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RESEARCH ARTICLE

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High-precision Sr and Nd isotope characterization of BHVO-2 reference material by thermal ionization mass spectrometry

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Rationale: Control over accuracy and precision in isotope geochemical analysis is highly necessary for reliable results. Use of reference materials in Sr and Nd isotope geochemistry provides a means of validating optimal sample preparation and instrument configurations.

Methods: A comprehensive data set of Sr and Nd isotope analyses of BHVO-2 reference material was obtained by thermal ionization mass spectrometry (TIMS). The intention is to assist other researchers in evaluating isotopic analyses of geological samples with similar chemical matrix.

Results: $^{87}Sr/^{86}Sr$ isotope ratios analyzed in BHVO-2 reference material over 88 replicas from 2015 to the present provide an average value of 0.703485 ± 0.000024. In turn, $^{143}Nd/^{144}Nd$ isotope ratios in 62 replicas show an average value of 0.512978 ± 0.000012. The high number of analyses here presented ensures a high reproducibility over time in a non-certified material for isotopic analysis of these two elements.

Conclusions: This high precision and reproducibility of Sr and Nd analysis by TIMS provide a basis for validation of analytical processes in the absence of certified reference materials and support the correlation of isotopic results between laboratories and the overall improvement in the interpretation of isotope results for geological, environmental and archeological samples.

1 | INTRODUCTION

The use of well-characterized geochemical reference materials (GRMs) represents an important and useful means for monitoring precision and accuracy in analytical studies.[1–3] Commonly used in calibrating sample preparation methods and configurations of analytical instruments, GRMs provide an invaluable tool to monitor reliability in geochemical and geochronological studies.[4–6] In isotope composition analysis in all types of materials (e.g., rocks, minerals, water, soils and archeological samples), it is also necessary to monitor the obtained results through the use of GRMs which, although not always certified, do allow one to track accuracy by checking the traceability of the complete analysis process in GRMs analyzed together with the samples.

The present paper includes a compilation set of high-precision $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios in BHVO-2 (United States Geological Survey, USGS). They all were analyzed in recent years (2015 to present) in the Geochronology Facility of Complutense University of Madrid. These analyses have been performed following the same preparation and instrumental methods using thermal ionization mass spectrometry (TIMS) and provide precise and accurate average values for both isotope ratios in this commonly used GRM.

Our aim is to help in establishing high-precision values for Sr and Nd isotope composition of BHVO-2 reference material and to help other researchers with the validation of their isotopic analyses.

2 | SAMPLES AND ANALYTICAL METHODS

BHVO-2 is a Hawaiian basalt powdered rock from the USGS and corresponds to a basaltic pahoehoe lava flow erupted at Halemaumau crater from the Kilauea volcano (Hawaii, USA).[7] Batch number 0869 is the BHVO-2 reference material used in this study for Sr and Nd isotope composition analysis. This GRM has been used in this laboratory since 2015 to perform internal calibration by analyzing BHVO-2 aliquots following the same dissolution process, chromatographic separation and instrumental analysis by TIMS as regular samples.

This section contains a brief description of chemical procedures and instrumental methods. Sr ($n = 88$) and Nd ($n = 62$) isotope analyses (supporting information) were performed by using a TIMS instrument (Phoenix-IsotopX). Previously weighed BHVO-2 fractions of approximately 0.1 g were dissolved in a pressure environment inside pre-cleaned PTFE bombs along with a mixture of 4 mL of 40% HF and 2 mL of 65% HNO_3 (Merck-Suprapur® ultraclean reagents). Bombs were placed in an oven at 120°C for 3 days. Solutions were dried over a hotplate at 120°C and 1 mL of 65% HNO_3 added for maximum evaporation of SiF_4. After that, 4 mL of Teflon-distillated 6 M HCl was added to the samples and placed again in an oven at 120°C for 24 h. Again, samples were dried over a hotplate at 120°C and reconstituted in 3 mL of Teflon-distillated and titrated 2.5 M HCl. The resulting solutions were passed through a double-step chromatographic separation: (1) using DOWEX AG®50x8 200–400 mesh resin (Bio-Rad Laboratories, Inc, USA) in order to separate the Sr fraction (Rb-free) and the complete rare earth element group from the bulk matrix of the sample and (2) using LnResin® (50–100 μm) resin (Eichrom Technologies, Lisle, IL, USA) for a complete separation of Nd fraction from the interference of Sm isotopes (Figure 1).

Sr purified fractions were loaded, together with 2 μL of ultrapure 1 M H_3PO_4 and 2 μL of Ta_2O_5, onto a pre-cleaned Re ribbon. They were analyzed with a mass spectrometer (Phoenix-TIMS IsotopX),

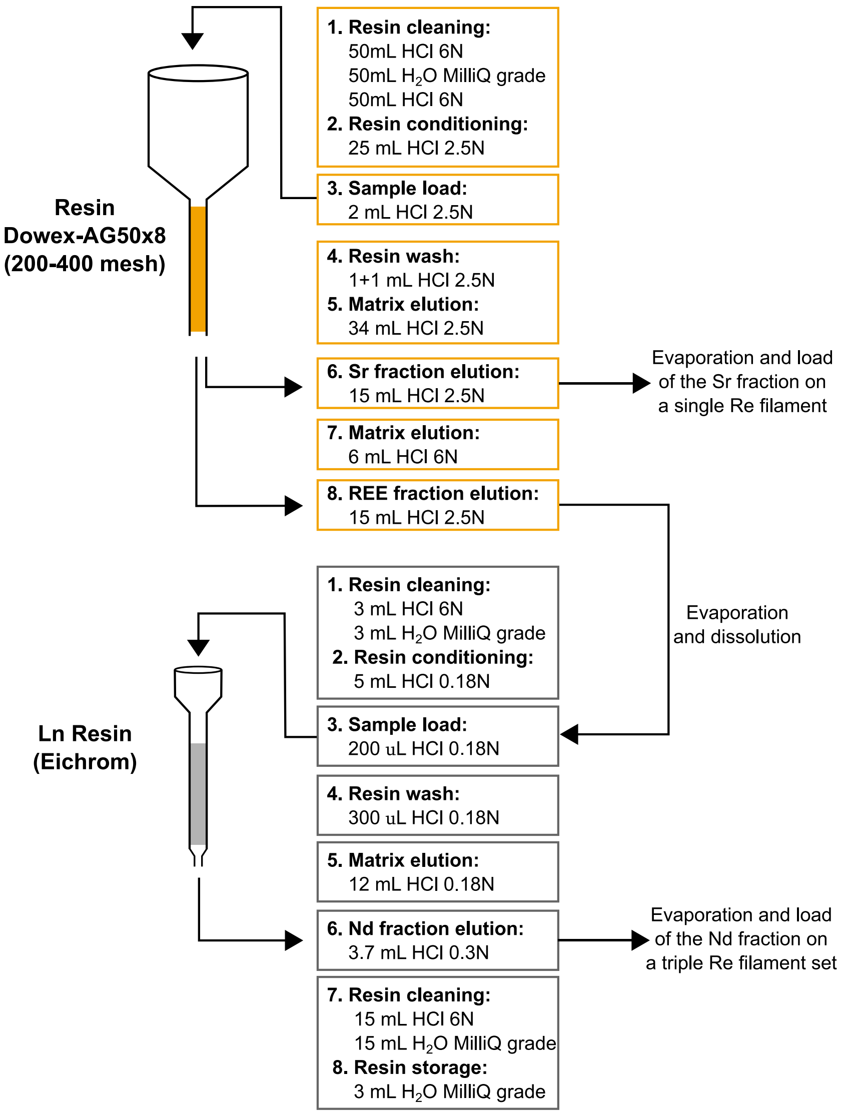

FIGURE 1 Schematic diagram of Sr and Nd chromatographic separation procedure followed for the isotopic analysis of the BHVO-2 (USGS) reference material. [Color figure can be viewed at wileyonlinelibrary.com]

following a multi-dynamic collection procedure isotope analysis maintaining a stable ion beam intensity of 3 V in mass ^{88}Sr for a maximum of 160 replicas, with a baseline integration time of 20 000 ms. Despite the fact that all analyses proved the absence of ^{85}Rb intensity, ^{87}Sr/^{86}Sr isotope ratios were corrected for possible ^{87}Rb interferences and potential fractionation was normalized to the ^{86}Sr/^{88}Sr ratio of 0.1194.[8] Final BHVO-2 Sr isotope ratios were also corrected considering the Sr isotope standard (NIST SRM 987), analyzed along with the samples (supporting information). Nd (Sm-free) fractions were loaded, together with 2 μL of ultrapure 0.05 M H_3PO_4, onto a lateral pre-cleaned Re ribbon in a triple Re ribbon arrangement. They were also analyzed using a multi-dynamic collection method. For this purpose, ^{144}Nd ion beam was kept stable at 1 V intensity during a maximum of 160 replicas, with a baseline integration time of 30 000 ms. A normalized value of 0.7219 for the ^{146}Nd/^{144}Nd ratio[9] was considered for a continuous correction of the Nd isotope fractionation. Absence of ^{142}Ce and ^{144}Sm isobaric interferences was continuously checked and corrected during the Nd isotope analysis. Nd reference standard JNdi-1[10] was run along with the BHVO-2 reference material. In each case, JNdi-1 average value was used for a final correction of the resulting ^{143}Nd/^{144}Nd isotope ratios (supporting information). Analytical errors for ^{87}Sr/^{86}Sr and ^{143}Nd/^{144}Nd ratios were estimated as 0.01% and 0.006%, respectively. Total Sr and Nd procedural blank was under 0.5 and 0.1 ng, respectively.

3 | RESULTS AND DISCUSSION

Supporting information shows the BHVO-2 reference material isotopic results (Sr and Nd) obtained from 2015 to present. In order to correct potential instrumental drifts, the ratios here included have been normalized to average values for Sr (NIST SRM 987) and Nd (La Jolla and JNdi-1) isotopic standards analyzed together with the GRM. ^{87}Sr/^{86}Sr and ^{143}Nd/^{144}Nd average values for these isotopic standards are included in supporting information for comparison, these ratios lying within the certified and published values. NIST SRM 987 analyses display a mean value of 0.710245 ($n = 367$ replicates) with a standard deviation of 0.000013 (2*s*), and values varying between 0.710230 and 0.710261. La Jolla Nd isotope standard was analyzed 49 times, yielding a ^{143}Nd/^{144}Nd average value of 0.511847, with a standard deviation of 0.000007 (2*s*), with 0.511841 and

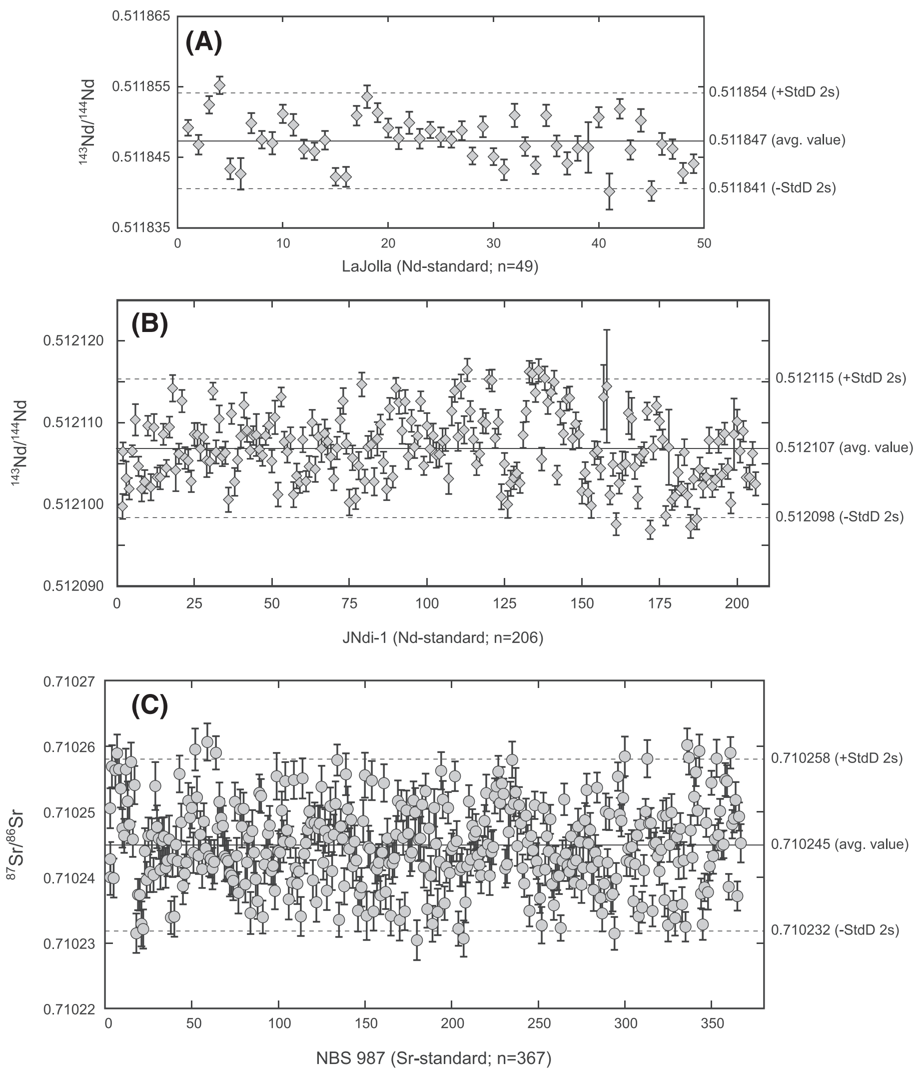

FIGURE 2 Sr and Nd isotopic results of isotope standards by TIMS: (A) La Jolla (Nd), (B) JNdi-1 (Nd) and (C) NIST SRM 987 (Sr). Average value and limited range defined by the standard deviation (2*s*) have been included in each case for comparison. Error bars correspond to the absolute standard error for individual analyses.

0.511854 as minimum and maximum values, respectively. In addition, JNdi-1 Nd isotope standard was analyzed 206 times along with the BHVO-2 reference material, displaying an average value of 0.512107 for $^{143}Nd/^{144}Nd$ ratio, with a standard deviation of 0.000008 (2*s*), and values ranging from 0.512098 to 0.512115 (Figure 2). Internal precision calculated for these three isotope standards is better than 0.3, 0.3 and 0.5 ppm for NIST SRM 987, JNdi-1 and La Jolla, respectively.

3.1 | BHVO-2 Sr isotope composition

Normalized $^{87}Sr/^{86}Sr$ ratios (considering 0.710248; literature values of NIST SRM 987) obtained for BHVO-2 (USGS) reference material (supporting information) display an average value of 0.703485 ± 0.000024 (2*s*; *n* = 88), with an internal precision below 2 ppm. Figure 3 shows the complete record of Sr isotope ratios for BHVO-2 analyzed in comparison with the average value and limited range

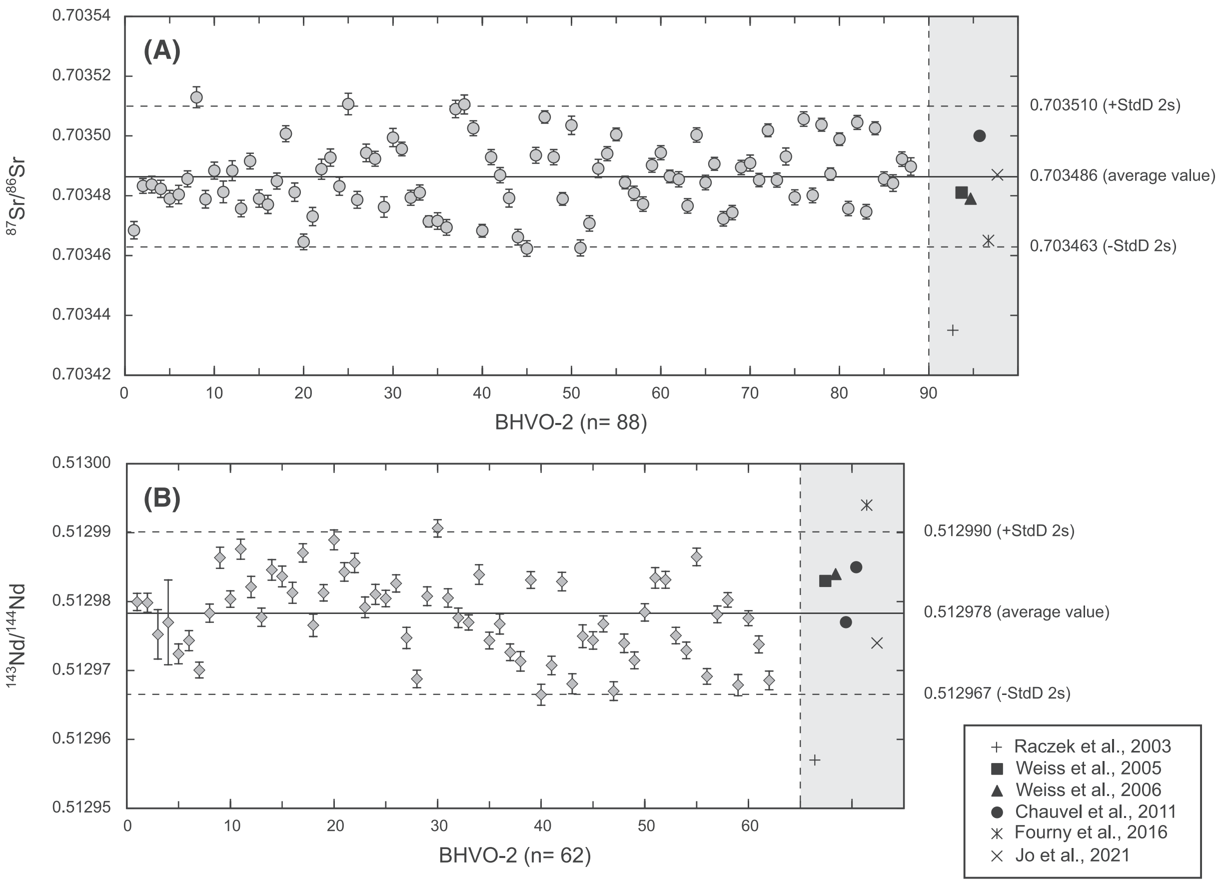

FIGURE 3 (A) Sr and (B) Nd isotopic results of BHVO-2 (USGS) reference material by TIMS. Other published isotope results for this GRM have been included for comparison. See text for additional information. Error bars correspond to the absolute standard error for individual analyses.

TABLE 1 Compilation of Sr and Nd isotope composition of BHVO-2 (USGS) reference material.

This study		$^{87}Sr/^{86}Sr$	2SD	*n*	$^{143}Nd/^{144}Nd$	2SD	*n*
	Non-normalized value	0.703485	0.000024	88	0.512974	0.000013	62
	Normalized value	0.703486	0.000024	88	0.512978	0.000012	62
Literature		$^{87}Sr/^{86}Sr$	**2SD**	***n***	$^{143}Nd/^{144}Nd$	**2SD**	***n***
Raczek et al[11]		0.703435	0.000034	3	0.512957	0.000038	3
Weis et al[12]	Unleached	0.703481	0.000020	10	0.512983	0.000010	9
Weis et al[13]	Normalized value	0.703479	0.000020	12	0.512984	0.000011	13
Chauvel et al[14]		0.703500	0.000030	1	0.512977	0.000010	1
					0.512985	0.000007	1
Fourny et al[15]		0.703465	0.000014	2	0.512994	0.000017	2
Jo et al[16]		0.703487	0.000003 (1SD)	4	0.512974	0.000006 (1SD)	4

defined by the standard deviation (2*s*). Considering the normalized values to the Sr isotope standard NIST SRM 987 in each individual case (supporting information), there is no significant changes from the non-corrected isotope values, with an average value of 0.703486 ± 0.000024. These BHVO-2 Sr isotope ratios here collected are in agreement with those previously published: 0.703435 (average value[11]); 0.703481 ± 20 (unleached fractions[12]); 0.703487 ± 19, with a normalized value of 0.703479 ± 20[13]; 0.703500 ± 11[14]; 0.703465 ± 14 (2SD)[15]; as well as 0703487 ± 3 (1*s*)[16] (Table 1).

3.2 | BHVO-2 Nd isotope composition

Nd analyses of BHVO-2 (USGS) reference material yield a normalized average value (considering 0.511858 for LaJolla[17] and 0.512115 for JNdi-1[10]) for ^{143}Nd/^{144}Nd ratios of 0.512978 ± 0.000012 (2*s*) for 62 replicas and a relatively high internal precision of under 1 ppm. Achieved ^{143}Nd/^{144}Nd ratios for BHVO-2 vary between 0.512966 and 0.512991 (supporting information), similar to the values defined by the standard deviation from the average value (Figure 3). No significant variation has been found for JNdi-1 non-normalized Nd isotope ratios, with an average value of 0.512974 ± 0.000013 (2*s*). BHVO-2 Nd isotope ratios here presented are consistent with those already published by Raczek et al[11] (0.512957, average value); Weis et al[12] (0512983 ± 10; unleached fractions); Weis et al[13] (0512984 ± 11; normalized value); Chauvel et al[14] (0.512977 ± 10 and 0.512985 ± 7); Fourny et al[15] (0.512994 ± 17; unleached fractions); and Jo et al[16] (1*s*; 0.512974 ± 0.000006) (Table 1).

4 | CONCLUSIONS

A complete data set of Sr and Nd isotope results is presented. These data can be used as a helpful means for verifying analytical instrument configuration and for validating Sr and Nd isotope analysis in unknown geological, environmental and archeological samples. The high internal precision and reproducibility, recorded through a relatively large number of isotope analyses of BHVO-2, provide a basis for assuring the quality of Sr and Nd isotopic analysis. This quality is highly necessary for the overall improvement in the interpretation of isotope results from different laboratories and even with different instruments. The absence of certified GRMs for isotopic analysis is a real disadvantage when comparing analytical methods. The increase in the available isotopic information for GRMs helps to improve the comparison of results between different laboratories and even between different techniques and instruments.

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DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in the supplementary material of this article.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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