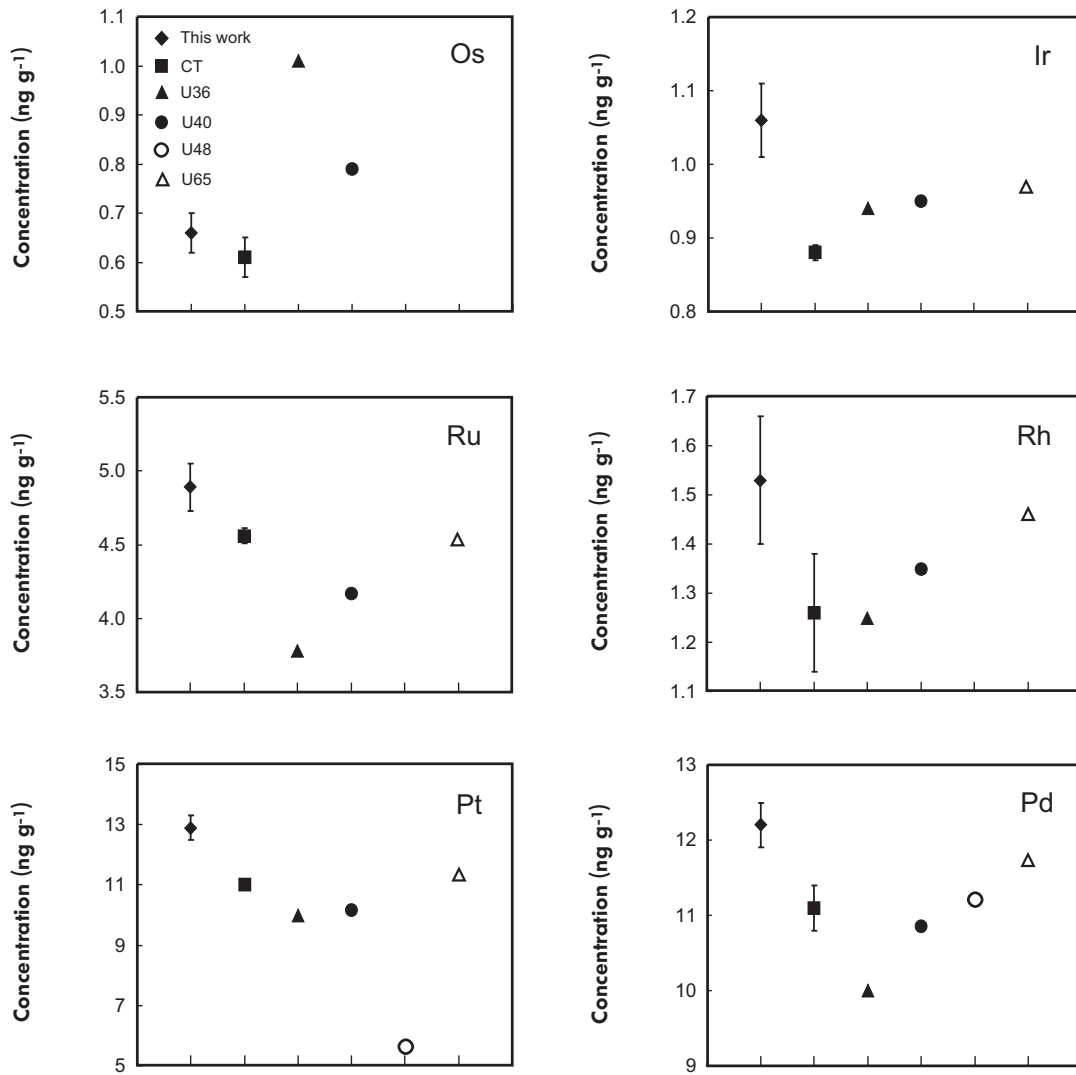


Figure 4. Comparison of values obtained by the Carius tube method and average results with information values from four laboratories.

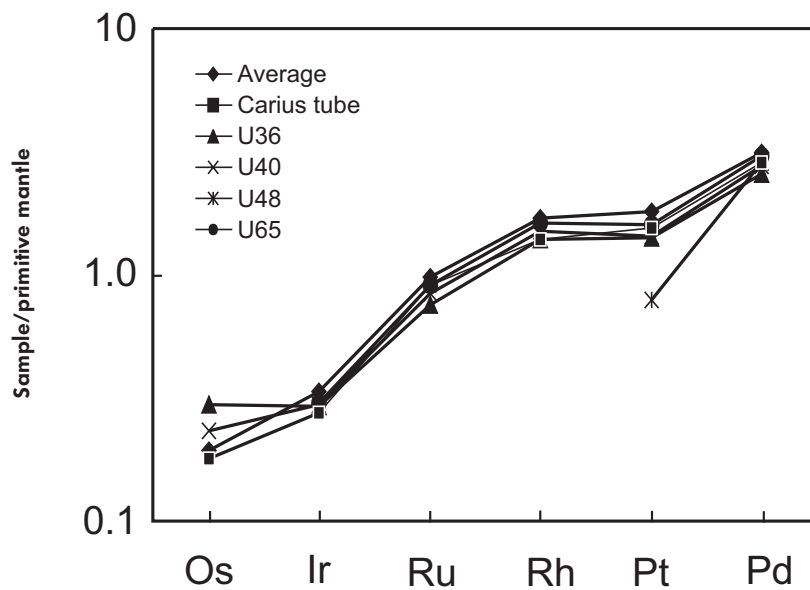


Figure 5. Primitive mantle-normalised PGE patterns for average PGE values obtained for OPY-1 compared with those obtained with the Carius tube technique and information values from four independent laboratories. The normalisation values are from Sun and McDonough (1989).

The % RSD of the PGEs for twelve independent preparations range from 2.6 to 8.6 (Table 6), indicating that the 2 g test sample portions level for OPY-1 is sufficiently homogeneous to be suitable as a reference material for method validation.

Conclusions

By measuring the PGEs in the residue of OPY-1 after Carius tube digestion, we found that about 4-15% of the PGEs are in the silicate phase and cannot be leached by *aqua regia* or digested even at 300 °C. Thus, complete digestion of ultramafic rocks is necessary for accurate measurement. The analytical results of OPY-1 for the Carius tube method are in good agreement with three international laboratories, but lower than those produced by the Carius tube combined with HF dissolution and the alkaline fusion techniques, indicating that both methods provide reliable means of determining PGEs in ultramafic rocks. For 2 g test sample portions, OPY-1 is sufficiently homogeneous as a reference material for method validation. We also provide new PGE data for OPY-1.

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