Evaluation of a technique for determining Re and PGEs in geological samples by ICP-MS coupled with a modified Carius tube digestion

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In the determination of Re and platinum group elements in geological samples, various techniques have been employed for digesting samples, including Carius tube, high-pressure asher (HPA-S), alkali fusion and nickel sulfide fire assay. The normal Carius tube technique is able to digest relatively small amount of sample and has a possible safety problem caused by a high internal pressure. This paper reports a modified Carius tube method which utilizes a sealed stainless steel high-pressure autoclave filled with water to prevent explosion of the tube. During heating, the external and internal pressures of the Carius tube increase simultaneously, such that the possible explosion of Carius tube can be avoided. Consequently, this technique allows a higher temperature (up to 330°C), a greater volume of aqua regia (up to 2/3 of the total volume of the Carius tube) and thus larger sample mass (12 g) relative to the normal Carius tube technique. Fairly good agreement were obtained for PGE poor mafic rocks (IPGE < 0.03 ng/g). The efficiency to dissolve ultramafic rocks and chromites at different temperatures was investigated. We demonstrate that this technique is more effective than normal Carius tube technique for ultramafic rocks and chromites containing refractory minerals and the detection limits and precision can be improved for PGE poor mafic samples. The total procedural blanks are lower than 0.003 ng for Os, 0.03 ng for Re, Ir, Ru and Rh and 0.4 ng for Pd and Pt.

Keywords: rhenium, PGEs, ICP-MS, Carius tube, high pressure autoclave

INTRODUCTION

Platinum group elements (PGEs) and Re are important for the understanding of petrogenetic processes and evolution of the Earth, e.g., core segregation, core-mantle, and mantle-crust interactions (Brandon *et al.*, 1998; Shirey and Walker, 1998). The determination of PGEs in geological materials is difficult because of their low abundance and heterogeneous distributions and the complexity of sample preparation. Methods for dissolving geological samples and thereby for concentrating PGEs include nickel sulfide (NiS) fire assay coupled with Te coprecipitation (Jackson *et al.*, 1990; Zhou *et al.*, 2001; Gros *et al.*, 2002; Juvonen *et al.*, 2002; Sun and Sun, 2005), acid attack combined with Na_2O_2 fusion (Morgan and Walker, 1989; Yi and Masuda, 1996; Dai *et al.*, 2001; Qi *et al.*, 2003, 2004), aqua regia dissolution in a sealed Carius tube, and high pressure asher (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; Pretorius *et al.*, 2003; Meisel and Moser, 2004). The advantages and disadvan-

tages of these methods have been discussed in several review papers (Barefoot, 1998; Barefoot and Van Loon, 1999; Reddi and Rao, 1999). Among these methods, the NiS fire assay technique utilizes relatively large amounts of sample, such that the effects of sample heterogeneity is largely reduced, but in general procedural blanks for PGEs are relatively high (Sun and Sun, 2005). Techniques combining the acid attack with Na_2O_2 fusion have lower procedural blanks (Qi *et al.*, 2004), but Os can not be measured because of the loss of volatile Os oxide, OsO_4 (Sun *et al.*, 2001).

Techniques using a Carius tube and HPA-S have total procedural blanks as low as 0.04 ng for Pt and 0.005 ng for other PGEs (Meisel *et al.*, 2003a), because small volumes of reagents in a sealed glass tube are used. These two techniques have been proved to be efficient in dissolving refractory PGE minerals in geological samples for simultaneously measuring Re, Os and other PGEs (Shirey and Walker, 1995; Cohen and Waters, 1996; Rehkämper *et al.*, 1998; Pearson and Woodland, 2000; Brauns, 2001; Meisel *et al.*, 2001, 2003a, 2003b; Pretorius *et al.*, 2003; Meisel and Moser, 2004). Because samples are dissolved in aqua regia under high temperatures (220–240°C for Carius tube, 300°C for HPA-S), all the PGEs are in their highest oxidation state with complete equili-

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bration between spikes and samples. However, 1–2 g sample is commonly used in a Carius tube and HPA-S (Pearson and Woodland, 2000; Meisel *et al.*, 2001, 2003a, 2003b; Meisel and Moser, 2004), with aqua regia less than one third of the total volume of the Carius tube to avoid possible crack caused by high internal pressure in the Carius tube.

Some samples, for example, PGE poor continental flood basalts and ocean island basalts, contain very low PGEs (Os, Ir and Ru < 0.02 ng/g), it is very difficult to obtain reliable results with sample mass of 1–2 g, especially for [99]Ru which has relatively low proportion (12.7% for [99]Ru). For ultramafic rocks and chromite, it is difficult to liberate all the PGEs from the samples only using aqua regia at temperature of about 220–240°C, because these samples contain refractory mineral, chromite. For these reasons, increasing the sample mass and elevating the digestion temperature are necessary to lower the detection limits and increase the recoveries for these kinds of samples.

Becker *et al.* (2006) used a steel pressure vessel containing 20 g dry ice to digest 2–3 g peridotite in a quartz glass Carius tubes at 345°C. The CO_2 pressure that builds up inside the pressure vessel upon warming supports the internal pressure in the Carius tube. They demonstrated that the spinels in peridotites were either completely dissolved, or oxidized.

In this study, the Carius tube is placed in a sealed stainless steel high pressure autoclave and filled with water to balance the internal pressure and to avoid the possible explosion. This modified approach allows us to digest 12 g of mafic samples, 10 g of ultramafic rocks and 2 g of chromite. We demonstrate that the improved technique is efficient for digesting mafic rocks, ultramafic rocks and chromites. The autoclave is of low cost and easy to maintain. Because methods for PGE pre-concentration and measurement were reported by many papers (Shirey and Walker, 1995; Birck *et al.*, 1997; Rehkämper *et al.*, 1998; Pearson and Woodland, 2000; Meisel *et al.*, 2001; Jensen *et al.*, 2003; Pretorius *et al.*, 2003), we focus on the efficiency of this modified technique for digesting geological samples at different temperature.

EXPERIMENTAL

Instrumentation

The instrument used in this study is a VG Plasma-Quad Excell ICP-MS in the Department of Earth Sciences, The University of Hong Kong. The solution introduction system, including the nebulizer, spray chamber, torch, and cones, are carefully cleaned to obtain low instrument blanks. Background counts for 2% HNO_3 solutions are normally <20 cps (counts per second) for Re and all PGEs. Relative standard deviations of 10 ppb PGE standard so-

Table 1. Instrumental operating parameters

Parameter	Value	Parameter	Value
Instrument	VG PQ Excell	Lens 1	–6.9 MV
Forward power	1350 W	Lens 2	–142 MV
Reflected power	<2 W	Lens 3	–156 MV
Cooling gas	13 L/min	Focus	19.1 MV
Auxiliary gas	0.80 L/min	Sampling cone (Ni)	1 mm
Nebulizer gas	0.75 L/min	Skimmer cone (Ni)	0.7 mm
Extraction	–599 MV	Detection mode	Peak jump

lution are typically less than 3% for raw counts. Throughout this study, sample solutions were introduced using self-aspiration instead of the peristaltic pump auto-sampler system, in order to shorten the length of the solution introduction tube and to reduce memory effects. The sensitivity of the instrument was adjusted to more than 50000 cps for 1 ng ml^{-1} of [115]In, in order to achieve the desired detection limits. The instrument settings are outlined in Table 1.

Reagents and solutions

HF, HCl and HNO_3 were purified by sub-boiling distillation, the first 100 ml of which was discarded. Water was obtained from 18 MΩ cm grade Millipore purification system.

Spike solutions with enriched stable isotopes, [185]Re, [190]Os, [101]Ru, [105]Pd, [193]Ir, and [194]Pt, were prepared from pure metals (US Services Inc., Oxbow, N.J.). Isotopic abundances of the spike are presented in Table 2. An ICP multi-element standard solution of 100 μg ml^{-1} Pt, Pd, Rh, Ru, Ir, and Au (AccuStandard, USA) was used and diluted as needed for calibration the spike and external calibration for the mono-isotopic element, Rh.

Te solution (about 2 mg ml^{-1}) was prepared by dissolving 0.5 g of TeO_2 in 10 ml of concentrated HCl, and diluted to 200 ml with distilled water.

The $SnCl_2$ solution (20%, w/v) was prepared by dissolving 50 g of $SnCl_2$ in 250 ml of 6 M HCl. This solution was purified using Te-coprecipitation from PGEs (Qi *et al.*, 2003).

Labware

Carius tubes used in this study are conventional borosilicate glass tubes similar to those described by Shirey and Walker (1995), which have length of 215 mm (the main body) with 21 mm inner diameter and 25 mm outer diameter. They have inner volume of about 75 ml and total volume of about 110 ml. The tubes were pre-cleaned with 60% aqua regia and heated to about 80°C for about 5 hours. After rinsed with water, the tubes were annealed at 560°C for about 8 hours to avoid possible cracking.

Isotope	Abundance (%)	Isotope	Abundance (%)
^{195}Pt	3.78	^{99}Ru	0.24
^{194}Pt	95.06	^{101}Ru	96.03
^{106}Pd	2.35	^{191}Ir	0.67
^{105}Pd	96.58	^{193}Ir	99.33
^{185}Re	94.36	^{190}Os	91.95
^{187}Re	5.64	^{192}Os	4.27

A high pressure autoclave to protect the Carius tube from explosion was custom-made of stainless steel (Fig. 1) and has inner volume of about 172 ml.

A custom-made distillation system was used to distill Os from the matrix. Prior to the experiment, all parts were cleaned with hot aqua regia, then rinsed with water, and heated to about 400°C to let all parts free of Os.

Analytical procedure

Sample powder was accurately weighed and placed in a Carius tube. Appropriate amount of enriched isotope spike solution containing ^{194}Pt, ^{105}Pd, ^{101}Ru, ^{193}Ir, ^{190}Os and ^{185}Re were accurately weighed and added to each sample. 15 ml of 10 M HCl and 20 ml of 16 M HNO$_3$ was added to the Carius tube, which was then sealed with a procedure similar to that described by Shirey and Walker (1995).

The sealed Carius tube was placed in a stainless steel high pressure autoclave, which was then filled with about 55 ml water. The autoclave was sealed and heated to 330°C in an electric oven for about 12 hours. After slowly cooled in air to room temperature, the autoclave was opened and the Carius tube was further cooled in a refrigerator for about 2 hours. The Carius tube was then opened in order to transfer the sample solution into a 50 ml centrifuge tube which was centrifuged at 2200 rpm for 6 minutes.

The upper part of the solution was transferred to a distillation system where the solution was heated to boiling (about 112°C for the aqua regia solution). The acid steam was cooled using a cooling water system and the OsO$_4$ vapor was trapped with 5 ml of 5% HCl solution cooled in an ice-water bath. About 95% of the Os was trapped after a 90 minutes distillation. This solution was used for measuring the Os concentration by ID-ICP-MS.

After the distillation, the residual solution with Re and PGEs in the distillation flask, was transferred to a 125 ml Savillex Teflon beaker and evaporated to dryness. Following this, 6 ml of concentrated HCl was added and evaporated to dryness. This procedure was repeated to let the solution free of HNO$_3$. The residue was dissolved with 50 ml of 3 N HCl. The resultant solution was then transferred to a 50 ml tube for centrifuging at 2200 rpm
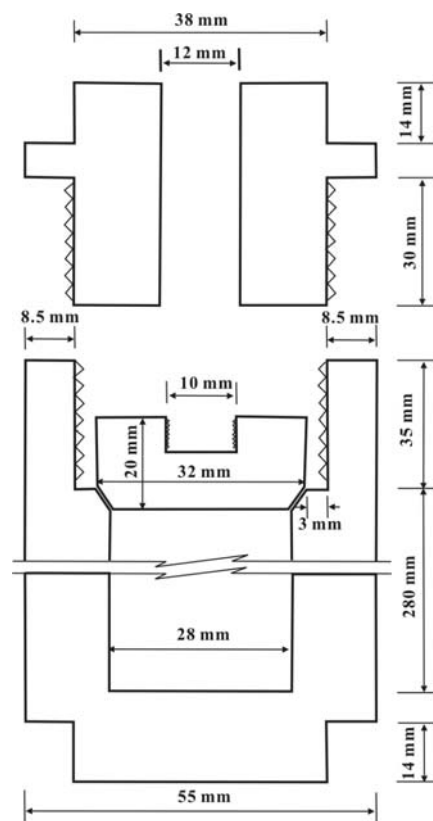
Fig. 1. A sketch diagram showing the design of a stainless steel high pressure autoclave.

for 6 minutes. About 10 ml of the centrifuged solution was used to separate Re from the matrix using AG 1-X8 anion exchange resin. The remaining 40 ml aliquot of this solution was used to preconcentrate PGEs by Te-coprecipitation. The solutions were then filtered using a Millipore membrane filter (type-HA, 0.45 μm).

The membrane was returned to the original beaker and dissolved using 3 ml aqua regia. The solutions were evaporated to near dryness on a hot plate before dissolved with 0.1 ml of HNO$_3$ and 10 ml of 0.5 M HCl. These solutions were passed through a mixed ion exchange column which contains 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, after the Te-coprecipitation (Qi *et al.*, 2004). The elution solution was evaporated to about 3–5 ml on a hot plate and then used for ICP-MS measurement. ^{195}Pt/^{194}Pt, ^{106}Pd/^{105}Pd, ^{99}Ru/^{101}Ru and ^{191}Ir/^{193}Ir ratios were measured by isotope dilution, whilst ^{194}Pt was used as the internal standard to calculate the abundance of the mono-isotope element Rh (Qi *et al.*, 2004). The mass bias was corrected with linear interpolation of the measured ratio of a 10 ng/ml natural Pt, Pd, Ru and Ir standard solution.

Table 3. PGE contents in Te solution (ng/ml), blank level (ng) and detection limits (DL, ng g^{-1})

Elements	Te solution	Blank-1	Blank-2	Blank-3	Blank-4	Blank-5	Average (ng)	DL (3σ)
Re		0.024	0.029	0.015	0.025	0.035	0.026	0.0018
Os		0.0032	0.0018	0.0016	0.0035	0.0028	0.0026	0.0002
Ir	0.014	0.022	0.026	0.035	0.022	0.018	0.025	0.0016
Ru	0.012	0.01	0.013	0.019	0.025	0.017	0.017	0.0014
Rh	0.010	0.033	0.017	0.027	0.029	0.024	0.026	0.0015
Pt	0.056	0.25	0.18	0.15	0.14	0.19	0.18	0.0108
Pd	0.150	0.26	0.33	0.41	0.45	0.38	0.37	0.0184

RESULTS AND DISCUSSION

Procedural blank and detection limit

The total procedural reagent blank was prepared using the same method as the sample decomposition and pre-concentration described above for real sample. The average of five total procedural reagent blanks are shown in Table 3. The blank levels range from 0.0026 ng (Os) to 0.37 ng (Pd). The detection limit (ng g^{-1}) is calculated as three times the standard deviation of five individual procedural reagent blanks (ng), divided by the sample weight (12 g). The detection limits (Table 3) range from 0.0002 ng g^{-1} (Os) to 0.018 ng g^{-1} (Pd). By examing the reagents used in this study, the blank are mainly from the Te solution (Table 3). The blank levels can be lowered if Te solution is further purified.

Usage of high pressure autoclave

The Carius tube technique and HPA-S are often used for digesting refractory PGE minerals in geological samples and Re–Os isotopic analyses (e.g., Shirey and Walker, 1995; Pearson and Woodland, 2000; Brauns, 2001; Meisel et al., 2003a, b; Pretorius et al., 2003; Meisel and Moser, 2004). Because of their low procedural blank compared to other techniques, these techniques leach and partially dissolve samples in a highly oxidizing solution (aqua regia) and can achieve full isotopic equilibration between spike and sample and avoid the loss of volatile species such as OsO$_4$. The amount of aqua regia normally used is less than one third of the total volume of the Carius tube with a temperature of about 220–240°C (Shirey and Walker, 1995; Cohen and Waters, 1996; Pretorius et al., 2003), because larger volumes and/or higher temperatures may rupture and create an explosion hazard.

In our modified Carius tube technique, a stainless steel high pressure autoclave is used and filled with water before sealed (Fig. 1). The external pressure produced by water when heated will balance the internal pressure of the Carius tube. This improved technique protects the Carius tube from explosion and the amount of aqua regia can be increased to about two thirds of the total volume of the Carius tube. Thus the Carius tube can be heated to 330°C for more effective sample leach and digestion.

Although Howard and Vocke (2004) and Becker et al. (2006) used dry ice to balance the internal pressure of Carius tube, however, the detail information of the steel pressure vessel, the Carius tube and the maximum of sample mass were not described. Dry ice may release at room temperature during sealing the autoclave and may have high pressure when open the autoclave. The suddenly decrease of pressure in autoclave may cause the crack of Carius tube, if internal pressure exist in carius tube. For using of water, the external and internal pressure of the Carius tube increase or decrease simultaneously during digestion, thus our method is more convenient and easy to operate.

Although we can prevent an explosion caused by the high internal pressure in the Carius tube, annealling during sealing of the Carius tube or some samples containing sulphide or carbonate may cause cracking of the glass tube, resulting in leakage of acid from the Carius tube. The reaction between acids and stainless steel can produce high pressure in the autoclave. To avoid any possible hazard, during the opening of the autoclave, the screw top of the autoclave was gently loosened. Then the copper stopper was loosened through a 12 cm diameter hole designed in the centre of the screw top of the autoclave and then the autoclave can be totally opened (Fig. 1). There are no cracks during the autoclave is heated if the Carius tube is well annealed and extra gas is not produced in Carius tube during the sample digestion. Otherwise, large amount of extra gas produced by sulphide or carbonate during digestion will cause cracks of Carius tube. The 172 ml autoclave filled with 160 ml water can reach to 400°C, therefore, it is safe to heat the autoclave to 330°C.

Separation and measurement of Os

In this study, the solution after aqua regia attack in the Carius tube was transferred to a custom made distillation system following the procedure described above. The solution was heated to boiling to distill Os using a clean air flow of about 2–4 bubbles per second. The liquid droplets containing acids and water were condensed and flowed back to the distillation system by a water cooling system. Only volatile Os was passed through and

trapped with 5% HCl solution cooled in an ice-water bath. About 95% of the Os was trapped after for a distillation for 90 minutes.

Osmium, at its highest valence (VIII), has stronger memory effect than other valence status in solution measurement, because of its volatile nature of Os–tetraoxide (Gregoire, 1990; Hassler *et al.*, 2000; Sun *et al.*, 2001; Norman *et al.*, 2002; Meisel and Moser, 2004). Sun *et al.* (2001) used 30% H_2O_2 and 5% HNO_3 to flush the sample introduction system alternately. It takes 10 minutes to reduce the ^{190}Os signal to its background level. We used 8% HCl solution to flush the sample introduction system. Only 90 seconds are needed to reduce an intensity of about 50000 cps to about 100 cps using the self-aspirating introduction system which has much shorter path than the peristaltic pump auto-sampler system. The memory effect of Os was thus significantly reduced, because Os is trapped with 5% HCl solution. The possible reason is that HCl may reduce the highest valence (VIII) of Os to its lower valence.

Separation of Re

Anion exchange resin AG 1-X8 has been successfully used to separate Re and PGEs from the matrix (Pearson and Woodland, 2000; Jensen *et al.*, 2003). Although Jensen *et al.* (2003) simplified the procedure of Pearson and Woodland (2000), the mono-isotope element, Rh, can not be measured, because of the poor recovery when an anion exchange resin is used.

In this study, 10 ml of solution containing Re and PGEs after Os distillation described above was only used for Re separation and measurement. The solution in 3 N HCl was passed through an anion exchange column (AG 1-X8) described above and washed with 20 ml of 3 N HCl, the matrix and some of the PGEs were eluted and then Re was eluted with 20 ml of 9 N HNO_3. After evaporated to dryness, the elutant was dissolved in 5 ml of 5% HNO_3 and mixed with 50 ng of commercial Ir (in solution) for mass bias correction. The solution is now ready for ICP-MS measurement.

APPLICATIONS TO GEOLOGICAL SAMPLES

Analyses of mafic rocks

Determination of low concentration of PGEs is very important for geochemical study. PGE poor continental flood basalts and ocean island basalts may have Os, Ir and Ru less than 0.02 ng/g, and Pt and Pd are less than 0.1 ng/g for some samples. Ruthenium has relatively low concentration and ^{99}Ru isotopic abundance compared to other PGEs in these samples. The sensitivity for most of the ICP-MS is about 50000 cps/ppb (except the new ICP-MS). Theoretically, the ^{99}Ru intensity will be about 25 cps when 1g of sample, of which Ru concentration is 0.02

Table 4. Analytical results (ng g⁻¹) of the reference material, WPR-1, GPt-1, GPt-3 and GPt-5.

Rock type	WPR-1 PGE-rich peridotite		GPt-1 Soil		GPt-3 Ultramafic rock			GPt-5 Chromite		
Temperature	300°C		330°C		240°C	330°C		240°C	330°C	
Time	12 h		12 h		12 h	12 h		12 h	12 h	
	This work (Mean ± S) n = 5	Certified*	This work (Mean ± S) n = 4	Proposed**	This work (Mean ± S) n = 3	This work (Mean ± S) n = 5	Proposed**	This work n = 1	This work (Mean ± S) n = 3	Proposed***
Re	10.67 ± 0.10		0.082 ± 0.003		0.045 ± 0.008	0.058 ± 0.004				
Os	14.5 ± 0.5	13	0.010 ± 0.001	~0.05	3.70 ± 0.18	6.49 ± 0.33	9.6 ± 2.0	158	346 ± 35	353 ± 27
Ir	13.4 ± 1.2	13.5	0.020 ± 0.003	~0.04	2.52 ± 0.12	4.15 ± 0.41	4.3 ± 0.5	76	139 ± 9	136 ± 10
Ru	22.5 ± 1.9	22	0.022 ± 0.002	~0.05	4.46 ± 0.08	11.0 ± 1.6	14.8 ± 2.7	237	539 ± 65	527 ± 91
Rh	12.7 ± 0.7	13.4	0.022 ± 0.001	~0.02	1.33 ± 0.17	1.34 ± 0.15	1.3 ± 0.3	6.5	10.5 ± 1.1	10 ± 2
Pt	276 ± 13	285	0.239 ± 0.019	0.26 ± 0.05	7.62 ± 0.42	7.78 ± 0.48	6.4 ± 0.9	14.9	21.5 ± 1.8	20 ± 4
Pd	231 ± 17	235	0.287 ± 0.074	0.26 ± 0.05	5.12 ± 0.21	4.82 ± 0.19	4.6 ± 0.6	6.8	10.5 ± 1.2	11.3 ± 1.5

*S = Standard Deviation, *Govindaraju (1994), **Yan et al. (1998).*

ng/g, is digested and conditioned with 5 ml of the final solution. This is because the abundance of [99]Ru is relatively low (12.7%), making it difficult to obtain good precision in Ru analysis with our instrument even if Ru recovery is 100%. Rehkämper *et al.* (1998) used only 12 ml of aqua regia to dissolve 10 g of silicate sample after a HF desilicification to remove silica. Using HF to remove silica can increase the sample mass and reduce the amount of aqua regia used, but the desilicification can possibly increase the procedural blanks, and makes the procedure more complicated, especially for transferring the residue to a Carius tube. In this study, we increase the sample mass to 12 g for mafic samples, and thus improve the detection limit and precision. 12 g of reference materials, GPt-1 (soil, with very low PGE contents similar to PGE poor mafic rocks), prepared by IGGE (Institute of Geophysical and Geochemical Exploration, China) was analyzed using the method described above. The results for Pt and Pd are in agreement with the reported values (Yan *et al.*, 1998) (Table 4). Despite the low concentration of Os, Ir, Ru and Rh (only approximately values were provided), fairly good agreement were obtained for 4 separate preparations (no information value for Re) using the proposed method (Table 4).

Digestion of ultramafic rocks and chromites at different temperature

Using the Carius tube technique, samples can be partially digested simply using aqua regia. Some samples, for example, WPR-1, a PGE-rich peridotite ($\sum$PGE > 500 ng g^{-1}), all PGE-hosting minerals can be easily dissolved with aqua regia in a Carius tube at 300°C. These minerals are base metal sulfide and can be easily dissolved. It is difficult to liberate all the PGEs from the refractory minerals in ultramafic samples and chromites, only using aqua regia. Puchtel and Humayun (2001) used a Carius tube to dissolve 40 mg of chromite at 220°C for 48 hours. Büchl *et al.* (2004) used HPA-S to dissolve 50 mg of chromite at 300°C for 16 hours. In this study, different temperature for digesting GPt-3 (ultramafic rock) and GPt-5 (a pure chromite) were examined by using the proposed method. The results are shown in Table 4. If sample was digested at 240°C for 12 hours, the results for Os, Ir and Ru are much lower than the certified values for GPt-3 and only about 55% of GPt-5 was dissolved (with about 45% undissolved residue). If the temperature increases to 330°C, GPt-5 can be totally dissolved (clear solution with little white residue). The results are in agreement well with the proposed value for GPt-3 and GPt-5 (Table 4), indicating that the PGE in the refractory minerals are effectively extracted by using the proposed method digested at 330°C for only 12 hours. Our results for Ru and Os are lower than the certified value for GPt-3, by measuring the PGE contents in the residue after

Carius tube digestion, Ru contents in the residue are less than 5% of the certified value, demonstrating that PGEs in the sample were extracted.

We also analyzed a CCRMP (Canadian Certified Reference Material Project) reference material, WPR-1 (Table 4). Our results of PGEs are in fairly good agreement with the certified value from Govindaraju, (1994) (no certified value for Re in this reference material).

CONCLUSIONS

The stainless steel high pressure autoclave can be used to balance the internal pressure of the Carius tube and to avoid possible explosion. With this relatively high-temperature digestion technique, the sample mass can be increased to 12 g for PGE poor mafic samples to improve the detection limits and precision. Ultramafic rocks and pure chromite can be dissolved effectively under relatively high temperature (330°C) for only 12 hours, indicating the proposed method is effective and time saving. The improved method is a low cost procedure compared with the HPA-S technique as well as a low maintenance approach. Compared to the traditional Carius tube digestion techniques, our method is effective and safe.

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