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Low-blank digestion of geological samples for platinum-group element analysis using a modified Carius Tube design

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Abstract We have developed a modified Carius Tube design that permits the low-blank digestion of geological samples prior to platinum-group element analysis. The new Carius Tubes incorporate a liner of high-purity quartz glass that retains the sample and acids during the digestion procedure. This dramatically reduces the comparatively high Pt blank associated with dissolutions in conventional Carius Tubes. Using the new Carius Tube design we are able to achieve total procedural blanks for the determination of the PGE in geological samples that are at the 1–15 pg/g level for Ru, Pd, Ir and Pt. This constitutes a reduction of blank values by a factor of ~10–100 compared to standard NiS fire assay sample preparation techniques.

Introduction

Abundance measurements of the platinum-group elements in geological samples have received particular attention in recent years. In part, this is due to the advent of inductively coupled plasma-mass spectrometry (ICP-MS). The high analytical sensitivity of ICP-MS renders this technique ideally suited for the determination of the PGE in rock samples [1–3], where PGE concentrations are typically in the ng/g to pg/g concentration range. Surprisingly, few abundance measurements by ICP-MS are performed using isotope dilution (ID) techniques, however, even though it has been demonstrated that this can achieve significant improvements in analytical precision and accuracy compared to standard ICP-MS procedures, where absolute signal intensities (as opposed to isotopic ratios) are used to determine elemental concentrations [4–6].

Most published ICP-MS methods for the determination of the PGE in rocks employ nickel sulfide fire assay methods [7, 8], often combined with Te-coprecipitation, for sample pre-treatment prior to analysis. A survey of the recent literature, however, reveals that NiS/Te-coprecipitation techniques are generally characterized by procedural blanks of 0.1–1 ng/g for the PGE and we have measured similar values in experiments conducted in our laboratory. The elements Ru, Pd and Pt appear to be particularly problematic in this respect. While procedural blank values in the range of 0.1–1 ng/g are acceptable for the analysis of geological samples with relatively high PGE concentrations (e.g., ores, peridotites, komatiites) they preclude the collection of high-quality data on samples with lower PGE

abundances such as many mantle derived basalts, continental rocks or some types of meteorites.

In our laboratory we apply the new technique of multiple collector inductively coupled plasma mass spectrometry (MC-ICPMS) [9, 10] to perform high-precision isotope dilution concentrations measurements of the PGE Ru, Pd, Ir and Pt in geological samples. Using a conventional Carius Tube sample digestion procedure (adopted from analytical methods for Re-Os studies [11]) and a new ion-exchange separation technique developed in this laboratory [12], we recently demonstrated that our ID techniques can achieve an external reproducibility of ~1.5–9% for the PGE in the ng/g to pg/g concentration range [13]. This paper summarizes our recent efforts in the evaluation of the procedural blanks for the PGE associated with this digestion technique and introduces a new, modified Carius Tube design suitable for the analysis of geological samples with extremely low PGE abundances.

Experimental

Reagents and materials

The tracer solutions for ID concentration measurements were prepared from enriched stable isotopes of ^{99}Ru , ^{105}Pd , ^{191}Ir and ^{198}Pt , obtained from the Oak Ridge National Laboratory. All mineral acids used in this study were purified once (HCl, HNO_3) or twice (HF) by sub-boiling distillation in quartz or Teflon stills, respectively. 18 M Ω -grade water from a Millipore purification system was used throughout. The bromine used for the preparation of bromine water (employed in the ion-exchange separation of the PGE [12]) was purified by extracting 5–10 mL portions of the reagent 3 \times with ~100 mL of water in a 125 mL FEP bottle.

The conventional Carius Tubes employed in our laboratory are identical in design to the digestion tubes employed by Shirey and Walker [11]. The modified Carius Tubes pioneered in this study are manufactured with a longer main body (33 vs. 20 cm), and contain a liner (31.5 cm long, 12 mm outer diameter, wall thickness ~0.8 mm) made of high-purity quartz glass, into which the sample and acid are inserted for digestion (Fig. 1). These tubes can accommodate silicate samples of up to 10 g together with ~12 ml of aqua regia. The quartz liner is inserted into the thick-walled outer shell of the Carius Tube during the fabrication process, prior to the sealing of the lower end of the latter. Proper sealing of the outer (borosilicate) shell without melting of the liner requires that the liner is approximately 1–2 cm shorter than the length of the shell.

Prior to use, all Carius Tubes are cleaned using the following procedure: the tubes are filled with aqua regia, placed in a waterbath and heated for at least 5 days. 1–2 days prior to use of the Carius Tubes the aqua regia is discarded. The tubes are then multiply rinsed with water and refilled with fresh aqua regia prepared from distilled reagents. Just prior to use, the tubes are emptied again, rinsed with copious amounts of water and dried to dispel any moisture from the inside.

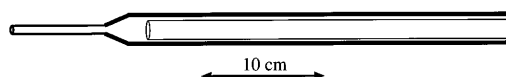


Fig. 1 Schematic diagram of the Carius tube with quartz glass liner employed in this study. The quartz liner fits loosely inside the outer, thick-walled borosilicate body and contains the sample and acid during the dissolution process

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Table 1 Comparison of procedural blank values for the PGE reported in the literature for NiS fire assay digestion methods with results from this study for Carius tube digestion techniques

Sample preparation technique	Reference	Sample size (g)	Procedural blank (pg/g)			
			Ru	Pd	Ir	Pt
NiS fire assay/Te-coprecipitation	[18]	10	30	610	10	260
NiS fire assay/Te-coprecipitation	[19]	15	1090	2430	50	300
NiS fire assay/Te-coprecipitation	[20]	15	780	120	40	150
Conventional Carius tube/ion-exchange	This study ^a	5	≤ 6	≤ 6	≤ 3	204
Carius tube with quartz liner/ion-exchange	This study ^b	5	≤ 6	≤ 6	≤ 3	≤ 15

^a The data represent mean or maximum results for three blanks measured in Jan.–March '97

^b The data represent maximum results of two measurements in Jan.–March '97

Analytical procedure

For the determination of the PGE procedural blanks we have processed blank samples using the same procedures that are commonly used in our laboratory for the treatment of 5 to 10 g-sized silicate samples. Prior to the Carius Tube digestion step, this involves desilicification of the samples with 15 mL of 30 mol/L HF and 2 mL of 11 mol/L HCl in 60 mL FEP screw-top beakers (Savillex™). Residual HF is then removed from the samples by drying down twice with 10 and 5 mL of 6 mol/L HCl, respectively.

Loading of the Carius Tubes is performed using procedures similar to those described by Shirey and Walker [11]. Namely, blank samples are dissolved in 6 to 9 mL of 11 mol/L HCl and the solutions transferred into Carius Tubes using an FEP funnel (Savillex™). Following chilling of the tubes in a chloroform-dry ice bath, 2 to 3 mL of 13.5 mol/L HNO₃ are added and the tubes then sealed in the flame of a natural gas-oxygen blow torch. Immediately after closure the seals are carefully annealed, first for ~2 min in the blue flame of a Bunsen burner followed by an additional 2 min in the yellow flame of the blow torch. Once closed, the Carius Tubes *must* be handled with extreme care since they pose the risk of explosion from the buildup of internal pressure. The reader is referred to previous publications for proper handling procedures [11, 14–16].

Following insertion of the tubes into stainless-steel jackets, they are placed into an oven and heated for 42–48 h at 230°C. Carius Tubes with quartz liners are stood up at an angle of ~45°, in order to prevent spilling of the reactants from the liner. Upon completion of the heating cycle, conventional Carius Tubes can be cooled quickly by removing them directly from the hot oven. For an unknown reason this procedure may not be employed for Carius Tubes containing quartz liners because such tubes will consistently burst if cooled too quickly. It is therefore imperative to slowly reduce the temperature of the oven to ambient levels, preferably within a time span of at least 3–5 h.

Following opening of the Carius Tubes (using procedures adapted from [11, 16]), the solutions are transferred back into the 60 mL FEP digestion beakers and evaporated to dryness on a hotplate. The residues are redissolved in 10 mL of 1 mol/L HCl that contains 10% bromine water, dried again, and then taken up in 10–20 mL of the same acid mixture. The solutions thus obtained are further processed using an anion-exchange separation protocol described in a previous publication [12]. The ion-exchange procedure permits the isolation of the PGE Ru, Pd and Pt-Ir in three elemental fractions suitable for ID concentration measurements. The PGE fractions obtained from the ion-exchange separation are dried down, evaporated twice with 1 drop of 13.5 mol/L HNO₃, and are then ready to be redissolved for PGE concentration measurements by MC-ICPMS.

PGE concentration measurements

All PGE concentrations were determined by ID techniques with the MC-ICPMS instrument Plasma 54 (VG Elemental) [9, 10], using instrumental procedures similar to those employed for the analysis of geological samples. By choosing extremely low dilution factors for the blank samples we were able to achieve sufficient analytical sensitivity to permit isotope ratio measurements by static multiple collection on the Faraday collectors of the Plasma 54. A full description of the instrumental procedures is outside of the scope of this paper and will be presented in a forthcoming publication.

Results and discussion

Table 1 displays a comparison of procedural blank values quoted in the literature for three conventional ICP-MS methods for the determination of PGE concentrations in rocks with results for the Carius Tube/ion-exchange procedures described in this study. The previously published ICP-MS techniques utilize standard NiS fire assay digestion methods and Te-coprecipitation for sample treatment prior to analysis. It is evident that the NiS/Te-coprecipitation techniques are generally associated with blank values of greater than 100 pg/g for the PGE Ru, Pd and Pt. Only for Ir are the procedural blank values at or below the 50 pg/g level.

In comparison, both Carius Tube/ion-exchange procedures described in this study are characterized by significantly lower blank values for the elements Ru, Pd and Ir (Table 1). For these elements the procedural blanks are lower than 10 pg/g, regardless of the type of Carius Tube employed. This constitutes a reduction of blank values by a factor of ~10–100 compared to standard NiS fire assay/Te-coprecipitation sample preparation techniques.

NiS fire assay methods require the use of relatively large quantities (~0.1–10 g) of several solid reagents such as Ni, S, Na₂B₄O₇ and Na₂CO₃. Importantly, these materials may carry a significant PGE blank and are difficult to purify by standard laboratory procedures. Ironically, studies conducted in this and other laboratories show that commercially available "ultrapure" reagents are often characterized by a higher PGE contamination than ordinary "reagent grade" quality compounds (e.g., [17]). Obtaining batches of particularly low-blank reagents therefore requires the analyses of different reagent qualities from a variety of manufacturers, a tedious and time-consuming procedure at best. The Carius Tube/ion-exchange techniques, on the other hand, do not require the use of solid reagents and utilize only mineral acids that are conveniently cleaned to a high degree of purity by sub-boiling distillation. This advantage is re-

flected in the significantly lower blank levels of the sample preparation techniques described in this study.

From Table 1, however, it is also evident that the use of conventional Carius Tubes is associated with a comparatively high Pt blank value of ~200 pg/g, comparable to the lowest values achieved by the NiS/Te-coprecipitation technique. Several observations suggest that the high Pt blank originates from the borosilicate-glass vessel material. Firstly, the Carius Tube digestion procedure is routinely associated with the dissolution of small amounts of silica from the inner walls of the sealed tubes at high temperature and pressure; secondly, a determination of the Pt concentration in the borosilicate glass of the Carius Tubes yielded a surprisingly high result of 670 pg/g. From this and the inner surface area of our conventional Carius Tubes (~78 cm²), it can be estimated that isotopic exchange between a surface layer of ~100 µm thickness and the sample solutions is sufficient to account for the measured Pt procedural blank.

The high Pt blank of conventional Carius Tubes can be circumvented, however, simply by inserting a liner, made of high-purity quartz glass, into the outer borosilicate shell. This liner retains the sample and acids during the high temperature digestion step and prevents intimate contact of the reactants with the borosilicate glass. As a result, the Pt blank of the Carius Tube/ion-exchange procedure is reduced by more than an order of magnitude to less than 15 pg/g (Table 1). This value is comparable to the procedural blanks observed for Ru, Pd and Ir (< 6 pg/g) using either conventional or quartz glass lined Carius Tubes.

Conclusions

Using a newly developed Carius Tube design, incorporating a liner of high-purity quartz glass inside the outer borosilicate shell, we achieve procedural blanks for the determination of the PGE in geological samples that are at the 1–15 pg/g level for the PGE Ru, Pd, Ir and Pt. These values are up to several orders of magnitude lower than the blank levels associated with conventional NiS fire-assay digestion techniques. The achievement of such low PGE blanks is of importance for a variety of geochemical studies, because many geological samples are characterized by PGE abundances of significantly less than 1 ng/g.

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