



Sectional power-law correction for the accurate determination of lutetium by isotope dilution multiple collector-inductively coupled plasma-mass spectrometry

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ABSTRACT

In this study, we employ a sectional power-law (SPL) correction that provides accurate and precise measurements of $^{176}\text{Lu}/^{175}\text{Lu}$ ratios in geological samples using multiple collector-inductively coupled plasma-mass spectrometry (MC-ICP-MS). Three independent power laws were adopted based on the $^{176}\text{Lu}/^{176}\text{Yb}$ ratios of samples measured after chemical chromatography. Using isotope dilution (ID) techniques and the SPL correction method, the measured lutetium contents of United States Geological Survey rock standards (BHVO-1, BHVO-2, BCR-2, AGV-1, and G-2) agree well with the recommended values. Results obtained by conventional ICP-MS and INAA are generally higher than those obtained by ID-TIMS and ID-MC-ICP-MS; this discrepancy probably reflects oxide interference and inaccurate corrections.

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1. Introduction

The changing abundance of ^{176}Hf associated with the long-lived radioactive β^- decay of ^{176}Lu ($T_{1/2} = 3.8 \times 10^{10}$ years; $\lambda = 1.865 \times 10^{-11} \text{ year}^{-1}$) [1,2] means that lutetium–hafnium is one of the most important isotopic systems for the dating of rocks and minerals and the tracing of geological processes. Although this system has been studied for more than two decades [3–5], its dating capability remains limited because of difficulties in both the chemical separation of lutetium, ytterbium, zirconium, titanium and hafnium, and the accurate measurement of lutetium and hafnium isotopic ratios by thermal ionization mass spectrometry (TIMS) [3–5] and hot-SIMS (secondary ionization mass spectrometry) [6,7].

Although hafnium isotopes can be precisely measured by MC-ICP-MS [8–12] with careful corrections for ytterbium interference and instrumental mass bias, accurate lutetium isotopic measurements remain difficult because of ytterbium interference and the lack of stable isotope couples such as strontium, neodymium, and hafnium for internal calibration. Moreover, because lutetium and ytterbium have similar physical chemistry and ytterbium has higher abundances than lutetium in natural geological samples, it is extremely difficult to obtain a pure lutetium solution with low ytterbium content.

The interference of ytterbium over lutetium is unavoidable using MC-ICP-MS, making correction the only way to deal with this issue [13]. Various methods have been proposed for correcting for mass bias

during MC-ICP-MS measurements, including those that employ linear, power, exponential, and generalized power laws [11,13–16]. Wombacher and Rehkämper (2003) demonstrated that the instrumental mass discrimination of MC-ICP-MS could be accurately corrected using a single best-fit mass bias law (generalized power law, GPL) providing that the best-fit n -value is well optimized. GPL is generally superior to other mass bias laws such as power laws, exponential (kinetic) laws, equilibrium laws, and linear laws. Although the empirically obtained n -value of GPL is different for different instruments or even different elements, careful calibration of the n -value may help in improving the accuracy of measurements of isotope ratios by MC-ICP-MS [15].

Previous studies have demonstrated that an exponential law is the most suitable method for correcting large mass bias effects. The observed mass bias is consistent with space charge as a possible cause, and the preferential extraction and transmission of the heavier ions in MC-ICP-MS [12,16–20]. Because the assumption of identical mass bias for neighbouring elements (notably lead and thallium, copper and zinc, and ytterbium and lutetium) is not useful in the case of Yb/Lu [11], an analytic formulation generated from a generalized law [15,21,22] has been proposed for correcting isotopic ratios measured by MC-ICP-MS [11].

In the present study, we propose an SPL correction protocol that yields precise and accurate measurements of the $^{176}\text{Lu}/^{175}\text{Lu}$ ratios of spiked geological samples by MC-ICP-MS (Nu Plasma). The success of this correction method means that complete chemical separation of ytterbium from lutetium is no longer a critical requirement of the measurement procedure. In addition, our modified one-step Lu–Hf separation technique can be applied to common geological samples. As an example of the use of this calibrating protocol, we evaluate and

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measure the lutetium concentrations of five commonly used United States Geological Survey igneous rock standards (BHVO-1, BHVO-2, BCR-2, AGV-2, and G-2).

2. Experimental

2.1. Instrumentation

A Nu plasma MC-ICP-MS (Nu Instruments, Wrexham, UK) was used for the measurement of isotopic compositions. This instrument is equipped with 15 fixed collectors (12 Faraday buckets and 3 ion multipliers) and a big-80 pump on the expansion chamber that provides for high sensitivity. Detailed descriptions of the fundamental features of this MC-ICP-MS can be found elsewhere [10,11]. A desolvator coupled with a perfluoroalkoxy (PFA) microflow nebulizer (DSN 100, Nu Instruments) was used for sample introduction. The typical uptake rate of the nebulizer is around 0.1 ml min^{-1} . The ion lens of the Nu Plasma was optimized with a solution containing lutetium (10 ng ml^{-1}) and ytterbium (1 ng ml^{-1}) to obtain maximum sensitivity and signal stability. Table 1 shows the instrumental parameters employed in data acquisition.

2.2. Reagent

All reagents used in this work were purified using quartz (for nitric acid and hydrochloric acid) and Teflon (for hydrofluoric acid) sub-boiling distillation methods. Deionized water was ultra-pure H_2O with an electrical conductivity of $18.2 \text{ M}\Omega \text{ cm}^{-1}$, as obtained from a MilliQ Element water purification system (Millipore, Billerica, USA).

The employed 1.0 mg ml^{-1} lutetium and ytterbium single standard solutions were purchased from Alfa Aesar (Ward Hill, MA, USA; Lot#: 62-015348A (lutetium) and 242227D (ytterbium)), and the enriched lutetium spike was obtained from ORNL (Oak Ridge National Laboratory, Batch NO. 21901). The concentration of the lutetium spike was calibrated with a pure Lu(III) oxide Reacton® purchased from Alfa Aesar (99.995%, metals basis; Lot# E02L14). A series of mixed ^{176}Lu – ^{178}Hf solutions (Lu & Hf contents of 0.77 and 46.85, 2.80 and 28.30, and 16.46 and 26.30 ng g^{-1}) were prepared because of the variable concentrations of lutetium and hafnium in natural geological samples [23].

2.3. Samples

To evaluate the accuracy and precision of the proposed method, we analyzed five United States Geological Survey (USGS) rock standards: three basalts (BHVO-1, BHVO-2, and BCR-2), one andesite (AGV-1), and one granite (G-2). Varying amounts of sample powder of these reference materials were weighed to yield 10–20 ng of hafnium in the final solutions.

The sample powder was weighed precisely and placed in a home-made polytetrafluoroethylene (PTFE) bomb with a Teflon-coated stainless steel cover. A suitable amount of mixed ^{176}Lu – ^{178}Hf spikes together with 1.5 ml of nitric acid and 1.5 ml of hydrofluoric acid were also added to the bomb inside a 10-grade clean hood. To achieve complete dissolution and equilibrium between the sample and spikes, we employed the following chemical steps: 1) the sealed bomb was heated in an oven at $195 \text{ }^\circ\text{C}$ for 2 days; 2) after cooling, the bomb was removed from the Teflon-coated steel jacket and placed in an ultrasonic bath at 100% power and $40 \text{ }^\circ\text{C}$ for 1 h; 3) the bomb was resealed in the steel jacket and placed in the oven at $195 \text{ }^\circ\text{C}$ for another 2 days; 4) after cooling, the samples were completely dissolved, ready for the one-step Ln-resin chemical chromatography to separate lutetium and hafnium once nitric acid and hydrofluoric acid had been replaced with 3.0 mol l^{-1} of hydrochloric acid. The chemical separation scheme is a one-column Lu–Hf separation technique [23] that is similar to a previously described technique using EICHROM Ln-Spec Resin [24], although modified in terms of the use of eluting acids and the granularity and volume of the resin bed. This method can be used to dissolve whole-rock samples as well as silicate mineral separates such as clinopyroxene and garnet.

2.4. Data acquisition

Lutetium isotopic compositions were measured by MC-ICP-MS under static mode. Collector configurations are shown in Table 2. We integrated the background signals for 30 s; the dwell time for each measurement was 10 s. The use of between 50 and 60 measurements normally yields a relative standard deviation (RSD) for $^{176}\text{Lu}/^{175}\text{Lu}$ (isotope dilution, ID) of better than 0.006%.

Fig. 1 $\Delta^{176}\text{Lu}/^{175}\text{Lu}$ (measured ratio from which the recommended ratio is subtracted) for samples with $^{176}\text{Lu}/^{176}\text{Yb}$ ratios ranging from 1 to >3000 (a); detailed comparisons are shown in (c) 2–40, (e) 40–130, and (g) 130–3000. Four simulated trend lines are shown based on polynomial, power, logarithmic, and exponential laws. The corresponding relative errors of the four simulated trend lines are shown in (b), (d), (f), and (h). The intensity of ^{176}Yb was calculated as the intensity of ^{173}Yb multiplied by 0.793045 [20]. Data collected on a standard block are shown by filled triangles (g); those measured with a U–Pb block are shown by open circles (a, c, e, g).

3. Results and discussion

The degree of mass bias in current MC-ICP-MS instruments is more than 10 times greater than that in conventional TIMS [8,10–12,19,25]. The mass-dependent ion yield is generally related to mass-dependent ionization, hydrodynamic entrainment by the expanding argon atoms behind the sampler cone and skimmer cone, space-charge effects within the electrical acceleration zone, and chromatic aberrations in the electrostatic sector [11,25,26]. However, theoretical methods for correcting for instrumental mass bias remain poorly understood, and various empirical methods have been proposed [11]. In the present study, we propose the SPL method (Method 1, see below) as a means of correcting measured $^{176}\text{Lu}/^{175}\text{Lu}$ ratios to their “true” value of 0.02656 [17]. The performances of four existing correction laws (Methods 2 to 5 below) [11,15] are also evaluated.

Table 1
MC-ICP-MS parameters.

MC-ICP-MS	Parameters
Model	Nu Plasma
Working mode	Faraday cups at static mode
Cooling gas	13 l min^{-1}
Auxiliary gas	0.8 l min^{-1}
Nebulizer gas	38 psi (via DSN)
RF power	1300 w
Data acquisition	
Blank acquisition	30 s
Integrated time per measurement	8 s
No. of measurements per block	50–60
No. of blocks	1
Analytical time	480–570 s

Table 2
Faraday collector configuration for Lu analysis.

Faraday bucket position	High 4	High 3	High 2	High 1	Axial 1	Low 1	Low 2
Nominal amu collected	177	176	175	174	173	172	171
Elements collected	Hf monitor	Lu with Yb and Hf interference	Lu	Yb	Yb	Yb	Yb

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