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The Design of Re-usable Carius Tubes for the Determination of Rhenium, Osmium and Platinum-Group Elements in Geological Samples

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The traditional Carius tube technique is cumbersome and requires skilful work to seal the Carius tube, which can be used only once. We describe a modification to the technique that does not require the use of a high-temperature welding torch to melt the Carius tube to seal it. The newly designed Carius tube consists of a main body with a 3 mm-thick glass wall, a neck and head with walls 4 mm in thickness, and an efficient screw-thread stopper. These new features allowed the tube to be used repeatedly. We demonstrate relatively low procedural blanks derived for Re and Os, and platinum-group elements (PGEs), using the redesigned tube. A temperature of 220 °C could be reached for about 5 ml of HNO_3 for a 47 ml tube and for 32 ml of inverse *aqua regia* for a 200 ml tube. This digestion technique can be used for routine analysis of Re and PGEs in geological samples.

Keywords: Carius tube, rhenium, osmium, platinum-group elements, molybdenite, ICP-MS.

La technique traditionnelle dite du «tube de Carius» est lourde à mettre en œuvre et nécessite un travail habile pour sceller le tube de Carius, qui ne peut être utilisé qu'une seule fois. Nous décrivons une modification de cette technique qui ne nécessite pas l'utilisation d'une torche de soudage à haute température pour faire fondre le tube de Carius afin de le sceller. Le tube de Carius nouvellement créé est constitué d'un corps principal avec une paroi de verre de 3 mm d'épaisseur, un col et une tête avec des parois de 4 mm d'épaisseur, et un bouchon à vis efficace. Ces nouvelles caractéristiques permettent une utilisation du tube à plusieurs reprises. Nous démontrons que nous avons obtenu des blancs de procédure relativement bas pour le couple Re-Os et les éléments du groupe du platine (PGEs), en utilisant le nouveau tube. Une température de 220 °C peut être atteinte pour environ 5 ml de HNO_3 pour un tube de 47 ml et pour 32 ml d'eau régale inverse pour un tube de 200 ml. Cette technique de digestion peut être utilisée pour l'analyse de routine du Re et des PGEs dans des échantillons géologiques.

Mots-clés : tube de Carius, rhénium, osmium, éléments du groupe du platine, molybdénite, ICP-MS.

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Carius tube and high-pressure asher (HPA-S) techniques are commonly employed for the determination of the platinum-group elements (PGEs) and Re-Os isotopes from geological samples (Shirey and Walker 1995, Birck *et al.* 1997, Pearson and Woodland 2000, Brauns 2001, Meisel *et al.* 2001, 2003a, b, Malinovsky *et al.* 2002, Pretorius *et al.* 2003, Meisel and Moser 2004a, b, Paliulionyte *et al.* 2006, Qi *et al.* 2007, 2010, Qi and Zhou 2008, Savard *et al.* 2010, Sun *et al.* 2010). They return low procedural blanks relative to other techniques for digesting geological samples. Using this technique, Re and all the PGEs are in their highest oxidation state with complete equilibration between spike and sample.

Previously used Carius tubes, essentially similar in shape to that reported in Shirey and Walker (1995), have included a main body and a narrow neck. The glass walls between the main body and the neck are usually inhomogeneous because the neck has a smaller internal diameter (about 6 mm), such that it is difficult to make an evenly thick glass

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wall. Such inhomogeneity can result in weakness and in the explosion of the Carius tube. Moreover, sealing conventional Carius tubes is difficult and requires high-pressure steel bottles of oxygen and propane (or coal gas) and a welding torch for use in sealing the glass tube. Well trained, experienced and skilful technicians are essential for the success of this operation. Carius tubes are normally used only once because the narrow neck makes them difficult to clean.

The quartz tube of the HPA-S technique is sealed by a covering PTFE tape and a piece of glass combined with high external nitrogen gas pressure. Although this is a convenient method of sealing the quartz tube, which itself can be used repeatedly, the equipment is costly. Moreover, acids may escape and corrode the instrument if samples containing carbonate, sulfide or organic matter generate additional gas during sample digestion.

Thus, the primary requirement to solve these difficulties would be an alternative design such that the Carius tube could be easily sealed and reused to allow the routine determination of Re and PGE in geological samples. In this paper, we report such a newly designed type of Carius tube for digesting geological samples that can be used repeatedly and easily sealed with a glass PTFE-lined stopper. We demonstrate that a temperature of 220 °C could be reached and that digestion was as efficient as the traditional Carius tube technique. This new design significantly simplifies the sealing procedure compared with the traditional Carius tube.

Experimental

Instrumentation

The instrument used in this study was an ELAN DRC-e ICP-MS located at the State Key Lab of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang. Background counts for 2% v/v HNO_3 solutions were normally < 10 cps (counts per second) for Re and the PGEs. The sensitivity of the instrument was adjusted to more than 30000 cps for 1 ng ml^{-1} ^{115}In. The instrument settings are given in Table 1.

Reagents and solutions

Hydrochloric acid was purified by double sub-boiling distillation. Water (18 MΩ cm grade) was obtained from a Millipore purification system. Nitric acid was first purified by bubbling clean air through boiled HNO_3 with H_2O_2 in a 3000 ml glass beaker to remove possible volatile OsO_4 and was purified further by sub-boiling distillation.

Table 1.
Instrumental operating parameters

Parameter	Value
RF power	1100 W
Plasma gas	15 l min^{-1}
Aux gas	1.20 l min^{-1}
Nebuliser gas	0.78 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

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

The new Carius tube system

The screw-topped, PTFE-lined stopper, stainless steel Carius tubes (Figure 1) used in this study were obtained from the Beijing Synthware Glass Instrument Company Limited, Chaoyang District, Beijing, China. Individual tubes had volumes of about 47 ml (for Re-Os dating of molybdenite) and 200 ml (for PGE in mafic and ultramafic rocks and poor Re-Os in sulfides). They consisted of a main body, neck and head. The main body had a 3 mm-thick wall, whereas both the neck and head had the same wall thickness (4 mm). The custom-made sealing system included a glass PTFE-lined stopper, a stainless steel screw cap and a stainless steel sheath.

The new Carius tube system was sealed by tightening the stainless steel screw cap and then heated to 220 °C for

Table 2.
Isotopic abundances of the spike

Isotope	Abundance (%)	Isotope	Abundance (%)
^{187}Os	0.014	^{106}Pd	2.35
^{190}Os	91.53	^{105}Pd	96.58
^{192}Os	4.82	^{99}Ru	0.24
^{185}Re	94.36	^{101}Ru	96.03
^{187}Re	5.64	^{191}Ir	99.33
^{195}Pt	3.78	^{193}Ir	0.67
^{194}Pt	95.06		

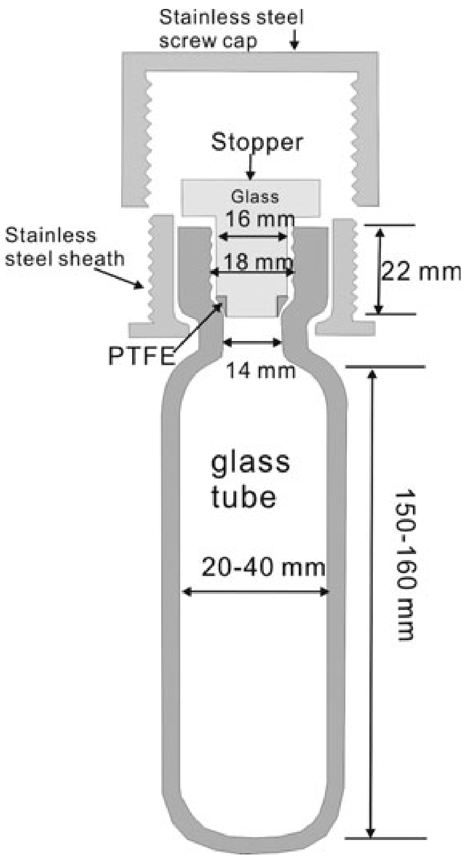

Figure 1. Sketch diagram showing the design of the custom-made Carius tube.

about 2 hr. After cooling to room temperature, the system was tightened again by turning the screw cap and then heated to 220 °C. This step was repeated several times to permit the Teflon stopper to fit the shape of the neck of Carius tube. The tube and PTFE stopper were pre-cleaned with 60% *aqua regia* with 1% v/v H_2O_2 and heated to boiling for about 2 hr. After rinsing with water, the tubes were heated to 220 °C with 5 ml of HNO_3 for about 2 hr, the same process as for sample digestion. Finally, the tube and stopper were rinsed with water and heated to 220 °C to minimise possible Os contamination.

Analytical procedure

To demonstrate the efficiency of sample digestion, molybdenite was used as an example. Molybdenite is a very important mineral that can be used for Re-Os dating (Suzuki *et al.* 1993, 1996, Stein *et al.* 1997, Du *et al.* 2004, Peng *et al.* 2006). Molybdenite separates (0.02–0.1 g) were accurately weighed and placed in the newly designed 47 ml Carius tubes and appropriate volumes of weighed rhenium and osmium spikes were added. The tubes were then placed into an ice water bath. Five millilitres of (refrigerator) cooled HNO_3 were added. The Carius tubes were immediately sealed with stainless steel screw caps as shown in Figure 1 and then placed in stainless steel jackets. The tubes were heated to 220 °C for about 12 hr. After being slowly cooled to about 50 °C, the tubes were further cooled in a refrigerator for 2 hr before being opened for *in situ* Os distillation using the procedure described in Qi *et al.* (2010). Osmium was trapped in 2 ml of water and measured using the ICP-MS.

After the distillation, the residual solution was transferred to a Savillex Teflon beaker (volume 125 ml) and evaporated to dryness twice with 5 ml of concentrated HCl to remove HNO_3. The resultant solution was then dissolved with 10 ml of 2 mol l^{-1} HCl for separating Re from the matrix using AG 1-X8 anion exchange resin as described by Qi *et al.* (2004).

Results and discussion

Comparison of the new and traditional Carius tube techniques

The traditional Carius tube technique involves melting the narrow glass neck using a high-temperature welding torch, thus sealing the tube. During this process, acids have to be frozen using an ethanol–dry ice slush to avoid the loss of volatile OsO_4 because of the relatively long time taken for sealing (Shirey and Walker 1995). The Carius tube is used only once, and the procedure for sealing is cumbersome. Due to the fragile nature of glass, if one wants to seal the tube without melting the glass, a soft stopper must be used. Due to its high-temperature stability (up to 250 °C) and resistance to acids, PTFE is the best material for sealing a glass tube.

This study used the newly designed Carius tube (Figure 1) for routine digestion of molybdenite and PGEs in mafic and ultramafic rocks. The new seal system included a glass PTFE-lined stopper, stainless steel screw cap and stainless steel sheath. The stainless steel sheath was cut into two pieces to fit the narrow neck of the tube. Due to the 4 mm-thick wall of the neck and the head of the Carius tube, the glass could bear relatively high stress. As shown in Figure 2A, the PTFE stopper and stainless steel sheath generated opposite pressures from the outside and inside of the glass. Thus, the stress from two directions was balanced to prevent the glass from cracking. As the expansion coefficient of PTFE is larger than glass, when the tube was heated during sample digestion, the expansion pressure of the PTFE stopper helped to make the seal more reliable.

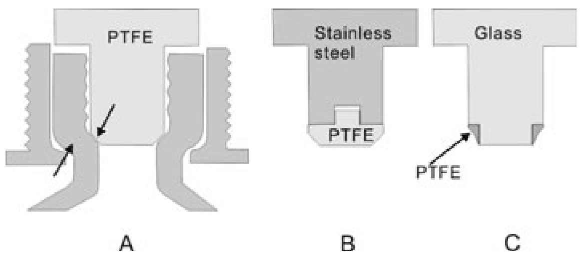

Figure 2. Sketch diagram showing the pressure direction for sealing the Carius tube and the stopper types investigated.

The PTFE stopper (Figure 2A), stainless steel PTFE-lined stopper (Figure 2B) and glass PTFE-lined stopper (Figure 2C) were all tested for their sealing properties. At a temperature of 220 °C, PTFE softens. If a stopper is made entirely of PTFE, the high internal pressure in the Carius tube would overcome the seal and result in the loss of acid. The glass PTFE-lined stopper design had a much smaller area of PTFE than the stainless steel PTFE-lined stopper; thus, cross-contamination of Os could be reduced. Furthermore, the glass PTFE-lined stopper was able to be cleaned directly with *aqua regia*. Thus, the glass PTFE-lined stopper was preferred for use in this study. The temperature reached 220 °C for 5 ml of HNO_3 in a 47 ml tube and 32 ml of *aqua regia* in a 200 ml tube with no explosion and no loss of Os.

The *in situ* distillation system used in this study (Figure 3) was similar to that reported previously by Qi *et al.* (2010). The Carius tube was sealed by tightening a screw-threaded PTFE stopper. The two holes (2 mm in diameter) were used to connect the inlet PTFE tube for the carrier gas and H_2O_2 and the outlet tube for Os gas. H_2O_2 was injected online by using a glass injector and pushed into the Carius tube by clean air. Water (2 ml) was used to trap Os, resulting in a recovery of more than 90%.

Due to the relatively large internal diameter of the neck (14 mm), the weighed sample powder was transferred readily to the Carius tube, and the residue in the tube after digestion was easily cleaned using a normal laboratory brush. Therefore, the new design was easy to seal and clean and was reusable.

Loss and cross-contamination of Os

It has been documented previously that OsO_4 can penetrate Teflon barriers under conditions of high temperature and pressure during sample digestion, causing partial loss of Os (Birck *et al.* 1997, Meisel *et al.* 2001, Malinovsky *et al.* 2002). OsO_4 can also penetrate at the scale of

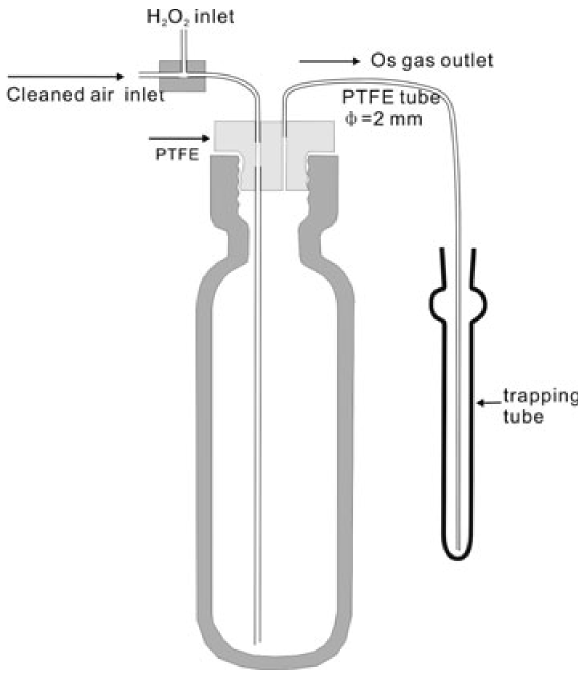

Figure 3. Sketch diagram showing the *in situ* distillation system (Qi *et al.* 2010).

millimetres into plastic materials. Even in Teflon, losses can reach 50% (Birck *et al.* 1997). To examine the loss or penetration of Os into the PTFE stopper during sample digestion, 1 ng of Os standard solution and 5 ml of HNO_3 were added to a new Carius tube before being sealed. The tube was heated to 220 °C in an electric oven for about 12 hr. After being cooled in air to room temperature, the tube was further cooled in a refrigerator for about 1 hr before Os was distilled in 2 ml of water as a trapping solution. Compared with the traditional Carius tube technique, the intensity of Os was just the same, indicating almost 100% recovery of Os by using the proposed new Carius tube. This recovery may be because the area of the PTFE of the stopper was much smaller than the whole internal area of the proposed Carius tube.

Osmium may penetrate PTFE and remain in the PTFE stopper, causing cross-contamination if the tube were to be reused. In this study, the stopper was wrapped with PTFE tape (0.1 mm × 15 mm), which was discarded each time after use. To investigate possible cross-contamination, we examined the procedural blank after digestion of Os-rich samples; 50 ng of Os and 5000 ng of Re standard solutions were digested with 5 ml of HNO_3 at 220 °C for 12 hr. After the digestion, both the tube and stopper were cleaned with 60% *aqua regia* and 1% v/v H_2O_2 at 80–90 °C for about 2 hr. After rinsing with water, the tube was

Table 3.
Procedural blank level (ng)

Elements	A $n = 5$	B $n = 5$	Average $n = 5$
Re	0.005	0.006	
Os	0.001	0.002	
Ir			0.021
Ru			0.019
Rh			0.012
Pt			0.19
Pd			0.25

A, new tube; B, after digestion with 50 ng of Os and 5000 ng of Re standard solution.

Table 4.
Analytical results of Re and Os of molybdenite separates, HLP, JDC

	JDC		HLP	
	This study (mean ± *s*) *N* = 5	Certified[a]	This study (mean ± *s*) *N* = 5	Certified[a]
Re ($\mu g\ g^{-1}$)	17.5 ± 0.4	17.39 ± 0.32	282 ± 5	283.8 ± 6.2
Os ($ng\ g^{-1}$)	25.6 ± 0.5	25.46 ± 0.60	658 ± 8	659 ± 14

s, standard deviation.
[a] Du *et al.* (2004).

heated to 220 °C with 5 ml of HNO_3 as for sample digestion. Finally, the tube and stopper were rinsed with water and heated to 220 °C for about 5 hr to permit the tube and stopper to become free of Os. The results of the blank for Re and Os, as well as the PGE are shown in Table 3. The procedural blank after digestion of Os-rich samples (blank B) had 2 pg Os and 6 pg Re, slightly higher than the new tubes (blank A), indicating that cross-contamination for Re and Os-rich molybdenite was insignificant.

Results for reference materials

The molybdenite reference materials JDC and HLP were used to investigate the efficiency of the proposed new Carius tube analyses. Samples were digested in 47 ml Carius tubes following the procedure described above. As shown in Table 4, the results for JDC and HLP were in fairly good agreement with the certified values, demonstrating the reliability of proposed new type Carius tube for determining Re and Os in molybdenites.

Reference materials WGB-1 (mafic rock) and UMT-1 (ultramafic rock) were used to investigate the efficiency of proposed new Carius tube for the determination of PGEs. Five grams of mafic sample and 3 g of ultramafic sample were digested at 240 °C in Carius tubes of 200 ml volume using 20 ml of inverse *aqua regia* for 24 hr. After cooling, Os was distilled using the procedure described above and trapped with 1.4 ml of water for the mafic sample and 5 ml of water for the ultramafic sample. After distillation and centrifugation, the upper portion of the solution was transferred to a Savillex Teflon beaker (volume 125 ml) and evaporated to dryness twice with 5 ml of concentrated HCl to remove HNO_3. The residue was dissolved with 40 ml of 3 mol l^{-1} HCl and transferred to a 50 ml tube. About 10 ml of the centrifuged solution was used to separate Re from the matrix using AG 1-X8 anion exchange resin. The remaining solution was used to pre-concentrate PGEs by Te-coprecipitation following the procedure described by Qi *et al.* (2011). As shown in Table 5, the blank-corrected results of WGB-1 and UMT-1 were in good agreement with the certified and reported values, demonstrating that the proposed new type of Carius tube can be used for determining PGEs from mafic and ultramafic rocks.

Table 5.
Analytical results ($ng\ g^{-1}$) of PGEs for reference materials

Elements	WGB-1			UMT-1		
	This study (mean ± *s*) *N* = 3	Meisel (2004)[a]	Certified[b]	This study (mean ± *s*) *N* = 3	Meisel (2004)[a]	Certified[b]
Re	1.19 ± 0.05	1.15		6.23 ± 0.16	6.65	
Ru	0.15 ± 0.02	0.144	0.3	10.6 ± 0.9	10.14	10.9 ± 1.5
Rh	0.19 ± 0.02	0.234	0.32 ± 0.21	8.55 ± 0.85	9.12	9.5 ± 1.1
Pd	14.0 ± 0.9	13.9	13.9 ± 2.1	108 ± 6	113	106 ± 3
Os	0.59 ± 0.03	0.54		8.09 ± 0.19	11.2	8
Ir	0.18 ± 0.03	0.211	0.33 ± 0.17	8.41 ± 0.55	8.61	8.8 ± 0.6
Pt	4.59 ± 0.65	6.39	6.1 ± 1.6	142 ± 8	146	128 ± 5

s, standard deviation.
[a] Meisel and Moser (2004b).
[b] Govindaraju (1994).

Conclusions

The newly designed Carius tube has significantly improved the traditional Carius tube technique. The new tube design much reduces the time taken for analysis, compared with the traditional technique, for a given test portion mass because of the larger diameter of the neck. The new technique does not require sealing the tube using a high-temperature torch, and the risk of explosion at high temperature is minimised due to the relatively thick wall of the neck of the tube. The proposed stoppered Carius tube can be used repeatedly, thus significantly reducing analytical costs. This improved technique is reliable, simple, low cost and suitable for routine sample preparation for Re and Os isotope determinations, particularly for molybdenite. It could also be used for the determination of PGEs in mafic and ultramafic rocks, as well as in Re- and Os-poor hydrothermal sulfides when the volume of the Carius tube was increased to about 200 ml.

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