Estimation of Isotopic Reference Values for Pure Materials and Geological Reference Materials

Wen Zhang and Zhaochu Hu*

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

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ABSTRACT: Reference materials (RMs) are the foundation in isotopic analysis, and the assignment of reference values of isotope ratios in RMs is a complex process. In this study, we established new isotopic reference values and its uncertainties for the Sr, Nd, Hf and Pb isotope ratios in 18 commonly used pure materials and rock RMs, and for Hf and O isotope ratios in five zircon RMs, following the ISO guidelines and procedures in the IAG Certification Protocol. The original data were collected from the geochemical database “GeoReM”. An estimation method for generating reference values of isotope ratios was developed, including a data filter process, technical criteria assessment and robust statistical calculation. The generated analytical results demonstrate the same instrumental performance with both TIMS and MC-ICP-MS for Sr and Nd isotopic analysis. However, significant discrete data for the Pb isotope ratios obtained by TIMS and MC-ICP-MS are evident, indicating existing challenges for accurate Pb isotopic analysis. It was found that 91500 is not a suitable Hf isotopic RM for micro-analysis due to the heterogeneous Hf isotopic composition and the Plešovice zircon may be a more ideal alternative. This study provides a powerful protocol and practical examples for estimating reference values of isotope ratios in frequently used RMs.

INTRODUCTION

Isotopic compositions may vary significantly in physicochemical reactions and various geochemical or biochemical processes. Therefore, isotope ratios offer numerous important applications, including the study of magmatic source components and geological evolution processes in geochemistry,¹⁻⁴ as well as the study of the distribution of metal stable isotopes in seawater and their potential impact on global biogeochemical cycles in the oceans.^{5,6} In recent years, thermal ionization mass spectrometry (TIMS) and multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) have become the mainstream instruments for high-precision isotopic analysis.⁷⁻¹¹ Reference materials (RMs) are the foundation in isotopic analysis,¹²⁻¹⁵ as they are always used in a measurement process for the calibration of instruments, assessment of a measurement procedure, and quality control. The accuracy of isotope ratios in RMs is the basis for the application of RMs. However, the assignment of isotope ratio

values in RMs is a complex process of combining the results from homogeneity to stability assessment and reliability of the determination methods.¹⁶⁻²⁰

ISO (International Organization for Standardization) has published guidelines on how to estimate a certified property value for RMs,^{21,22} especially with respect to the evaluation of measurement uncertainties and establishment of metrological traceability. In the field of geochemistry, there are also many institutes or researchers dedicated to reliably estimate the true values for geological RMs, such as IAG (International Association of Geoanalysts) or the GeoReM website (<http://GeoReM.mpch-mainz.gwdg.de>).^{16,18-20,23} Many valuable works have been published. For example, Jochum *et al.* assigned more reliable sets of reference values and the respective uncertainties for major, minor and a large group of trace elements for 19 USGS, GSJ and GIT-IWG rock RMs.¹⁶ The GeoReM website is a well-known geochemical database and provides the "GeoReM preferred

values" for users, which are estimated from certified data or high-precision and definitive methods.²⁴ However, previous studies mainly assign the reference values for elemental concentrations in geological RMs, but rarely for isotopic compositions. The "GeoReM preferred values" for isotopic compositions on the GeoReM website are just the average of a population, which is not an adequate estimation. For example, the "GeoReM preferred value" of $^{87}\text{Sr}/^{86}\text{Sr}$ in BCR-2 (a frequently used rock RM) is 0.70492 ± 0.00055 (SD, standard deviation), which may present an overestimation for uncertainty.

GeoReM is an excellent geochemical database. It contains a large number of elemental and isotopic data of geological reference materials. Therefore, it is an opportunity to use this database for the estimation of isotopic compositions in geological RMs. Our aim was to establish new isotopic reference values and its uncertainties following the ISO guidelines and procedures in the IAG Certification Protocol.^{19, 25, 26} The original data obtained from the GeoReM were checked carefully using a strict data reduction method. As a result, we assigned a new set of reference values and uncertainties for the Sr, Nd, Hf, and Pb isotope ratios in 18 frequently used pure materials and rock RMs, and the Hf and O isotope ratios in five zircon RMs.

ESTIMATION METHOD FOR ISOTOPE RATIOS IN RMs

Based on the ISO guidelines (ISO GUIDE 35:2017),²² the characterization of an operationally defined measurand (isotope ratio in this study) can be achieved by using a network of competent laboratories. GeoReM has collected a large number of raw data from different laboratories around the world, using different instruments over time. These data are naturally random and well match the ISO requirements for a network of laboratories. However, we should note that some laboratories may not have high-precision isotopic analysis capabilities. Therefore, it is important to carefully check the raw data quality based on some technical criteria. Fig. 1 shows a flow chart of the data reduction method used in this study. The Sr isotopic RM (NIST 987) is selected as an example to illustrate our data reduction method and the statistical calculation process.

The first step is collecting data. We used all published $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios in the GeoReM database (Fig. 2). There are more than 2000 raw data in the database obtained by different methods/instrumentation. The majority of data was provided for instrument types, such as TIMS or MC-ICP-MS, but some data were reported without the information on instrument type. In addition, in some cases, the information on uncertainties of isotope ratios was not recorded (Fig. 2).

Therefore, in the second step of data reduction, we designed two data rejection rules. First rule: only the data produced by TIMS or MC-ICP-MS are retained, because both instruments are

Fig. 1 The flow chart of the reference value estimation strategy.

Sr isotope of NIST 987		0.701243 710250 2053 values (compiled: 0.71034)	
Unclear analytical method	Unclear uncertainty type	0.000008	SD
		0.000005	2SE
		0.00001	

Fig. 2 The information of isotope ratios for NIST 987 in GeoReM database.

well known as being reliable for high-precision isotope ratio analysis. Second rule: only retain data that have correct uncertainty expression, such as SD, sigma, 95% confidence level. The data without reporting uncertainty or SE (standard error) as uncertainty were rejected. Because SE is a measure of the precision of the sample mean, it is not an estimate of the variability of the population from which the sample was drawn, and it does not evaluate the data quality of an entire analysis process.

The third step is the statistical treatment of remaining data and calculation of reference values. In general, after the first round of filtering the data, some remaining data still show large uncertainties, indicating the unqualified analysis processes. Therefore, these data cannot be accepted in the reference value assignment. According to ISO recommendations, in proficiency testing by interlaboratory comparison (ISO 13528), the repeatability and reproducibility standard deviations from a previous collaborative study of precision of a measurement method should be used for the determination of the criteria for the evaluation of performance.²¹ We designed a technical criterion to judge the quality of isotopic data. The basic idea is to use the existing data population to calculate a reasonable uncertainty range, which then is used as a technical criterion of isotopic analysis, as detailed below.

(1) First, the entire data was divided into the TIMS group and the MC-ICP-MS group. In each group, a kernel density plot is used for identifying possible bimodalities or lack of symmetry. As shown in Fig. 3, it is clear that the uncertainty distribution is not a normal distribution in both groups. The non-normal data can be highly variable and makes conventional statistical techniques,

Fig. 3 The kernel density plot of uncertainties of $^{87}\text{Sr}/^{86}\text{Sr}$ in NIST 987. The entire data was divided into TIMS group and MC-ICP-MS group.

Fig. 4 The kernel density plot of $^{87}\text{Sr}/^{86}\text{Sr}$ in NIST 987.

including the mean and standard deviation, unreliable. Therefore, we selected three robust statistical techniques to evaluate the population mean and uncertainty, such as the median, Algorithm A and Hampel estimator. Robust statistics provide a large collection of statistical methods that explicitly allow for the presence of outlying values in an otherwise approximately normally distributed data set.²² The three robust statistical techniques used in this study are cited from ISO 13528²¹ and implemented by python code.

(2) The statistical results of the population mean and SD are listed in Table 1, and the obtained results by three robust statistical techniques are similar. For example, the uncertainties of population mean for the TIMS group are 0.000014, 0.000016 and 0.000015, respectively, whereas for the MC-ICP-MS group are 0.000016, 0.000018 and 0.000017, respectively. Therefore, we only selected one robust technique (Algorithm A) for the subsequent evaluation and calculation. Algorithm A transforms the original data to provide alternative estimators of mean and SD for near-normal data, and is the most useful where the expected proportion of outliers is below 20%. The working condition of Algorithm A is suitable for the sample population. As shown in Table 1, we found that the analytical uncertainties of $^{87}\text{Sr}/^{86}\text{Sr}$ should be in the range of 0.000015 ± 0.000017 (SD, $k=2$) and 0.000016 ± 0.000016 (SD, $k=2$) for the TIMS group and the MC-ICP-MS group, respectively. The technical criterion values in the TIMS group and the MC-ICP-MS group can be determined as 0.000032 and 0.000032 (mean + $2 \times \text{SD}$), respectively. The obtained similar technical criteria in TIMS and MC-ICP-MS indicate a similar instrumental performance. Thus, the remaining data with uncertainties larger than the technical criterion values were then removed.

(3) Another key factor is whether there is a systematic measurement error between TIMS and MC-ICP-MS. As shown in Fig. 4, kernel density plots show a complex $^{87}\text{Sr}/^{86}\text{Sr}$ ratio distribution in both groups. But the robust statistical results by Algorithm A are 0.710246 ± 0.000008 (SD) and 0.710250 ± 0.000010 (SD) for the TIMS group and the MC-ICP-MS group, respectively, clearly indicating no systematic error between both methods. Therefore, all of the data in both groups can be integrated to estimate the final result of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in NIST 987.

(4) Now the final sample population that was measured by TIMS and MC-ICP-MS, filtered according to the technical criterion, was obtained. With reference to the ISO guidelines, the assignment of property values and their uncertainties in the final sample population should exclude the outliers using the Grubb's test.^{21, 22} After the outlier rejection procedure, the kernel density plot is used to characterize the final sample population. If it is a non-normal distribution, robust statistical techniques (Algorithm A in this study) should be used to estimate the robust sample mean

Table 1. The Uncertainty Distribution of $^{87}\text{Sr}/^{86}\text{Sr}$ in NIST 987. Three Robust Statistical Techniques Were Used to Calculate the Mean and Standard Deviation, Respectively

Procedure	The uncertainty ranges of $^{87}\text{Sr}/^{86}\text{Sr}$ in NIST 987			
	Mean		Standard deviation	
	TIMS (n=1536)	MC-ICP-MS (n=326)	TIMS (n=1536)	MC-ICP-MS (n=326)
Arithmetic mean and standard deviation	0.000019	0.000021	0.000046	0.000031
Robust: Median and MADe	0.000014	0.000016	0.000009	0.000007
Robust: Algorithm A (x^* , s^*)	0.000015	0.000016	0.000008	0.000008
Robust: Hampel + Qn	0.000015	0.000017	0.000009	0.000009

Table 2. Pure Materials, Rock RMs and Micro-analysis Solid RMs Investigated in this Study

RMs	Provider	Type	Isotopes
Pure materials			
NIST SRM 987	NIST	Strontium carbonate powder: SrCO ₃	Sr
IAPSO	Ocean Scientific International Ltd.	Sea water solution	Sr
EIMER-AMEND	Elmer and Amend	Strontium carbonate powder: SrCO ₃	Sr
JNdi-1	Shin-Etsu Chemical Co., Ltd.	Nd ₂ O ₃ powder	Nd
La Jolla Nd	Lugmair and Carlson	Solution	Nd
JMC-Nd	Johnson Matthey	Nd ₂ O ₃ powder ((JMC 231)	Nd
AMES-Nd	-	Pure metal	Nd
JMC-475	Johnson Matthey	Solution	Hf
NIST 981	NIST	Lead metal	Pb
Rock RMs			
BCR-1	USGS	A basalt from washington, USA	Sr-Nd-Hf-Pb
BCR-2	USGS	A basalt from washington, USA	Sr-Nd-Hf-Pb
BHVO-1	USGS	A basalt from kilauea volcano, Hawaii, USA	Sr-Nd-Hf-Pb
BHVO-2	USGS	A basalt from kilauea volcano, Hawaii, USA	Sr-Nd-Hf-Pb
BIR-1	USGS	A basalt from Iceland	Sr-Nd-Hf-Pb
AGV-1	USGS	An andesite from Oregon, USA	Sr-Nd-Hf-Pb
AGV-2	USGS	An andesite from Oregon, USA	Sr-Nd-Hf-Pb
RGM-1	USGS	A rhyolite from California, USA	Sr-Nd-Hf-Pb
JB-2	GSJ	A basalt from oshima, Tokyo, Japan	Sr-Nd-Hf-Pb
JB-3	GSJ	A basalt from oshima, Tokyo, Japan	Sr-Nd-Hf-Pb
Micro-analysis RMs			
91500	Wiedenbeck <i>et al.</i> (1995) ³⁹	Zircon, the Harvard Museum	Hf-O
GJ-1	Jackson <i>et al.</i> (2004) ⁴²	Gem zircon	Hf
Plešovice	Sláma <i>et al.</i> (2008) ⁴³	Zircon, the Blanský les granulite body, in the southern Bohemian Massif, Czech Republic	Hf
TEMORA-1	Black <i>et al.</i> (2003) ⁴⁰	Zircon, Middledale Gabbroic Diorite of the PalaeozoicLachlan Fold Belt of eastern Australia	Hf-O
TEMORA-2	Black <i>et al.</i> (2004) ⁴¹	Zircon, Middledale Gabbroic Diorite of the PalaeozoicLachlan Fold Belt of eastern Australia	Hf-O

Fig. 5 The reference values of $^{87}\text{Sr}/^{86}\text{Sr}$ in NIST 987 obtained from 12 independent labs and this study (1583 data).

and uncertainty. As shown in Fig. 4, the kernel density plot of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of NIST 987 is not a normal distribution. Consequently, the Algorithm A method was used, and a new statistical value of $^{87}\text{Sr}/^{86}\text{Sr}$ for NIST 987: 0.710248 ± 0.000024 (SD, $k=2$) was obtained. In this example, there were 2053 original data for NIST 987, but only 1583 data contributed to the final result. The utilization efficiency of the original data was 77%. Most removed data were due to a lack of information on instrument type, uncertainty unit and the large uncertainty.

In order to verify the reliability of the proposed method, Fig. 5 shows the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of NIST 987 measured by 12 independent labs.²⁷⁻³⁸ These labs reported the long-term results of $^{87}\text{Sr}/^{86}\text{Sr}$ in NIST 987, which were recorded in the GeoReM database. However, these $^{87}\text{Sr}/^{86}\text{Sr}$ ratios show an obvious larger dispersion (0.710244 ± 0.000056 , SD, $K=2$), which will undoubtedly prevent the selection of the reference value. Moreover, the certified value of $^{87}\text{Sr}/^{86}\text{Sr}$ in NIST 987 (0.710340 ± 0.000260 , SD, $K=2$) obviously deviated from all reported values. In this study, a new and more precise reference value for NIST 987 was obtained based on a large sample population and use of a robust statistical method. Therefore, our results provide a good constraint for the reference value of NIST 987.

MATERIALS

Three sample types were analyzed in this study and include pure materials, rock RMs and micro-analytical solid RMs. Pure materials are mainly used to monitor instrumental conditions, isotope ratio drift during the analysis process and data reduction. Rock RMs can be analyzed with unknown samples to monitor the entire isotopic analysis process, including sample digestion, chemical purification and the instrument measurement process.

Table 3. The Technical Criteria Values for Sr, Nd, Hf and Pb Calculated in NIST 987, JNdi-1, JMC-475 and NIST 981, respectively

Isotope ratios	TIMS		MC-ICP-MS		Technical criteria
	Mean	SD, k=2	Mean	SD, k=2	
$^{87}\text{Sr}/^{86}\text{Sr}$ (NIST 987)	0.000015	0.000017	0.000016	0.000016	0.000032
$^{143}\text{Nd}/^{144}\text{Nd}$ (JNdi-1)	0.000009	0.000011	0.000011	0.000010	0.000021
$^{176}\text{Hf}/^{177}\text{Hf}$ (JMC-475)			0.000011	0.000011	0.000022
$^{206}\text{Pb}/^{204}\text{Pb}$ (NIST 981)	0.007	0.011	0.003	0.005	0.008
$^{207}\text{Pb}/^{204}\text{Pb}$ (NIST 981)	0.007	0.012	0.003	0.004	0.007
$^{208}\text{Pb}/^{204}\text{Pb}$ (NIST 981)	0.019	0.032	0.007	0.011	0.018

Table 4. New Reference Values of Sr, Nd, Hf and Pb Isotope Ratios for Nine Pure Materials

Name	Mean	SD	Original sample number	Final sample number	Utilization efficiency (%)
$^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios					
NIST 987	0.710248	0.000012	2058	1583	77
IAPSO	0.709169	0.000012	22	8	36
EIMER-AMEND	0.708011	0.000016	40	14	35
$^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratios					
JNdi-1	0.512107	0.000012	586	503	86
La-Jolla	0.511850	0.000010	1020	679	67
JMC-Nd	0.511134	0.000038	149	97	65
AMES-Nd	0.512077	0.000081	200	129	65
$^{176}\text{Hf}/^{177}\text{Hf}$ isotope ratios					
JMC-475	0.282157	0.000008	384	260	68
Pb isotope ratios					
$^{206}\text{Pb}/^{204}\text{Pb}$	16.938	0.005	586	349	60
$^{207}\text{Pb}/^{204}\text{Pb}$	15.494	0.006	568	308	54
$^{208}\text{Pb}/^{204}\text{Pb}$	36.710	0.019	568	318	56

Fig. 6 The kernel density plot of $^{143}\text{Nd}/^{144}\text{Nd}$ in JNdi-1.

In the micro-analysis of isotopes, solid RMs are used for isotopic fractionation correction or monitoring data quality. Based on the GeoReM database, the most popular RMs are selected and listed in Table 2. For pure materials and rock RMs, we mainly analyzed the four isotope systems of Sr, Nd, Hf and Pb. In addition, five

zircon RMs, reported as U-Pb dating, were analyzed for Hf and O.³⁹⁻⁴³

RESULTS AND DISCUSSION

Pure materials. According to our proposed analysis strategy, the technical criteria for the Sr, Nd, Hf and Pb isotope systems should be determined first. The results from pure materials are most suitable for this work because they are free of interfering elements and provide the best analytical data. Four popular pure materials (NIST 987, JNdi-1, JMC-475 and NIST 981) were selected to assess the technical criteria values of Sr, Nd, Hf and Pb, respectively. The statistical results are listed in Table 3. As described above, this consistent uncertainty range of the Sr isotope ratio between TIMS and MC-ICP-MS indicates that both instruments have similar analytical capabilities for Sr isotope ratio analysis. Therefore, the mean value of technical criteria for both TIMS and MC-ICP-MS was used as the final technical criteria value of Sr isotope analysis. The same situation was found for the Nd isotopic data by TIMS and MC-ICP-MS, where the mean value of 0.000021 was obtained for the technical criteria for Nd isotope analysis.

For the Hf isotope system, most data were determined by MC-ICP-MS. The technical criteria of MC-ICP-MS were used for Hf isotope analysis. For the Pb isotope system, the TIMS method presents a large distribution of uncertainty. The technical criteria with TIMS for the Pb isotope ratio is generally more than 2 times higher than that with MC-ICP-MS. Therefore, the technical criteria of MC-ICP-MS were selected for Pb isotope analysis (Table 3).

The technical criteria calculated above will help to screen the original data. If the uncertainty of a data from GeoReM is higher than the corresponding technical criteria value, then that data will be rejected for the calculation.

After the first two steps in the estimation method, the final sample populations were obtained (Table 4). For the Sr isotope system, the above discussion for NIST 987 has shown that there is no systematic statistical error between TIMS and MC-ICP-MS for $^{87}\text{Sr}/^{86}\text{Sr}$ analysis. Therefore, the $^{87}\text{Sr}/^{86}\text{Sr}$ values measured by TIMS and MC-ICP-MS were integrated to estimate the robust mean and SD. The new $^{87}\text{Sr}/^{86}\text{Sr}$ reference values obtained for three pure materials (NIST 987, IAPSO and EIMER-AMEND) are 0.710248 ± 0.000012 (SD, k=1), 0.709169 ± 0.000012 (SD, k=1) and 0.708011 ± 0.000016 (SD, k=1), respectively.

For the Nd isotope system, the $^{143}\text{Nd}/^{144}\text{Nd}$ results of JNdi-1 determined by TIMS and MC-ICP-MS were compared and found to be consistent with each other (Fig. 6). Therefore, the $^{143}\text{Nd}/^{144}\text{Nd}$ values measured by TIMS and MC-ICP-MS were integrated to estimate the robust sample mean and SD. The new $^{143}\text{Nd}/^{144}\text{Nd}$ reference values obtained for four pure materials

(JNdi-1, La-Jolla, JMC-Nd and AMES-Nd) are 0.512107 ± 0.000012 (SD, $k=1$), 0.511850 ± 0.000010 (SD, $k=1$), 0.511134 ± 0.000038 (SD, $k=1$) and 0.512077 ± 0.000081 (SD, $k=1$), respectively. The large SD values in JMC-Nd and AMES-Nd indicate the heterogeneous Nd isotopic compositions in different batches.

A high-precision Hf isotopic analysis can only be achieved by MC-ICP-MS. According to the final sample population of Hf isotopic data, the new $^{176}\text{Hf}/^{177}\text{Hf}$ reference value of JMC-475 is 0.282157 ± 0.000008 (SD, $k=1$).

For the Pb isotope system, the Pb isotopic compositions in NIST 981 obtained by TIMS and MC-ICP-MS show large variations (Fig. 7). This phenomenon cannot be explained by the heterogeneous Pb isotopic composition in NIST 981. The main reason could be that the Pb isotopic analysis methods used in many laboratories may not be mature, especially for the isotopic fractionation correction and the control of potential Pb contamination. Nevertheless, the robust statistical results for the Pb isotope ratios are consistent for both the TIMS and MC-ICP-MS instrumentation. The Pb isotopic data from TIMS and MC-ICP-MS were integrated to estimate the robust sample mean and SD. The new $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ reference values of NIST 981 are 16.938 ± 0.005 (SD, $k=1$), 15.494 ± 0.006 (SD, $k=1$) and 36.710 ± 0.019 (SD, $k=1$), respectively.

Rock RMs. Although there are many isotopic RMs in the geochemistry community, only a portion of RMs were widely used and reported for isotopic results. In order to ensure adequate statistical power for the final sample population, we collected the frequently used rock RMs for Sr, Nd, Hf and Pb for data compilation, such as BCR-1, BCR-2, BHVO-1, BHVO-2, BIR-1, AGV-1, AGV-2, JB-2 and JB-3. The compilation results are listed in Table 5.

After the data reduction process, the final utilization efficiency was about 53%. Most of these geological RMs are produced by USGS. Some of them were sampled at the same place but in different production batches, such as BCR-1, BCR-2, BHVO-1, BHVO-2, AGV-1 and AGV-2. Our data show consistent Sr, Nd and Hf isotopic compositions within the uncertainty range in different batches. In contrast, the Pb isotope ratios have significant variations up to 0.25% between different batches. For example, the values of $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ for BHVO-1 are 18.687 ± 0.007 (SD, $k=1$), 15.572 ± 0.004 (SD, $k=1$) and 38.347 ± 0.021 (SD, $k=1$), respectively, in comparison to 18.647 ± 0.022 (SD, $k=1$), 15.532 ± 0.007 (SD, $k=1$) and 38.226 ± 0.024 (SD, $k=1$), respectively, for BHVO-2. Similar variations in Pb isotope ratios are observed for AGV-1 and AGV-2.

Solid reference materials for micro-analysis: Hf and O isotope ratios in zircon. The Hf and O isotopic analysis in zircon is the most widely used micro-analysis application in the geological field. *In situ* Hf isotopic analysis in zircons is generally performed

by LA-MC-ICP-MS, and the O isotope ratio is measured by SIMS. We collected a few common zircon RMs for Hf and O isotopic analysis, such as GJ-1, 91500, Plešovice, TEMORA-1 and TEMORA-2.

In order to assess the technical criteria value of the Hf isotope ratio, the analytical uncertainties of GJ-1, 91500 and Plešovice in the original data were calculated. The kernel density of uncertainties is shown in Fig. 8. It is clear that most uncertainties fall in the range of 0.000005–0.000022. Thus, the technical criteria value of the Hf isotopic analysis using LA-MC-ICP-MS was set

Fig. 7 The kernel density plots of $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ in NIST 981.

Fig. 8 The kernel density plots of uncertainties of $^{176}\text{Hf}/^{177}\text{Hf}$ in GJ-1, 91500 and Plešovice.

Table 5. New Reference Values of Sr, Nd, Hf and Pb Isotope Ratios for nine Rock RMs

Name	Mean	2SD	Original sample number	Final sample number	Utilization efficiency (%)	
<i>⁸⁷Sr / ⁸⁶Sr isotope ratios</i>						
BCR-1	0.705008	0.000020	48	32	67	
BCR-2	0.705012	0.000020	164	115	70	
BHVO-1	0.703478	0.000005	29	9	31	
BHVO-2	0.703480	0.000016	128	70	55	
BIR-1	0.703107	0.000009	18	7	39	
AGV-1	0.703988	0.000007	22	9	41	
AGV-2	0.703988	0.000013	45	25	56	
JB-2	0.703679	0.000015	30	8	27	
JB-3	0.703407	0.000028	14	7	50	
<i>¹⁴³Nd / ¹⁴⁴Nd isotope ratios</i>						
BCR-1	0.512634	0.000017	178	99	56	
BCR-2	0.512626	0.000008	240	179	75	
BHVO-1	0.512988	0.000011	46	23	50	
BHVO-2	0.512983	0.000010	154	94	61	
BIR-1	0.513095	0.000021	32	21	66	
AGV-1	0.512788	0.000005	14	5	36	
AGV-2	0.512787	0.000007	46	28	61	
JB-2	0.513095	0.000006	31	14	45	
JB-3	0.513055	0.000010	29	19	66	
<i>¹⁷⁶Hf / ¹⁷⁷Hf isotope ratios</i>						
BCR-1	0.282871	0.000006	32	17	53	
BCR-2	0.282869	0.000009	84	48	57	
BHVO-1	0.283105	0.000005	50	30	60	
BHVO-2	0.283100	0.000009	104	74	71	
BIR-1	0.283271	0.000021	30	19	63	
AGV-1	0.282976	0.000016	10	7	70	
AGV-2	0.282974	0.000010	31	20	65	
JB-2	0.283261	0.000021	22	7	32	
JB-3	0.283226	0.000008	17	14	18	
<i>Pb isotope ratios</i>						
BCR-1	²⁰⁶ Pb/ ²⁰⁴ Pb	18.819	0.004	24	11	46
	²⁰⁷ Pb/ ²⁰⁴ Pb	15.634	0.005	24	11	46
	²⁰⁸ Pb/ ²⁰⁴ Pb	38.722	0.015	24	11	46
BCR-2	²⁰⁶ Pb/ ²⁰⁴ Pb	18.753	0.008	104	48	46
	²⁰⁷ Pb/ ²⁰⁴ Pb	15.621	0.004	101	54	53
	²⁰⁸ Pb/ ²⁰⁴ Pb	38.725	0.022	100	54	54
BHVO-1	²⁰⁶ Pb/ ²⁰⁴ Pb	18.687	0.007	16	8	50
	²⁰⁷ Pb/ ²⁰⁴ Pb	15.572	0.004	15	11	73
	²⁰⁸ Pb/ ²⁰⁴ Pb	38.347	0.021	15	9	60
BHVO-2	²⁰⁶ Pb/ ²⁰⁴ Pb	18.647	0.022	53	18	34
	²⁰⁷ Pb/ ²⁰⁴ Pb	15.532	0.007	52	17	33
	²⁰⁸ Pb/ ²⁰⁴ Pb	38.226	0.024	52	24	46
BIR-1	²⁰⁶ Pb/ ²⁰⁴ Pb	18.848	0.005	17	12	71
	²⁰⁷ Pb/ ²⁰⁴ Pb	15.659	0.003	16	10	63
	²⁰⁸ Pb/ ²⁰⁴ Pb	38.495	0.008	16	10	63
AGV-1	²⁰⁶ Pb/ ²⁰⁴ Pb	18.940	0.002	28	10	36
	²⁰⁷ Pb/ ²⁰⁴ Pb	15.654	0.004	29	15	52
	²⁰⁸ Pb/ ²⁰⁴ Pb	38.561	0.005	29	12	41
AGV-2	²⁰⁶ Pb/ ²⁰⁴ Pb	18.866	0.003	46	24	52
	²⁰⁷ Pb/ ²⁰⁴ Pb	15.615	0.004	46	26	57
	²⁰⁸ Pb/ ²⁰⁴ Pb	38.532	0.010	46	27	59
JB-2	²⁰⁶ Pb/ ²⁰⁴ Pb	18.342	0.002	48	20	42
	²⁰⁷ Pb/ ²⁰⁴ Pb	15.562	0.001	48	16	33
	²⁰⁸ Pb/ ²⁰⁴ Pb	38.277	0.004	48	19	40
JB-3	²⁰⁶ Pb/ ²⁰⁴ Pb	18.294	0.002	18	13	72
	²⁰⁷ Pb/ ²⁰⁴ Pb	15.536	0.004	20	15	75
	²⁰⁸ Pb/ ²⁰⁴ Pb	38.251	0.006	20	11	55

Fig. 9 The kernel density plots of $^{176}\text{Hf}/^{177}\text{Hf}$ in GJ-1, 91500, Plešovice, TEMORA-1 and TEMORA-2. Note that the data of TEMORA-1 and TEMORA-2 are integrated.

Table 6. New Reference Values of Hf and O Isotope Ratios for Five Zircon RMs

Name	Mean	SD	Original sample number	Final sample number	Utilization efficiency (%)
<i>$^{176}\text{Hf}/^{177}\text{Hf}$ isotope ratios</i>					
GJ-1	0.282009	0.000010	342	268	78
91500	0.282300	0.000011	352	229	65
Plešovice	0.282478	0.000008	73	49	67
TEMORA-1	0.282684	0.000008	35	22	63
TEMORA-2	0.282683	0.000008	63	33	52
<i>$\delta^{18}\text{O}$</i>					
91500	9.89	0.12	51	27	53
TEMORA-1	8.08	0.16	9	6	67
TEMORA-2	8.19	0.05	58	19	33

as 0.000022. The results of the Hf isotope ratios obtained after the data reduction process are listed in Table 6. The final utilization efficiency is about 63%. The new $^{176}\text{Hf}/^{177}\text{Hf}$ reference values for five zircon RMs (GJ-1, 91500, Plešovice, TEMORA-1 and TEMORA -2) are 0.282009 ± 0.000010 (SD, $k=1$), 0.282300 ± 0.000011 (SD, $k=1$), 0.282478 ± 0.000008 (SD, $k=1$), 0.282684 ± 0.000008 (SD, $k=1$) and 0.282683 ± 0.000008 (SD, $k=1$),

respectively. TEMORA-1 and TEMORA-2 show consistent Hf isotopic compositions, indicating no significant variation in Hf isotopic composition between different batches of TEMORA zircon.

The final statistical results in five zircon RMs gave similar uncertainties of Hf isotope ratios. However, the kernel density plots show a clear secondary peak in 91500 zircon at a value of 0.282270 (Fig. 9). This indicates that the Hf isotopic composition in 91500 zircon may be heterogeneous and, therefore, is not a suitable RM for *in situ* Hf isotopic analysis. Plešovice presents a more symmetric distribution of the Hf isotope ratios in comparison to GJ-1, TEMORA-1 and TEMORA-2 (Fig. 9); hence, it is a better RM for Hf isotopic analysis by LA-MC-ICP-MS.

The assessment of uncertainties of the O isotope ratios produced a value of 0.42 as the technical criterion value for the O isotopic analysis by SIMS. After the data reduction process, the compilation results of the O isotope ratios obtained are listed in Table 6. The new $\delta^{18}\text{O}$ reference values for three zircon RMs (91500, TEMORA-1 and TEMORA-2) are 9.89 ± 0.12 (SD, $k=1$), 8.08 ± 0.16 (SD, $k=1$) and 8.19 ± 0.05 (SD, $k=1$), respectively.

CONCLUSIONS

The reference values of RMs can be obtained through a long-term analysis process in an independent laboratory, but this approach has the risk of systematic bias. Using data from laboratories around the world has many advantages, including a better randomness and independence. Based on the selected statistical models, the obtained statistical values can be used for better evaluation or approximation of the reference values in RMs. A similar approach was used in this study to estimate the reference values of total elemental concentrations, which provides a powerful protocol for the estimation of reference values of isotope ratios from all data reported in the GeoReM database platform. Here, new reference values of Sr, Nd, Hf and Pb isotope ratios in 18 pure materials and rock RMs, and Hf and O isotope ratios in five zircon RMs were generated. The proposed reference value estimation strategy can also be applied to other isotope systems, such as stable isotope systems or new RMs when more laboratory data are available.

AUTHOR INFORMATION

Corresponding Author

*Z. C. Hu

Email address: zchu@vip.sina.com

Notes

The authors declare no competing financial interest.

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