

Boron isotope ratio determination in carbonates *via* LA-MC-ICP-MS using soda-lime glass standards as reference material

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A new *in situ* method using LA-MC-ICP-MS (193 nm excimer laser) for the determination of stable boron isotope ratios ($\delta^{11}\text{B}$) in carbonates was developed. Data were acquired *via* a standard sample standard bracketing procedure typically providing a reproducibility of 0.5‰ (SD) for samples containing 35 ppm of boron. A single ablation interval consumed about 5 μg of sample corresponding to about 0.2 ng of boron. The major finding was the similar instrumental fractionation behaviour of carbonates, soda-lime glass and sea salt with respect to boron isotopes. As no matrix induced offset was detectable between these distinct materials we propose the use of NIST glasses as internal standards for boron isotope ratio measurements *via* LA-MC-ICP-MS. This finding overcomes the problem of a missing matrix matched carbonate standard for *in situ* boron isotope studies. As a first application a set of coral samples from a culturing experiment was analysed. $\delta^{11}\text{B}$ values range from 19.5 to 25‰ depending on the pH of the water used in the particular treatment. This is in good agreement with the results of earlier studies.

Introduction

The element boron has two stable isotopes, ^{10}B (~19.9%) and ^{11}B (~80.1%), respectively. Boron isotope ratio data are usually reported relative to NIST-SRM951 using the δ -notation:

$$\delta^{11}\text{B}[\text{‰}] = 1000 \times \frac{(^{11}\text{B}/^{10}\text{B})_{\text{sample}}}{(^{11}\text{B}/^{10}\text{B})_{\text{NIST951}}} - 1000$$

All $\delta^{11}\text{B}$ data reported in this paper are expressed relative to the NIST-SRM951 too. Uncertainties are given as SD in brackets for the last significant digits (*e.g.* 20.41(33) means 20.41 ± 0.33 (SD)).

Boron is a volatile element with a high relative mass difference between its isotopes of about 10%. As a consequence it is strongly fractionated in different major reservoirs of the earth.

Of particular interest in marine geochemistry is the fractionation of boron isotopes during the precipitation of carbonates from seawater ($\delta^{11}\text{B}_{\text{seawater}} = 39.5\text{‰}$). Boron is present in seawater in two different species: $\text{B}(\text{OH})_3$ dominating at low pH and $\text{B}(\text{OH})_4^-$ at high pH, respectively.¹ Between the two species a strong equilibrium fractionation of about 20–30‰ exists.^{2–5}

Carbonates (calcite, aragonite) precipitated from seawater are believed to incorporate primarily the borate ion $\text{B}(\text{OH})_4^-$ into their lattice.^{6–10} Thus, the boron isotopic signature of $\text{B}(\text{OH})_4^-$ as a consequence of its pH dependent abundance and equilibrium fractionation relative to $\text{B}(\text{OH})_3$ is recorded in the precipitate.

In recent years several studies focussed on the application of this systematic to reconstruct seawater pH from $\delta^{11}\text{B}$ data.¹¹

To a certain degree many biogenic marine carbonates deviate from the $\delta^{11}\text{B}$ –pH relation determined for inorganically precipitated carbonates.¹²

The latter is a result of the influence of biological control on the process of calcification referred to as “vital effects”. On the one hand this leads to a need for species-specific calibrations, on the other hand it provides the fascinating option to study the process of biomineralisation itself.

Several analytical techniques for the determination of boron isotopes were used so far:

- (1) thermal ionisation mass spectrometry (N-TIMS,^{7,13–15} P-TIMS^{16,17}),
- (2) inductively coupled plasma mass spectrometry (MC-ICP-MS,^{18,20} LA-MC-ICP-MS)¹⁹ and
- (3) secondary ion mass spectrometry (SIMS).^{21–23}

The TIMS method is perhaps the most commonly used approach to date. TIMS and MC-ICP-MS provide the highest precision and accuracy.²⁴ The strength of the third technique is the high spatial resolution of several μm measuring directly at the solid sample surface.

A recent inter-laboratory calibration study revealed certain limitations of the different analytical methods reporting a significant spread in the results reported by the participating labs.²⁴

There are several analytical challenges inherent in boron isotope measurements. Unlike other elements (*e.g.* Ca, Pb, U, ...) boron just has two stable/long-lived isotopes which prevents the application of double- or triple-spike methods. This fact is a serious burden for all methods where a separation of boron from the sample matrix is required as no control is possible for any fractionation induced by the sample separation procedure. It is also a limitation for methods where a strong variable fractionation during the measurement occurs. Contamination is another issue for boron analyses. In particular for the *in situ* $\delta^{11}\text{B}$ measurements in carbonates the major limitation so far was the absence of any solid-state matrix standard.

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The stated obstacles and limitations justify the need for improved analytical methods to further develop and strengthen applications of boron isotopes in geochemistry.

Experimental

Standard and sample preparation

Three types of standards were used in this study:

- (1) soda-lime glass SRM (NIST610/611/612),
- (2) carbonate pressed powder pellets (TIMS calibrated sponge aragonite Ce95-1, 125 ky old coral aragonite FCA) and
- (3) seawater evaporates (NIST-SRM951 boric acid mixed with IAPSO seawater standard, NASS-5 seawater standard).

All carbonate samples were bleached to remove organic compounds using 10% NaClO (1% active chlorine). The bleaching was done over a period of 3 days, renewing the NaClO each day including ultrasonication for about 10 min. To finally remove NaClO the samples were washed several times using MilliQ water (18.2 MΩ cm⁻¹). This water was adjusted to a pH ≈ 9 by adding small amounts of NH₄OH to prevent dissolution of the carbonates.

Carbonate powder standards Ce95-1 and FCA were pressed as pellets. For easier handling and stabilisation these pellets were set into epoxy resin. A blank pellet of the epoxy resin was prepared too. Ablation of this pellet yielded no detectable boron signal. After removing the surface contamination with the first ~10 shots the signals of both boron isotopes decayed rapidly to the background level. The rest of the 900 shots just showed typical background signals.

The TIMS calibration measurement was done on a split from a larger Ce95-1 bulk sample which was bleached according to the described procedure. From another split of this already bleached bulk powder the pellet for this study was prepared. Thus, the material used for both techniques was completely equal.

A set of *Pocillopora* sp. coral aragonite samples from a culturing experiment carried out at the Hebrew University Jerusalem was prepared as a first test application. The corals grew in aquaria at different pH levels (pH = 7.8–8.3). Details of the culturing experiment will be presented elsewhere. Despite from bleaching no further treatment was done with these samples.

Two sea salt evaporite standards were prepared from seawater (IAPSO seawater standard). 2 ml of seawater were evaporated in a vacuum cabinet at 20 °C. One of the two solutions was enriched in boron by a factor of 20 using boric acid (NIST-SRM951).

Instrumentation, data acquisition and evaluation

All measurements were performed on a Thermo Fisher MC-ICP-MS AXIOM (originally designed and manufactured by VG) connected to an ESI New Wave Research UP193FX excimer laser ablation system equipped with an ESI New Wave Research LFC (large format cell). Typical operation parameters can be found in Table 1.

Data for amu10 and amu11 were simultaneously collected using the outermost Faraday Cups (L4 and H4). For the data reduction no separate baseline measurement was carried out,

Table 1 Instrumental parameters

AXIOM MC-ICP-MS	
Cool gas	14 l min ⁻¹
Auxiliary gas	1.8 l min ⁻¹
Nebulizer gas	0.9 l min ⁻¹ (Ar)
RF power	1250 W
Reflected power	3 W
Accelerating voltage	4972 V
Cones	R.A. Chilton RAC19/RAC705
Resolution	500res
UP193FX	
Ablation cell gas	0.6 l min ⁻¹ (He)
Spot size	100–150 μm
Fluence	2.5 J cm ⁻²
Repetition rate	30 Hz
Scan mode	Spot analysis (500–900 shots)

because the breaks between ablation periods were sufficient to collect the respective gas blank data.

Our method differs from the published laser-based analytical method¹⁹ for boron isotope ratio determination using an AXIOM MC-ICP-MS, too, threefold:

- (1) use of an 193nm excimer in contrast to a 213nm solid-state LA system,
- (2) data collection using Faraday Cups instead of multi-ion counting and
- (3) different data reduction.

Despite the fact that some earlier studies^{19,20} already made clear statements on the absence of disturbing interferences on both masses this is still disputed in the community. Thus, we did collect for both spectral areas the signals in low (500 res) and high resolution (5500 res) with and without ablation. The results are summarized in Fig. 1.

Prior to analysis all areas intended to be analysed were pre-ablated (3 s@10 Hz; 30 shots ~3 μm depth) to remove contaminations from the sample surface.

Running the laser at a repetition rate of 30 Hz using a spot diameter of 150 μm provided a total B signal of about 70 mV for a sample containing 35 ppm of boron. During one ablation interval of 30 s the laser excavated to a depth of about 100 μm corresponding to a sample amount of 5 μg (~0.2 ng total B).

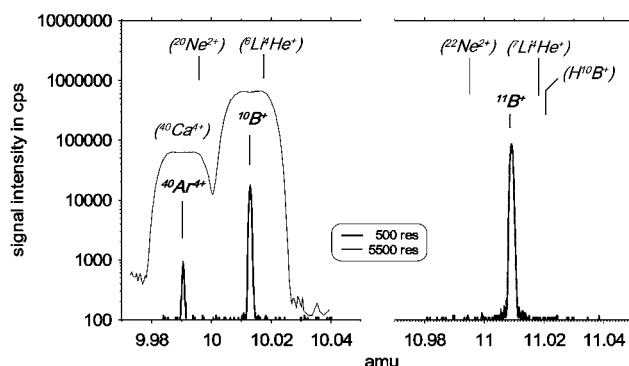


Fig. 1 Spectra around ¹⁰B and ¹¹B in low and high resolution mode. Besides the boron peaks the ⁴⁰Ar⁴⁺ could be clearly identified *via* its exact mass in the high-resolution spectra. The latter peak did not change regardless of the ablation running or not indicating no additional occurrence of ⁴⁰Ca⁴⁺ from ablated material (NIST 612). Other possible interferences (italic in brackets) indicated by their expected position in the spectra were not observed.

After each ablation period the laser was paused for 60 s. Due to the superior washout characteristic of the LFC ablation cell the signal dropped to the baseline level within less than 3 s. We did not observe any deviations from this performance depending on the position within the LFC but excluded the area closer than 1 cm from the outer boundaries.

Test measurements comparing spot and raster analysis revealed no measurable differences (while keeping the aspect ratio during the spot ablation below 1). As this method is supposed to be used for high spatial resolution work we continued with spot ablation.

Measurements were performed using the standard sample standard bracketing procedure. Typically, one analysis included 7 ablation periods of the sample bracketed by 8 ablation periods of the standard (see example in Fig. 2). Thus, the whole analysis of one sample took less than 30 min. Data were collected using integration times of 6 s.

Initially all measurements were done using the Ce95-1 as bracketing standard as this carbonate was independently determined *via* TIMS for its boron isotopic composition. The only exception was the first test of IAPSO *vs.* IAPSO–NIST–SRM951 mixture.

After establishing the constant isotopic difference between Ce95-1 and the NIST glass standards we did switch to the NIST SRM610 glass as bracketing standard due to its higher boron concentration (improved internal precision).

Data collected during one ablation period and the backgrounds prior and after ablation were evaluated as single data-sets using the procedure initially developed for laser ablation Cl and Sr isotope ratio determination.^{25,26} In the case of boron isotopes the slope of the linear fit of ¹¹B plotted against ¹⁰B intensities is used, covering the whole simultaneous signal development for both isotopes from baseline to maximum intensities. The merits of this method when compared to a conventional baseline reduction were already explained in detail in the references mentioned above.^{25,26}

For samples with low boron concentration (or if high spatial resolution limitates the sample amount) a slightly modified instrumental setup was tested. Instead of using two Faraday Cups a combination of one Faraday Cup (H5: ¹¹B) and one

electron multiplier (MH: ¹⁰B) was used. When running the laser at 30 Hz with 150 μm spots both methods show a comparable precision for samples containing about 10–15 ppm of boron. For lower concentrations the multiplier/cup combination is preferable as the amplifier noise limits the precision of the cup/cup combination (*e.g.* 5–10 μV noise; ¹⁰B signal of 3 mV at 10 ppm B). On the other hand the multiplier/cup combination is limited by the fact that the multiplier is tripping frequently at signal intensities of higher than 100 000 cps restricting its use to low concentration/high spatial resolution applications. This is not due to the normal trip level ($\sim 2\,000\,000$ cps) but a consequence of the much to steep signal increase when the laser starts ablating. The latter activates the multiplier self-protection.

Results and discussion

Standards

A summary of all standard $\delta^{11}\text{B}$ results are given in Table 2. First test measurements were carried out using the two seawater evaporite standards (IAPSO; IAPSO mixed with NIST–SRM951 boric acid). For the combined standard we had to consider the contribution of both materials to the isotopic composition of the mixture. The NIST–SRM951 ($\delta^{11}\text{B} = 0\text{‰}$) contributed 95% of the total B. The IAPSO boron isotopic composition was calculated from the results of the pure and mixed evaporite standards to $\delta^{11}\text{B}_{\text{IAPSO}} = 39.2(5)\text{‰}$ (SD), being in good agreement to the published seawater value of 39.5‰ .^{27,28}

The two in-house carbonate standards Ce95-1 (recent sclerosponge aragonite) and FCA (prepared from 125 ky old fossil coral aragonite) were measured against each other. The Ce95-1 was previously measured by TIMS at IFM–GEOMAR, Kiel, Germany for boron isotopes yielding a $\delta^{11}\text{B}$ of $20.4(6)\text{‰}$ and $19.4(9)\text{‰}$ at Bristol University.²⁹ Using the first value as a reference we calibrated the FCA to $\delta^{11}\text{B} = 24.0(4)\text{‰}$ ($n = 9$) being a reasonable result for a coral.³⁰ Prior to this analysis the homogeneity of both standards was tested by ablating randomly distributed regions of the respective standard. $\delta^{11}\text{B}$ variations were below 0.5‰ in both standards, being insignificant with respect to the reproducibility of the measurements.

The influence of the amount of material introduced into the plasma by ablation was tested by firing the laser at different repetition rates (from 5 to 40 Hz) ablating the FCA standard.

Table 2 $\delta^{11}\text{B}$ results of standards analyzed

Seawater evaporites	$\delta^{11}\text{B}$ in ‰; n repeats
IAPSO	39.2(5); 4
NASS-5	39.4(3); 7
Carbonates	
Ce95-1	20.4(6) ^a
FCA	24.0(4); 9
FCA (rep. rate 5 Hz)	23.5(5); 10
FCA (rep. rate 10 Hz)	24.5(3); 10
FCA (rep. rate 20 Hz)	23.9(4); 10
FCA (rep. rate 40 Hz)	23.8(3); 10
Silicate glasses	
NIST610	−0.55(53); 16
NIST611	−0.48(31); 5
NIST612	−0.56(49); 20

^a TIMS result used for calibration (uncertainties as SD in brackets).

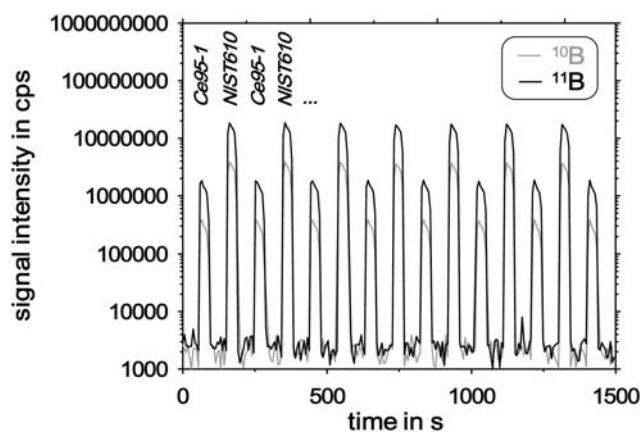


Fig. 2 One analytical run of 7 ablation periods on NIST610 (as unknown sample) bracketed by 8 ablation periods on Ce95-1 as bracketing standard. Applying the TIMS value for the Ce95-1 ($\delta^{11}\text{B} = 20.4\text{‰}$) this analysis yielded a $\delta^{11}\text{B}$ of $-0.41(39)\text{‰}$ for NIST SRM610.

The FCA used as bracketing standard was ablated at 20 Hz. No systematic influence of the repetition rate on the $\delta^{11}\text{B}$ result could be found (see Table 2) indicating the robustness of the method with respect to variable matrix loads introduced into the plasma.

Typically, during a single ablation period (900 shots, 30 Hz, 150 μm spot) the laser penetrated about 100 μm deep into the sample surface. This corresponds to a sample amount of approximately 5 μg or 0.15–0.25 ng of boron (for B concentrations of 30–50 ppm). For this sample amount the $^{11}\text{B}/^{10}\text{B}$ ratio was determined with a reproducibility of 0.5‰ (SD) determined in long-term reproducibility test measurements using NIST612 as unknown and NIST610 as bracketing standard.

To evaluate the matrix induced systematic offsets, soda-lime glass standards (NIST610, 611, and 612) were analysed using the two carbonate in-house standards for the bracketing. Despite the fact that the B concentration differs by one order of magnitude within this set of silicate standards (35–360 ppm B) the $\delta^{11}\text{B}$ values are indistinguishable for all three NIST glasses analyzed. This appears to be reasonable, pointing at the same B source used for the preparation of these standards by NIST.

NIST610 and NIST611 should yield the same result anyway as both standards were prepared from the same bulk material just cut differently with respect to thickness of the glass discs.³⁴ Nevertheless, we wanted to provide data for both standards as some databases also report values for these standards separately.

The results agree with published results obtained by solution MC-ICP-MS and TIMS, reporting $\delta^{11}\text{B}$ values ranging from -0.2 to -1.2 ‰.^{19,22,32,33} Surprisingly, this indicates that no matrix related offset seems to exist between soda-lime glass and carbonates when applying the described method. Both matrices show an identical behavior during ablation as well as evaporation and ionization within the plasma. Boron isotopes undergo the same degree of instrumental mass fractionation regardless of ablation from a carbonate or silicate glass matrix.

This is a major difference to the behaviour boron isotopes show during SIMS measurements. Typically, SIMS boron isotopic ratio results from NIST glass show an offset of about +50‰ when compared to carbonates.²² Obviously, the mass fractionation of boron isotopes during ion sputtering is to a large degree dependent on the local composition of the sample, but fairly insensitive to the latter during ablation using 193 nm deep-UV laser radiation.

This result has an important consequence. So far *in situ* B isotope studies in carbonates were difficult due to the absence of any carbonate standard being homogeneous and certified for boron isotopic ratios. In this study we showed that soda-lime glass standards like the NIST glasses may serve as an adequate reference material for this particular field of application.

With the observed matrix insensitivity for carbonates and silicate glasses we carried out further test measurements. NIST glasses were used as internal standards for boron isotope ratio determination of a freshly prepared seawater evaporite sample (produced from NASS-5 seawater standard). We measured a $\delta^{11}\text{B}$ value of 39.4(3)‰ ($n = 7$) being in accord with the published seawater value of 39.5‰. Again we found no measurable matrix induced offset.

For the three investigated matrices (CaCO_3 , Si–Na–Ca–Al glass, and NaCl) boron isotopes behave matrix-insensitive within the limits of measurement uncertainty.

Coral samples

A set of coral samples (*Pocillopora* sp.) from a lab-culturing experiment carried out at the Hebrew University Jerusalem (Israel) was used to test the application of the described method.

The corals were grown in aquaria at a constant temperature of 25 °C and five different pH levels (7.8–8.3). Branch tips (~ 5 mm in size) of the corals were bleached (see above). The aragonite precipitated during the culturing was analyzed using either FCA carbonate or NIST612 glass standard for bracketing during different analytical sessions.

Within the limits of uncertainty the results were identical regardless which standard was used. The mean results are given in Table 3.

In Fig. 3 our coral $\delta^{11}\text{B}$ data are compared with widely used theoretical and measured boron isotope fractionation curves for $\text{B}(\text{OH})_4^-$ and the results from earlier coral culturing experiments are shown.^{2,5,30,31} In general the LA-MC-ICP-MS results from this study plot in a comparable range as published coral data show a clear dependence on the ambient water pH. Nevertheless, deviations from both, the theoretical curve and results of earlier studies were found. The latter can be due to several reasons:

- (1) species-specific offsets (“vital effects”): different coral species were used in the experiments,
- (2) culturing setup: water conditions and method used for pH adjustment differ in the studies and
- (3) analytical offsets: as shown in a recent cross-calibration study $\delta^{11}\text{B}$ results from different labs show a significant variability.²⁴

The comparison of theoretical $\delta^{11}\text{B}$ fractionation curves with the coral results provides an interesting observation. The best fit for the coral data is:

$$\delta^{11}\text{B} = \frac{39.5 + 18.93 \times 10^{((8.53 - \text{pH})/0.553)}}{1 + 10^{((8.53 - \text{pH})/0.553)}}$$

This corresponds to a $^{11-10}K_{\text{B}} = 1.0202$ (close to the 1.0194 of Kakhana) and an apparent boric acid dissociation constant of $\text{p}K^* = 8.53$ (close to the $\text{p}K_{\text{B}}$ of 8.60 for seawater at 25 °C and open ocean salinity).¹ The major difference to the theoretical curves is the value of 0.553 in the denominator of the exponents. This parameter can be interpreted as the activity factor $a_{\text{B}(\text{OH})_4^-}$ for the $\text{B}(\text{OH})_4^-$ ion in the respective solution. While the theoretical curve was calculated with the total concentration we consider the activity of $\text{B}(\text{OH})_4^-$ being the appropriate representative as the conditions are far from an ideal (infinitely diluted) solution.

For future studies we propose the three parameters:

- (1) fractionation factor $^{11-10}K_{\text{B}}$,

Table 3 $\delta^{11}\text{B}$ results of cultured corals (pH treatment, NBS scale) (uncertainties as SD in brackets)

Culturing water pH	$\delta^{11}\text{B}$ in ‰; n repeats
7.77	19.75(36); 18
7.92	19.81(60); 12
8.06	21.51(47); 17
8.19	22.90(23); 18
8.32	24.98(10); 6

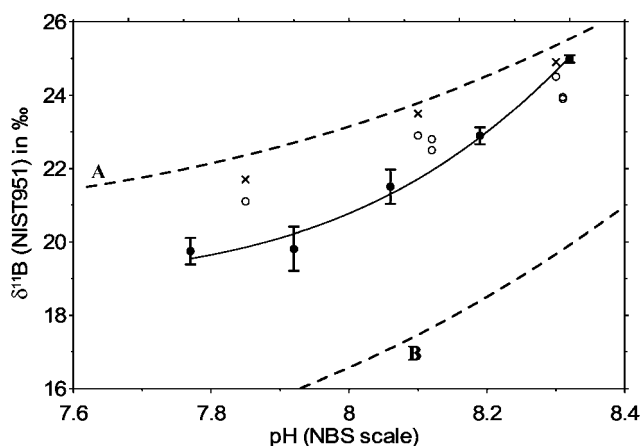


Fig. 3 $\delta^{11}\text{B}$ in corals cultured under different pH conditions. *Pocillopora* sp. samples (filled circles) from this study measured by LA-MC-ICP-MS; *Acropora* (open circles) and *Porites* (crosses) data from the previous studies measured via N-TIMS.^{30,31} For comparison published data for the theoretical and measured $\delta^{11}\text{B}$ fractionation curves of $\text{B}(\text{OH})_4^-$ are provided (A: $^{11-10}K_{\text{B}} = 1.0194$ and B: $^{11-10}K_{\text{B}} = 1.0272$).^{2,5}

(2) apparent dissociation constant $\text{p}K^*$ and

(3) activity factor $a_{\text{B}(\text{OH})_4^-}$ as a base to evaluate and compare the results for the pH dependent $\delta^{11}\text{B}$ fractionation in carbonates.

Conclusions

A new *in situ* method for the determination of $\delta^{11}\text{B}$ using LA-MC-ICP-MS was presented. Using the standard-sample-standard bracketing approach single periods of sample ablation typically provided $\delta^{11}\text{B}$ reproducibilities of 0.5‰ (SD) consuming about 0.2 ng of total boron.

We could overcome the long-standing issue of standardization for boron isotope solid-state analytics. No matrix-related offsets could be found within the limits of uncertainty for three distinct matrices: soda-lime glass, carbonate and sea salt (evaporated seawater). Thus, we propose the use of soda-lime glass standards (e.g. NIST glasses) as internal standard for boron isotope studies in carbonates.

A first application of the new method shows a strong dependence of $\delta^{11}\text{B}$ in coral aragonite on the ambient water pH. The deviation of the observed boron isotope systematic from theoretical curves points to the importance of considering the activity of $\text{B}(\text{OH})_4^-$ for the boric acid dissociation instead of the total concentration.

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