

Determination of the Isotopic Composition of an Enriched Lutetium Spike by MC-ICP-MS

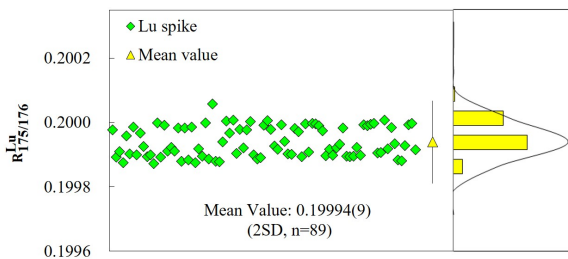
Ran Lin, Keqing Zong,* Jie Lin, Ao Yang, Kang Chen, Zhaochu Hu, and Yongsheng Liu

State Key Laboratory of Geological Processes and Mineral Resources, School of Earth Sciences, China University of Geosciences, Wuhan, 430074, China

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ABSTRACT: In geochronology, the isotope dilution (ID) method has been developed as an analytical method that provides accurate and precise element concentration and isotope ratio. For the ideal application of spiked sample, the critical prerequisite is the accurate isotopic composition of spike, which is commonly challenging to determine accurately. In this study, we report the first independent measurement of lutetium (Lu) isotopic composition in a Lu spike by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) using an optimized regression mass bias correction model. The rhenium (Re) reference material (NIST SRM 3143), previously calibrated against the NRC CRM IRIS-1 isotopic iridium (Ir), was selected as the primary calibrant to calibrate the Lu isotope ratio in Lu spike. The obtained ratio of $R_{175/176}^{\text{Lu}}$ was 0.19994 ± 0.00050 (u, k=1), which meets the required precision levels for the Lu-Hf isotopic system application. The accuracy of the Lu - Hf isochron age was improved by the application of the precisely calibrated Lu spike, and this Lu spike was successful applied for the determination of Lu concentration in geological reference material. The application of the optimized regression model was further broadened by determining the isotopic composition of the Lu spike.



INTRODUCTION

Lutetium (Lu) is one of a heavy rare earth element and has a single stable isotope (^{175}Lu) and a long-lived radioactive isotope (^{176}Lu).¹ Radioactive decay of ^{176}Lu to hafnium-176 (^{176}Hf) provides numerous applications of Lu - Hf isotopic system in geosciences. For instance, the ^{176}Lu - ^{176}Hf radiogenic isotopic system is a powerful tool for mineral-scale geochronology and isotopic tracer studies.²⁻⁷ Therefore, the Lu - Hf isotopic system has played an important role in understanding Earth's early crustal evolution, deciphering the chemical evolution of the Earth, and constraining the sources of magma and sediment.⁸⁻¹⁵ Because isotope dilution (ID) was first applied to geological problems in the 1950s, the ID method became a widely applied tool to determine the isotopic composition (IC) and concentration for a wide range of samples.¹⁶ The ID method can minimize the uncertainties in elemental concentration and the calculated ages of rocks.¹⁷⁻²² Therefore, ID has been developed as one of the analytical methods that provides accurate and precise mass fraction values, and it has specifically

played an important role in geochronology.¹⁸ For an ID analysis, a known quantity of an element having a non-natural IC, the spike, is added to a known quantity of sample by measuring the IC in the spike-sample mixture using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). However, to determine the isotope ratio and concentration of an element using ID, the accurate IC of the spike is crucial. The accuracy and precision of the concentration and isotope ratio calculated by ID critically depends on the accuracy and precision of the IC of the spike.²²

The application of MC-ICP-MS has grown significantly over the last two decades, because of its simple sample introduction, high ionization efficiency, and high sensitivity.^{11,23} However, MC-ICP-MS exhibits a larger mass bias than TIMS, which needs to be properly corrected for accurate isotope measurements.²⁴⁻²⁷ It is difficult to preclude the instrumental mass bias and obtain the spike IC accurately and precisely because of its non-natural IC.²¹ Currently, standard-sample bracketing (SSB),^{28,29} combined standard-sample bracketing with internal standard (C-SSBIN),³⁰

linear, power-law,³¹ and exponential³² methods are commonly employed for mass bias correction. The exponential law, with the assumption of identical mass bias for the analyte and the reference isotope ratio, is applied for the mass bias correction of the Lu isotope ratio in most studies.^{30–33} However, the mass bias factors of various elements are not always identical.²⁵ In addition, based on a previous study, the precision and accuracy of SSB and C-SSBIN do not meet the requirement of a spike.²¹ Furthermore, matrix matching of analyte and internal standard concentrations is required in the standard and the sample to yield accurate isotope ratios. Therefore, the methods mentioned above are not suitable for spike determination. Therefore, a cost-effective regression model for the Lu isotopic ratio measurements was employed in this study. The regression model for the determination of absolute IC was initially proposed by Maréchal et al.³⁴ and was revised by measuring the increments of radio frequency (RF) power.^{25,35} It allows calibration of the isotope ratio using a nearby and isobaric interference-free isotope ratio of other elements as a calibrant by observing the correlated temporal drift of isotope ratios measured by MC-ICP-MS. Owing to the small incremental changes in the plasma RF power, the measurement time was significantly shortened from several hours to 10–30 min per session, making the optimized regression model (ORM) suitable for applications requiring small sample sizes.^{21,25} It is important to note that the ORM is capable of correcting both mass-dependent and mass-independent isotopic fractionation occurring in MC-ICP-MS. In addition, the analyte and calibrant are measured from the same solution, matrix separation is not strictly required if no significant spectroscopy interference exists.²⁵ In this way, the regression model does not invoke the traditional mass fractionation assumptions and allows isotope ratio measurements between various elements regardless of the fact that each element undergoes slightly different isotope ratio fractionation. The ORM was also compared with the full gravimetric isotope mixture method (a primary calibration method) in molybdenum and lead isotope ratio measurements, both showing excellent agreement.^{36,37} This method has been validated in several ways and successfully applied for the determination of the IC of Ir,³⁸ Yb,³⁹ Hf,⁴⁰ Re,²¹ Os,⁴¹ and Pb.³⁷

The aim of this study is to provide the calibrated Lu isotopic composition of an enriched Lu spike by the regression mass bias correction model using the NIST SRM 3143 isotopic Re as a primary standard without assuming the identical mass bias for the Lu and Re. Additionally, the state-of-art ORM was also extended to the determination of the Lu IC in spike. The calibrated Lu spike applied for Lu isotope ratio and concentration measurements in Lu-Hf isotopic system.

EXPERIMENTAL

Instrumentation. A Neptune *Plus* MC-ICP-MS (Thermo Fisher Scientific, Germany) was used for isotope ratio measurements in the low mass resolution mode at the State Key Laboratory of Geological Processes and Mineral Resources (GPMR), China University of Geosciences, Wuhan. The instrument was equipped with nine Faraday cups, and all Faraday cups were equipped with $10^{11} \Omega$ amplifier resistors. The sample solution was introduced using a standard introduction system (PFA nebulizer $\sim 50 \mu\text{L min}^{-1}$) and a quartz glass spray chamber coupled with an autosampler (ASX-112FR, Cetac Technologies, Omaha, Nebraska, USA). The Neptune *Plus* was operated in static mode using twenty-four cycles with an integration time of 4.149 s. To improve the instrumental sensitivity, the X skimmer cone and Jet sample cone combination, as well as the guard electrode, were applied. The Faraday cup configuration and typical operating conditions are listed in Table 1. Intensities of all isotopes in the blank of 2 % HNO_3 solution were subtracted from the standard and sample measurements. With the wash of 2% HNO_3 for 90 s, the blank intensity values of ^{176}Lu and ^{187}Re were reduced to ~ 3.2 mV. Gain calibration of the Faraday cups was performed at the beginning of each day's session to cross-calibrate the gain of each amplifier.

Reagents and reference material. Ultrapure water ($18.2 \text{ M}\Omega \text{ cm}$) was acquired from a Milli-Q Element system (Millipore, Bedford, MA, USA). Commercially available nitric acid (HNO_3) and hydrochloric acid (HCl) were further purified twice using a DST-1000 acid purification system (Savillex, Eden Prairie, MN, USA).

Table 1. Neptune *Plus* MC-ICP-MS Operating Conditions

Cup-configuration	L2(^{173}Yb) L1(^{175}Lu) C(^{176}Lu) H1(^{180}Hf) H2(^{185}Re) H3(^{187}Re)
Resistors, Ω	10^{11}
RF power, W	1046 to 1110
Plasma gas flow, L min^{-1}	16.0
Auxiliary gas flow, L min^{-1}	0.94
Sample gas flow, L min^{-1}	0.99
Interface cones	Jet sample cone + X skimmer cone
Block \times cycle	6×5
Integration time, s	4.194
Mass resolution $m/\Delta m$ (at 5% and 95% peak height)	400
Sensitivities, $\text{V}/\mu\text{g g}^{-1}$	16–22 for ^{176}Lu and ^{187}Re
Blank, mV	3.2 for ^{176}Lu and ^{187}Re

Table 2. Certificate Isotopic Composition of Lu Spike

Isotope	Abundance	Certificate isotopic value (¹⁷⁵ Lu normalized to ¹⁷⁶ Lu)
¹⁷⁵ Lu	0.1669(40)	0.2003(40)
¹⁷⁶ Lu	0.8331(40)	1

The 2% HNO₃ solution consisted of concentrated HNO₃ was diluted with ultrapure water. The Re certified reference material solution NIST SRM 3143 (Lot No. 010816, 1000 µg g⁻¹, National Institute of Standards and Technology, NIST, Gaithersburg, MD, USA), previously calibrated against the NRC CRM IRIS-1 isotopic Ir,²¹ which was used to calibrate the Lu spike. The enriched Lu spike (Oak Ridge National Laboratory, USA, Lot No. TEAC 4-09-0, which is Lu₂O₃ digested with concentrated HCl) was evaporated to dryness and then re-dissolved in 2% HNO₃. The certificate isotopic compositions of the spike are listed in Table 2.

Sample preparation and analysis. For the regression correction model, the mixtures of each mono-elemental Lu spike and NIST SRM 3134 Re were prepared by dilution with 2% HNO₃ to approximately 1.5–2 µg g⁻¹. Recent developments in the regression model have significantly shortened the measurement time from 6–15 h to 10–30 min per session by measuring at equal increments of plasma RF power.^{25, 37–41} Like the determination of Ir, Re, Os, and Hf IC, the instrument plasma RF power was increased stepwise from the optimum value P₀ (corresponding to the highest sensitivity and stable signal, at 1046 W in this study) to P_{max} (Lu isotope signals decreased by approximately 25% compared to the sensitivities at P₀, typically at 1110 W in this study). The purpose of incrementally increasing the RF power during a measurement session was to induce a shift in the mass bias in a shorter measurement time (10–30 min per session). The IC of all samples was determined by incrementally increasing the RF power with values of P = (P_{max}–P₀)/N/3 where N = 0, 1, 2, and 3 for a measurement session that forms a linear regression data set. All signals of monitored isotopes at every point (P₀ to P_{max}) were subtracted from the corresponding intensities in 2% HNO₃ at optimum RF power, P₀.

Spectral interferences. Potential spectral interferences of Lu and Re isotopes that could occur in samples, including isobaric and polyatomic interferences are summarized in Table 3. Possible polyatomic interference degrades the accuracy of the Lu isotope ratio and requires elimination or correction. Quantitative analysis of sample solutions containing 2 µg g⁻¹ Lu and Re by ICP-MS revealed that the mass fractions of Ba, Ce, Gd, Dy, Er, Sm, Tm, Nd, Yb, Hf, W, and Os were all less than 0.03 ng g⁻¹. Such concentrations are insignificant to form isobaric interferences because the mass fractions of Lu and Re in the analyzed samples were many orders of magnitude higher, producing 0.00008 mV 0.00008 mV for ¹⁷⁶Yb in the 2 µg g⁻¹ Lu and Re test solutions. Moreover, owing to the low abundance of ¹⁷⁵Lu in the Lu spike,

Table 3. List of Potential Interferences in Lu and Re Isotopes Analyzed by MC-ICP-MS

Isotopes*	Isobaric interference	Polyatomic interferences
¹⁷⁵ Lu (16.69)	-	-
		¹⁷⁵ Lu (16.69) ¹ H (99.86)
		¹⁶² Er (0.14) ¹⁴ N (99.63)
		¹⁶¹ Dy (18.90) ¹⁵ N (0.37)
¹⁷⁶ Lu (83.31)	¹⁷⁶ Yb (12.76), ¹⁷⁶ Hf (5.26)	¹⁶⁰ Gd (21.86) ¹⁶ O (99.76)
		¹⁶⁰ Dy (2.34) ¹⁶ O (99.76)
		¹³⁶ Xe (8.90) ⁴⁰ Ar (99.60)
		¹³⁶ Ba (7.85) ⁴⁰ Ar (99.60)
		¹³⁶ Ce (0.19) ⁴⁰ Ar (99.60)
¹⁸⁵ Re (37.4)	-	¹⁶⁹ Tm (100) ¹⁶ O (99.76)
		¹⁴⁵ Nd (8.30) ⁴⁰ Ar (99.60)
		¹⁸⁶ W (28.60) ¹ H (99.86)
		¹⁸⁶ Os (1.58) ¹ H (99.86)
¹⁸⁷ Re (62.6)	¹⁸⁷ Os (1.6)	¹⁷³ Yb (16.12) ¹⁴ N (99.63)
		¹⁷¹ Yb (14.30) ¹⁶ O (99.76)
		¹⁴⁷ Sm (15.00) ⁴⁰ Ar (99.60)

*The Numbers in Brackets are Isotope Abundances (%).

the mass fraction of ¹⁷⁵Lu¹H only produced 0.0003 mV for the ¹⁷⁶Lu in 2 µg g⁻¹ Lu spike and Re mixed standard solution, as compared to intensities of 4.4, 22, 12.3, and 20.7 V for ¹⁷⁵Lu, ¹⁷⁶Lu, ¹⁸⁵Re, and ¹⁸⁷Re, respectively. Such interference with the ¹⁷⁶Lu isotope was observed to be insignificant. Therefore, the above-mentioned matrix elements do not induce significant polyatomic interference in the Lu and Re isotopes.

RESULTS AND DISCUSSION

Correction for instrumental mass bias

To determine the Lu isotope ratio precisely and accurately, a regression model was employed with using the NIST SRM 3143 Re isotopic standard as the calibrant. The regression model is based on the observed correlated temporal drift between the isotope ratios of the analyte and calibrant occurring in MC-ICP-MS using the following equation 1:

$$\ln r_{175/176}^{\text{Lu}} = a_i + b_i * \ln r_{187/185}^{\text{Re}} \quad (1)$$

where $r_{187/185}^{\text{Re}}$ and $r_{175/176}^{\text{Lu}}$ are the measured isotope ratios of Re and Lu, respectively; and coefficients a_i and b_i are the intercept and slope of the corresponding linear regression, respectively, which are obtained using least squares fitting of data.^{25, 37–41} Assuming that the true isotope ratio (R) is directly proportional to the measured ratio (r) by a correction factor K . (equation 2):

$$R_{175/176}^{\text{Lu}} = K_{175/176}^{\text{Lu}} * r_{175/176}^{\text{Lu}} \quad (2)$$

According to the above equations, the true Lu isotope ratios of $R_{175/176}^{Lu}$ can be derived based on equation 2 and the true $R_{187/185}^{Re}$ ratio (1.6742 ± 0.0005 , $u, k = 1$):^{21,42}

$$R_{175/176}^{Lu} = e^{a_i} \cdot (R_{187/185}^{Re})^{b_i} \quad (3)$$

It is important to note that equation 3 is not derived from either the exponential or Russell's law, and is able to correct both mass dependent and mass independent fractionation occurring in MC-ICP-MS.²⁵ In addition, the above equations effectively calibrate the Lu isotope ratio without assuming that Lu and Re must both undergo identical isotopic fractionation for different isotope pairs.^{43,44} The analyte and the calibrant are both measured simultaneously in the same solution, thereby eliminating the effect of the sample matrix and alleviating the need to match the mass fractions of the analyte and calibrant.³⁸ In addition, both the analyte and calibrant are measured simultaneously in the same solution; thus, the sample matrix effect is minimized and there is no need to match the mass fractions of the analyte and calibrant.³⁸ All Lu and Re isotope ratios were measured at varying RF powers from P_0 to P_{max} , as shown in Fig. 1, with linear relationships between the measured $\ln R_{187/185}^{Re}$ vs $\ln R_{175/176}^{Lu}$.

Taking advantage of these features, in this study, a regression model was applied for the characterization of the Lu IC in this Lu spike by using the primary isotopic calibrant, NIST SRM 989 Re. Eighty-nine sets of $\ln R_{187/185}^{Re} - \ln R_{175/176}^{Lu}$ were acquired from Re-Lu mixtures over three months. Consequently, the relationships were linearly correlated and exhibited high coefficients of regressions ($R^2 \geq 0.9996$). As shown in Fig. 1, the typical measured $\ln R_{175/176}^{Lu}$ and $\ln R_{187/185}^{Re}$ isotope ratio showed a well-defined log-linear relationship in accordance with equation 1.

Measurement results of isotope ratio in Lu spike. Lu isotope ratio measurements in the Lu spike were performed with replicate solutions containing $1.5 - 2.0 \mu\text{g g}^{-1}$ of Lu spike and Re. A total of eighty-nine sets of Lu - Re regressions were collected during a three-month period from May to July 2022. The relationships of $\ln R_{187/185}^{Re} - \ln R_{175/176}^{Lu}$ were linearly correlated and exhibited high correlation coefficients ($R^2 \geq 0.9996$) (such as Fig. 1). With a good linear correlation between $\ln R_{187/185}^{Re}$ and $\ln R_{175/176}^{Lu}$, the final value of $R_{175/176}^{Lu}$ in the Lu spike was 0.19994 ± 0.00009 (2 SD, $n = 89$) (Fig. 2), which was calculated using equation (3). Over the long-term measurements, the obtained Lu isotope ratios exhibited little variation, even with different daily optimization conditions, demonstrating the robustness of the regression model. In addition, the frequency histograms and probability density curves of $R_{175/176}^{Lu}$ showed that the measured Lu isotope ratio followed a Gaussian distribution.

The combined uncertainties included all uncertainty contributions from the measurement of the calibrated Lu isotope ratio estimated using a Monte Carlo method,^{25,38} in which the uncertainty of the primary calibrant NIST SRM 3134 Re ($R_{187/185}^{Re} = 1.6742 \pm 0.0005$, $u, k = 1$), was calibrated against the

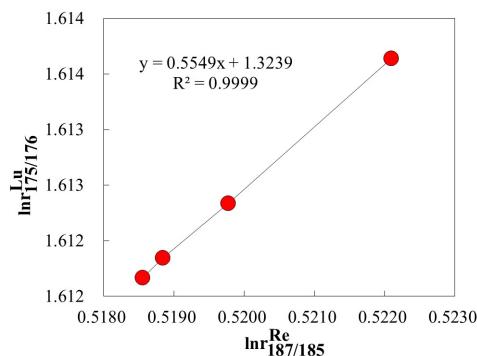


Fig. 1 Typical MC-ICP-MS log-linear regression plots of $\ln R_{175/176}^{Lu}$ against the calibrator of $\ln R_{187/185}^{Re}$ in (Lu spike + NIST SRM 3134 Re) solutions.

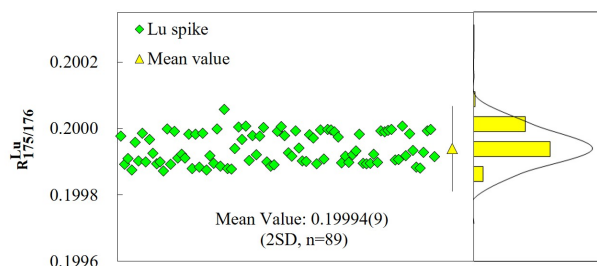


Fig. 2 Calibrated Lu isotope ratios using the optimized regression model (ORM). Uncertainties are analytical uncertainty (2SD).

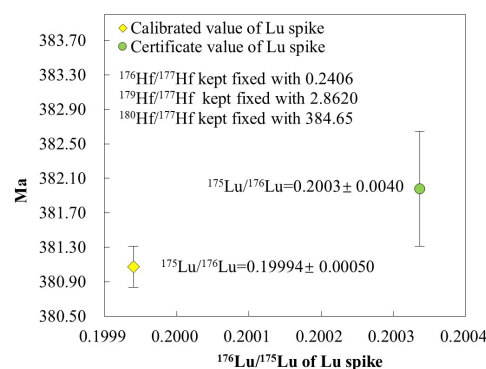


Fig. 3 Deviation in calculated isochron ages between the different precision of the Lu spike when using the calibrated and certificate isotopic composition (IC).

ratio estimated using a Monte Carlo method,^{25,38} in which the uncertainty of the primary calibrant NIST SRM 3134 Re ($R_{187/185}^{Re} = 1.6742 \pm 0.0005$, $u, k = 1$), was calibrated against the NRC IRIS - 1 isotopic Ir.^{21,42} The combined uncertainty of $R_{175/176}^{Lu}$ was 0.00050 ($u, k = 1$), which met the required precision level for applying the ID method.

Effect of isotopic precision in Lu spike on calculated isochron age. For the application of the ID method, the precise determination of the isotope ratio is influenced by the accuracy and uncertainty of the spike,²² which also affect the isochron age.^{10,45} Therefore, the spike purchased from the Oak Ridge National

Table 4. Lu concentrations ($\mu\text{g g}^{-1}$) of BHVO-2 determined using the ID method

Sample	Conc. Lu ($\mu\text{g g}^{-1}$)	2SE	Mean (Calculated by calibrated IC)	Mean (Calculated by certificated IC)	Recommended Conc. Lu ($\mu\text{g g}^{-1}$)*
BHVO-2	0.2754	0.0031	0.2748 ± 0.0010 (2SD, n=5)	0.2810 ± 0.0056 (2SD, n=5)	0.274
	0.2745	0.0022			
	0.2742	0.0026			
	0.2751	0.0018			
	0.2749	0.0023			

*Recommended value was determined by ID-TIMS ⁴⁸

National Laboratory should be re-calibrated.²¹ As detailed elsewhere, compared with the SSB and C-SSBIN methods, the IC precision in enriched spike calibrated by the regression model was significantly improved.²¹ The isotope ratio of $R_{175/176}^{\text{Lu}}$ in the Lu spike and the isotope ratios of $R_{176/177}^{\text{Hf}}$, $R_{179/177}^{\text{Hf}}$ and $R_{180/177}^{\text{Hf}}$ in the Hf spike are needed to calculate the isochron age. To investigate the effect of the increase in precision on the calculation on the Lu - Hf isochron age calculation, the isotope ratios ($R_{175/176}^{\text{Lu}}$) in this Lu spike were varied, while the values ($R_{176/177}^{\text{Hf}}$, $R_{179/177}^{\text{Hf}}$ and $R_{180/177}^{\text{Hf}}$) of the Hf spike were held constant (Fig. 3). Compared with the certificate (0.2003 ± 10) and calibrated IC (0.19994 ± 0.00050) of this Lu spike, there was a potential approximate 0.84 Ma offset of the calculated isochron age (Fig. 3). In addition, when the certificate IC and was applied, there was a potential ~ 0.67 Ma offset of the isochron age. When the calibrated IC was used, the offset was only ~ 0.24 Ma. Therefore, it was essential to calibrate the spike, and the precision of the enriched Lu spike calibrated by the regression model was improved. In addition, the uncertainty in measuring the mass fraction of Lu was significantly reduced by the application of the calibrated spike, and the accuracy of the Lu-Hf chronometer was also improved.

Application of the calibrated Lu spike for the geological reference materials

The ID method is commonly applied in geoscience, most notably in geochronology, where element concentrations with high accuracy and precision are required. The main advantage of the ID method over other methods is that the concentration of an element does not depend on the calibration of the method relative to an external reference material.^{46,47} Rather, the sample concentration can be directly determined from the masses of the sample and spike, and the measured ICs of the sample, spike, and sample-spike mixture.²² It is essential to verify the applicability of the calibrated Lu spike, which can measure the concentration with high accuracy and precision.

The silicate rock reference material, BHVO-2 (basalt powder) obtained from the United States Geological Survey (USGS) was used to evaluate the applicability of the calibrated Lu spike. In accordance with the optimum proportion of the spike-sample mixture, the reference material was separately mixed with the Lu

spike. To avoid the parent-daughter isotope ratios that differ from those of the bulk sample, the entire geological reference material should be spiked before digestion. In addition, the concentration of the Lu spike in this study were also re-calibrated as $0.58021(5)$ (2SE) $\mu\text{g g}^{-1}$. According to the principles of ID,²² the concentration of an element in the reference material can be calculated using the measured IC of the sample-spike mixture, known IC and atomic weight of the spike and sample, measured sample and spike weight, and concentration of the spike. After calculation, the obtained Lu concentrations of the BHVO-2 with a high precision of 0.2 % (relative error) were within the recommended value range. The uncertainty of mean Lu concentration calculated by the certificated isotopic composition of Lu spike was significantly improved by the calibrated isotopic composition of Lu spike, which proved the necessity of re-calibration, and the calibrated Lu spike was appropriate for the ID method (Table 4).

CONCLUSION

The regression model successfully determined the IC of an enriched Lu spike for the first time. The obtained isotope ratio $R_{175/176}^{\text{Lu}}$ was 0.19994 ± 0.00050 (u , $k = 1$) in this Lu spike. Compared to the certificate value of Lu spike, the isochron age calculated by the calibrated Lu spike was improved as 0.43 Ma, and the uncertainties of the calculated isochron age were also improved by the application of the calibrated Lu spike. In addition, the calculated Lu concentrations of the geological reference materials (BHVO-2) were within the recommended value range, which demonstrated that the calibrated Lu spike was appropriate for the ID method. Therefore, the Lu spike in this study is suitable for application to the ID method. In addition, the regression model can eliminate mass dependent and mass independent fractionation during MC-ICP-MS measurements. By taking the advantage of these features, the regression model can be applied to determine of the isotopic composition (IC) of spike.

AUTHOR INFORMATION



Keqing Zong is a professor at the State Key Laboratory of Geological Processes and Mineral Resources, School of Earth Sciences, China University of Geosciences, Wuhan (CUG-Wuhan). He received his B.S. (2004) and Ph.D. (2010) degrees in geochemistry from CUG-Wuhan. His main interest was the method and application of trace element geochemistry. He is currently working on trace

elemental analysis and its application in planetary science, the deep carbon cycle, and the early evolution of the Earth. He has published over 100 peer-reviewed scientific articles in ISI-index journals.

Corresponding Author

*K. Q. Zong

Email address: zongkeqing@cug.edu.cn

Notes

The authors declare no competing financial interest.

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