



Refinement of high precision Ru isotope analysis using negative thermal ionization mass spectrometry



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ARTICLE INFO

Article history:

Received 14 September 2015
Received in revised form 5 February 2016
Accepted 6 February 2016
Available online 8 March 2016

Keywords:

Ruthenium isotope
 ^{100}Ru
Thermal ionization mass spectrometry
N-TIMS

ABSTRACT

A refined method for the isolation, purification, and high precision measurement of Ru isotope compositions in natural samples by negative thermal ionization mass spectrometry (N-TIMS) is reported. After chemical purification of Ru using ion exchange chromatography and microdistillation techniques, the Ru isotopic composition is measured as RuO_3^- via N-TIMS. Data are corrected for oxide interferences using the simultaneously measured oxygen isotope composition, and subsequently for mass fractionation using an exponential law. Repeat analyses of an *Alfa Aesar* Ru standard solution demonstrate external reproducibility of $^{100}\text{Ru}/^{101}\text{Ru}$ to ± 6.4 ppm (2SD). This level of precision is more than two times better than prior techniques. Repeat analyses of gravimetrically prepared mixtures of a natural *Alfa Aesar* Ru standard and a ^{100}Ru enriched spike show that isotopic differences of ≥ 13 ppm can be resolved by single measurements of a material using this method. Repeat analyses of diverse terrestrial materials (chromitites and Os-Ir-Ru alloys) are characterized by compositions that are identical to the *Alfa Aesar* standard, and the external reproducibility for these materials is also identical to that of the chemically pure standard, demonstrating that chemical separation/purification methods introduce no bias to the analysis. These materials likely define the Ru isotopic composition of the Earth's mantle.

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1. Introduction

Mass-independent nucleosynthetic isotopic anomalies have been observed in Ru present in whole rock meteorites and their components [1–7]. The nature and magnitude of the anomalies have been used to investigate the stellar origins of matter in our solar system, as well as nebular mixing processes. Ruthenium isotopes ($^{96}\text{Ru} = 5.52\%$; $^{98}\text{Ru} = 1.87\%$; $^{99}\text{Ru} = 12.8\%$; $^{100}\text{Ru} = 12.6\%$; $^{101}\text{Ru} = 17.1\%$; $^{102}\text{Ru} = 31.6\%$; $^{104}\text{Ru} = 18.6\%$) are well suited for this task. This is because of the diverse nucleosynthetic processes by which Ru isotopes were made (*p*-, *s*-, *r*-process; [33]), and the high condensation temperature of Ru ($T_c = 1565$ K, where T_c is the temperature at which 50% of the element is condensed; [8]). Additionally, there are two short-lived chronometers associated with the Ru isotope system, ^{98}Tc - ^{98}Ru and ^{99}Tc - ^{99}Ru ($t_{1/2} = 4.2$ – 10 Ma and $t_{1/2} = 0.21$ Ma, respectively; [9]). Conclusive evidence for either chronometer, however, is yet to be identified. Further, given the variations in Ru isotopic compositions among early solar system materials, Ru isotopes show great promise for providing genetic fingerprints of diverse, late-stage accretionary additions

to the Earth and Moon [10,11]. This is possible because the Ru present in, for example, lunar impact melt rocks produced by basin-forming events, is primarily derived from the impactor (e.g., [12]).

High precision isotopic analytical capability is required to fully pursue these cosmochemical and geochemical objectives. Ruthenium isotopes have previously been measured using either thermal ionization mass spectrometry (TIMS; [6,13]) or multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS; e.g., [7,14]). The current state-of-the-art for $^{100}\text{Ru}/^{101}\text{Ru}$ is ± 31 ppm using TIMS [6] and ± 13 ppm using (MC-ICP-MS [7]), where uncertainties are 2SD, defined by repeat analyses of laboratory standards. Here, we present refined chemical and mass spectrometric procedures to precisely measure Ru isotopic compositions in natural samples. The new method offers a better than twofold improvement in precision for some Ru ratios, compared to the existing techniques.

2. Methods

2.1. Samples

The in house laboratory standard used in this study was a Ru *Alfa Aesar Specpure*[®] plasma standard solution (1000 $\mu\text{g}/\text{ml}$,

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RuCl_3 in 20% HCl). In order to confirm that our chemical isolation/purification and measurement procedures did not impart systematic biases, as well as to define the Ru isotopic composition of modern terrestrial mantle, chromitites from the 492 Ma Shetland ophiolite complex [15] and Os-Ir-Ru alloy grains from the 162 Ma Josephine ophiolite complex [16] were analyzed (EA1). In order to test the procedures for cosmochemical materials, and to enable comparisons of data with data from prior studies, the group IVB iron meteorite Hoba was also analyzed (EA1). Each sample type has a chemically distinct matrix, thus making this suite well suited to testing the robustness of our chemical separation and mass spectrometric protocols.

2.2. Sample preparation

Chromitites (C1, C2, C3) were cut into 2–3 g pieces using a MK Diamond Products (Inc.) water-cooled tile saw with a 25.4 cm diameter diamond blade. The pieces were abraded using silicon carbide sandpaper, in order to remove visible saw marks, rinsed with distilled water, and then fragmented into 0.1–0.5 g chips using a hammer wrapped in plastic film. The fragments were then carefully ground to a fine ($\sim 10 \mu\text{m}$) powder using an agate mortar and pestle dedicated to chromitites and other terrestrial rocks with high Ru abundances. Between samples, the mortar and pestle were mechanically cleaned by grinding multiple aliquots of silica grains, using new aliquots of silica grains each time. The mortar and pestle were then cleaned in dilute *aqua regia* overnight at $\sim 40^\circ\text{C}$, followed by a few hours in Milli-Q (water deionized to a resistivity of 18.2 M Ω cm) at the same temperature. The Os-Ir-Ru alloy grains analyzed here are a small subset of the grains studied in [16]. No sample preparation prior to digestion was required. Approximately 10 g of the meteorite Hoba was obtained from the Smithsonian Institution National Museum of Natural History (USNM 6506). The sample was cut into a 0.7 g piece using a distilled water-cooled Leco “Vari-cut” saw with a 12.7 cm diamond wafering blade. The blade was cleaned with carborundum before cutting the sample (as detailed in [17]). Pieces with or near fusion crust and rust patches were avoided. The cut sample was abraded using silicon carbide sandpaper, and then sonicated in Milli-Q water three times for 10 min at a time, using fresh Milli-Q water each stage. This was done to remove any adhering material from the sample.

2.3. Sample digestion

The Carius tube digestion technique employed to digest chromitites and Os-Ir-Ru alloys is based on the method adapted by [18]. Between 0.9 and 1.2 g of a powdered chromitite sample, or a single Os-Ir-Ru alloy grain (0.05–0.1 g), 3 ml of quartz-distilled concentrated hydrochloric acid (HCl) and 6 ml of quartz-distilled concentrated nitric acid (HNO_3) were placed in a chilled, thick-walled Pyrex® Carius tube. The distilled acids were made from either Sigma Aldrich® ACS grade or BDH Aristar® ACS grade commercial acids. The Carius tube was sealed promptly after addition of the acids in order to avoid possible loss of volatile RuO_4 (boiling point (BP) = 40°C ; [19]), which is produced on the addition of an oxidizing agent to a sample. Digestions of the samples were performed at 240°C for 4–5 days. Although not critical here, complete dissolution of the sample was typically not achieved. After digestion, the Carius tube was chilled in an ice bath, opened, and the acid phase was transferred to a 60 ml Savillex Teflon® beaker containing ~ 20 ml of quartz-distilled 6 M HCl. The mixed solution was gently dried down to ~ 2 ml using an ultraviolet heat lamp. The solution from the Carius tube was mixed with the 6 M HCl to promote the reduction of the volatile RuO_4 to a non-volatile form, thus reducing its loss during evaporation. The gentle and incomplete dry down at this stage also limited the loss of RuO_4 . Approximately 5 ml of 6 M

quartz-distilled HCl was added to the beaker to continue converting the Ru in solution to a chloride form. This solution was gently evaporated down to ~ 1 ml of residual solution. This step was repeated once.

At this point, Os-Ir-Ru alloy samples were dried down to ~ 0.2 ml and transferred to the cap of a 5 ml conical bottom Savillex Teflon® beaker for microdistillation, as described below. The Ru present in the chromitite samples, however, required further purification before microdistillation, and this was achieved by separating the Ru from the matrix via ion exchange chromatography. In preparation for this, the remaining ~ 1 ml of solution was evaporated down to a slurry using the heat lamp, after which 5 ml of 0.15 M quartz-distilled HCl was added. This solution was again evaporated to slurry, subsequently taken up in 10 ml of 0.15 M quartz-distilled HCl, and left to dissolve at room temperature. The sample was then transferred to a 10 ml centrifuge tube and centrifuged for 10 minutes at 7000 rpm. The supernatant was then removed for ion exchange chromatography.

The sanded and sonicated meteorite piece was added to 30 ml of 9 M quartz-distilled HCl in a 60 ml Savillex Teflon® beaker and left capped at 130°C on a hotplate for 12 h to digest. Following this, another 20 ml of 9 M quartz-distilled HCl was added to the beaker. The beaker was sonicated for 10 min, and then returned to the hotplate and left at 150°C for 24 h. After this treatment, the sample was completely dissolved. The sample was then gently evaporated to slurry, after which 5 ml of 0.15 M HCl was added, and the solution again slowly evaporated to slurry. The slurry was taken up in 5 ml of 0.15 M quartz-distilled HCl and left to dissolve at room temperature. The sample was transferred to a 10 ml centrifuge tube and centrifuged for 10 min at 7000 rpm. Finally, the supernatant was removed for ion exchange chromatography.

2.4. Ion exchange chromatography

Ruthenium has commonly been isolated using one- or two-stage ion exchange chromatographic procedures and then further purified using microdistillation [6,7,20]. Consistently achieving high recovery and high purity Ru with these techniques has been problematic. This is mainly due to the tendency of Ru to exist in multiple oxidation states (0 to +8; [21]), many of which exhibit different redox potentials and cation/anion exchange behaviors. This can lead to loss of Ru during chemical purification, as well as variable efficiency of chromatographic separations and microdistillation.

In this study, a two-step ion exchange chromatographic procedure was initially adapted from previous studies (e.g., [6,20]), in order to isolate Ru from the large amount (~ 1 g) of sample matrix used for chromitite and meteorite analyses. This method works by removing the majority of chromium (chromitites) or iron (iron meteorites) from the Ru and other highly siderophile elements (HSE: Re, Os, Ir, Pt, Rh, Pd, Au), in a primary (1°) cation column using an HCl-based chemistry. Ruthenium is separated from the other HSE using a secondary (2°) anion column, and an HCl- HNO_3 based chemistry (Table 1). The yields, however, from the 2° column were only $\sim 50\%$. This is likely a result of on-column reduction and retention of Ru-complexes in different oxidation states during the elution protocol, in addition to the loss of some RuO_4 during evaporation of the Ru-Re fraction (HNO_3). Subsequently, for those samples requiring column chromatography, better Ru yields were achieved by proceeding directly from the 1° column chemistry to a microdistillation.

In detail, the 1° column cation exchange chromatography used ~ 10 ml of pre-cleaned Eichrom AG50WX8 200–400 mesh cation exchange resin equilibrated in Milli-Q water (see EA2 for pre-cleaning steps and Table 1 for elution protocol). This resin was transferred to a Biorad column (1.5 cm \times 12 cm) as a slurry, then further cleaned using 4×10 ml 6 M HCl (quartz distilled). The columns

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