

The reliability of geochemical and isotopic data acquired at the metal-free chemical clean room and LA-MC-ICP-MS system of the institute of geological sciences, VAST

Tran Tuan Anh, Nguyen Hoang^{*}, Le Duc Luong, Tran Thi Huong,
Cu Sy Thang, Pham Ngoc Can

*Institute of Geological Sciences, Vietnam Academy of Science and Technology (VAST),
Alley 84 Chua Lang Str., Dong Da, Ha Noi, Viet Nam*

^{*}Email: nghoang@igs.vn

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Abstract. The newly constructed ISO5-class metal-free chemical clean room at the Institute of Geological Sciences requires verification for its cleanliness standards, while the recently installed Laser Ablation system, integrated with a Multi-Collector Inductively Coupled Plasma Mass Spectrometry (LA-MC-ICP-MS), must be certified for its analytical precision and accuracy before operational use. To assess both the clean room and the mass spectrometry system's reliability, a set of radiogenic isotope and geological reference samples was processed through chemical chromatography and mass spectrometry, with intercalated blanks included for control. The reference samples used in the evaluation included magmatic standards JA-2 and JB-1a from the Geological Survey of Japan, as well as radiogenic isotope solutions for Sr (NIST987), Nd (JNdi-1), Pb (NIST981), and Hf (JMC475). Trace element compositions were analyzed using a Quadrupole ICP-MS (Q-ICP-MS), while isotopic ratios were measured via MC-ICP-MS at both the Department of Physics and Earth Sciences, University of the Ryukyus (Okinawa, Japan), and the Institute of Geological Sciences (IGS). Results from both laboratories were compared to evaluate repeatability and accuracy, thereby providing a comprehensive assessment of the analytical reliability of IGS's facilities.

Keywords: metal-free clean room, mass spectrometry, radiogenic isotope, geochemical composition, relative standard deviation.

Classification numbers: 3.2.1, 3.7.3, 5.7.1.

1. INTRODUCTION

The Institute of Geological Sciences (IGS) has recently bolstered its research capabilities by establishing a state-of-the-art metal-free chemical clean room and installing a modern laser ablation-multi-collector inductively coupled plasma mass spectrometry system (LA-MC-ICP-MS). This advanced analytical facility will enable precise analysis of the chemical composition

and age of geological and mineral formations, positioning IGS as one of the leading institutions in material composition research.

The newly constructed clean room adheres to ISO/IEC 17025:2005 standards and features P100 class clean benches within a P100,000 environment, specifically designed for the digestion and separation of metallic elements from rocks and ores. Built by MK Versuchsanlagen und Labbedarf e.K. of Germany, the clean room covers 40 m², with 25 m² designated as working space and 15 m² allocated to support areas such as technical rooms, buffers, changing rooms, and weighing rooms. Operational since mid-2022, this facility plays a crucial role in sample preparation for trace element and radiogenic isotope analysis using thermal ionization or plasma source mass spectrometers (Fig. 1).



Figure 1. The ISO 5 class, metal-free chemical clean room at the Institute of Geological Sciences, Vietnam Academy of Science and Technology (VAST).

In early 2023, IGS further enhanced its capabilities by acquiring the NU Plasma 3 analyzer, a high-precision multi-collector plasma source mass spectrometer (MC-ICP-MS), integrated with the NWR213 laser ablation system (LA; www.nwrlasers.com) (Fig. 2). The NU Plasma 3 is renowned for its exceptional repeatability and accuracy, allowing simultaneous measurement of multiple isotopic ions ranging from lithium to actinide elements (3 to 300 amu). It achieves this through a unique variable dispersion Zoom lens and a static collection array of 16 Faraday cups and up to 6 ion counters. This advanced system is indispensable for analyzing isotopic ratios of elements such as U, Pb, Th, and Hf in minerals like zircon, facilitating the determination of both isotopic composition and age.

Notably, the IGS clean room and LA-MC-ICP-MS system are the first of their kind in Southeast Asia and the first installations in Vietnam. However, before the official deployment of these systems for geochemical data processing and analysis, it is essential to verify their cleanliness and reliability. Evaluating the cleanliness of a geochemical and isotope laboratory can be approached in several ways. For instance, processing geological samples of varying masses and subsequently analyzing their geochemical and isotopic compositions can help assess the repeatability (precision) and accuracy of results compared to published data. Additionally, analyzing blank samples alongside geological samples can help detect any contamination of tools and materials used, as well as potential cross-contamination during sample processing and analysis.

To assess the reliability of the IGS clean room and mass spectrometry system in processing and analyzing geological samples, we undertook the chemical treatment and chromatographic analysis of several geological reference materials and blanks in the IGS clean room. These samples were then analyzed for trace geochemical compositions using a Quadrupole (Q)-ICP-MS and isotopic ratios using MC-ICP-MS, first at the Department of Physics and Earth Sciences, University of the Ryukyus, Okinawa (Japan), and subsequently at IGS. The results from both laboratories will be compared to evaluate the repeatability and accuracy relative to standard data.

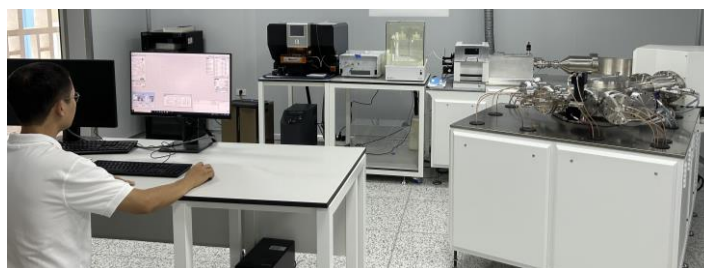


Figure 2. A laser ablation system (LA) connected with a multi-collector inductively coupled plasma mass spectrometry NU Plasma 3 (LA-MC-ICP-MS) recently installed at the Institute of Geological Sciences.

2. MATERIALS AND METHODS

2.1. Processing Geological Reference Samples for Elemental Analysis

Two powdered geological reference materials from the Geological Survey of Japan, JA-2 and JB-1a, and two blank samples were selected for chemical composition testing analysis. JA-2 is a typical volcanic arc andesite with low Nb, Ta, and Zr concentrations and high Ba, Rb, and K contents. In contrast, JB-1a is a (within-plate) continental volcanic basalt with higher contents of all the above elements than JA-2. The two reference samples are popular among geochemists as geochemical endmembers and geoscientists as two tectonic-volcanic representatives (<https://gbank.gsj.jp/geostandards/welcome.html>). Additionally, a range of geological reference materials from the Japan and United States Geological Surveys, including BIR-1, BRR-1, JB-2, JB-3, JA-1, JGb-1, JA-2, BCR-1, AGV-1, JB-1a, BHVO-2, and BEN - were processed and analyzed to construct an external calibration line and compare the results.

JA-2 and JB-1a powdered samples were weighed in 15 ml Teflon bottles, with each sample weighed twice at 50 mg (± 0.00005) and 100 mg (± 0.000010). Concentrated HNO_3 acid ($> 60\%$) was added in volumes of 1 ml and 2 ml for the 50 mg and 100 mg samples, respectively, and the same procedure was followed for the two blank samples (Blank A and Blank B). After gently shaking to ensure the acid was fully absorbed, 2 ml and 4 ml of HF acid ($> 30\%$) were added to the sample and blank bottles, respectively. The Teflon bottles were then tightly sealed and placed on a hotplate at $125 - 135\text{ }^\circ\text{C}$ for at least 48 hours. Following this, the samples were completely evaporated at $135 - 145\text{ }^\circ\text{C}$ for about 3 hours. To ensure complete dissolution, 1 ml of concentrated HNO_3 was added to the dry samples and evaporated again.

Next, 1-2 ml of concentrated HCl acid ($> 30\%$) or HClO_4 ($> 70\%$) was added to the dry samples while still on the hotplate. The samples were gently shaken to allow the acid to permeate evenly, the temperature was reduced to $60 - 70\text{ }^\circ\text{C}$, and the Teflon bottle caps were closed. After 30 minutes, the caps were opened, the temperature was increased to $135\text{ }^\circ\text{C}$, and approximately 5 ml of milli-Q water was added to the samples. The samples were allowed to evaporate completely over about 4 hours, preparing them for dilution and subsequent analysis by plasma mass spectrometry (Q-ICP-MS). All acids and milli-Q water used in the chemical treatment process were double-distilled in the clean room of the Institute of Geological Sciences.

Following complete evaporation, the samples were dissolved in 3 ml of 2M HNO_3 and diluted approximately 60 times. They were then placed on a heating plate at around $60\text{ }^\circ\text{C}$ to ensure complete dissolution and equilibration. About 0.164 - 0.165 grams of the sample solution

were transferred into a 15 ml Nalgene tube, to which approximately 10 grams of 0.3M HNO₃ acid (1.5 %) was added, diluting the solution up to 4000 (\pm 0.0010) times for analysis.

Quantitative analysis was performed using a Quadrupole (Q)-ICP-MS Thermo Scientific X Series 2 at the Geochemistry Laboratory, Department of Physics and Earth Sciences, University of the Ryukyus, Okinawa, Japan, according to the procedure detailed in the reference document. Below is a brief introduction to the spectrometer's running parameters. The plasma gas flow is fixed at 12 liters/minute, the RF (radio frequency) is 27.12 MHz, and the output power is 750 – 1500 W, optimized at 1150 W. The sample solutions are 0.3 M HNO₃ and in 15 ml Nalgene tubes, which are introduced into the spray chamber using a Cetac autosampler. Each sample was analyzed three times, with 45-second intervals between each run to allow the sample syringe to be rinsed in 5 % HNO₃ acid.

2.2. Chromatographic procedures for metal separation

Chromatographic chemical processing is one effective way to separate metals from rock and ore samples, an essential input for analyzing their isotopic composition. The chromatographic processing must be clean, and the chromatographic operating environment must also comply with strict international standards for cleanliness.

The most used radioactive isotope ratios in geological research today are strontium (⁸⁷Sr/⁸⁶Sr), neodymium (¹⁴³Nd/¹⁴⁴Nd), lead (²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb, and ²⁰⁸Pb/²⁰⁴Pb), and hafnium (¹⁷⁶Hf/¹⁷⁷Hf) [1 - 4]. They are used alone or in combination with other isotopic components to interpret issues about the origin of geological formations or magmatic rock formations related to critical geodynamic and mineralogy processes in a particular area's evolutionary history and development [5 - 6]. To increase the reliability of the obtained data, the isotope ratios used in the interpretation of the above geological problems, especially petrology, and geochemistry of magmatic rocks, must have minimal errors (2 σ) to be acceptable [7 - 11].

The chromatographic technique applied in the Institute of Geological Sciences clean room is called micro-column chromatography, using Eichrom company resins (Figs. 3 and 4), with experimental sample sizes as tiny as 10 - 15 mg.

Multi-collector inductively coupled plasma mass spectrometers (MC-ICP-MS) such as the NU Plasma 3, can measure Sr, Nd, Pb, and Hf isotopes at concentrations of 20 to 250 μ g/L, 20-30 μ g/L, 20-30 μ g/L, and 10-20 μ g/L, respectively, under standard conditions.

The geological isotope standards NIST987 (Sr), JNdi-1 (Nd), NIST981 (Pb), and JMC475 (Hf) were prepared in dilute HNO₃ or HCl at concentrations of 20,000 mg/L, 10,000 mg/L, 5,000 mg/L, and 2,000 mg/L, respectively. The standard solutions used for the chromatographic experiments should be calculated to yield at least 200 nanograms (ng) of Sr, 30 ng of Nd and Pb, and 20 ng of Hf, assuming a 75 % recovery of the chromatographic process for these metals. For the geological standard solutions JA-2, JB-1a, and blanks (Blank A and B) remaining after the trace element analysis are kept in 2.5M HNO₃ acid, they can continue to be used for the chromatographic experiments to compare with the standard data to determine the accuracy of the analysis. For example, the NIST987 standard solution has a concentration of 20,000 μ g/L; therefore, 15 mg should be weighed to yield at least 200 ng Sr.

2.2.1. Separation of Sr and Pb

The elements Sr and Pb were separated using Eichrom Sr-spec resin. The amount of resin used was about < 50 microliters (□ 1) and the chromatographic column was a 1 ml pipette tip (Fig. 3) [8, 12 - 15].

The resin was washed with 4 - 5 ml of 6M HCl acid, followed by 1 ml of dilute HNO₃ (0.05 M), and then washed with 0.5 ml of 2.5 M HNO₃ to return the resin to a nitric environment. Calculate the sample to be just enough in about 0.5 ml of 2.5 M HNO₃ acid. Wash the sample with 1 ml of 2.5M HNO₃, then with 0.5 ml of 7 M HNO₃. Sr is collected in 1 ml of 0.05 M HNO₃ acid, then transferred to 1.5 to 2 ml of 2 % HNO₃ for analysis by inductively coupled plasma mass spectrometry (MC-ICP-MS). After separating the Sr metal, transfer the Sr-spec resin to an HCl environment by slowly passing 0.6 to 1 ml of 2 M HCl acid through the chromatographic column. Collect Pb in 1.5 ml of 6M HCl acid. Let the solution evaporate completely, then dilute in 1.5 to 2 ml of 2 % HNO₃ for analysis.

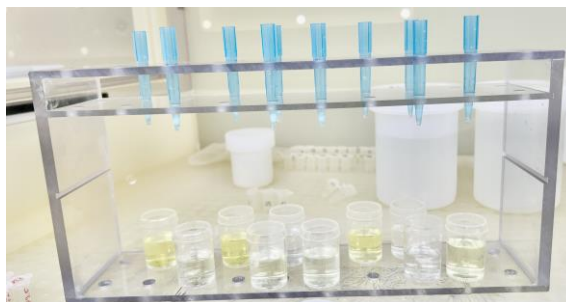


Figure 3. 1-ml pipette tips as chromatographic micro-columns using Sr-spec resin to separate Sr and Pb.

2.2.2. Separation of Nd and Hf

Separate Nd and Hf using 1 ml of Ln-spec resin (Eichrom) in a 10 ml Nalgene plastic tube as a chromatographic column (Fig. 4). The experimental sample, calculated to obtain a concentration of > 20 µg/L for both the metals and the initial sample size does not exceed 10 mg to meet the resin volume of 0.9 ml [9, 16 - 17], is in about 0.1 to 0.15 ml of dilute HNO₃ (0.05M) for loading. For the JNdi-1 standard solution (10 mg/L concentration), drop 5 µl (50 ng of Nd) and 2.5 µl (25 ng) directly onto the resin in the two chromatographic columns. For the JMC475, a hafnium isotope reference solution having a concentration of 5 mg/L, add 5 µl (25 ng of Hf) and 2.5 µl (12.5 ng) directly on to the Ln-spec resin columns for chromatographic work (Fig. 4).



Figure 4. Eichrom Ln-spec resin in 10 ml Nalgene columns for separation of Nd, Sm, and Hf metals.

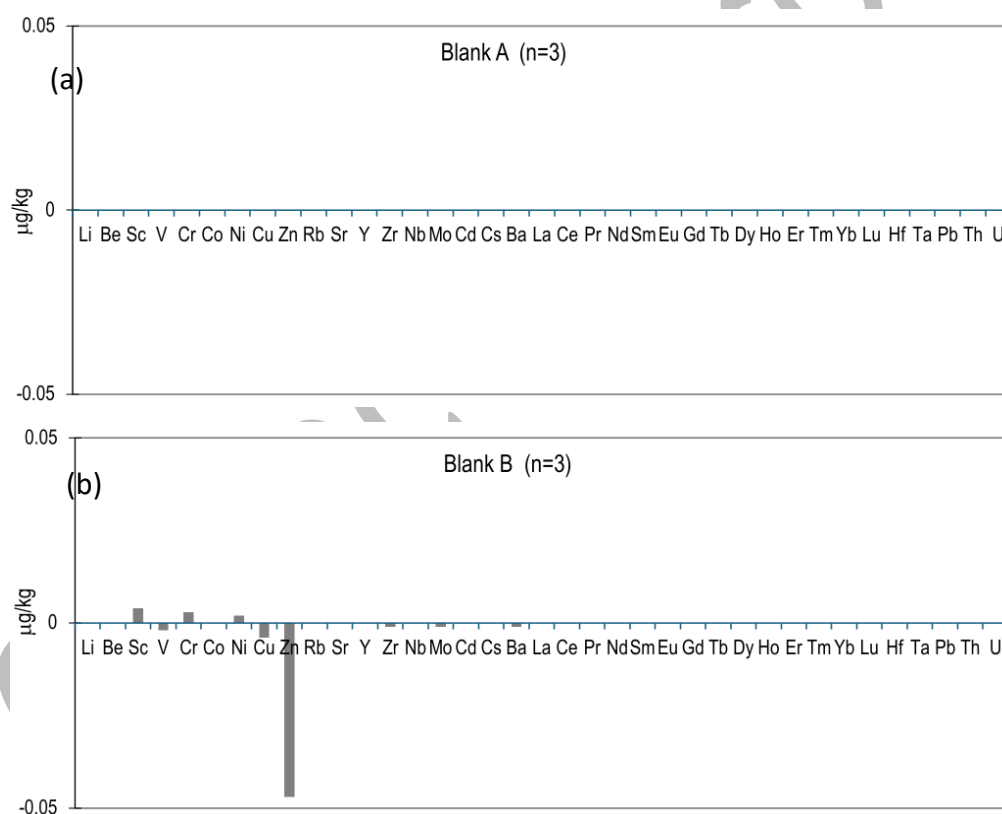
Wash the light rare earth elements (La, Ce, and Pr) with 5 ml of 0.2 M HCl, and collect the Nd in 2.2 to 2.5 ml of 0.2M HCl. Evaporate completely, add a drop of concentrated HNO₃ to the dry sample, and continue evaporating. Dissolve the sample in 1.5 to 2 ml of 2 % HNO₃ for Nd isotope ratio analysis.

After Nd separation, remove the silicate components and medium and heavy rare earth elements (Sm, Eu, Gd, ... Yb, Lu) with 4 to 6 ml of 6 M HCl. Release the high-field strength elements (such as Nb, Ta, Zr, and Ti) from the resin with 8 ml of a 0.1M HF and 2 M HCl mixture. Hf metal was collected in 1.5 ml of a mixture of 0.2 M HF and 2 M HCl and evaporated completely [9, 16 - 17]. The Hf was dissolved in 1.5 to 2 ml of 2 % HNO₃, ready to analyze the ¹⁷⁶Hf/¹⁷⁷Hf isotope ratio.

3. RESULTS AND DISCUSSION

3.1. Elemental Composition Analysis Using Quadrupole (Q)-ICP-MS

3.1.1. Blank samples



The representative elements to be analyzed include those with low isotopes, such as ⁷Li and ⁹Be, medium isotopes, such as ⁵¹V, ⁵³Cr, or ⁶⁰Ni, or high isotopes, such as rare earth elements, ¹³⁹La, ¹⁴⁰Ce, ..., ¹⁷³Yb, and ¹⁷⁵Lu, and the elements with very high isotopic masses such as ¹⁷⁸Hf, ¹⁸¹Ta, ²⁰⁸Pb, ²³²Th, and ²³⁸U. In total, 37 representative elements are analyzed.

The results of the three analyses ($n = 3$) were averaged (\bar{x}) to report and determine the analytical error (σ) and the relative standard deviation ($\%RSD = \sigma/\bar{x} * 100$) (Fig. 5a, b).

The highest deviation for blank A occurred at Zn (-0.076, 0.0167, and 0.059 $\mu\text{g/kg}$), resulting in a 1σ error of 0.069; however, the average of the three analyses was 0. Thus the $\%RSD$ was 0. The highest deviation for blank B also appeared at Zn, with the three analyses being -0.116, -0.038, and 0.013, respectively, and the average of Zn was -0.047; the 1σ error was 0.002, and the $\%RSD$ was 0 (Fig. 5a-b).

3.1.2. JA-2 geological standard

Each standard sample with different masses was divided into two portions for analysis. The JA-2-1 and JA-2-2 portions were separated from the sample with the 50 mg weight; JA-2-3 and JA-2-4 were divided from the sample of 100 mg weight.

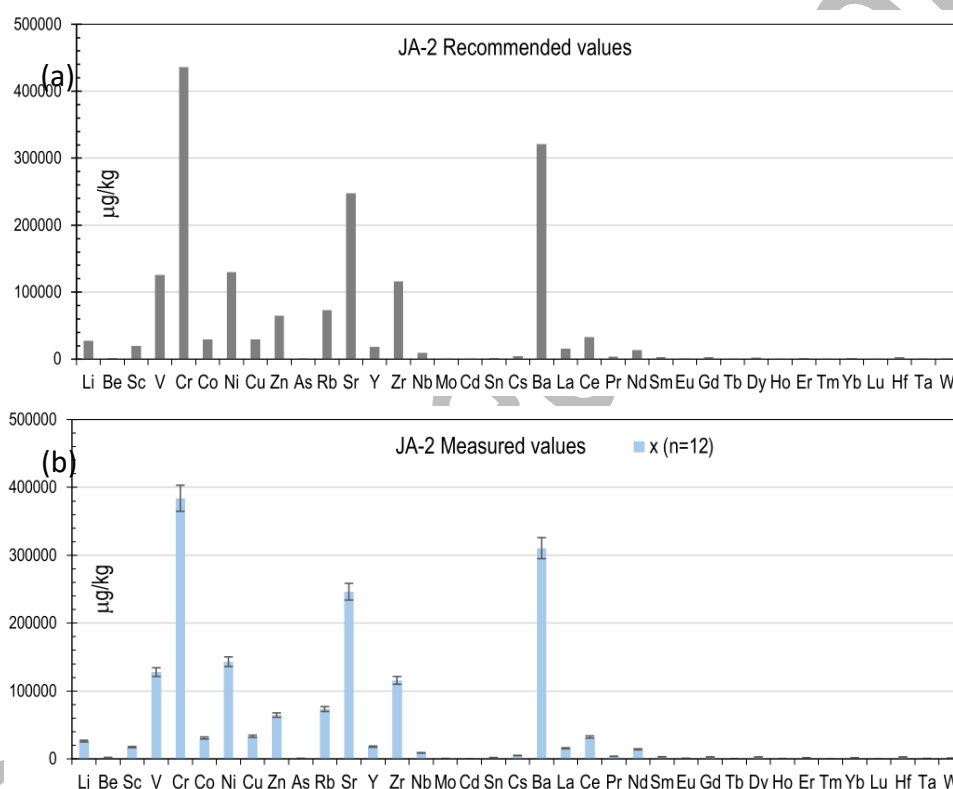


Figure 6a, b. The chemical composition of the experimental JA-2 standard sample compared to the recommended data (b) officially published at <https://gbank.gsj.jp/geostandards/igneous.html>. The $\%RSD$ are expressed as error bars (I) and are shown at the top of each element concentration.

The results of the four analyses of sample JA-2 are illustrated in Fig. 6a, b. Each analysis was performed three times, 45 seconds apart, and the average (\bar{x}), error (1σ), and percentage of standard deviation ($\%RSD$) were calculated based on the three analyses. The results of the JA-2-1 and JA-2-2 runs were quite different, especially for low-mass elements such as Li, Be, V, and Cr, or elements with multiple isotopes such as U. The fluctuations of these elements were relatively strong in the JA-2-1 runs. However, their precision was significantly improved in subsequent analyses, starting from the JA-2-2 runs. For example, the variation in percent

standard deviation (%RSD) of Li, Be, V, and Cr was 7.35, 16.44, 16.66, and 18.16, respectively, which became 0.18, 2, 0.47, and 0.84. The results of the JA-2-3 and JA-2-4 portions are presented in Fig. 6a, b. Like the previous analyses, the low-isotopic elements had quite large errors in the first analysis. For example, the elements such as Li, Be, Sc, and V had percent standard deviations of 15.43, 16.2, 15.96, and 9.26, respectively; however, in the following analysis, the above coefficients improved, becoming 3.36, 3.25, 2.59, and 2.49, resulted in the %RSD varies from 1 to 5 % for all the elements.

3.1.2. JB-1a standard sample

Like JA-2, the JB-1a sample was split into four parts for analysis: JB-1a-1 and JB-1a-2 extracted from the 50 mg sample solution, and JB-1a-3 and JB-1a-4 extracted from the 100 mg sample. The results are illustrated in Fig. 7a, b.

For the JB-1a standard sample, except for some elements such as Sc, Cr, Co, and Cd with relative standard deviation (RSD) of 4 - 5 %, all the remaining elements are lower than 3 %. Li has the lightest isotope (7) in the analyzed element series, with the highest standard deviation percentage of 2.01 %. Light rare earth elements such as La, Ce, and especially Nd, are elements with many isotopes in nature, so they are affected by interference during the mass spectral recording process. However, their RSD are significantly low, < 3.56 %, compared to the usual standard deviation of 6 % [8]. As with high-field strength elements such as Nb, Ta, Zr, or Hf, interference effects often occur very strongly between these elements, and the strongly affected element is Nb.

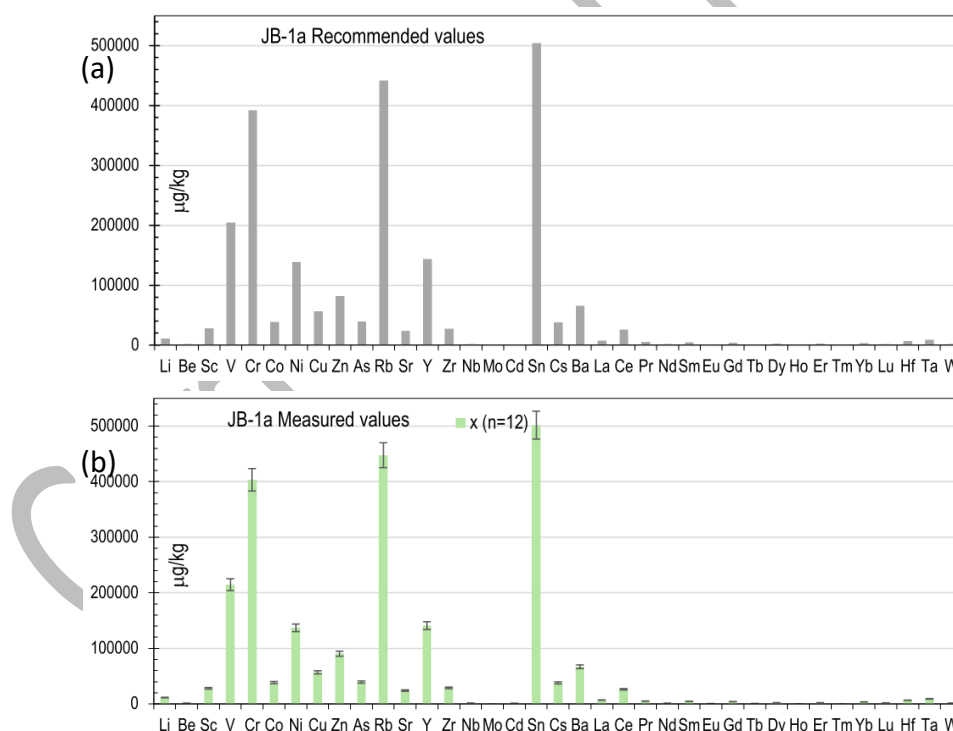


Figure 7a, b. Chemical composition of the experimental standard sample JB-1a (b) compared to the recommended value (a) published at <https://gbank.gsj.jp/geostandards/igneous.html>. The %RSD (I) are shown as error bars, varying from 1 to 5 %.

In this experiment, the Nb data compared to the standard value has an error of 6.4 %. However, this error is acceptable in studies using the high-field strength element (HFSE) group (Fig. 7a, b).

1.1. Processing and Analyzing Sr-Nd-Hf-Pb Isotopic Ratios of Reference Materials

The Sr-Nd-Hf-Pb isotopic ratios of sample solutions were first analyzed at the Department of Physics and Earth Sciences, University of the Ryukyus (Okinawa, Japan) using a Neptune Plus MC-ICP-MS equipped with 9 Faraday cups and 7 ion counters that can measure isotopic ratios of elements ranging from 3 to 255 amu (atomic mass units). The RF power is 1200 W, and the gas flow rate is fixed at 15 liters/minute, whereas the extraction voltage is about 2 kV.

The same set of solution samples was later re-analyzed at the Institute of Geological Sciences using a NU Plasma 3 MC-ICP-MS equipped with 16 Faraday and five ion cups to measure isotope ratio data with high precision for elements across the mass range from 3 to 300 amu. The argon gas flow is about 20 liters/minute with a purity of nearly 100 %. The power input is 6 kV; the RF generator is 27 MHz, inducing an oscillating electromagnetic field within the ICP torch, which sustains an argon plasma. Currently, only various Faraday cups are used to measure Sr-Nd-Hf-Pb isotopic ratios. For example, Sr is measured using 6 cups, 9 cups for Nd, 6 cups for Hf, and 7 cups are for Pb measurement.

3.1.3. Sr isotope analysis

Strontium fractionation was corrected to $^{87}\text{Sr}/^{86}\text{Sr} = 0.1194$, and data were reported relative to $^{87}\text{Sr}/^{86}\text{Sr} = 0.71025 \pm 0.000015$ for the NBS987 standard. During the analysis, the strontium running procedure was programmed to minimize the interference of ^{84}Kr and ^{85}Rb to the data reliability and accuracy.

Sr was analyzed in the concentration range of 100 to 150 $\mu\text{g/kg}$ (corresponding to the ^{88}Sr spectral intensity of 4 to 6 volts). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was measured in 5 or more blocks; each block had 20 ratios, the average value of each block was taken, and the error (1σ) was calculated. The procedure for measuring 4 (or 5) Sr isotope samples was performed as follows. Start with 2 NIST987 standards and a Blank, then 4 (or 5) unknown samples, and end with 2 standards. Use the Blank results to assess the possibility of material contamination between samples and the results of the standards used to determine the analyzed samples' standard deviation and correction factor [10-11].

The correction factor, according to the NIST987 standard, is determined as follows:

The ratio $^{87}\text{Sr}/^{86}\text{Sr} = 0.71025 \pm 0.000015$ of the NIST987 standard is accepted at the Geochemistry Laboratory of University of the Ryukyus, Okinawa, based on the average value of hundreds of measurements in recent years. The standards are measured simultaneously with the research samples, and the correction factor F is determined = $[0.71025/(\text{NIST987-1} + \text{NIST987-2} + \text{NIST987-3} + \dots + \text{NIST987-8})/8]$ (Table 1A). The final Sr isotope ratio of the sample will be:

$$\text{NIST987-1} = F \times ^{87}\text{Sr}/^{86}\text{Sr}(\text{measured}) = 0.999989 \times 0.710263 = 0.710255 \pm 0.000024$$

The two chromatographic NIST987-test1 and NIST987-test2 reference samples gave ^{88}Sr intensities of 4.6 volts and 13.4 volts for 100 $\mu\text{g/kg}$ (extracted from a 10-mg solution) and 200 $\mu\text{g/kg}$ (from a 20-mg solution), respectively. These chromatographically experimental samples were analyzed, intercalated with the standards presented in Table 1A, and were corrected by

F = 0.999989, yielding results of 0.710240 ± 0.000024 and 0.710242 ± 0.000012 , respectively (Table 1A).

Table 1A. The $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios of the NIST987 reference material and correction factor (F) acquired at the University of the Ryukyus, Okinawa, Japan.

Sample ID	^{88}Sr (volt)	$^{87}\text{Sr}/^{86}\text{Sr}$ measured	$\pm\sigma$	$^{87}\text{Sr}/^{86}\text{Sr}$ corrected	$\pm 2\sigma$
NIST987-1	3.9	0.710263	0.000012	0.710255	0.000024
NIST987-2	3.8	0.710249	0.000012	0.710241	0.000024
NIST987-3	3.8	0.710255	0.000014	0.710246	0.000028
NIST987-4	3.7	0.710254	0.000011	0.710246	0.000023
NIST987-5	3.6	0.710267	0.000012	0.710258	0.000025
NIST987-6	3.6	0.710245	0.000013	0.710237	0.000025
NIST987-7	3.5	0.710267	0.000011	0.710259	0.000022
NIST987-8	3.5	0.710265	0.000013	0.710257	0.000027
Average		0.710258	0.000012		
F= 0.999989†					
NIST987-test1	4.6	0.710248	0.000012	0.71024	0.000024
NIST987-test2	13.4	0.71025	0.000006	0.710242	0.000012

(†): NIST987 compositions are normalized to 0.71025 as recommended value

Table 1B. Results of the NIST987 samples and two chromatographically experimental reference sample analyzed at the Institute of Geological Sciences

Sample ID	^{88}Sr (volt)	$^{87}\text{Sr}/^{86}\text{Sr}$ measured	$\pm\sigma$	$^{87}\text{Sr}/^{86}\text{Sr}$ (corrected)	$\pm 2\sigma$
NIST987-1	5.4	0.710272	0.000011	0.710268	0.000021
NIST987-2	5.7	0.710258	0.000008	0.710254	0.000016
NIST987-3	5.6	0.710273	0.000007	0.710269	0.000015
NIST987-4	5.4	0.710266	0.000007	0.710262	0.000014
NIST987-5	2.8	0.710264	0.000012	0.71026	0.000023
NIST987-6	5.3	0.71026	0.00001	0.710256	0.000019
NIST987-7	5.1	0.710257	0.000008	0.710253	0.000016
Average		0.710264	0.000009		
F= 0.999994					
NIST987-test1	6.2	0.710258	0.00001	0.710254	0.000019
NIST987-test2	9.6	0.710257	0.000008	0.710253	0.000016

(†) NIST987 compositions are normalized to 0.71026 as recommended value for IGS's labs.

Results of $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios of seven NIST987 and two chromatographical reference samples NIST987-test1 and -test2 were acquired at the Institute of Geological Sciences using a NU Plasma 3 MC-ICP-MS to determine the analytical precision and accuracy. The data are shown in Table 1B.

An average of seven results yielded a value of 0.710264 ± 0.000009 (2σ). Therefore, the acquired compositions were normalized to 0.71026, as a value recommended for the reference material at the IGS analytical facility, to determine a standard deviation correction F at 0.999994 (Table 1B). The correction factor was then used to corrected for all the Sr isotopic analyses, including two experimental reference samples, NIST987-test1 and -test2, showing, respectively, 0.710254 ± 0.000019 and 0.710253 ± 0.000016 (Table 1B).

The Geological Survey of Japan's geological reference samples were also subjected to chemical chromatography and mass spectrometry to check the repeatability and cleanliness of the IGS's metal-free chemical clean room. The results were reported relative to the NIST987 strontium reference isotopic ratio of 0.71026 and shown in Table 1C.

Table 1C. Sr isotopic composition of the geological standard samples of the Geological Survey of Japan (GSJ). Reference data are at <https://gbank.gsj.jp/geostandards/igneous.html>

Sample ID	^{88}Sr (volt)	$^{87}\text{Sr}/^{86}\text{Sr}$ measured	$\pm\sigma$	$^{87}\text{Sr}/^{86}\text{Sr}$ corrected (\dagger)	$\pm 2\sigma$	$^{87}\text{Sr}/^{86}\text{Sr}$ (*)
JA-2	2.5	0.706366	1.10E-05	0.706348	2.20E-05	0.70637
JA-2 (2)	4.3	0.706354	1.13E-05	0.706336	2.26E-05	
JB-1a	4.4	0.70411	1.01E-05	0.704092	2.02E-05	0.704097
JB-1a (2)	7.4	0.704166	7.40E-06	0.704148	1.40E-05	0.7041

(\dagger) Correction factor F = 0.999994 calculated based on the results of seven NIST987 analyses.

(*) The $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios of the standard samples are recommended for use by the GSJ.

3.1.4. Nd isotope analysis

Unlike Sr, which is present in relatively high concentrations in the JA-2 (248 mg/kg) and JB-1a (442 mg/kg) reference samples, the Nd content is significantly lower, at only 13.9 mg/kg and 26 mg/kg for JA-2 and JB-1a, respectively. Given that the dissolved sample for chromatographic work is expected to yield at least 50 $\mu\text{g/L}$ of Nd, and assuming a chromatographic efficiency of 80 %, using a sample size of less than 10 mg for JA-2 ($80 \times 13.9 \text{ ng} = 111.2 \text{ ng}$) and 5 mg for JB-1a is appropriate.

After chromatographic separation, the JNdi-1, a Geological Survey of Japan Nd isotopic reference sample, was diluted in 1.5 ml of 2% HNO_3 to achieve Nd concentrations between 20 and 25 $\mu\text{g/L}$ for analysis. During the analysis, the $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were fractionation-corrected to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ and reported relative to a reference value of $^{143}\text{Nd}/^{144}\text{Nd} = 0.512115$ for the JNdi-1 neodymium standard. The sample was analyzed in 6 blocks, comprising 20 ratios ($^{143}\text{Nd}/^{144}\text{Nd}$). The average value and the 1-sigma (1σ) error for each block were calculated, and the overall average value was used to determine the 2-sigma (2σ) error.

The deviation error can be higher since the low Nd content produces lower signal intensities. Therefore, more standard samples can be intercalated between experimental samples. For example, when analyzing 2-4 experimental samples, 4-6 standard samples are needed to

correct for deviation and report the data (as shown in Table 2A). The data correction method follows the same approach described earlier for Sr isotopes.

Table 2A. The $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratios of the Geological Survey of Japan's JNdi-1, a neodymium isotopic reference material analyzed at the University of the Ryukyus, Okinawa, Japan.

Sample ID	^{145}Nd (volt)	$^{143}\text{Nd}/^{144}\text{Nd}$ (measured)	$\pm \sigma$	0.512115 normalized	$\pm 2\sigma$
JNdi-1-1	1.2	0.512053	0.000006	0.512103	0.00001
JNdi-1-2	2	0.512067	0.000009	0.512117	0.00002
JNdi-1-3	2.2	0.512069	0.000004	0.512119	0.00001
JNdi-1-4	2.1	0.51207	0.000005	0.51212	0.00001
JNdi-1-5	1.9	0.512063	0.000008	0.512113	0.00016
Average		0.5120641	0.000006		
F=1.000098					
JNdi-1-test1	2.5	0.512068	0.000005	0.512118	0.00001
JNdi-1-test2	3.5	0.512071	0.000007	0.512121	0.00001

Table 2B. The $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratios of the JNdi-1 reference sample analyzed at the IGS and the correction factor $F = 1.000099$ according to the $^{143}\text{Nd}/^{144}\text{Nd}$ recommended value at 0.512115.

Sample ID	^{145}Nd (volt)	$^{143}\text{Nd}/^{144}\text{Nd}$	$\pm 2\sigma$	0.512115 normalized	$\pm 2\sigma$	$^{143}\text{Nd}/^{144}\text{Nd}$ (†)
JNdi-1 1	4.9	0.512055	0.000006	0.512106	0.000011	
JNdi-1 2	5	0.51207	0.000005	0.512121	0.000011	
JNdi-1 3	4.9	0.512068	0.000007	0.512119	0.000015	
JNdi-1 4	5.1	0.512046	0.000007	0.512097	0.000013	
JNdi-1 5	5.2	0.512041	0.000006	0.512092	0.000011	
JNdi-1 6	5.1	0.512043	0.000005	0.512093	0.00001	
JNdi-1 7	4	0.512086	0.000008	0.512137	0.000016	
JNdi-1 8	3.9	0.51209	0.000011	0.512141	0.000022	
JNdi-1 9	3.7	0.512075	0.00001	0.512126	0.00002	
JNdi-1 10	3.7	0.512067	0.000011	0.512118	0.000023	
Average		0.5120644	0.000007			
F = 1.000099						
JNdi-1-test1	3.2	0.512063	0.000006	0.512114	0.000012	
JNdi-1-test2	5.3	0.51206	0.000005	0.512111	0.00001	
JA-2	2.3	0.512491	0.000005	0.512542	0.000009	0.512536
JA-2-2	3.1	0.512502	0.000003	0.512553	0.000007	0.512552
JB-1a	2.2	0.512725	0.000004	0.512776	0.000008	0.512761
JB-1a-2	3.2	0.512738	0.000004	0.512789	0.000008	0.512768

(†) Data analyzed at the University of the Ryukyus using a Neptune Plus MC-ICP-MS.

Five JNdi-1 reference samples were run at 1.2 to 2.2 volts, corresponding to Nd concentrations from 15 to 25 $\mu\text{g/L}$. Two additional experimental samples, JNdi-1-test1 and JNdi-1-test2, were run at 2.5 and 3.5 volts, respectively, with sample solution volumes of 2.5 μl (ca. 25 $\mu\text{g/L}$) and 5 μl (ca. 50 $\mu\text{g/L}$) used for chromatographic work. The average of the five $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratios was used to define a standard correction factor (F) relative to the recommended value of 0.512115, yielding $F = 1.000098$ (Table 2A). All acquired $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were corrected using this factor to report the final isotopic results. The corrected values for JNdi-1-test1 and JNdi-1-test2 were 0.512118 ± 0.000010 and 0.512121 ± 0.000016 , respectively, as shown in Table 2A.

The chromatographic experiments on two JNdi-1, JA-2, and JB-1a reference samples were analyzed interspersed with 10 JNdi-1 reference solutions at the Institute of Geological Sciences, using a NU Plasma 3 MC-ICP-MS. The Nd isotopic analysis procedure at the IGS is identical to that used with the Thermo Scientific Neptune Plus MC-ICP-MS at the University of the Ryukyus, except that the Nd samples at IGS were analyzed at higher intensities (Table 2B). The average of ten $^{143}\text{Nd}/^{144}\text{Nd}$ ratios was normalized to 0.512115, the recommended ratio for the GSJ JNdi-1 reference material, resulting in a standard deviation correction factor of 1.000099. This factor was applied to correct the results for JNdi-1-test1, JNdi-1-test2, JA-2, and JB-1a, yielding values of 0.512114 ± 0.000012 , 0.512111 ± 0.000010 , 0.512542 ± 0.000009 , and 0.512776 ± 0.000008 , respectively (Table 2B).

3.1.5. Pb isotope analysis

During the lead isotopic analysis, thallium (Tl) was added to the lead solution at about 1:8 (e.g., 0.125 portion) for internal mass-fractionation correction [18-19] and NIST981, a lead standard, was embedded between samples throughout the analytical process.

Lead is analyzed at intensities from 2 to 8 volts (^{208}Pb) in 6 cycles; each cycle consists of 20 ratios. Each 20 ratios are calculated for a one-sigma error (1σ), and a total of 120 ratios is calculated for a two-sigma error (2σ) (Table 3A). Each set of 4 samples is sandwiched between two NIST981 standards and two blanks. The error is determined based on the repeatability (or precision) of the measurements; the accuracy is determined based on geological standard (reference) samples that are chemically treated and mass spectrometry analyzed at the same time as the unknown samples after comparing with the results of the NIST981 standard samples (Table 3A).

NIST981-1-1 and NIST981-1-2 and two GSJ geological reference samples, JA-2 and JB-1a, were prepared for chromatography and acid dilution at the IGS. The samples were measured simultaneously with the NIST981 standard solutions using a Neptune Plus MC-ICP-MS at the University of the Ryukyus and later, at the Institute of Geological Sciences using a NU Plasma 3 MC-ICP-MS (Tables 3A and 3B). The lead data were reported relative to $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ of NBS981 at 16.939 ± 0.0006 , 15.493 ± 0.0005 , and 36.710 ± 0.0016 , respectively. These isotopic ratios were used for accuracy verification and data correction. The data are shown in Tables 3A and 3B [18].

Table 3A. Lead isotope ratios of the NIST981 reference sample analyzed at the Department of Physics and Earth Sciences, University of the Ryukyus at Nishihara, Okinawa, using a Neptune Plus MC-ICP-MS.

Sample ID	$^{206}\text{Pb}/^{204}\text{Pb}$	$\pm 2\sigma$	$^{207}\text{Pb}/^{204}\text{Pb}$	$\pm 2\sigma$	$^{208}\text{Pb}/^{204}\text{Pb}$	$\pm 2\sigma$
NIST981-1	16.941	0.0006	15.4963	0.0006	36.716	0.0016
NIST981-2	16.940	0.0005	15.4948	0.0005	36.712	0.0012
NIST981-3	16.941	0.0005	15.496	0.0005	36.715	0.0012
NIST981-4	16.934	0.0004	15.495	0.0005	36.711	0.0012
NIST981-5	16.941	0.0006	15.496	0.0006	36.714	0.0015
NIST981*	16.939	0.0006	15.493	0.0005	36.710	0.0016
NIST981-1-1	16.944	0.0005	15.497	0.0005	36.711	0.0013
NIST981-1-2	16.947	0.0004	15.501	0.0004	36.709	0.0011

Table 3B. The lead isotopic ratios of the NIST981 reference material measured at the Institute of Geological Sciences, using a NU Plasma 3 MC-ICP-MS. F, a standard deviation correction factor according to the NIST981 recommended (\ddagger) values.

Sample ID	$^{206}\text{Pb}/^{204}\text{Pb}$	$\pm 2\sigma$	$^{207}\text{Pb}/^{204}\text{Pb}$	$\pm 2\sigma$	$^{208}\text{Pb}/^{204}\text{Pb}$	$\pm 2\sigma$
NIST981-1	16.9359	0.0003	15.49	0.0003	36.6951	0.0007
NIST981-2	16.9368	0.0003	15.4906	0.0003	36.6962	0.0009
NIST981-3	16.9374	0.0003	15.4908	0.0003	36.6971	0.0007
NIST981-4	16.9348	0.0004	15.4888	0.0003	36.6919	0.0009
NIST981-5	16.9358	0.0003	15.4899	0.0003	36.6953	0.0007
NIST981-6	16.9364	0.0003	15.4904	0.0003	36.6959	0.0007
NIST981-7	16.936	0.0003	15.4897	0.0004	36.6945	0.0009
NIST981-8	16.9343	0.0004	15.4884	0.0003	36.6913	0.0008
NIST981-9	16.9351	0.0003	15.4889	0.0003	36.6917	0.0008
NIST981-10	16.9345	0.0003	15.4886	0.0003	36.6911	0.0009
NIST981-11	16.9362	0.0003	15.4902	0.0003	36.6969	0.0007
NIST981-12	16.936	0.0003	15.4901	0.0003	36.6945	0.0009
Average	16.9357	0.0003	15.4896	0.0003	36.6941	0.0008
F	1.00019		1.00041		1.00048	
NIST981(\ddagger)	16.939	0.0006	15.493	0.0005	36.71	0.0016
NIST981-1-1	16.95	0.0005	15.508	0.0005	36.721	0.0012
NIST981-1-2	16.947	0.0005	15.504	0.0006	36.729	0.0013
JA-2-1	18.399	0.0005	15.61	0.0006	38.672	0.0014
JA-2 \dagger	18.418		15.61		38.66	
JB-1a-1	18.377	0.0006	15.568	0.0005	38.646	0.0014
JB-1a \dagger	18.36		15.54		38.62	

(\dagger) Data recommended at <https://gbank.gsj.jp/geostandards/igneous.html>

3.1.6. Hf isotope analysis

Hf was analyzed at 10 to 20 µg/L (or ppb), using an Aridus 3 desolvating nebulizer system to introduce the sample to the ion chamber. $^{176}\text{Hf}/^{177}\text{Hf}$ ratios were measured in 6 cycles. The value of $^{176}\text{Hf}/^{177}\text{Hf}$ of JMC475, a hafnium isotopic standard, showed 0.282160 ± 0.000007 [20], was used for data correction and report.

Each of the two Hf isotopic reference samples chromatographically extracted was divided into two portions for the NU Plasma 3 analysis. Note that, sample JMC475-a was half of the 12.5-ng size extracted sample, whereas JMC475-b was half of the 25-ng sample (Table 4). Compared to a JMC475 reference material solution of 25 µg/L, equivalent to approximately 10 to 12 volts, the running JMC475-a and JMC475-b measured at 2.3 and 4.5 volts, thus, equivalent to roughly 6 and 12 µg/L, respectively.

Two experimental JMC475-a and -b samples were analyzed and intercalated with seven JMC475 reference samples using a NU Plasma 3 MC-ICP-MS at the Institute of Geological Sciences. The $^{176}\text{Hf}/^{177}\text{Hf}$ isotopic ratios are presented in Table 4.

Table 4. The JMC475 $^{176}\text{Hf}/^{177}\text{Hf}$ isotopic ratios for chromatographically experimental samples (JMC475-a and -b) and reference solutions (JMC475-1 to -7) acquired at the IGS.

Sample ID	$^{176}\text{Hf}/^{177}\text{Hf}$	$\pm\sigma$	Total Hf beam (v)	$^{176}\text{Hf}/^{177}\text{Hf}$ corrected	$\pm 2\sigma$
JMC475-1	0.282167	0.000008	11.77	0.282181	0.000016
JMC475-2	0.282113	0.000003	11.12	0.282127	0.000006
JMC475-3	0.28212	0.000004	11.56	0.282134	0.000008
JMC475-4	0.282145	0.000004	11.77	0.282159	0.000008
JMC475-5	0.282151	0.000006	9.88	0.282165	0.000012
JMC475-6	0.28216	0.000006	11.66	0.282174	0.000012
JMC475-7	0.282165	0.000006	11.25	0.282179	0.000012
Average	0.282146	0.000005			
F (correction factor) = 1.000050(†)					
JMC475-a	0.282163	0.000008	2.31	0.282177	0.000016
JMC475-b	0.282126	0.000003	4.5	0.28214	0.000006

(†) $F = 0.28216/0.282146$; where 0.28216 is the $^{176}\text{Hf}/^{177}\text{Hf}$ recommended value for JMC47

3.2. Discussion

3.2.1. Blank samples

In the blanks A and B analyses, except for Li, Sc, V, Cr, Ni, Cu, and Zn-which showed concentrations ranging from 0.002 to 0.069 µg/kg - all other elements were either zero or below the detection limit (negative values). The one sigma errors (1σ) did not exceed 0.013, and the relative standard deviations (%RSD, calculated as $100 \cdot \sigma/x$, where x is the average content) were zero. Therefore, the blank samples were almost 'blank'. Additionally, there were no

significant differences between blanks A and B, despite blank B containing twice the amount of acid as blank A. This evidence indicates that the quantity of acid used did not affect the analysis results and that the acid used was exceptionally clean.

3.2.2. The JA-2 reference sample

For the JA-2 reference samples (JA-2-1 and JA-2-2) extracted from the 50-mg-size sample, results for low-mass elements (Li, Be, V, and Cr) and elements with multiple isotopes, such as U, showed relatively large variations. However, repeatability improved significantly in subsequent analyses (Fig. 3a), with the %RSD of Li, Be, and V reduced to 0.18, 2, and 0.84, respectively. The initial analyses for JA-2-3 and JA-2-4, extracted from the 100-mg-size sample, showed relatively larger standard deviations for low-isotopic elements. These deviations, however, decreased by 3-5% to just 3.36, 3.25, 2.59, and 2.49 for Li, Be, Sc, and V, respectively. Overall, the Q-ICP-MS analyses of all four samples extracted from the 50-mg and 100-mg JA-2 standard samples exhibited much lower relative standard deviations (Figs. 6a, b).

Furthermore, the results obtained from the JA-2 reference samples of different weights were almost identical across the four divisions. This consistency suggests that using sample weights of 50 mg and 100 mg, and consequently different amounts of acids and other substances during sample digestion and chromatography did not significantly impact the analytical results. Compared to the standard values published by the Geological Survey of Japan (JA-2†) illustrated in Fig. 5a, b, the results for some light elements in JA-2-1 showed relative variability. However, the analytical results for JA-2-2, JA-2-3, and JA-2-4 portions demonstrated high repeatability, low %RSD, and high accuracy, suggesting that the chemical processing and mass spectrometry of the JA-2 sample are reliable (Figs. 6a, b). It is worth noting that since the JA-2-1 and JA-2-2 solutions were derived from a 25-mg sample, the larger variability in light elements may be attributed to the smaller sample size.

3.2.3. The JB-1a reference sample

For the JB-1a standard sample, most elements, except for a few such as Sc, Cr, Co, and Cd with relative standard deviations of 4-5%, had %RSDs lower than 3%. Li, the lightest isotope (7) in the analyzed series, had the highest standard error percentage of 2.01% (JB-1a-2; Fig. 7a, b). Light rare earth elements such as La, Ce, and Nd, which have many isotopes in nature, were affected by interference during isotope spectral recordings. However, their %RSDs remained significantly low, at less than 3.56%, compared to the usual relative standard deviation of 6% [8]. High-field strength elements such as Nb, Ta, Zr, and Hf often experience strong interference effects, particularly Nb. In this experiment, the Nb data showed an error of 6.4% compared to the standard value, which is acceptable in studies involving high-field strength elements (HFSE) (Fig. 7a, b).

Typically, the lower the element content, the higher the standard error, as observed with Ho (710 µg/kg), which had an analytical error of up to 14%. Similarly, Lu, a heavy rare earth element with a standard content of 330 µg/kg, had an error of 6.4% compared to the standard, equivalent to ±20 µg/kg (Fig. 7a, b). Compared to the recommended values, except for the elements with %RSDs as noted above, most element groups ranging from low to high atomic masses exhibited low %RSDs relative to the reference sample concentrations. These findings suggest that the chemical digestion, dilution, and mass spectrometric procedures used to analyze these standards ensure clean and efficient results.

Nevertheless, in (Quadrupole) Q-ICP-MS analysis, some metals, like Sc, Cr, Cu, Sn, and others, can have higher relative standard deviation percentage (%RSD >10-14%) than many other elements (Figs. 6, 7). There are many reasons for the higher %RSD observed in several metals, but the primary ones may include: (1) The elemental concentration is too low; (2) Matrix effects: some metals are more susceptible to matrix interferences. For example, Sn and Cr are known to suffer from matrix effects, which can lead to variability in signal, hence resulting in a higher %RSD; (3) Polyatomic spectral interferences occur due to overlapping peaks at the same m/z (atomic mass to the number of protons) as the analyte. For example, in the case of Cr (m/z 52), interferences from polyatomic species like $^{40}\text{Ar}^{12}\text{C}^{40}\text{Ar}^{12}\text{C}$ or $^{40}\text{Ar}^{12}\text{O}^{40}\text{Ar}^{12}\text{O}$ can occur; (4) The solution conditions do not match the target element, making the elements less efficiently ionized. Some elements, such as Sn, can exhibit more significant variability. Certain elements may require specific treatments, such as adding a small amount of HF to HNO_3 or using an HCl-based solution; (5) Certain elements are more likely to form oxides during analysis. Oxides can cause signal suppression, leading to signal instability. Metals like Sc and Sn can quickly form oxides, thus showing a higher %RSD due to the variable extent of oxide formation [21].

1.1.1. Strontium isotopic data

Two NIST987 solution samples, NIST987-test1 and -test2, were measured along with 9 NIST987 reference solutions at the University of the Ryukyus (UR), Okinawa, Japan, and the Institute of Geological Sciences. At the UR, the samples were run at 4.6 volts and 13.4 volts for NIST987-test1 and -test2 and yielded $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios at 0.710240 ± 0.000024 and 0.710242 ± 0.000012 , respectively. The ratios were corrected and reported relative to the value of 0.71025, which was recommended for the NIST987 Sr isotopic standard at the UR's geochemistry laboratory (Table 1A).

The two similar chromatographically treated samples were also measured for $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios, and 7 NIST987 prepared reference samples at the Institute of Geological Sciences (IGS) using a NU Plasma MC-ICP-MS. The test samples were run at 6.2 and 9.6 volts for NIST987-test1 and -test2 and showed $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios at 0.710254 ± 0.000019 and 0.710253 ± 0.000016 , respectively. The data were corrected and reported relative to 0.71026, the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio recommended for the NIST987 Sr isotopic reference at the Institute of Geological Sciences (Table 1B).

Despite having different sample weight sizes and being normalized by various isotopic ratios from different laboratories the four portions of the NIST987 reference samples showed almost identical results. Similarly, JA-2 and JB-1a, the Geological Survey of Japan's geological reference samples, were each measured in two portions at two mass spectrometry laboratories with different intensities (e.g., weights) (Tables 1A and 1B); however, the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios acquired for each of the reference samples were close mostly similar, with minor 2-sigma errors (Table 1A).

1.1.2. Neodymium isotopic data

The chromatographically experimental reference samples, JNdi-1-test1 and JNdi-1-test2, were analyzed simultaneously with 5 JNdi-1 standard solutions at the University of the Ryukyus (Table 2A). Using the correction factor (F) computed from these standard samples, the

$^{143}\text{Nd}/^{144}\text{Nd}$ isotopic composition results were 0.512118 ± 0.00001 and 0.512121 ± 0.00001 , corrected and reported relative to the recommended value of 0.512115. The same samples were also measured interbedded with 10 JNdi-1 reference solutions at the Institute of Geological Sciences. The acquired $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratios were corrected and reported relative to the value of 0.512115, respectively, 0.512114 ± 0.000012 and 0.512111 ± 0.000010 (Table 2B).

As presented in Tables 2A and 2B, the average values of JNdi-1 measured at the UR and the IGS are nearly identical at 0.5120641 ± 0.000006 and 0.5120644 ± 0.000007 . Additionally, two experimental reference samples, JNdi-1-test1 and JNdi-1-test2, were analyzed at different laboratories, showing mostly the similar values of 0.512111 to 0.51221 ± 0.00001 , despite having different sample weights and running conditions (e.g., mass spectrometers, and intensities).

Furthermore, a set of the Geological Survey of Japan's geological standard samples (GSJ) was chemically processed, and mass spectrometry measurements were conducted at the Institute of Geological Sciences (Table 2B). The data were corrected and reported relative to the $^{143}\text{Nd}/^{144}\text{Nd}$ value at 0.512115 and compared with those acquired at the UR laboratory. The isotope results were comparable with a minor standard deviation error range (Table 2B).

1.1.3. Lead isotopic data

The isotopic ratios of two experimental lead isotope reference samples, NIST981-1-1 and NIST981-1-2, were acquired at the University of the Ryukyus at Nishihara, Okinawa, Japan. These samples were analyzed and intercalated with 5 NIST981 standard solutions. The two experimental samples and two GSJ's geological samples interbedded with 12 NIST981 reference solutions were analyzed at the Institute of Geological Sciences. The data were corrected and reported relative to the lead isotopic ratios recommended for the NIST981, as shown in Tables 3A and 3B.

The samples, NIST981-1-1 and NIST981-1-2, analyzed at the UR laboratory showed isotopic ratios of $16.9438\text{--}16.9465 \pm 0.00045$, $15.4974\text{--}15.5012 \pm 0.00045$, and $36.7109\text{--}36.7094 \pm 0.0012$, respectively, for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$. Compared with those acquired at the IGS that showed $16.950\text{--}16.947 \pm 0.0005$, $15.508\text{--}15.504 \pm 0.0006$, and $36.721\text{--}36.729 \pm 0.0035$. Average the values of two samples of each set shows 16.945 ± 0.0005 , 15.499 ± 0.0006 , and 36.710 ± 0.0012 ; and 16.949 ± 0.0005 , 15.506 ± 0.0006 , and 36.725 ± 0.0035 , for the second set. Compared to the recommended lead isotopic ratios of 16.939 ± 0.0006 , 15.493 ± 0.0005 , and 36.710 ± 0.0016 , for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$, respectively, except for the $^{208}\text{Pb}/^{204}\text{Pb}$ ratios measured at the IGS that is slightly higher, the isotopic ratios of the experimental reference samples are mostly acceptable within the given deviation ranges. Two GSJ's geological reference samples, JA-2 and JB-1a, analyzed at the IGS, show isotopic ratios almost comparable with the recommended values with minor standard deviation errors (Table 3B).

1.1.4. Hafnium isotopic data

The average of $^{176}\text{Hf}/^{177}\text{Hf}$ isotopic ratios of 7 reference solution samples is 0.28215 ± 0.000005 ; the value is normalized to the JMC475 recommended value of 0.28216 (Wiedenbeck et al., 1995), resulting in an isotope correction factor (F) of 1.00005. The correction factor was used to correct and report the $^{176}\text{Hf}/^{177}\text{Hf}$ isotopic ratios of the experimental samples, JMC475-a

and JMC475-b, which show 0.282177 ± 0.000016 and 0.282140 ± 0.000006 , respectively. The samples were run at 2.3 and 4.5 volts (total Hf beam), equivalent to 6 and 12 $\mu\text{g/L}$, comparable to the JMC475 reference solution of 25 $\mu\text{g/L}$, equivalent to 11 volts (Table 4).

Despite low Hf running concentrations, the results are exceptionally excellent compared to the composition of the Hf isotope reference material of 0.28216.

4. CONCLUSIONS

From the experimental results, the following conclusions can be drawn:

1) For the andesite standard sample (JA-2), most elements exhibit low percentage errors when compared to the recommended reference data, except for Sc, Cr, Cu, Sn, and W, which show slightly higher errors (>10-14%). For the basalt standard sample (JB-1a), only one heavy rare earth element (Ho) shows a significant percentage error. Additionally, the nearly identical results obtained for JA-2 and JB-1a using different sample weights (50 mg and 100 mg) demonstrate that sample weight does not affect the analytical outcomes.

2) Two reference samples, NIST987-test1 and NIST987-test2, were processed chromatographically at the Institute of Geological Sciences (IGS) and analyzed at 4.6 volts and 13.4 volts for concentrations of 100 and 200 $\mu\text{g/kg}$, respectively. The $^{87}\text{Sr}/^{86}\text{Sr}$ results (0.710254 ± 0.000019 and 0.710253 ± 0.000016) were compared to those from the University of the Ryukyus (UR), Okinawa, Japan (0.710240 ± 0.000024 and 0.710242 ± 0.000012). Both sets of results are consistent with the recommended value for the NIST987 reference sample ($^{87}\text{Sr}/^{86}\text{Sr} = 0.71026 \pm 0.000009$).

4) The Nd reference samples, JNdi-1-1 and JNdi-1-2, processed at IGS, yielded $^{143}\text{Nd}/^{144}\text{Nd}$ results of 0.512114 ± 0.000012 and 0.512111 ± 0.000010 , which closely match those obtained at UR (0.512118 ± 0.00001 and 0.512121 ± 0.00001). These values, corrected against the recommended reference material (0.512115), show minor errors of ± 0.00001 .

5) The lead isotope standard samples, NIST981-1 and NIST981-2, analyzed at IGS, yielded isotopic ratios of $^{206}\text{Pb}/^{204}\text{Pb}$: 16.950-16.947 ± 0.0005 , $^{207}\text{Pb}/^{204}\text{Pb}$: 15.508-15.504 ± 0.0006 , and $^{208}\text{Pb}/^{204}\text{Pb}$: 36.721-36.729 ± 0.0035 . These results were compared to those obtained at UR ($^{206}\text{Pb}/^{204}\text{Pb}$: 16.9438-16.9465 ± 0.00045 , $^{207}\text{Pb}/^{204}\text{Pb}$: 15.4974-15.5012 ± 0.00045 , and $^{208}\text{Pb}/^{204}\text{Pb}$: 36.7109-36.7094 ± 0.0012). Both sets of data align well with the recommended values for NIST981 ($^{206}\text{Pb}/^{204}\text{Pb}$: 16.939 ± 0.0006 , $^{207}\text{Pb}/^{204}\text{Pb}$: 15.493 ± 0.0005 , and $^{208}\text{Pb}/^{204}\text{Pb}$: 36.710 ± 0.0016).

6) The average $^{176}\text{Hf}/^{177}\text{Hf}$ isotopic ratio of seven reference solution samples (JMC475) analyzed at IGS was 0.28215, closely aligning with the recommended value of 0.28216. Two chromatographic reference samples, corrected and reported relative to the recommended ratio, yielded $^{176}\text{Hf}/^{177}\text{Hf}$ values of 0.282177 ± 0.000016 and 0.282140 ± 0.000006 , respectively.

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Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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