GEOSTANDARDS and
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RESEARCH

NIST RM 8301 Boron Isotopes in Marine Carbonate (Simulated Coral and Foraminifera Solutions): Inter-laboratory δ^{11}B and Trace Element Ratio Value Assignment

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The boron isotopic ratio of $^{11}\text{B}/^{10}\text{B}$ ($\delta^{11}\text{B}_{\text{SRM951}}$) and trace element composition of marine carbonates are key proxies for understanding carbon cycling (pH) and palaeoceanographic change. However, method validation and comparability of results between laboratories requires carbonate reference materials. Here, we report results of an inter-laboratory comparison study to both assign $\delta^{11}\text{B}_{\text{SRM951}}$ and trace element compositions to new synthetic marine carbonate reference materials (RMs), NIST RM 8301 (Coral) and NIST RM 8301 (Foram) and to assess the variance of data among laboratories. Non-certified reference values and expanded 95% uncertainties for $\delta^{11}\text{B}_{\text{SRM951}}$ in NIST RM 8301 (Coral) (+24.17‰ ± 0.18‰) and NIST RM 8301 (Foram) (+14.51‰ ± 0.17‰) solutions were assigned by consensus approach using inter-laboratory data. Differences reported among laboratories were considerably smaller than some previous inter-laboratory comparisons, yet discrepancies could still lead to large differences in calculated seawater pH. Similarly, variability in reported trace element information among laboratories (e.g., Mg/Ca ± 5% RSD) was often greater than within a single laboratory (e.g., Mg/Ca < 2%). Such differences potentially alter proxy-reconstructed seawater temperature by more than 2 °C. These now well-characterised solutions are useful reference materials to help the palaeoceanographic community build a comprehensive view of past ocean changes.

Keywords: boron isotopes, trace elements, reference materials, coral, foraminifera.

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Anthropogenic carbon emissions since the industrial revolution have impacted both Earth's radiative balance and seawater carbonate chemistry, resulting in surface warming and ocean acidification (Doney *et al.* 2009, Stocker *et al.* 2013). The scientific community requires details of (a) spatial/temporal changes in ocean pH and temperature, and (b)

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levels of atmospheric carbon dioxide (CO_2) during intervals of climate change in the geological past, to better understand and anticipate potential future changes to the ocean/atmosphere system and the impacts on marine bio-carbonate organisms. To this end, attention has been focused on the development of ocean pH proxies, with the differences in boron isotopic composition (expressed as $\delta^{11}B_{SRM951}$, relative to National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 951 Boric Acid, in parts per thousand; $\delta^{11}B = (R(^{11}B/^{10}B)_{Sample}/R(^{11}B/^{10}B)_{SRM951} - 1))$ of modern and fossilised marine calcifying organisms (e.g., coral and foraminifera) showing particular promise (Hemming and Hanson 1992).

In addition to boron, the trace element composition of marine carbonates is vital to understanding past ocean characteristics and composition (e.g., Algeo and Rowe 2012). For this reason, palaeoceanographers routinely measure carbonate molar ratios of Mg/Ca (sometimes also paired with Li/Ca) and Sr/Ca as proxies for temperature (Beck *et al.* 1992, Anand and Elderfield 2003, Case *et al.* 2010); Al/Ca, Mn/Ca, Fe/Ca, and Ba/Ca to assess seawater metal content (Lea and Boyle 1989, Guzmán and Jiménez 1992) and sample diagenesis/contamination (Barker and Greaves 2003); Cd/Ca to estimate nutrient content (Rickaby and Elderfield 1999); and U/Ca to assess carbonate ion saturation states and calcification rates (Russell *et al.* 2004, DeCarlo *et al.* 2015). In this way, trace element proxy data can provide a holistic view of past and present ocean–climate interactions.

Before palaeoceanographic interpretation can be made from any $\delta^{11}B_{SRM951}$ or trace element dataset, rigorous assessment of uncertainty is required. Initial inter-laboratory comparison exercises measuring boron isostopes in natural materials revealed large discrepancies in results across laboratories (>> ±1‰; Gonfiantini *et al.* 2003, Aggarwal *et al.* 2009). Despite much analytical improvement since then, recent inter-laboratory studies still report significant inter-laboratory disagreement for both boron isotope (Foster *et al.* 2013) and trace element (Hathorne *et al.* 2013) measurements. Hence, well-characterised boron isotopic reference materials in a carbonate matrix are urgently needed to assess the accuracy and precision of carbonate $\delta^{11}B_{SRM951}$ measurements through the entire procedural treatment: from dissolution of carbonate, ionic separation of boron from the carbonate matrix, to the final $\delta^{11}B_{SRM951}$ measurement. To date, only two authentic carbonate boron isotope reference materials exist that have been value-assigned by the palaeoceanographic community: JCp-1 (*Porites* coral) and JCt-1 (Giant Clam) (Okai *et al.* 2002, Inoue *et al.* 2004, Hathorne *et al.* 2013) (see companion inter-laboratory study by Gutjahr *et al.* (2020 in press). While many carbonate geochemistry laboratories routinely use these materials in-house, recent changes to regulations by Convention on International Trade in Endangered Species of Wild Fauna and Flora (CITES) now restrict the distribution of both biogenic carbonates due to their animal origins. NIST has therefore supplemented these with NIST RM 8301 *Boron Isotopes in Marine Carbonate (Simulated Coral and Foraminifera Solutions)*, hereafter abbreviated as NIST RM 8301, providing new solution-based inorganic carbonate boron reference materials synthetically produced to imitate typical coral (NIST RM 8301 (Coral)) and foraminiferal (NIST RM 8301 (Foram)) $\delta^{11}B_{SRM951}$ and trace element contents (Li, B, Na, Mg, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Mo, Ag, Cd, Sn, Sb, Cs, Ba, Nd, W, Pb, U). The solutions comprising NIST RM 8301 will not only ensure quality control of procedural chemistry post-dissolution across laboratories, but have the added benefits of having a high mass fraction of B to ensure stability during storage (NIST RM 8301 (Coral) ≈ 7.1 $\mu g\ g^{-1}$ and RM 8301 (Foram) ≈ 1.9 $\mu g\ g^{-1}$), free from any shipping restrictions associated with shipment of protected species, and are in abundant supply (5000 bottles each) to ensure long-term continuity of measurements into the future. Here, we present $\delta^{11}B_{SRM951}$ and trace element data from NIST and other leading boron isotope laboratories to assign values to NIST RM 8301 and evaluate analytical performance between these laboratories.

Methodology

NIST RM 8301 reference material production

The production of NIST RM 8301 reference materials is summarised in Figure 1. Six kilograms of high-purity powdered calcium carbonate (ACS 337 calcium carbonate, chelometric material; GFS Chemicals, OH, USA; Lot # C474630) was dissolved in TraceMetal™ Grade concentrated nitric acid (Fisher Scientific, MA, USA) while cooled in a water bath. The dissolved solution was passed through Whatman® GF/F 0.7 μm microfibre filters (142 mm diameter; 0.42 mm thickness; Cat # 1825-142) to remove small quantities (< 3 g total mass) of residual solids (trace oxides, organics, and/or silicates) that formed during the dissolution process. After filtration, the solution was transferred into two acid-cleaned 20 L HDPE carboys: one for NIST RM 8301 (Coral), and one for NIST RM 8301 (Foram). The matching carbonate matrix of these two solutions means that they share a common RM identifier (8301). However, with their contrasting boron isotope and trace element composition (see below) we distinguish between the two levels of this RM as 'Coral' and 'Foram'. The end user is not necessarily

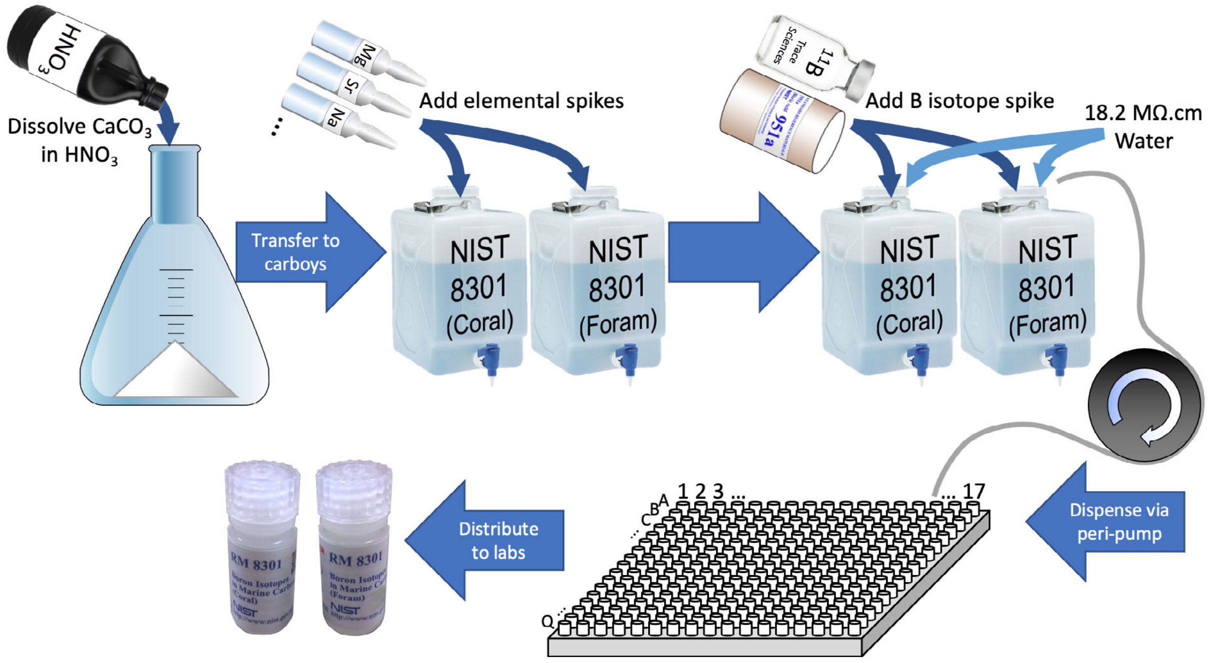


Figure 1. Production of NIST RM 8301 including (i) dissolution of carbonate powder in nitric acid, (ii) addition of trace elements, (iii) addition of boron isotope spike, (iv) dispensing into acid clean vials and (v) distribution to participants.

expected to use both solutions in tandem as part of their quality control procedure; rather, they should choose the solution most appropriate to their sample type of interest.

Single-element trace element solutions were added in suitable quantities to each solution of the RM to reproduce the trace element to calcium ratios typical of a dissolved coral aragonite and foraminiferal calcite. The stock solution used for each element and the masses added to each RM solution are given in Table 1. Note that these values are given for reference to show the approximate element/Ca ratios in the solutions. Gravimetric concentrations are provided for documenting the production procedure, and the masses in Table 1 do not account for concomitant trace elements contained within the starting powdered carbonate and single-element standards, or for ions leached during dissolution and filtration. Inter-laboratory consensus information values for the trace element composition of the RMs are reported later in the manuscript.

The boron isotope spike customised and added to each trace element-doped dissolved carbonate RM solution was a mixture of NIST SRM 951a boric acid ($\delta^{11}B = 0‰$; $^{11}B/^{10}B = 4.0437$) and a $> 99\%$ enriched ^{11}B spike (Trace Sciences) to give B/Ca and $^{11}B/^{10}B$ ratios typical of coral (B/Ca ≈ 550 µmol mol^{-1}; $\delta^{11}B_{SRM951} \approx 25‰$) and foraminifera (B/Ca ≈ 150 µmol mol^{-1}; $\delta^{11}B_{SRM951} \approx 15‰$) (Table 1). NIST SRM 951a was dissolved in boron-free high-purity water while the more recalcitrant ^{11}B-enriched metal was microwave-digested in Optima™ concentrated nitric acid and hydrogen peroxide (Fisher Scientific) using quartz vessels in an Anton Parr Multiwave 3000 Microwave Reaction System. Following addition of this final boron isotope spike, the resultant solutions were diluted with boron-free water (resistivity: 18.2 MΩ cm) to yield a total volume of 20.2 l in each carboy and final calcium concentrations of approximately 50 mg ml^{-1} and nitric acid content of approximately 3 mol l^{-1}. Gravimetric calibration and measurement by inductively coupled plasma-mass spectrometry (ICP-MS) revealed final calcium mass fractions of 49.7 and 51.3 mg g^{-1} for NIST RM 8301 (Coral) and NIST RM 8301 (Foram), respectively (see Analytical techniques section). The boron isotope spike weights given in Table 1 are for reference to show the target boron mass fraction and $^{11}B/^{10}B$ ratio of the solutions. As above, gravimetric preparation values are expected to differ from actual B/Ca and $^{11}B/^{10}B$ ratios in the RM solutions as small amounts of boron are added from the original carbonate and/or leached during dissolution. Each NIST RM 8301 solution was well mixed and aliquoted sequentially through preconditioned peristaltic pump tubing into 5000 acid cleaned 4 ml HDPE screw top vials for production. All vial cleaning and RM dispensing were carried out in the NIST Biorepository ISO Class 5 clean room at the NIST Charleston Laboratory.

Inter-laboratory comparison outline

For the NIST contribution to the inter-laboratory study, nine vials of each RM were selected for measurement of $\delta^{11}B_{SRM951}$ and trace element composition. Additional participant laboratories include LSCE, GEOMAR, Yale and Universities of Southampton, St Andrews, and National Cheng Kung that were selected based on their active research on boron isotopes in marine carbonates. Each laboratory was assigned a laboratory number at random to protect data anonymity. Participants were sent three vials (selected by random number generator) of each simulant of NIST RM 8301 and asked to make at least three separate boron isotopic measurements of each vial, providing a relevant citation detailing their matrix separation and analytical protocol of choice. The high nitric acid content in NIST RM 8301 (approximately 3 mol l^{-1}) makes these solutions unsuitable for negative thermal ionisation mass spectrometry (e.g., Hönisch and Hemming 2004, B. Hönisch pers. comm.). All laboratories in this study therefore opted to employ multi-collector (MC)-ICP-MS analytical techniques.

Participants were asked to provide supplementary data for each vial for their typical carbonate trace element suite (element ratioed to calcium); however, these analyses were optional. In order for us to present a wide array of useful trace element ratios in these solutions, we did not ask laboratories to produce a detailed uncertainty budget beyond a combined estimation of analytical reproducibility and variability between the vials measured. For this reason, an expanded uncertainty is not provided for trace element values presented here. Consequently, they cannot be used to establish metrological traceability to the mol or kg, but are nonetheless useful guide values determined by inter-laboratory consensus. Trace element data were provided by NIST, LSCE, GEOMAR, Southampton and St. Andrews. Additional trace element data were provided by the Universities of Bristol and Oxford; however, these two laboratories measured fewer individual vials. Laboratories providing trace element data were again assigned a random number to protect data anonymity. All laboratories used either quadrupole or sector-field ICP-MS instrumentation to analyse the solutions, matrix-matching samples and calibration solutions with calcium mass fractions of between 25 and 100 µg g^{-1}. Note that the laboratory numbers used for boron isotopic comparison in Figure 2 do not correspond to the same laboratory number reporting elemental ratios in Figures 4 and 5.

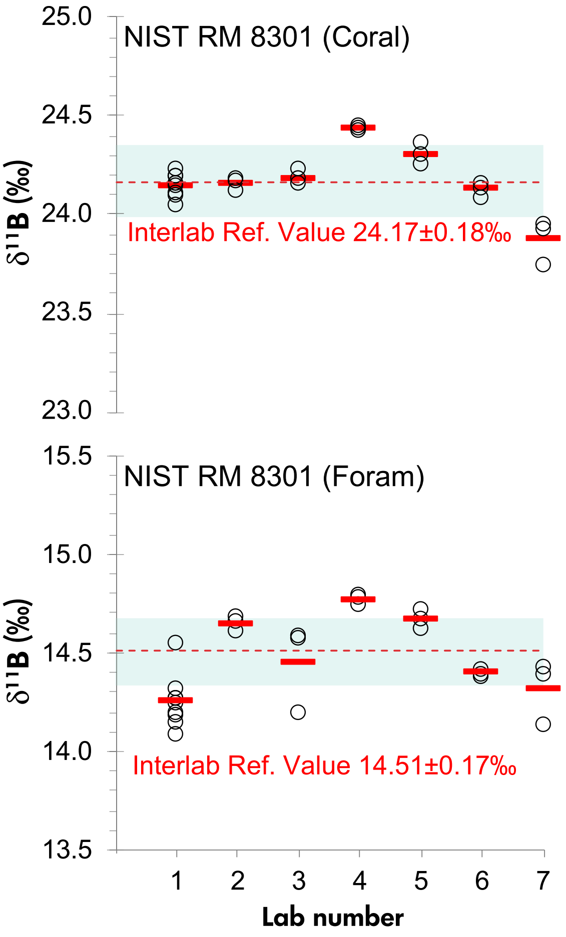


Figure 2. **$\delta^{11}B_{SRM951}$ results for NIST RM 8301 (Coral) and NIST RM 8301 (Foram). NIST lab is number 1, other laboratories have been anonymised. Circles and thickdashes denote, respectively, mean values measured for each vial and the mean value for that laboratory. The dashed line shows the inter-laboratory consensus reference value for $\delta^{11}B_{SRM951}$ of all seven contributing laboratories. Shaded zones show the 95% expanded uncertainty on consensus reference values.**

Analytical techniques

Analytical techniques used by the participant laboratories are summarised in Tables 2 and 3. Details of the analytical approach used by NIST are given below.

Boron isotope measurements at NIST: Analyses at NIST followed protocols previously described in Foster (2008), Rae *et al.* (2011) and Foster *et al.* (2013). The exact volume of RM used varied between column batches, yet in all cases more than 100 ng of B was targeted for each analysis (typically 15 and 50 µl of NIST RM 8301

Table 1.
Mass of calcium carbonate, boron isotopic spike and single-element stock solutions added to each level of NIST RM 8301

	Stock source	Stock concentration	Lot #	Matrix (*v*/*v*)	NIST RM 8301 (Coral) mass added		NIST RM 8301 (Foram) mass added	
	$CaCO_3$ 337 powder		C474630		3029	g	3031	g
	NIST SRM 951a Boric Acid Isotopic Standard powder				1.0	g	0.3	g
	Trace Sciences ^{11}B powder (99% enriched)				3.8	mg	0.6	mg
Sr	HP 10M53-1	10 mg ml^{-1}	1414835	1% HNO_3	2167	g	325.054	g
Na	HP 10M52-1	10 mg ml^{-1}	1505109	1% HNO_3	1439	g	215.831	g
Mg	HP 10M31-2	10 mg ml^{-1}	1413333	10% HCl	304	g	191.627	g
Zn	HP 10M68-1	10 mg ml^{-1}	1326125	4% HNO_3	8.0	g	1.978	g
Al	HP 10M1-1	10 mg ml^{-1}	1516016	10% HNO_3	4.4	g	8.596	g
Cu	HP 10M14-1	10 mg ml^{-1}	1502217	4% HNO_3	3.9	g	1.125	g
P	NIST 3139a	10016 µg g^{-1}	60717	0.8% HNO_3	3.7	g	2.757	g
Ba	HP 10M4-1	10 mg ml^{-1}	1406438	2% HNO_3	2.1	g	1.205	g
Fe	HP 10M26-1	10 mg ml^{-1}	1508449	10% HNO_3	1.7	g	3.536	g
Ni	NIST 3136	10003 µg g^{-1}	120619	8% HNO_3	1.2	g	1.033	g
U	HP 10M64-1	10 mg ml^{-1}	1435233	4% HNO_3	0.6	g	0.023	g
Mn	HP 10M32-1	10 mg ml^{-1}	1413613	4% HNO_3	0.3	g	8.575	g
Co	NIST 3113	9996 µg g^{-1}	630	10% HNO_3	0.2	g	0.094	g
W	NIST 3163	9991 µg g^{-1}	80331	7% HNO_3 + 4% HF	127	mg	73	mg
Sb	NIST 3102a	10015 µg g^{-1}	61229	10% HNO_3 + 2% HF	94	mg	44	mg
Li	HP 10M29-1	10 mg ml^{-1}	1428019	1% HNO_3	90	mg	179	mg
Nd	HP 10M35-1	10 mg ml^{-1}	1412002	4% HNO_3	65	mg	2259	mg
V	NIST 3165	4860 µg g^{-1}	992706	10% HNO_3	50	mg	37	mg
Pb	HP 10M28-1	10 mg ml^{-1}	1322626	4% HNO_3	45	mg	34	mg
Cd	HP 10M8-1	10 mg ml^{-1}	1312905	4% HNO_3	35	mg	176	mg
Cr	NIST 3112a	9922 µg g^{-1}	30730	10% HNO_3	33	mg	24	mg
Mo	NIST 3134	9999 µg g^{-1}	130418	10% HCl	31	mg	23	mg
Rb	NIST 3145a	10040 µg g^{-1}	891203	4% HNO_3	27	mg	20	mg
Sn	NIST 3161a	10010 µg g^{-1}	70330	5% HNO_3 + 1% HF	19	mg	14	mg
Ag	NIST 3151	10010 µg g^{-1}	992212	10% HNO_3	3	mg	3	mg
Cs	NIST 3111a	10006 µg g^{-1}	50614	1% HNO_3	0.5	mg	0.3	mg

These guide values show the relative proportions of elements in each RM.
HP = high-purity standards, Inc. (all traceable to NIST SRM 3100 series).

(Coral) and NIST RM 8301 (Foram), respectively). Each aliquot from the individual RM 8301 vials was buffered in 2 mol kg^{-1} sodium acetate to 0.5 mol kg^{-1} acetic acid (20:1 buffer to sample ratio) before boron was separated from the carbonate matrix using 20 µl micro-columns containing IRA 743 boron-specific anionic exchange resin (Kiss 1988). All boron must be recovered from columns to avoid isotopic fractionation; therefore, following elution of the boron fraction, an additional elution was checked to ensure > 99% of sample boron was recovered.

At NIST, the purified boron samples were diluted to a boron mass fraction of approximately 100 ng g^{-1} for analysis on a Nu Plasma II MC-ICP-MS concurrently with NIST *SRM 951a Boric Acid Isotopic Standard* at matrix-matched mass fractions of B and acid concentration (0.5 mol l^{-1} HNO_3). An on-peak zero was acquired as a 60 s acid blank measurement before each sample. Immediately after sample wash in, a peak centre was performed using the ^{11}B mass before both boron isotopes were collected on H8 and L4 Faraday cups. Sample data were acquired as one block of sixty cycles each with an integration time of 2 s. Data acquisition was followed by a 2 min wash between samples to ensure minimal sample carry over (i.e., blank intensity < 1% of sample). Note that all laboratories in this study used either SRM 951 or SRM 951a to correct for mass bias, using similar sample-standard bracketing techniques.

The precision of $\delta^{11}B_{SRM951}$ results in the NIST laboratory was assessed by repeat measurements of boric acid standard BAM ERM-AE121 (certified value, 19.9‰ ± 0.6‰; Vogl and Rosner 2012) during analytical runs. In addition, assessment of the full powdered sample processing methodology was performed using the carbonate reference material JCp-1 (robust mean including robust

Table 2.
Boron isotope method summary for inter-laboratory study participants

Participant	Matrix separation	Instrument	Type	Run concentration [B] (ng g^{-1})	Source of traceability	Method reference
NIST	Amberlite gravity columns	MC-ICP-MS	Nu Plasma II	100	NIST SRM 951	Foster (2008)
GEOMAR	Amberlite gravity columns	MC-ICP-MS	Thermo Neptune Plus	36	NIST SRM 951	Foster (2008), Jurikova *et al.* (2019)
LSCE	Amberlite gravity columns	MC-ICP-MS	Thermo Neptune Plus	200	NIST SRM 951	Douville *et al.* (2010), Lazareth *et al.* (2016)
Nat. Cheng Kung Univ.	Microsublimation	MC-ICP-MS	Thermo Neptune	50	NIST SRM 951	Hönisch and Hemming (2005), Wang *et al.* (2010)
Univ. of Southampton	Amberlite gravity columns	MC-ICP-MS	Thermo Neptune	30–50	NIST SRM 951	Foster (2008)
Univ. of St Andrews	Amberlite gravity columns	MC-ICP-MS	Thermo Neptune Plus	18–30	NIST SRM 951	Foster (2008), Rae *et al.* (2018)
Yale	Amberlite gravity columns	MC-ICP-MS	Thermo Neptune Plus	35	NIST SRM 951	Foster (2008), Zhang *et al.* (2017)

All laboratories used sample-calibrator bracketing to correct for instrument-induced mass bias. Order of laboratories listed here does not reflect randomly assigned laboratory number.

Table 3.
Trace element method summary for inter-laboratory study participants

Participant	Instrument	Type	Run concentration [Ca] (μg g^{-1})	Method reference
NIST	ICP-MS	Thermo Element 2	80	Marchitto (2006)
Univ. of Bristol	ICP-MS	Thermo Element XR	80	Marchitto (2006)
GEOMAR	ICP-MS	Agilent 7500cx Quad	25	Hathorne *et al.* (2013)
LSCE	ICP-MS	Xseries II Quad	100	Montagna *et al.* (2014), Hathorne *et al.* (2013)
Univ. of Oxford	ICP-MS	Perkin Elmer NexION 350D	60	Rosenthal and Field (1999), Day and Henderson (2013)
Univ. of Southampton	ICP-MS	Thermo Element XR	80	Henehan *et al.* (2013)
Univ. of St Andrews	ICP-MS	Agilent 7500a Quad	40	Ni *et al.* (2007)

Order of laboratories listed here does not reflect randomly assigned laboratory number.

standard deviation ($2s^*$) of oxidatively cleaned JCp-1 from companion inter-laboratory study: 24.25‰ ± 0.22‰; Gutjahr *et al.* 2020). Measurements for these additional reference materials at 100 ng g^{-1} B mass fraction during sample analysis were, respectively, 19.71‰ ± 0.07‰ ($2s$; $n = 39$; no matrix separation) and 24.18‰ ± 0.39‰ ($n = 6$; matrix removed by micro-columns). Similar results for BAM ERM-AE121 were also provided by five out of seven laboratories in this study that vary by 0.17‰ (19.71, 19.60, 19.55, 19.75 and 19.60‰; Lab 1–5, respectively; $2s$).

Six total procedural blank measurements were made at NIST alongside samples in this study (mean absolute blank of 116 pg of boron). These blanks are small relative to the sample size (< 0.09% of sample boron) resulting in minimal impact on $\delta^{11}B_{SRM951}$ results (i.e., < 0.1‰); hence, a total procedural blank correction was not applied.

Elemental determination at NIST: Determinations were carried out on an Element XR sector-field ICP-MS and broadly followed the protocol of Marchitto (2006) to yield Li/Ca, B/Ca, Na/Ca, Mg/Ca, Al/Ca, Mn/Ca, Fe/Ca, Sr/Ca, Cd/Ca, Ba/Ca, Nd/Ca and U/Ca ratios. Sample aliquots were diluted to an equal mass fraction of Ca (80 μg g^{-1}), and every three samples were bracketed by a matrix-matched, gravimetrically prepared, primary calibrant that was traceable to NIST 3100 series single-element solutions. Measured intensities (counts per second) of each individual

Table 4.
Compiled boron isotope measurement results of NIST RM 8301 from all inter-laboratory study participants

NIST RM 8301 (Coral)		Vial mean	NIST RM 8301 (Foram)		Vial mean
Vial	δ^{11}B (‰)	δ^{11}B (‰)	Vial	δ^{11}B (‰)	δ^{11}B (‰)
2A2	24.09	24.15	2A2	14.28	14.18
	24.20			14.00	
	24.17			14.26	
3A2	23.87	24.09	3A2	14.41	14.17
	24.29			14.44	
	24.14			14.11	
	24.05			13.72	
3G14	23.95	24.13	3G14	14.47	14.31
	24.36			14.17	
	24.09			14.29	
4K11	23.97	24.10	4K11	13.76	14.07
	24.12			14.27	
	24.23			14.18	
5A2	24.11	24.18	5A2	14.30	14.23
	24.20			14.12	
	24.24			14.27	
15A2	24.09	24.05	15A2	14.67	14.54
	23.76			14.60	
	24.28			14.35	
16A2	24.29	24.23	16A2	14.21	14.26
	24.15			14.21	
	24.24			14.36	
17A2	24.30	24.19	17A2	14.60	14.25
	24.36			14.41	
	23.90			13.76	
17G15	23.94	24.15	17G15	14.07	14.14
	24.29			14.71	
	24.22			13.63	
NIST Lab 1	**Mean (±2*s*)**	**24.14 ± 0.11**	**NIST Lab 1**	**Mean (±2*s*)**	**14.24 ± 0.27**
14E16	24.31	24.17	14E16	14.60	14.59
	24.00			14.61	
	24.14			14.57	
	24.22				
1T3	24.26	24.18	1T3	14.63	14.67
	24.03			14.71	
	24.25			14.68	
6A3	24.12	24.12	6A3	14.61	14.64
	24.13			14.78	
	24.11			14.53	
Lab 2	**Mean (±2*s*)**	**24.16 ± 0.06**	**Lab 2**	**Mean (±2*s*)**	**14.64 ± 0.08**
6Q16	24.08	24.17	6Q16	14.14	14.18
	24.25			14.34	
	24.19			14.07	
14M7	24.15	24.15	14M7	14.59	14.57
	24.05			14.47	
	24.27			14.64	
17J13	24.26	24.22	17J13	14.49	14.56
	24.16			14.65	
	24.24			14.54	
Lab 3	**Mean (±2*s*)**	**24.18 ± 0.07**	**Lab 3**	**Mean (±2*s*)**	**14.44 ± 0.44**
4A17	24.44	24.44	4A17	14.73	14.77
	24.44			14.80	
	24.44			14.80	
6G14	24.36	24.43	6G14	14.74	14.73
	24.46			14.73	
	24.46			14.72	
11K5	24.51	24.42	11K5	14.78	14.76
	24.42			14.79	
	24.34			14.72	

Table 4 (continued).
Compiled boron isotope measurement results of NIST RM 8301 from all inter-laboratory study participants

NIST RM 8301 (Coral)		Vial mean	NIST RM 8301 (Foram)		Vial mean
Vial	δ^{11}B (‰)	δ^{11}B (‰)	Vial	δ^{11}B (‰)	δ^{11}B (‰)
Lab 4	**Mean (±2*s*)**	**24.43 ± 0.02**	**Lab 4**	**Mean (±2*s*)**	**14.76 ± 0.05**
1N12	24.40	24.25	1N12	14.59	14.65
	24.24			14.60	
	24.10			14.77	
4F10	24.45	24.36	4F10	14.75	14.71
	24.29			14.68	
	24.34			14.70	
7B3	24.34	24.29	7B3	14.64	14.61
	24.33			14.53	
	24.21			14.67	
Lab 5	**Mean (±2*s*)**	**24.30 ± 0.12**	**Lab 5**	**Mean (±2*s*)**	**14.66 ± 0.10**
12G5	24.19	24.13	12G5	14.39	14.38
	24.05			14.35	
	24.16			14.39	
11B8	24.07	24.08	11B8	14.33	14.37
	24.06			14.36	
	24.12			14.43	
7O8	24.16	24.15	7O8	14.34	14.40
	24.12			14.38	
	24.18			14.49	
Lab 6	**Mean (±2*s*)**	**24.12 ± 0.07**	**Lab 6**	**Mean (±2*s*)**	**14.38 ± 0.03**
1I4	23.71	23.74	1I4	14.34	14.41
	23.83			14.52	
	23.67			14.39	
9G8	24.04	23.92	9G8	14.33	14.12
	23.72			13.89	
	24.01			14.16	
17C12	23.78	23.94	17C12	14.27	14.38
	24.09			14.23	
	23.95			14.63	
Lab 7	**Mean (±2s)**	**23.87 ± 0.23**	**Lab 7**	**Mean (±2s)**	**14.30 ± 0.32**

sample were blank corrected using blank acids measurements before and after each sample. Typical precision (1*s*) for these element/calcium ratios is < 4% based on repeat measurements (*n* = 38) of an in-house matrix-matched gravimetric solution.

Reference value assignment for $\delta^{11}B_{SRM951}$ and supplemental data

Reference values and expanded uncertainties for $\delta^{11}B_{SRM951}$ in NIST RM 8301 (Coral) and NIST RM 8301 (Foram) published in the final NIST Report of Investigation for NIST RM 8301 were determined from all inter-laboratory study data using the DerSimonian-Laird analysis method within the NIST Consensus Builder (Koepke *et al.* 2017). Value assignment such as this, by consensus approach involving multiple participants, is not conducive to obtaining a fully comprehensive uncertainty budget (e.g., Vogl and Rosner 2012, Geilert *et al.* 2019). The DerSimonian-Laird method was therefore chosen to account for 'dark uncertainty' (unaccounted sources of uncertainty among laboratories) as the reported data only included uncertainties related to replication. Because no comprehensive uncertainty budgets were reported, traceability to the SI cannot be established. For this reason, we do not advocate the use of NIST RM 8301 for calibration purposes (e.g., using as a bracketing calibrator) or establishing metrological traceability. Consensus element/calcium ratios published in the final NIST Report of Investigation for NIST RM 8301 as non-certified information values, are based on the overall means calculated from the mean values reported for each material from each participant laboratory.

Results and discussion

Boron

All boron isotope data for NIST RM 8301 collected by the seven contributing laboratories are shown in Table 4 and summarised in Table 5 and Figure 2. These data show the mean of three $\delta^{11}B_{SRM951}$ values for individual vials of NIST RM 8301 (Coral) and NIST RM 8301 (Foram) that range from 23.74‰ to 24.44‰ and 14.07‰ to 14.77‰, respectively. The range in mean $\delta^{11}B_{SRM951}$ values for all vials reported by each laboratory is similar for both RMs: by 0.56‰ for NIST RM 8301 (Coral) (23.87–24.43‰), and 0.52‰ for 8301 (Foram) (14.24–14.76‰). Inter-laboratory consensus-based NIST reference values were calculated as 24.17‰ ± 0.18‰ and 14.51‰ ± 0.17‰ for NIST RM 8301 (Coral) and NIST RM 8301 (Foram), respectively, using DerSimonian-Laird analysis and 95% expanded uncertainty. These values are extremely close to the mean of all laboratory mean values of 24.17‰ ± 0.35‰ and 14.49 ± 0.39‰ (2*s*). This suggests that the NIST laboratory, contributing results from more than three vials of each RM and with its poorer reproducibility of some vials (e.g., NIST RM 8301(Foram) vial 17G15 > ±1‰; 2*s*), did not unduly influence the overall consensus value.

Expanded uncertainties estimated using this approach are small (< ±0.2‰) in comparison with the laboratory mean values (> ±0.3‰; 2*s*). DerSimonian-Laird consensus values are weighted with uncertainty surrounding the consensus value decreasing roughly in proportion to the square root of the number of results being combined. Therefore, this approach can underestimate dark uncertainty in cases such as this where the number of laboratories is small. However, we note the alternative hierarchical Bayesian approach available in the NIST Consensus Builder offers similar results (± 0.20‰ expanded uncertainty at 95% confidence), suggesting that DerSimonian-Laird analysis provides a reasonable estimate of the consensus value and its uncertainty.

Non-certified values such as this are a best estimate of the true value; however, they may reflect only the measurement repeatability and may not include all sources of uncertainty (May *et al.* 2000). An example of unaccounted uncertainty could be from the boron isotope ratio of NIST SRM 951 bracketing standard itself that was used by all laboratories in this study (NIST SRM 951 $^{10}B/^{11}B$ absolute abundance ratio of 0.2473 ± 0.0002). While the $\delta^{11}B$ value of NIST SRM 951 of 0‰, by definition, carries no uncertainty, heterogeneities between different batches of NIST SRM 951 used in each laboratory could potentially have an impact on absolute reported $\delta^{11}B$ values. We consider this source of uncertainty and its impact on inter-laboratory results small; however, because of the close agreement of boric acid standard BAM ERM-AE121 (no matrix removal step required) measurements provided by five out of seven laboratories in this study.

Inter-laboratory measurement discrepancy and calculated pH: Boron isotope measurements in marine carbonates are commonly used to calculate seawater pH values using the simplified relationship described in Equation (1) (Zeebe and Wolf-Gladrow 2001); see also full expression in Rae (2018):

$$\mathrm{pH} = \mathrm{p}K_B^{*} - \log\left(-\frac{\delta^{11}B_{sw} - \delta^{11}B_{borate}}{\delta^{11}B_{sw} - \alpha_B\delta^{11}B_{borate} - 1000(\alpha_B - 1)}\right) \tag{1}$$

where α_B is the fractionation factor between the two major species of boron in seawater (boric acid and borate; 1.0272; Klochko *et al.* 2006), $\mathrm{p}K_B^{*}$ is the dissociation constant for boric acid in seawater, and $\delta^{11}B_{borate}$ and $\delta^{11}B_{sw}$ are the respective boron isotopic ratios of the borate ion (thought to be incorporated into marine carbonates) and total boron in seawater (39.61‰; Foster and Pogge von Strandmann 2010). Although the inter-laboratory range in mean $\delta^{11}B_{SRM951}$ values reported from each laboratory was similar (approximately 0.5‰) for each RM, if treated as a true carbonate sample (assuming a sensitivity of $\delta^{11}B_{SRM951}$ to pH equal to borate ion; Equation 1), seawater pH values calculated using these $\delta^{11}B_{SRM951}$ values result in a range in pH of 0.02 pH units for NIST RM 8301 (Coral) and a larger 0.10 pH unit range for NIST RM 8301 (Foram). This difference largely reflects the non-linear relationship between carbonate $\delta^{11}B$ and pH (Equation 1) but also highlights the significant potential differences in calculated pH from boron isotope data produced in different laboratories, hence the need for reference materials like NIST RM 8301 to help tighten pH reconstructions using this proxy.

Boron isotope values and NIST RM 8301 homogeneity testing: Although the solutions comprising NIST RM 8301 were dispensed from carboys into the 4 ml distribution vials and capped as soon as possible, the sequential nature of the dispensing through single lengths of tubing has the potential to introduce heterogeneities across a reference material batch. Despite such potential bias, $\delta^{11}B_{SRM951}$ values for each vial from all participant laboratories agree well across the entire seventeen racks (each rack contained 289 vials) of each reference material (Figure 3). Vial $\delta^{11}B_{SRM951}$ values from the start (first four racks; first 24% of vials; $n = 9$) and end (last four racks; last 24% of vials; $n = 8$) of the dispensing sequence vary by < 0.03‰ in both RM 8301 (Coral) solution (with a typical processed aliquot size of ≈ 10 μl), and NIST RM 8301 (Foram) solution (with a typical processed aliquot size of ≈ 50 μl). The individual vial differences are indistinguishable at the quoted precision. Sampling of the population was limited by the

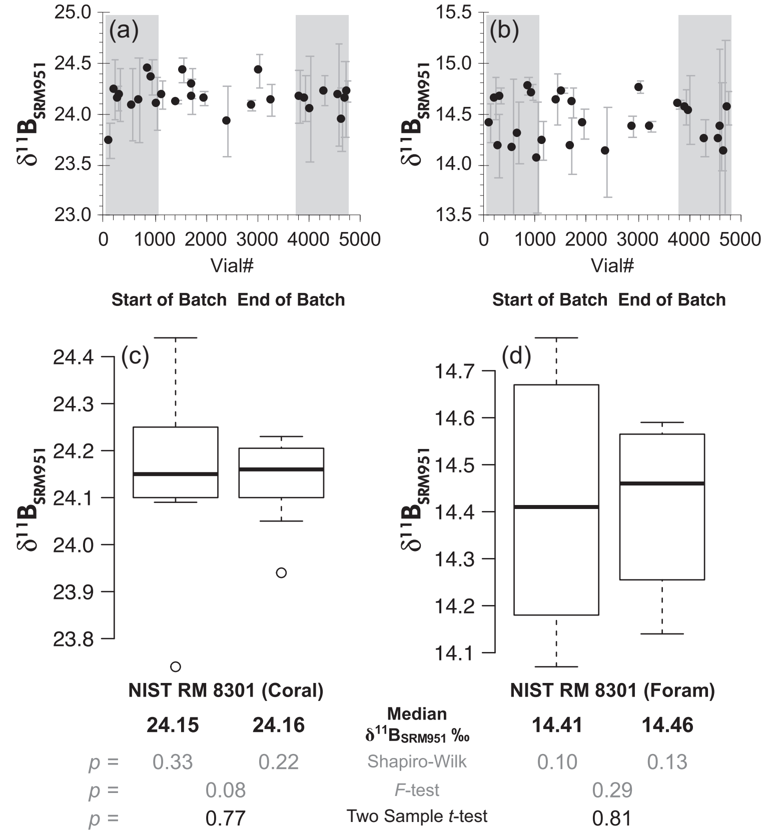


Figure 3. $\delta^{11}B_{SRM951}$ **homogeneity testing of NIST RM 8301 (Coral) and NIST RM 8301 (Foram) across the batches of seventeen racks. Panels (a) and (b) plot vial** $\delta^{11}B_{SRM951}$ **mean (data from all participants; range bars represent 2*s* of replicates) arranged by order dispensed (1 to 5000). Grey bars highlight vials from start (first 24% of vials;** $n = 9$**) and end (last 24% of vials;** $n = 8$**) of dispensing sequence. Box plots in panels (c) and (d) show median and interquartile range of vial** $\delta^{11}B_{SRM951}$ **from start and end of batch. Shapiro-Wilk and *F*-tests show data subsets are, respectively, normally distributed and of similar variance (**$p > 0.05$**). A parametric two-sample *t*-test was therefore applied, which revealed no statistically significant (**$p > 0.05$**) difference between mean** $\delta^{11}B_{SRM951}$ **across each batch of RM.**

labour-intensive nature of boron isotope data collection. Shapiro-Wilk and *F*-tests show data subsets are, respectively, normally distributed and of similar variance ($p > 0.05$). A two-sample *t*-test comparing available data could therefore be performed that showed no statistically significant difference ($p > 0.05$) could be resolved between mean $\delta^{11}B_{SRM951}$ values for vials at the start and end of the batch and speak for homogeneity of the reference materials.

Stability of reference materials is also of great importance; however, as yet insufficient time has elapsed for a rigorous investigation into NIST RM 8301 stability. Release of these solutions for use by the community, without lengthy delay, was considered a priority. We note that many inter-laboratory participants have continued to use these solutions for more than 1 year and have obtained similar results to those that they report here. Full stability testing will be performed by NIST at a later date, with results made available on the NIST website (https://www.nist.gov/srm) along with recommendations of storage conditions.

NIST RM 8301 (Foram) reproducibility issues: Multiple laboratories using the well-established ion exchange column matrix separation technique reported poorer reproducibility when using the lower B mass fraction NIST RM 8301 (Foram) solution. As an example, NIST results for this solution varied by ± 0.55‰ (2*s*) across all replicates in contrast with ± 0.31‰ variation across replicates of the higher boron mass fraction NIST RM 8301 (Coral) solution, despite a similar mass of boron being loaded. Even the lower boron concentration solution NIST RM 8301 (Foram) has a relatively large boron mass fraction at 2 µg g^{-1}. Therefore, we consider true heterogeneities within a single vial solution to be unlikely. Furthermore, the impact of the

Table 5.
Summary of inter-laboratory boron isotope results for NIST RM 8301

Lab	Matrix removal	Vial	NIST RM 8301 (Coral)		NIST RM 8301 (Foram)	
			Mean vial $\delta^{11}B$ (‰)	Lab mean $\delta^{11}B$ (‰)	Mean vial $\delta^{11}B$ (‰)	Lab mean $\delta^{11}B$ (‰)
NIST (1)	Amberlite columns	2A2	24.15	24.14	14.18	14.24
		3A2	24.09		14.17	
		3G14	24.13		14.31	
		4K11	24.10		14.07	
		5A2	24.18		14.23	
		15A2	24.05		14.54	
		16A2	24.23		14.26	
		17A2	24.19		14.25	
		17G15	24.15		14.14	
2	Amberlite Columns	14E16	24.17	24.16	14.59	14.64
		1T3	24.18		14.67	
		6A3	24.12		14.64	
3	Amberlite Columns	6Q16	24.17	24.18	14.18	14.44
		14M7	24.15		14.57	
		17J13	24.22		14.56	
4	Amberlite Columns	4A17	24.44	24.43	14.77	14.76
		6G14	24.43		14.73	
		11K5	24.42		14.76	
5	Amberlite Columns	1N12	24.25	24.30	14.65	14.66
		4F10	24.36		14.71	
		7B3	24.29		14.61	
6	Amberlite Columns	12G5	24.13	24.12	14.38	14.38
		11B8	24.08		14.37	
		7O8	24.15		14.40	
7	Microsublimation	1I4	23.74	23.87	14.41	14.30
		9G8	23.92		14.12	
		17C12	23.94		14.38	
Interlab consensus reference value				**24.17**		**14.51**
Expanded uncertainty				**± 0.18**		**± 0.17**
Overall interlab mean				24.17		14.49
2*s*				0.35		0.39

NIST reference values and 95% expanded uncertainties (reported at the bottom of the table in bold) were determined from reported laboratory data using the DerSimonian-Laird analysis method within the NIST Consensus Builder (Koepke *et al.* 2017). 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 repeatability and may not include all sources of uncertainty (May *et al.* 2000).

total procedural blank is also considered to be negligible (pg level) compared with the high mass of boron used per analysis (> 100 ng; *cf.* foraminifera samples often < 10 ng of B; Foster 2008). However, $^{11}B/^{10}B$ ratios are known to fractionate strongly on ion exchange columns unless near complete recovery of boron (> 99%) is achieved (Lemarchand *et al.* 2002). Boron can be lost at two stages during matrix separation (i) during sample loading and (ii) during sample elution steps; both being potentially detrimental to the isotopic integrity of the sample. While elution tails at NIST were all found to be low (less than 0.11 ng of B) and boron recovery from the columns was considered complete (> 100 ng loaded; tail < 0.1% of sample), boron loss during loading was not accurately quantified; thus, small amounts of B loss cannot be discounted.

Significant loss of boron during loading of foraminiferal calcite samples using these techniques has not been documented previously; however, the acid concentration in these RMs (21% by volume; 3 mol l^{-1} HNO_3) is considerably higher than that commonly used to dissolve marine carbonates (e.g., 0.5 mol l^{-1} HNO_3). A greater volume of buffer is therefore required to raise the pH of the solution before loading onto columns (20:1; *cf.* 2:1 Foster 2008). Rapid loading of high volume (> 1 ml) samples will cause solutions to pass quickly through the resin, reducing sample–resin interaction times and

Table 6.
Summary of inter-laboratory trace element determination of NIST RM 8301

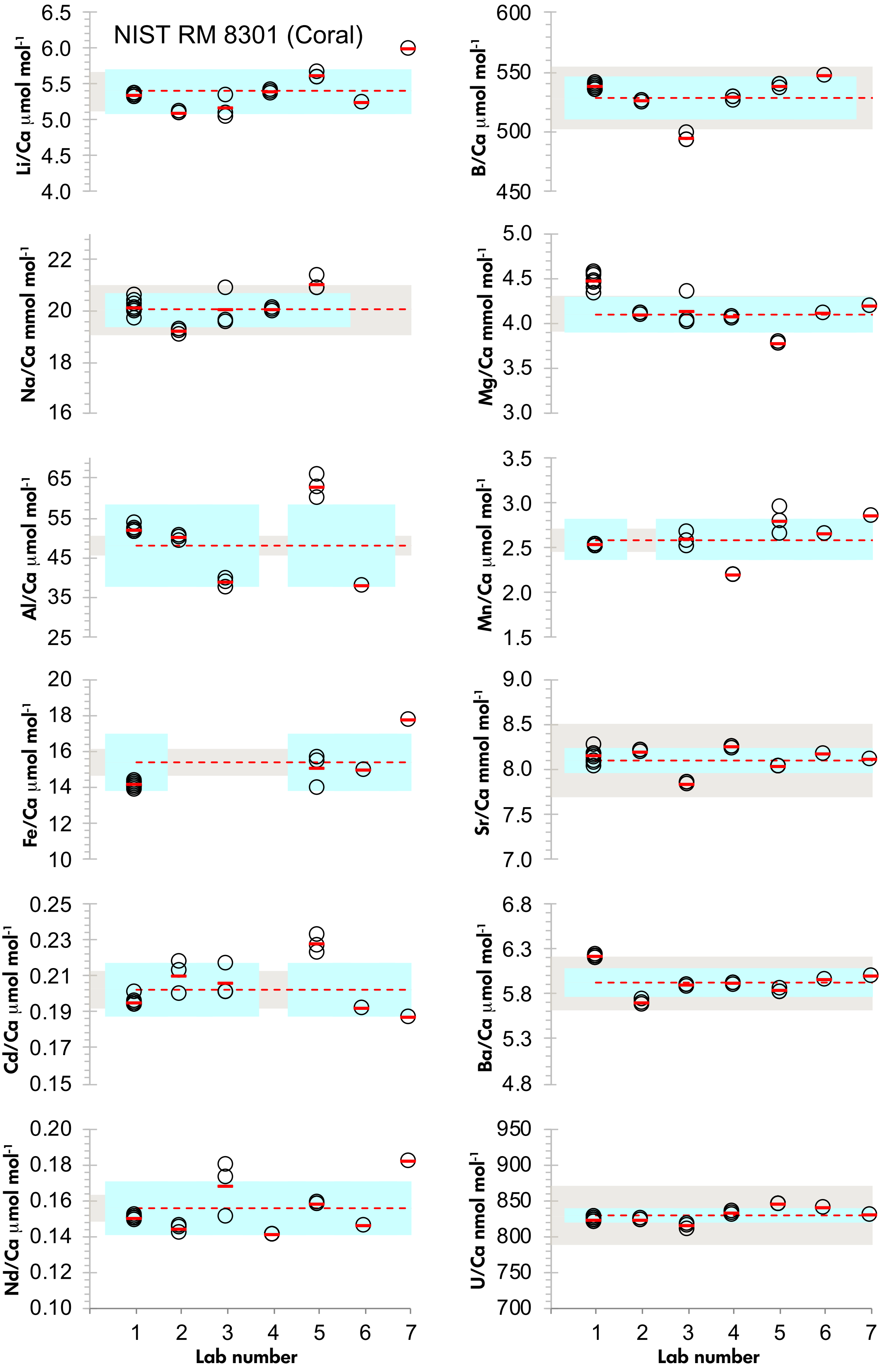
	n	Li/Ca		B/Ca		Na/Ca		Mg/Ca		Al/Ca		Mn/Ca		Fe/Ca	
		µmol mol^{-1}	% RSD	µmol mol^{-1}	% RSD	mmol mol^{-1}	% RSD	mmol mol^{-1}	% RSD	µmol mol^{-1}	% RSD	µmol mol^{-1}	% RSD	µmol mol^{-1}	% RSD
NIST RM 8301 (Coral)															
NIST Lab 1	9	5.34	0.3	537.0	0.4	20.08	1.3	4.46	1.8	51.85	1.2	2.52	0.3	14.09	1.1
Lab 2	3	5.09	0.4	525.2	0.2	19.15	0.5	4.09	0.2	49.82	1.4				
Lab 3	3	5.15	3.1	494.2	0.7	19.99	3.7	4.13	4.6	38.63	3.0	2.58	3.0		
Lab 4	3	5.39	0.3	528.0	0.3	20.01	0.2	4.06	0.1			2.19	0.0		
Lab 5	3	5.61	0.7	537.9	0.3	20.99	1.3	3.77	0.1	62.54	4.7	2.79	5.5	15.01	6.1
Lab 6	1	5.23	1.0	546.5	1.6			4.10	1.0	37.78	3.1	2.65	3.8	14.88	16.2
Lab 7	1	5.99	3.3					4.18	1.1			2.85	4.9	17.76	5.5
Mean		**5.40**		**528.1**		**20.04**		**4.11**		**48.13**		**2.59**		**15.44**	
1*s*		0.31		18.3		0.65		0.20		10.27		0.23		1.60	
% RSD		5.8		3.5		3.3		4.9		21.		9.0		10.4	
Number of laboratories		7		6		5		7		5		6		4	
NIST RM 8301 (Foram)															
NIST Lab 1	9	8.90	1.2	143.5	2.3	2.99	1.8	2.87	1.9	97.61	0.9	50.39	0.1	24.17	1.3
Lab 2	3	8.59	0.5	123.5	1.7	2.95	0.5	2.63	0.4	101.07	2.7	50.01	0.2	26.49	1.4
Lab 3	3	8.76	2.1	136.8	1.7	3.02	0.3	2.60	0.3	74.30	5.7	50.04	0.2		
Lab 4	3	9.20	0.1	143.1	0.6	3.07	0.2	2.64	0.1			44.57	0.1		
Lab 5	3	9.34	2.3	141.6	2.0	3.25	1.5	2.38	0.3	109.16	6.5	50.58	0.3	25.19	2.0
Lab 6	1	8.75	1.0	145.1	2.2			2.59	1.4	72.41	2.8	50.19	0.9	23.56	4.4
Lab 7	1	9.52	1.1					2.60	2.1			50.01	2.0	27.70	2.2
Mean		**9.01**		**138.9**		**3.06**		**2.62**		**90.91**		**49.40**		**25.42**	
1*s*		0.35		8.1		0.12		0.14		16.58		2.14		1.69	
% RSD		3.9		5.8		3.9		5.4		18.2		4.3		6.6	
Number of laboratories		7		6		5		7		5		7		5	

	n	Sr/Ca		Cd/Ca		Ba/Ca		Nd/Ca		U/Ca		Li/Mg	
		mmol mol^{-1}	% RSD	µmol mol^{-1}	% RSD	µmol mol^{-1}	% RSD	µmol mol^{-1}	% RSD	nmol mol^{-1}	% RSD	mmol mol^{-1}	% RSD
NIST RM 8301 (Coral)													
NIST Lab 1	9	8.14	0.9	0.19	1.2	6.21	0.2	0.15	0.5	822.6	0.3	1.20	1.7
Lab 2	3	8.19	0.1	0.21	4.4	5.69	0.7	0.14	1.6	822.3	0.2	1.25	0.3

Table 6 (continued).
Summary of inter-laboratory trace element determination of NIST RM 8301

	n	Sr/Ca		Cd/Ca		Ba/Ca		Nd/Ca		U/Ca		Li/Mg	
		mmol mol^{-1}	**% RSD**	**µmol mol^{-1}**	**% RSD**	**µmol mol^{-1}**	**% RSD**	**µmol mol^{-1}**	**% RSD**	**nmol mol^{-1}**	**% RSD**	**mmol mol^{-1}**	**% RSD**
Lab 3	3	7.83	0.1	0.21	4.6	5.88	0.1	0.17	9.0	813.4	0.5	1.25	1.6
Lab 4	3	8.24	0.2			5.90	0.2	0.14	0.0	831.0	0.3	1.33	0.1
Lab 5	3	8.03	0.0	0.23	2.3	5.83	0.3	0.16	0.3	844.4	0.1	1.49	0.8
Lab 6	1	8.17	0.9	0.19	1.5	5.94	0.9	0.15	4.0	840.0	1.1	1.28	1.3
Lab 7	1	8.11	0.8	0.19	8.5	5.99	3.6	0.18	11.2	828.6	2.8	1.43	3.3
Mean		**8.10**		**0.20**		**5.92**		**0.16**		**828.9**		**1.32**	
1*s*		0.13		0.01		0.16		0.01		10.7		0.11	
% RSD		1.7		7.3		2.7		9.6		1.3		8.1	
Number of laboratories		7		6		7		7		7		7	
NIST RM 8301 (Foram)													
NIST Lab 1	9	1.39	0.6	0.55	0.6	4.06	0.4	5.04	0.3	67.9	0.5	3.11	1.9
Lab 2	3	1.35	0.0	0.60	0.3	3.88	0.6	5.27	0.2	68.9	0.5	3.26	0.8
Lab 3	3	1.31	0.3	0.60	0.6	3.96	1.5	5.10	1.7	70.6	6.4	3.37	2.4
Lab 4	3	1.35	0.1			3.74	0.0	4.71	0.1	67.1	0.3	3.48	0.1
Lab 5	3	1.32	0.4	0.63	0.7	3.77	0.7	5.22	0.5	69.2	0.4	3.93	2.6
Lab 6	1	1.32	1.1	0.56	1.0	3.90	1.0	4.93	0.7	68.6	1.2	3.38	1.2
Lab 7	1	1.36	0.6	0.56	8.6	3.97	2.8	5.15	2.7	68.6	2.9	3.66	2.1
Mean		**1.34**		**0.58**		**3.90**		**5.06**		**68.7**		**3.45**	
1*s*		0.03		0.03		0.11		0.19		1.1		0.27	
% RSD		2.2		5.3		2.9		3.8		1.6		7.8	
Number of laboratories		7		6		7		7		7		7	

Mean values and percentage relative standard deviation based on the replicate analysis of *n* vials are shown. Where only one vial was measured within laboratory, precision is based on replicate analysis of the same vial.


NIST RM 8301 (Coral)
Li/Ca µmol mol⁻¹
6.5
6.0
5.5
5.0
4.5
4.0
B/Ca µmol mol⁻¹
600
550
500
450
Na/Ca mmol mol⁻¹
22
20
18
16
Mg/Ca mmol mol⁻¹
5.0
4.5
4.0
3.5
3.0
Al/Ca µmol mol⁻¹
65
55
45
35
25
Mn/Ca µmol mol⁻¹
3.5
3.0
2.5
2.0
1.5
Fe/Ca µmol mol⁻¹
20
18
16
14
12
10
Sr/Ca mmol mol⁻¹
9.0
8.5
8.0
7.5
7.0
Cd/Ca µmol mol⁻¹
0.25
0.23
0.21
0.19
0.17
0.15
Ba/Ca µmol mol⁻¹
6.8
6.3
5.8
5.3
4.8
Nd/Ca µmol mol⁻¹
0.20
0.18
0.16
0.14
0.12
0.10
U/Ca nmol mol⁻¹
950
900
850
800
750
700
1
2
3
4
5
6
7
Lab number
Lab number

potentially resulting in incomplete and variable boron adherence on columns. Other participating laboratories loading only 300 µl maximum per column and step did not encounter these problems.

Occurrences of some boron loss during loading may account for the slightly lower mean $\delta^{11}B_{SRM951}$ value for NIST RM 8301 (Foram) measured at NIST (14.24‰) with the lowest replicate measurement more than 0.8‰ lower than the inter-laboratory consensus reference value of 14.51‰. This effect was less pronounced or absent in analyses of the higher B mass fraction in NIST RM 8301 (Coral) (NIST mean only 0.03‰ lower than consensus reference value) where smaller volumes of RM were needed to achieve ≈ 100 ng of B, keeping total loading volumes low (≈ 300 µl). We note, however, that removal of the NIST RM 8301 (Foram) vials for which NIST $\delta^{11}B_{SRM951}$ values were most variable (> ± 0.5‰, 2*s*; 3A2, 4K11, 17A2, 17G15) increases the NIST mean $\delta^{11}B_{SRM951}$ value of NIST RM 8301 (Foram) by only 0.06‰ and thus has little impact on the overall consensus values.

Although the influence on final consensus values is considered small, compiled data here suggest the potential impact of incomplete boron loading onto columns on individual replicates of NIST RM 8301 (Foram) is potentially large, so RM 8301 users should evaluate their routine B separation methods carefully before processing the material. This highlights the importance of adequate buffering of samples prior to column loading and suggests that loading of samples low in B (e.g., dissolved foraminifera) should be performed slowly, in sequential small volumes (e.g., 100 µl), to maximise initial boron adhesion to the resin.

Trace elements

Trace element determinations were contributed by seven participant laboratories (Table 6). As laboratories were only asked to run their typical method for carbonate samples, not all laboratories were able to provide data for all trace elements that were added during the preparation of these RMs. We therefore only present means of trace element values provided by four or more laboratories as summarised in Figures 4 and 5.

For all analytes investigated here, the variance of measurements across vials within each laboratory (relative standard deviation up to ± 9% for Nd/Ca and ± 16% for Fe/Ca, but typically ± 2%; 1*s*) was better than the overall variance of elemental ratios in these RMs reported among laboratories (up to ± 21% for Al/Ca, but typically ± 6%; 1*s*). Similarly, poor reproducibility of values across laboratories was observed in the inter-laboratory study for carbonate powders JCp-1 and JCt-1 (Li/Ca, B/Ca, Ba/Ca, U/Ca, > ± 10% (1*s*); Hathorne *et al.* 2013). This struggle for accuracy, particularly for challenging to measure elements like Al, further highlights the need for reference materials for this type of analyses. While analytical offsets across laboratories for any trace element have the potential to bias interpretation of palaeoceanographic results, here we consider the impact on commonly used temperature proxies in corals and foraminifera Mg/Ca, Li/Mg (i.e., (Li/Ca)/(Mg/Ca)), and Sr/Ca that typically reproduced well within each laboratory.

The ambient seawater temperature in which biogenic carbonates were formed is routinely estimated using these trace element ratios (given in mmol mol^{-1}) and calibration equations such as:

$$T(^\circ C) = (\ln(Li/Mg) - 1.69)/-0.05 \qquad (2)$$

$$T(^\circ C) = 99 - 7.9 \times Sr/Ca \qquad (3)$$

$$T(^\circ C) = \ln(Mg/Ca)/0.061 \qquad (4)$$

Equations (2) (Stewart *et al.* 2020) and (3) (Alpert *et al.* 2016) are based on multiple species of coral. Equation (4) (Gray and Evans 2019) is a multispecies calibration of planktonic foraminifera simplified by assuming pH and salinity values of 8 and 35 psu, respectively. Mean Li/Mg ratios of NIST RM 8301 (Coral) for each laboratory vary between 1.20 and 1.49 mmol mol^{-1}. These measured Li/Mg values would yield reconstructed seawater temperatures of 30.2 and 25.8 °C, respectively, if treated like a true coral sample (Equation 2). Thus, we find inter-laboratory measurement discrepancy yields potentially more than 4 °C inaccuracy in reconstructed temperature, even before calibration uncertainty is incorporated. Inter-laboratory

Figure 4. Trace element results for NIST RM 8301 (Coral). NIST lab is number 1, other laboratories have been anonymised. Circles and thick red bars denote, respectively, values measured for each vial and the mean value for that laboratory. The dashed red line shows the overall inter-laboratory mean of all contributing labs, blue shaded band shows 1 standard deviation of the laboratory means, grey shaded band is the mean plus or minus an arbitrary 5% to help demonstrate the varying spread in results for each element. Laboratory numbers differ from those in Figure 2.

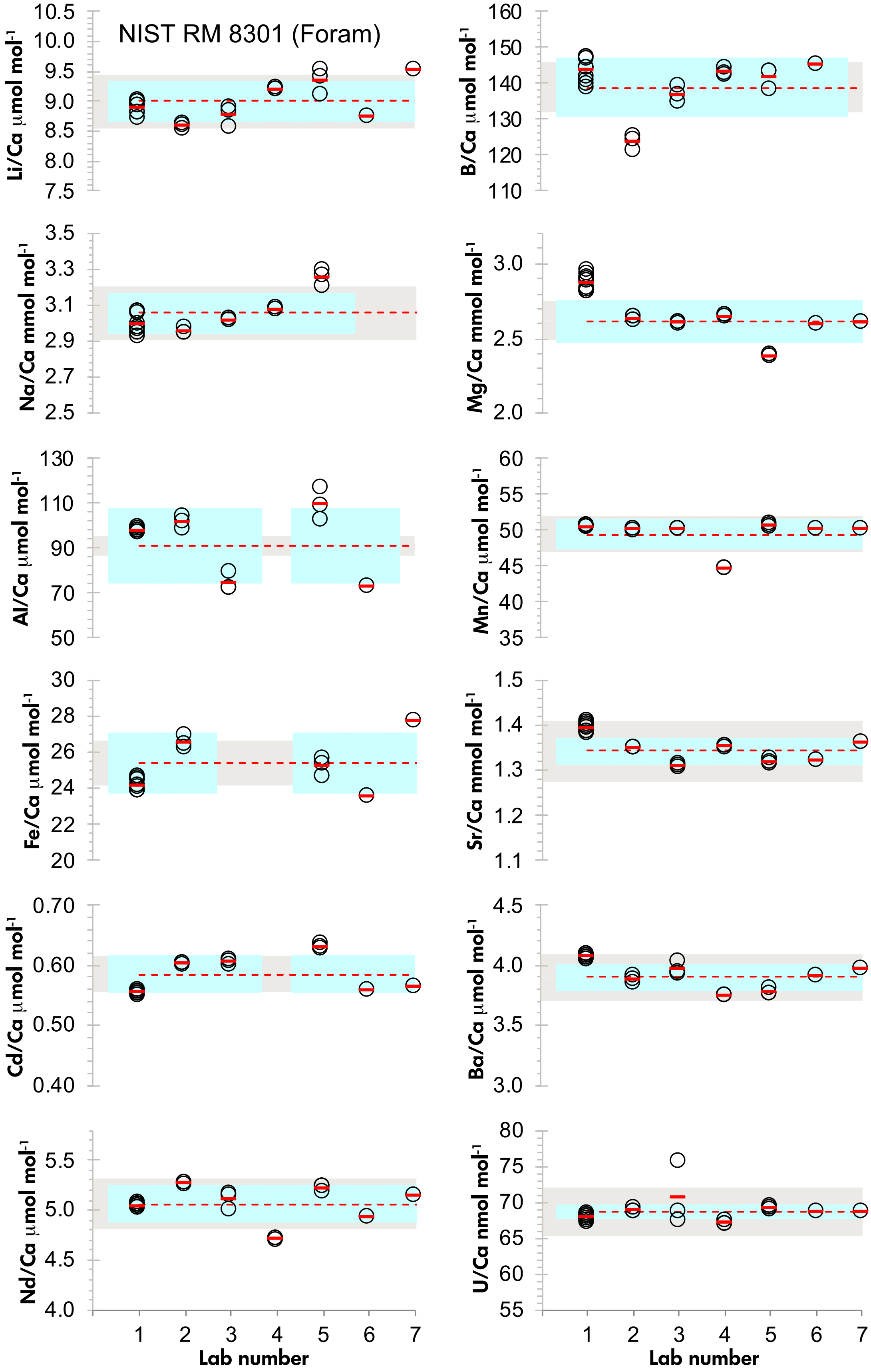


Figure 5. Trace element results for NIST RM 8301 (Foram). Symbols as in Figure 4.

discrepancies therefore far outweigh the approximate ± 1.5 °C calibration uncertainty typically quoted for this proxy (Case *et al.* 2010, Montagna *et al.* 2014, Fowell *et al.* 2016, Cuny-Guirriec *et al.* 2019, Stewart *et al.* 2020). Laboratory mean Sr/Ca ratios for NIST RM 8301 (Coral) vary by only ± 1.7% (1*s*); however, using Equation (3), such discrepancy results in more than 3 °C difference in calculated seawater temperatures. We note however that Sr/Ca values in NIST RM 8301 (Coral) (≈ 8.1 mmol mol^{-1}) are slightly lower than typical coral values (≈ 9 mmol mol^{-1}); thus, reconstructed temperatures based on this calibration (≈ 35 °C) are higher than those typically found in the surface ocean. Similarly, for NIST RM 8301 (Foram), laboratory mean Mg/Ca values vary by ± 5.4% (1*s*); therefore, using Equation (4), implied seawater temperatures would vary by more than 3 °C (maximum 17.3 °C; minimum 14.2 °C). This again exceeds typically quoted calibration uncertainty for temperature estimated from foraminiferal Mg/Ca (± 1.2 °C; Gray and Evans 2019).

This exercise highlights the large uncertainties that are potentially introduced to palaeoceanographic proxy reconstructions by discrepancies between laboratories and underestimated measurement uncertainties. With good within laboratory precision, but little accuracy with respect to known reference materials, data produced by a single methodology will yield results that elucidate robust relative palaeoceanographic changes (e.g., temperature rise or fall); however, absolute target values may be inaccurate. Such inaccuracies become especially significant in cases where paired carbonate trace element values are used to assess temperature-induced temporal changes in pK_B^* for δ^{11}B-based pH or $p\text{CO}_2$ records (e.g., Martínez-Botí *et al.* 2015). Commutability of data is particularly important in calibration studies that set the ground work for proxy application and where data are often compiled from multiple laboratories (e.g., Montagna *et al.* 2014, Fowell *et al.* 2016, Marchitto *et al.* 2018, Cuny-Guirriec *et al.* 2019, Stewart *et al.* 2020).

Summary

We used boron isotope data compiled from seven leading research laboratories to assign respective NIST reference values and 95% expanded uncertainties for $\delta^{11}\text{B}_{\text{SRM951}}$ of 24.17‰ ± 0.18‰ and 14.51‰ ± 0.17‰ to the new marine carbonate reference materials NIST RM 8301 (Coral) and NIST RM 8301 (Foram). These reference values were assigned by consensus approach and by their nature do not necessarily account for all sources of uncertainty. However, these solutions were found to be homogeneous across the batches of vials and had characteristics suitable for use as analytical quality controls.

Trace element data were provided by seven participants, and inter-laboratory consensus information values for key trace elements in marine carbonates that include Li/Ca, B/Ca, Na/Ca, Mg/Ca, Al/Ca, Mn/Ca, Fe/Ca, Sr/Ca, Cd/Ca, Ba/Ca, Nd/Ca and U/Ca are given here. For all analytes in question, reported trace element values for RMs were considerably more variable across laboratories than reported precision based on a single methodology. The simulated marine carbonate solutions comprising NIST RM 8301 will not be subject to CITES limitations restricting distribution of authentic biogenic material and will help minimise analytical artefacts caused by sample pre-treatment in respective laboratories (e.g., oxidative cleaning and/or dissolution; Gutjahr *et al.* 2020). NIST RM 8301 (Foram) and NIST RM 8301 (Coral) are therefore valuable tools for evaluating the quality of marine carbonate geochemical analyses, thus improving confidence in palaeoceanographic interpretation.

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Data availability statement

All inter-laboratory data are available in the tables within this paper. Reported NIST reference values for $\delta^{11}\text{B}_{\text{SRM951}}$ along with the element/calcium ratios given here are based only on the data contained in the original NIST Report of Investigation issued at the time of this publication. Updates to the officially assigned values for NIST RM 8301 can be accessed by via the latest version of the NIST Report of Investigation for *RM 8301 Boron Isotopes in*

Marine Carbonate (Simulated Coral and Foraminifera Solutions), available on the NIST SRM website, https://www.nist.gov/srm. Any mention of commercial products is to specify adequately the analytical procedures used. It does not imply recommendation or endorsement by NIST or that the products mentioned are necessarily the best available for the intended purpose. Handling of NIST RM 8301 solutions will result in possible exposure to nitric acid, and appropriate personal protective equipment should be used.

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