National Institute of Standards & Technology

Report of Investigation

Reference Material 8301

Boron Isotopes in Marine Carbonate (Simulated Coral and Foraminifera Solutions)

This Reference Material (RM) is intended for use in developing and evaluating methods for measuring relative differences in boron (B) isotope-number ratios, $R(^{11}B/^{10}B)$. It is specifically designed to evaluate B isotope-number ratio measurements normalized to SRM 951 (hereafter designated as $\delta^{11}B_{SRM951}$ or simply $\delta^{11}B$ measurements) in marine carbonate samples [1]. Even though the $\delta^{11}B$ values are reported as reference and not certified values [2], the use of RM 8301 will serve as an effective harmonization standard to improve the comparability of data among different laboratories.

A unit of RM 8301 consists of three vials each of two simulated solutions, labeled as RM 8301 (Coral) and RM 8301 (Foram), each containing approximately 4 mL of a gravimetrically prepared solution with a nominal 50 mg/g mass fraction of calcium in approximately 3 mol/L nitric acid in water. The synthetic materials have been designed to reflect typical $\delta^{11}B$ values and trace element content of authentic coral skeleton and foraminiferal test (invertebrate shell) samples (hence the "Coral" or "Foram" designations in RM 8301).

Expiration of Value Assignment: RM 8301 is valid, within the measurement uncertainty specified, until **31 July 2030**, provided this RM is handled and stored in accordance with instructions given in this Report of Investigation (see "Instructions for Storage and Use"). The reference values are nullified if the RM is damaged, contaminated, or otherwise modified.

Reference Values: Reference values and expanded uncertainties for $\delta^{11}B_{SRM951}$ are shown in Table 1. These values were determined from inter-laboratory study data using the DerSimonian-Laird analysis method within the NIST Consensus Builder [3].

Table 1. Reference Values[(a)] and Expanded Uncertainty Estimates for the Relative B Isotope-Number Ratio Differences of RM 8301 (Coral) and RM 8301 (Foram) solutions

RM Solution	Reference Value $10^3\ \delta^{11}B_{SRM951}$[(b)]	Expanded Uncertainty $10^3\ \delta^{11}B_{SRM951}$[(b)]
8301 (Coral)	+24.17	± 0.18
8301 (Foram)	+14.51	± 0.17

[(a)] A reference value is a non-certified value that is the best estimate of the true value; however, the value may reflect only the measurement precision and may not include all sources of uncertainty [2].

[(b)] The $\delta^{11}B$ value is expressed as $x \pm 2u(x)$, where x is a mean value and $u(x)$ is its associated standard uncertainty. While the best estimate of the delta value lies within the interval $x \pm 2u(x)$ with approximately 95 % confidence, this interval may not include the true value.

Relative Differences in Isotope-Number Ratio Values: The difference in the measured isotope-number ratio of boron isotopes in a sample p, $R(^{11}B/^{10}B)_p = [N(^{11}B)_p/N(^{10}B)_p]$ is reported as a $\delta^{11}B$ value [1]. The relative difference in isotope-number ratios for boron is referenced to SRM 951 where:

$$\delta^{11}B = [R(^{11}B/^{10}B)_{sample} / R(^{11}B/^{10}B)_{SRM951}] - 1$$

SRM951 refers to the boron SRM 951 delta scale, which is defined by assigning a $\delta^{11}B$ value of 0 ‰ to SRM 951 [1], where the symbol ‰ is part per thousand and is equal to 0.001.

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Report Issue Date: 06 January 2021

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Maintenance of RM: NIST will monitor this RM over the period of its validity. If substantive technical changes occur that affect the value assignment before the expiration of this report, NIST will notify the purchaser. Registration (see attached sheet or register online) will facilitate notification.

Technical aspects involved in the design, manufacture, and issuance of this RM were coordinated by S. Christopher of the NIST Chemical Sciences Division and J. Stewart and R. Day, formerly of NIST.

Statistical analyses were performed by B. Toman of the NIST Statistical Engineering Division.

Design and coordination of the inter-laboratory comparison exercise were performed by J. Stewart and R. Day. The institutions listed in Table 2 provided the $\delta^{11}B_{SRM951}$ data used to assign the reference values in Table 1 and/or the supplemental elemental data for RM 8301 listed in Appendix A.

Boron measurements at NIST were provided by J. Stewart and R. Day. Material bottling was performed by C. Davis, R. Day, D. Ellisor, J. Hoguet, A. Moors, J. Ness, R. Pugh, and J. Stewart.

Support aspects involved in the issuance of this RM were coordinated through the NIST Office of Reference Materials.

INSTRUCTIONS FOR STORAGE AND USE

CAUTION: This RM contains an acidic solution sealed in screw top plastic vials. All appropriate safety precautions should be taken during opening and handling. This includes the use of gloves and other appropriate personal protective equipment.

STORAGE: Unopened vials should be stored under normal laboratory conditions in an upright position inside the original packaging supplied by NIST.

USE: The amount of material in each individual vial of RM 8301 (Coral) or RM 8301 (Foram) far exceeds the amount typically needed for boron isotope ratio mass spectrometry. NIST recommends opening the vials individually when needed and aliquoting the opened solutions into pre-cleaned secondary containers for subsequent dilution. This will minimize the potential for contamination and allow for cross-checking. Also, by tightly resealing the secondary containers with paraffin film, the potential for the solutions to undergo isotopic fractionation will be minimized.

Table 2. Laboratories Contributing $\delta^{11}B$ Data and/or Mole Fraction (Element/Ca Ratio) Data for RM 8301

Institution	Location
Department of Earth Sciences, National Cheng Kung University	Tainan, Taiwan
GEOMAR Helmholtz Center for Ocean Research Kiel	Kiel, Germany
Laboratoire des Sciences du Climat et de l'Environnement	Paris, France
National Institute of Standards and Technology	Charleston, SC, USA
University of Bristol	Bristol, United Kingdom
University of Oxford	Oxford, United Kingdom
University of Southampton	Southampton, United Kingdom
University of St. Andrews, STAig Laboratory	St. Andrews, Scotland
Yale University Metal Geochemistry Centre	New Haven, CT, USA

MATERIAL SOURCE, PREPARATION AND ANALYSIS[(1)]

Material Source and Preparation: The simulated solutions comprising RM 8301 (Coral) and RM 8301 (Foram), were prepared at NIST by gravimetric addition and blending of acidified solutions of single element standards, NIST SRM 951a *Boric Acid Isotopic Standard* [4] and an enriched (>99 %) elemental ^{11}B spike to separate 20 L volumes of two different acidified calcium carbonate source solutions. The synthetically created solutions are representative of the expected trace element content, together with a $\delta^{11}B_{SRM951}$ value within the natural range found in authentic coral or foraminifera samples. Supplemental mass fraction data for boron and calcium, and mole fraction data (element/Ca ratios) for various elements in the RM 8301 (Coral) and RM 8301 (Foram) solutions are listed in Appendix A to provide additional information about the solution matrixes. The boron mass fraction values in Appendix A can be used to estimate the amount of solution required for B isotope purification and analysis methods.

Homogeneity Testing: The inter-laboratory study for $\delta^{11}B$ showed good agreement (<0.03 ‰ difference) for twenty-seven vials of RM 8301 (Coral) at a 10 µL typical aliquot size, and RM 8301 (Foram) at a 50 µL typical aliquot size, that were randomly selected from across the entire production batch. Shapiro-Wilk and *F*-Tests on vials measured from the first and last quartiles of the production batch suggested that the data were normally distributed and of similar variance (p>0.05). Parametric two-sample t-tests applied revealed no statistically significant difference (p>0.05) between mean $\delta^{11}B_{SRM951}$ values for either RM 8301 solution.

Analytical Methods: The $\delta^{11}B$ reference values for RM 8301 are based on an inter-laboratory study using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), of which NIST was one of the participants. Most laboratories (including NIST) employed anion exchange chromatography using a boron-chelating resin (Amberlite IRA743) [5] to eliminate matrix effects prior to MC-ICP-MS analysis. The matrix separations were performed after buffering the samples of RM 8301 to an approximate pH of 5 using a sodium acetate-acetic acid buffer. The buffered samples were loaded onto the resin, followed by column washing. Boron was then eluted with nitric acid. One laboratory performed micro-sublimation [6] prior to MC-ICP-MS. All laboratories calibrated their multi-collector instruments using a standard-sample bracketing approach with NIST SRM 951 *Boric Acid or* SRM 951a *Boric Acid Isotopic Standard*. Additional boron isotopic RM materials with published $\delta^{11}B_{SRM951}$ values were processed and measured concurrently with the RM 8301 samples to verify that the measurements were in control [7].

Additional Resource: Fuller details on the production, analysis, and statistical evaluation of RM 8301 are provided in [7].

NOTICE TO USERS

NIST strives to maintain a RM inventory supply but cannot guarantee the continued or continuous supply of any specific RM or SRM. Accordingly, NIST encourages the use of this RM as a primary benchmark for the quality and accuracy of the user's in-house reference materials and working standards. As a benchmark, this RM should be used to validate the more routinely used isotopic reference materials present in a laboratory. Comparisons between this RM and in-house reference materials or working measurement standards should take place at intervals appropriate to the conservation of the RM and the stability of the relevant in-house materials. For further guidance on how this approach can be implemented, contact NIST by email at srms@nist.gov.

(1) Certain commercial equipment, instruments or materials are identified in this certificate to adequately specify the experimental procedures. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

REFERENCES

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Users of this RM should ensure that the Report of Investigation in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; e-mail srminfo@nist.gov; or via the Internet at https://www.nist.gov/srm.

Appendix A

Supplemental data for RM 8301 were collected from the inter-laboratory test for $\delta^{11}B$ [7]. These data provide complementary information about the material, which may be useful to the RM user. However, the data in Table 3 are not certified and should not be used for calibration, validation, or establishing metrological traceability.

Table 3. Non-Certified Values for RM 8301 Boron Isotopes in Marine carbonate (Simulated Coral and Foraminifera Solutions), reported in units of mass fraction for boron and calcium, or mole fraction for element/calcium ratios

Constituent	RM 8301 (Coral)	RM 8301 (Foram)	Units
Boron	7.1	1.9	mg/kg
Calcium	49.7	51.3	mg/g
Al/Ca	48.1	90.9	µmol/mol
B/Ca	528.1	138.9	µmol/mol
Ba/Ca	5.9	3.9	µmol/mol
Cd/Ca	0.2	0.6	µmol/mol
Fe/Ca	15.4	25.4	µmol/mol
Li/Ca	5.4	9.0	µmol/mol
Mg/Ca	4.1	2.6	mmol/mol
Mn/Ca	2.6	49.4	µmol/mol
Na/Ca	20.0	3.1	mmol/mol
Nd/Ca	0.2	5.1	µmol/mol
Sr/Ca	8.1	1.3	mmol/mol
U/Ca	828.9	68.7	nmol/mol