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Boric acid and borate incorporation in inorganic calcite inferred from B/Ca, boron isotopes and surface kinetic modeling

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Abstract

The boron concentration (B/Ca ratio) and isotopic composition (δ^{11} B) of biogenic calcite are widely applied to reconstruct past changes in seawater carbonate chemistry. Knowledge of B incorporation pathways into calcite is critical for these applications and for improving the theoretical basis of B proxies. While the canonical interpretation of δ^{11} B holds that B in calcite predominantly derives from dissolved borate anion in seawater, recent studies of the B content, coordination, and isotopic composition in calcite suggest more complex B incorporation pathways. To provide new insights into these pathways, here we present δ^{11} B of inorganic calcite precipitated from saline solutions of varying pH, calcium and dissolved inorganic carbon (DIC) concentration for which B/Ca data were previously reported by Uchikawa et al. (2015). Results show that calcite δ^{11} B significantly increases with increasing pH and decreases with increasing [Ca²⁺] and [DIC]. In combination, these experiments show that the difference in $\delta^{11}B$ between solid calcite and aqueous borate linearly decreases with increasing calcite precipitation rate. To interpret these data, we present the first application of surface kinetic modeling (SKM) to boron incorporation. The SKM can simultaneously explain ratedependent B/Ca and δ^{11} B patterns observed in our and previously published inorganic calcite precipitation experiments when both aqueous borate and boric acid contribute to boron in inorganic calcite. If the B incorporation mechanism shown here for inorganic calcite is applicable to biogenic calcite, precipitation rate variations could modify δ^{11} B patterns by changing the contributions of aqueous boric acid and borate to boron in calcite. However, better knowledge of biogenic calcite precipitation mechanisms and rates is needed to assess the importance of this effect for applications of B proxies in biogenic carbonates. © 2018 Elsevier Ltd. All rights reserved.

Keywords: Boron; Inorganic calcite; Boron isotopes; B/Ca; Surface kinetic modeling; Precipitation rate; Paleo-pH

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1. INTRODUCTION

Gas exchange between the ocean and atmosphere regulates atmospheric carbon dioxide concentrations and affects the hydrogen ion activity of seawater. Today, the ocean is absorbing about 2.6 Gt C of anthropogenic carbon per year (Le Quéré et al., 2016). As a consequence, seawater $[H^+]$ is increasing, leading to reduced pH (pH = $-\log[H^+])$ in a

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process termed "ocean acidification" (e.g., Caldeira and Wickett, 2003). As instrumental records of ocean pH are limited in length and number, proxy records of past seawater pH are central for understanding both rates and magnitudes of past ocean acidification events, and the relationship between past changes in ocean carbonate chemistry and global climate.

Boron (B) concentrations and B isotopic compositions of marine carbonates are primary tools for reconstructing past ocean carbonate chemistry, including seawater pH (Spivack et al., 1993; Rae, 2018; Hönisch et al., 2019). These proxies are based on acid-base chemistry of B compounds in seawater. In aqueous solutions such as seawater, B predominantly occurs as trigonally coordinated boric acid (B(OH)₃) and tetrahedrally coordinated borate anion (B(OH)₄⁻) (see Table 1 for definitions of commonly used terms in this manuscript), with the abundance of each species dependent on pH (Fig. 1):

$$B(OH)_3 + H_2O \iff B(OH)_4^- + H^+ \tag{1}$$

Because the boron-oxygen bonds are stronger in B(OH)₃ than in B(OH)₄ (e.g., Zeebe, 2005), B(OH)₃ is preferentially enriched in ¹¹B over B(OH)₄ by ~26 to 27 parts per thousand (‰) (Klochko et al., 2006; Nir et al., 2015). B isotope ratios are reported in delta notation (δ ¹¹B) relative to the NIST 951 standard (Catanzaro et al., 1970):

$$\delta^{11}B = \left(\frac{\left[\frac{11}{10B}\right]_{sample}}{\left[\frac{11B}{10B}\right]_{NIST951}} - 1\right) * 1000$$
(2)

B is a conservative element in seawater (Lee et al., 2010) and the B isotopic composition of total B in modern seawater is constant ($\delta^{11}B_{sw} = 39.61\%$, Foster et al., 2010). Since

Table 1 Terms used throughout the manuscript.

the δ^{11} B of seawater and the B isotope fractionation are constant, but the contribution of B(OH)₃ and B(OH)₄⁻ to the total boron concentration ([B_T]) in seawater varies as a function of pH, the δ^{11} B of both B species must change with pH to maintain mass balance. Specifically, as pH increases, B(OH)₄⁻ becomes more dominant relative to B (OH)₃, and both B(OH)₃ and B(OH)₄⁻ become more enriched in ¹¹B (i.e., their respective δ^{11} B increases) (Fig. 1).

Calcareous skeletons of marine organisms contain B at concentrations of $\sim 1-100$ parts per million by weight (Vengosh et al., 1991; Hemming and Hanson, 1992). Provided that the incorporation pathway of B into carbonates is systematic, δ^{11} B measurements of marine carbonates may serve as archives of past variations in ocean pH. Based on B concentrations and δ^{11} B of marine carbonates, Hemming and Hanson (1992) proposed that $B(OH)_4^-$ substitution for bicarbonate ion (HCO_3^-) is the dominant pathway for B incorporation into carbonates, specifically through substitution of HBO₃²⁻ groups for CO_3^{2-} . This appears logical. because negatively charged $B(OH)_4^-$ will be attracted to positively charged calcite surfaces (see Section 4.2.2), whereas uncharged $B(OH)_3$ will not (Hemming and Hanson, 1992). In this framework, the δ^{11} B of marine carbonates records ocean pH because carbonate δ^{11} B tracks the δ^{11} B of B(OH)⁻₄ (hereafter δ^{11} B_{borate}), which itself is a function of pH (Fig. 1).

Although Hemming and Hanson's (1992) $B(OH)_4^$ model remains a useful first-order scheme for understanding B incorporation into carbonates, subsequent studies have illustrated notable inconsistencies with this model. It was noted early on that the tetrahedral coordination of B $(OH)_4^-$ contrasts with observations of trigonally coordinated B in calcite from nuclear magnetic resonance

Term	Equation	Definition
B(OH) ₃ (or B3)	(1)	Aqueous boric acid (trigonal coordination)
$B(OH)_4^-$ (or B4)	(1)	Aqueous borate anion (tetrahedral coordination)
B/Ca	(4), (5)	Boron concentration of calcite (measured via ICP-MS and normalized to calcite Ca content)
[B _T]	(5)	Total boron concentration (sum of boric acid and borate anion concentrations)
с	_	Intercept of linear relationship between $\delta^{11}B_{\text{calcite}}$ and $\delta^{11}B_{\text{borate}}$
Ι	_	Solution ionic strength
$K_{\rm B}^{*}$	(3)	Conditional equilibrium constant for boric acid dissociation (on log scale when expressed as $pK_{\rm B}^*$)
K _D	(4)	Partitioning parameter of calcite B/Ca to fluid borate to bicarbonate ratio
$^{3,4}K_{\rm b}$	(9)	Partitioning of boric acid (3) and borate (4) detachment from the crystal surface
$^{3,4}K_{\rm f}$	(9)	Partitioning of boric acid (3) and borate (4) attachment to the crystal surface
т	_	Slope of linear relationship between $\delta^{11}B_{calcite}$ and $\delta^{11}B_{borate}$
$^{c}R_{b}$	(8), (9)	Ion detachment rate for SKM
$^{c}R_{f}$	(8), (9)	Ion attachment rate for SKM
R_p		Calcite net precipitation rate (usually expressed as $\log_{10}R_p$ in mol m ⁻² s ⁻¹)
SEMO	_	Surface entrapment model (Watson, 2004)
SI	_	Saturation index (SI = $\Omega_{calcite} - 1$)
SKM	_	Surface kinetic model (DePaolo, 2011; Branson, 2018)
$\alpha_{\rm B}$	_	Aqueous isotopic fractionation factor between boric acid and borate
$\delta^{11}\mathbf{B}_{calcite}$	(2)	Boron isotopic composition of calcite (in ‰ vs. NIST951)
$\delta^{11} \mathbf{B}_{borate}$	(2)	Boron isotopic composition of borate anion (in ‰ vs. NIST951)
ε _B	_	Aqueous isotopic fractionation (in ‰) between boric acid and borate
ε _{c-b}	_	Difference between $\delta^{11}B_{\text{calcite}}$ and $\delta^{11}B_{\text{borate}}$ (in % vs. NIST951)
$\lambda_{\mathbf{B}}$	(5)	Partitioning parameter of calcite B/Ca to fluid B_T to DIC ratio



Fig. 1. Concentration (a) and isotopic composition (b) of boric acid (dashed line) and borate (solid line) in aqueous solution as a function of pH (NBS scale). Note that the concentrations (a) and isotopic compositions (b) are defined for the parent solution of the control inorganic calcite precipitation experiment, with $[B_T] = 432 \mu mol/kg$ and $pK_B^* = 8.956$ (calculated using the PITZER database in PHREEQC). Isotopic compositions in (b) are defined using $\varepsilon_B = 26\%$ (Nir et al., 2015) and solution $\delta^{11}B_w$ (-12.19‰, mean of experimental solutions).

(NMR) and synchrotron X-ray micro-spectrometric analyses (Sen et al., 1994; Klochko et al., 2009; Rollion-Bard et al., 2011; Branson et al., 2015; Cusack et al., 2015; Noireaux et al., 2015). However, B coordination is not sufficient to define incorporation pathways due to possible coordination changes and intermediary B compounds during incorporation (Sen et al., 1994; Hemming et al., 1995; Klochko et al., 2009; Balan et al., 2016).

Furthermore, if $B(OH)_4^-$ is the only B species incorporated into calcite, then calcite B/Ca and δ^{11} B should track $[B(OH)_4^-]$ and $\delta^{11}B_{\text{borate}}$ in the parent solution. While B concentrations of biogenic calcite (foraminifera) are tightly linked with solution $[B(OH)_4^-]/[HCO_3^-]$ or $[B(OH)_4^-]/DIC$ (Allen et al., 2012; Haynes et al., 2017), inorganic calcite precipitation experiments imply additional controls from solution pH, precipitation rate, and the solution [B_T]/DIC (Gabitov et al., 2014; Mavromatis et al., 2015; Uchikawa et al., 2015, 2017). δ^{11} B tightly correlates with δ^{11} B_{borate} in calcite produced by marine calcifiers, but this correlation is often not unity (e.g., Sanyal et al., 1996, 2001; Henehan et al., 2013; Farmer et al., 2015; but see Rae et al., 2011; Henehan et al., 2016). In laboratory culturing experiments where symbiont-bearing marine calcifiers are grown under controlled conditions, calcite δ^{11} B values are generally elevated above $\delta^{11}B_{\text{borate}}$ at lower pH and converge toward δ^{11} B_{borate} at higher pH (Sanyal et al., 1996, 2001; Rollion-Bard and Erez, 2010; Henehan et al., 2013). This pattern is also observed in inorganic calcite (Sanyal et al., 2000; Noireaux et al., 2015; Farmer et al., 2016), suggesting that deviations between $\delta^{11}B_{\text{calcite}}$ and $\delta^{11}B_{\text{borate}}$ are not solely related to biological "vital effects" or organismal pH regulation (Rollion-Bard and Erez, 2010; Trotter et al., 2011), although those effects may further complicate δ^{11} B interpretation in biogenic carbonates. Evidence for isotopic fractionation of $B(OH)_4^$ at near-equilibrium calcite precipitation conditions during structural incorporation (Balan et al., 2018) and adsorption (Saldi et al., 2018) provides another potential complication to relationships between $\delta^{11}B_{\text{calcite}}$ and $\delta^{11}B_{\text{borate}}$. However, the effect of non-equilibrium (kinetic) processes on $\delta^{11}B_{calcite}$ is poorly

understood even in simpler inorganic systems (Kaczmarek et al., 2016).

In this study, we seek to further advance our understanding on B incorporation pathways using paired B/Ca and δ^{11} B data of inorganic calcites precipitated from solutions of controlled pH, calcium and DIC concentrations (Uchikawa et al., 2015). Previous B/Ca measurements on these samples suggested potential precipitation ratedependent partitioning of B(OH)₃ into calcite (Uchikawa et al., 2015). To evaluate this hypothesis and assess the influence of precipitation rate on δ^{11} B_{calcite}, we present calcite δ^{11} B measurements and employ a surface kinetic modeling approach (Branson, 2018) to infer mechanisms of B incorporation into inorganic calcite from our paired B/Ca and δ^{11} B data.

2. MATERIALS AND METHODS

2.1. Calcite precipitation and analyses

Inorganic calcite samples were precipitated from NaCl-CaCl₂-B(OH)₃-Na₂CO₃ parent solutions using a seeded calcite overgrowth technique (see details in Uchikawa et al., 2015). Calcite precipitation occurred in an airtight acrylic chamber monitored with a pH electrode and connected to an auto-titrator that added Na₂CO₃ titrant to maintain reaction chamber pH within ± 0.01 unit. Precipitation was initiated by introduction of B-free calcite seeds, and the experiments were stopped when the mass of experimental overgrowth approximately equaled that of the initial seeds. An important distinction from recent inorganic precipitation experiments (Gabitov et al., 2014; Mavromatis et al., 2015; Noireaux et al., 2015; Kaczmarek et al., 2016) is that in our experiments, parameters of interest (DIC, [Ca²⁺], pH) were individually manipulated from the same starting control solution, allowing the influence of individual solution parameters to be investigated.

The overgrown seeds were homogenized with a mortar and pestle. B/Ca measurements were obtained on \sim 300 µg of homogenized sample using a Thermo Element XR

ICP-MS at the Marine Analytical Laboratory of the University of California, Santa Cruz (see detailed methodology and B/Ca results in Uchikawa et al., 2015). B isotopes were measured via multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) using a Thermo Neptune Plus at the Lamont-Doherty Earth Observatory (LDEO) following the procedures given in Farmer et al. (2016). Briefly, a sufficient quantity of homogenized sample to provide 10–20 ng B (0.5-7 mg calcite depending on B/Ca) was transferred to HCl-cleaned 0.5 mL polypropylene vials and rinsed ten times in B-free MilliO water (resistivity 18.2 MOhm) under sonication. Rinsed samples were dissolved in ultrapure 0.5 N HNO₃, buffered to pH \sim 6 by adding B-free acetic acid/sodium acetate buffer solution, and passed through 20 uL microcolumns of Amberlite IRA-743 resin to isolate B from the sample matrix. B was eluted using 450 µL of ultrapure 0.5 N HNO₃. Sample analyses were bracketed by NIST 951 standards. All samples were measured at least in duplicate, with uncertainty reported as the 2sd of all sample replicate analyses. Parent solution composition, calcite precipitation rate, and calcite B/Ca and δ^{11} B ratios are given in Table 2.

2.2. Boron speciation and $\delta^{11}B_{\text{borate}}$ of precipitating solutions

The conditional equilibrium constant for boric acid dissociation (K_B^*) defines the pH-dependent partitioning of B (OH)₃ and B(OH)₄⁻:

$$K_B^* = \frac{[B(OH)_4^-] \times [H^+]}{[B(OH)_3]}$$
(3)

The respective concentrations of B(OH)₃ and B(OH)₄ from K_B^* are used to calculate $\delta^{11}B_{\text{borate}}$. While $\delta^{11}B_{\text{borate}}$ has traditionally been calculated from B(OH)₃ and B (OH)₄⁻ concentrations, the boron isotope fractionation (α_B and ε_B , where $\varepsilon_B = 1000 * [\alpha_B - 1]$) and the boron isotopic composition of the parent solution ($\delta^{11}B_T$), Rae (2018) noted that this approach is an approximation of the true mass balance due to the use of isotope ratios (δ -values) instead of individual isotope abundances ($^{11}B_1^{10}B_1$, Eq. (2)). Therefore, we calculated $^{11}B_1^{10}B_{\text{borate}}$ using the strict mass balance equation (the root of equation 5.8 in Rae, 2018) using $\delta^{11}B_T$ of $-12.19 \pm 0.32\%$ ($^{11}B_T/^{10}B_T = 3.9944 \pm 0.0013$, average for all experiments), and α_B (ε_B) of 1.026 (26%) from Nir et al. (2015). $\delta^{11}B_{\text{borate}}$ values were then calculated from $^{11}B_1^{10}B_{\text{borate}}$ and Eq. (2).

The primary variables influencing $\delta^{11}B_{\text{borate}}$ are the solution B speciation (K_B^*), and the isotope fractionation between the aqueous species (α_B ; ε_B). The value of K_B^* is sensitive to solution chemistry due to interactions between B(OH)⁴ and major cations, particularly Ca²⁺ and Mg²⁺ (Hershey et al., 1986; Simonson et al., 1988). K_B^* has been determined for synthetic seawater as a function of temperature and salinity (Dickson, 1990). However, the solution composition for inorganic precipitation experiments is generally much simpler than seawater, therefore B speciation is more properly defined using an aqueous chemical speciation model (Nir et al., 2015; Noireaux et al., 2015; Kaczmarek et al., 2016). Previous inorganic precipitation

B speciation. Mavromatis et al. (2015) and Noireaux et al. (2015) used the MINTEQA2 database (Allison et al., 1991) within PHREEOC (Parkhurst and Appelo, 2013). Kaczmarek et al. (2016) used the MINTEQA2 database within Visual MINTEQ (Gustafsson, 2008) with modified K_B , K_1 and K_2 . Uchikawa et al. (2015) used the WATEQ4 database (Ball and Nordstrom, 1991) within PHREEQC. For the purposes of B speciation, both the MINTEQA2 and WATEQ4 databases calculate activity coefficients (and thus $K_{\rm B}^*$) using the Davies equation (Davies, 1962), which is suitable for solutions with low ionic strengths (I < 0.5, Allison et al., 1991). The MINTEO approach is therefore appropriate for the dilute solutions (I = 0.1-0.2)used by Noireaux et al. (2015), but may be problematic for higher ionic-strength solutions, including those of Kaczmarek et al. (2016) (I \approx 0.7) and seawater (I = 0.71).

Variations in the methods used to calculate B speciation between previous inorganic calcite studies complicate direct comparison of their data. To identify which method facilitates internally consistent comparison of all available data, we have evaluated the MINTEQA2 and PITZER (Plummer et al., 1988) databases within PHREEQC and the MyAMI seawater speciation model (Hain et al., 2015) by comparing predicted and measured $K_{\rm B}^*$ in simple (NaCl, KCl) and complex (artificial seawater) ionic solutions (Electronic Annex 1). We find that no method exactly reproduces the measured $K_{\rm B}^*$ in all conditions (Supplementary Fig. 1). The MyAMI model accurately predicts $K_{\rm B}^*$ in artificial seawater at lower ionic strengths, but poorly predicts $K_{\rm B}^{*}$ in simple ionic solutions at all ionic strengths, and is unsuitable for the above inorganic precipitation experiments. Both the PITZER and MINTEQA2 databases within PHREEQC perform similarly in all conditions, although importantly the size and sense of the offset between observed $K_{\rm B}^*$ and MINTEQA2-based $K_{\rm B}^*$ varies with ionic strength in simple solutions. This makes the MINTEQA2 database a poor choice for comparing data between simple solutions with varying ionic strength (i.e., existing inorganic precipitation experiments). In contrast, PITZER within PHREEQC calculates $K_{\rm B}^*$ values that slightly underestimate measured $K_{\rm B}^*$ values (calculated pK_B^* 0.1–0.15 higher than measured pK_B^*), but this offset appears independent of ionic strength. Based on this, and in line with the suggestions of Nir et al. (2015), we favor calculating $K_{\rm B}^*$ using the PITZER database within PHREEQC over the range of ionic strengths in existing inorganic precipitation experiments (I = 0.1-0.7), and use PITZER-PHREEQC to recalculate B speciation for these experiments. Given the lack of a single technique for reconciling $K_{\rm B}^*$ values for seawater and simple solutions, and differences in aqueous borate complexation with cations between PIT-ZER and MINTEQA2, we recommend that inorganic precipitation studies publish the full details of their solution compositions to facilitate future recalculation of $K_{\rm B}^*$, as we have provided in the Electronic Annex for all studies that have published paired B/Ca and δ^{11} B analyses.

Alongside variations in speciation calculation methods, past studies have also chosen different values of $\alpha_{\rm B}$; for example, Noireaux et al. (2015) use $\alpha_{\rm B} = 1.026 \pm 0.001$ (Nir et al., 2015, all errors 2 *s*), Kaczmarek et al. (2016)

Table 2					
Calcite and	solution	compositions	in	this	study.

Solution compo	osition	pН	[H+]	[Ca ²⁺]	[Cl-]	[Na+]	$[B_T]$	Ion. strength	[DIC]	$[HCO_3^-]$	$[CO_{3}^{2-}]$	$[B(OH)_4^-]$	[B(OH) ₃]	$K_{\rm B}^*$	$\delta^{11} B(OH)_4^-$
Experiment	Sample ID	(NBS)	(µmol/kg)	(µmol/kg)	(mol/kg)	(mol/kg)	(µmol/kg)	(mol/kg)	(µmol/kg)	(µmol/kg)	(µmol/kg)	(µmol/kg)	(µmol/kg)		(‰, JR18)
Control	8C & 8F	8.25	5.61E-09	3851	0.4599	0.4545	432	0.47	2393	2217	160	6.851E-05	3.634E-04	1.057E-09	-33.27
pH	15A	8.37	4.27E-09	3851	0.4595	0.4546	432	0.47	2393	2174	207	8.576E-05	3.462E-04	1.057E-09	-32.27
	9B	8.50	3.17E-09	3851	0.4599	0.4547	432	0.47	2393	2114	270	1.080E-04	3.239E-04	1.057E-09	-30.99
	10A	8.65	2.25E-09	3852	0.4599	0.4549	432	0.47	2393	2022	365	1.382E-04	2.936E-04	1.057E-09	-29.24
pH(10x [B])	4B	8.00	9.98E-09	3852	0.4599	0.4550	4317	0.47	2393	2272	92	4.134E-04	3.904E-03	1.057E-09	-34.84
	2B	8.25	5.63E-09	3852	0.4599	0.4552	4317	0.47	2393	2217	160	6.823E-04	3.635E-03	1.057E-09	-33.28
	1C	8.50	3.18E-09	3852	0.4600	0.4561	4318	0.47	2393	2115	270	1.079E-03	3.239E-03	1.057E-09	-30.99
DIC	13C	8.25	5.59E-09	3851	0.4589	0.4532	432	0.46	1795	1662	120	6.864E-05	3.632E-04	1.057E-09	-33.26
	12B	8.25	5.63E-09	3852	0.4605	0.4569	432	0.47	3589	3325	240	6.824E-05	3.636E-04	1.057E-09	-33.28
	11A	8.25	5.64E-09	3853	0.4616	0.4593	432	0.47	4787	4435	320	6.823E-05	3.637E-04	1.057E-09	-33.29
Ca	19 B	8.25	5.61E-09	4817	0.4615	0.4546	432	0.47	2393	2214	164	6.840E-05	3.635E-04	1.057E-09	-33.27
	17 B	8.25	5.63E-09	5778	0.4634	0.4546	432	0.47	2393	2210	167	6.826E-05	3.638E-04	1.056E-09	-33.28
	16B	8.25	5.63E-09	7706	0.4675	0.4549	432	0.48	2394	2204	174	6.813E-05	3.640E-04	1.054E-09	-33.28
Calcite compos	ition		$\log_{10}R$	2sc	I B/C	Ca _{Sample}	2sd	B/Ca _{OG}	2sd	$\delta^{11}\mathbf{B}$		2sd	n ε (ca	lcite - borat	e) 2sd
Experiment	Sample	ID	(mol/m ² /s	ec) \pm	(µn	nol/mol)	\pm	(µmol/mol)	\pm	(‰ vs N	BS951)	(%)	(‰)		(‰)
Control	8C & 8	F	-5.70	0.0	3 16.	7	3.2	29.5	4.7	-27.68		0.56	7 5.21		0.64
pH	15A		-5.50	0.0	0 52.	5	3.2	102.1	4.9	-26.74		0.58	4 5.07		0.66
1	9B		-5.38	0.0	1 83.)	3.7	162.9	5.3	-25.87		0.22	4 4.57		0.39
	10A		-5.21	0.0	1 156	.5	6.9	305.8	8.3	-23.95		0.23	2 4.68		0.39
pH(10x [B])	4B		-6.59	0.0	1 29.4	4	3.2	75.4	7.8	-27.16		0.68	6 7.67		0.75
	2B		-5.80	0.0	3 179	.7	7.8	334.5	10.6	-26.86		0.3	4 6.40		0.44
	1C		-5.50	0.0	1 560	.9	24.7	1068.1	24.9	-26.54		0.31	6 4.43		0.45
DIC	13C		-5.85	0.0	0 20.2	2	3.2	37.5	4.8	-27.08		0.31	2 5.81		0.45
	12B		-5.40	0.0	0 51.	1	3.2	97.7	4.8	-27.91		0.21	2 4.98		0.38
	11A		-5.24	0.0	0 62.4	4	3.2	119.2	4.7	-28.50		0.21	2 4.38		0.38
Ca	19 B		-5.55	0.0	0 47.	5	3.2	98.9	5.5	-27.63		0.24	2 5.27		0.40
	17 B		-5.42	0.0	0 72.	7	3.2	139.2	4.7	-28.20		0.22	2 4.71		0.39
	16 B		-5.32	0.0	0 100	.5	4.4	194.1	5.6	-28.74		0.25	2 4.18		0.41

use $\alpha_{\rm B} = 1.025 \pm 0.0005$ (Klochko et al., 2006, for KCl solutions), while studies of marine carbonates typically use $\alpha_{\rm B} = 1.0272 \pm 0.0006$ (Klochko et al., 2006 for artificial seawater). Variations in the choice of $\alpha_{\rm B}$ therefore have the potential to alter data interpretation by 1–2‰. As the sensitivity of $\alpha_{\rm B}$ to solution chemistry is debated (e.g., Klochko et al., 2006 vs. Nir et al., 2015), and given that the KCl and artificial seawater $\alpha_{\rm B}$ values from Klochko et al. (2006) fall within uncertainty of Nir et al.'s (2015) estimate ($\alpha_{\rm B} = 1.026 \pm 0.001$), we opt here to apply the $\alpha_{\rm B}$ value of Nir et al. (2015) to our data and all previously published studies to allow internally consistent comparison.

3. RESULTS

Fig. 2 shows calcite B/Ca and δ^{11} B data for the four experiments measured in this study: variable pH at [B_T]_{ctrl} (432 μ mol/kg) and 10x[B_T]_{ctrl} (Fig. 2a-b), variable [Ca²⁺] at pH_{ctrl} ($pH_{NBS} = 8.25$) (Fig. 2c-d), and variable DIC at pHctrl (Fig. 2e-f). Calcite B/Ca increases with increasing pH in the [B_T]_{ctrl} and 10x[B_T]_{ctrl} experiments (Fig. 2a), and increases with increasing $[Ca^{2+}]$ (Fig. 2c) and DIC (Fig. 2e) (Uchikawa et al., 2015). Calcite δ^{11} B increases with pH in both the [B_T]_{ctrl} (measured in Farmer et al., 2016) and $10x[B_T]_{ctrl}$ experiments, although with less $\delta^{11}B$ change per unit pH change in 10x[B_T]_{ctrl} experiment. This is expected because the 10x[B_T]_{ctrl} experiments were performed at lower pH than the [B_T]_{ctrl} experiments (Fig. 2b). In both pH experiments, $\delta^{11}B_{calcite}$ is elevated above precipitating solution $\delta^{11}B_{\text{borate}}$ by >4‰ (Table 2). $\delta^{11}B_{calcite}$ decreases approximately linearly with increased $[Ca^{2+}]$ or increased [DIC] (Fig. 2d, f). The magnitude of $\delta^{11}B_{\text{calcite}}$ change from each manipulation is similar, with $\delta^{11}B_{\text{calcite}}$ decreasing by 0.3‰ per 1 mmol/kg [Ca²⁺] increase, and decreasing by 0.43‰ per 1 mmol/kg [DIC] increase. $\delta^{11}B_{\text{calcite}}$ is similarly elevated over $\delta^{11}B_{\text{borate}}$ by >4‰ in [Ca²⁺] and [DIC] experiments. Note that $\delta^{11}B_{\text{borate}}$ is effectively constant (-33.28 ± 0.02‰) in both [Ca²⁺] and [DIC] experiments (Table 2).

4. DISCUSSION

4.1. Inorganic calcite δ^{11} B, B/Ca and precipitation rate (R_p)

Variations in pH, [Ca²⁺] and [DIC] all affect calcite precipitation rate (R_n) , which influences the amount, and possibly species of B incorporated into inorganic calcite (Hobbs and Reardon, 1999; Gabitov et al., 2014; Mavromatis et al., 2015; Uchikawa et al., 2015, 2017; Kaczmarek et al., 2016). To investigate the potential influence of precipitation rate on B incorporation, Uchikawa et al. (2015) presented relationships between R_p and various B partitioning parameters, which relate the B content of inorganic calcite to ratios of B and DIC species in solution and imply different underlying B incorporation mechanisms. For example, the framework of Hemming and Hanson (1992) for B incorporation (i.e., $B(OH)_4^-$ exchanging for HCO_3^-) would allow B incorporation to be described by the fluid-calcite partitioning parameter K_D :

$$K_D = \frac{(B/Ca)_{CaCO_3}}{\left(\frac{[B(OH)_{\tilde{a}}]}{[HCO_3]}\right)_{fluid}}$$
(4)



1

Fig. 2. B/Ca (a, c, e) and $\delta^{11}B_{calcite}$ (b, d, f) of inorganic calcites from precipitation experiments: pH at $[B_T]_{ctrl}$ (red triangles) and pH at 10x $[B_T]$ (blue squares; a-b); $[Ca^{2+}]$ (purple triangles; c-d); and [DIC] (green triangles; e-f). Gray circle in each panel indicates the Control experiment. Black lines in (b) indicate $\delta^{11}B_{borate}$ as a function of pH_{NBS} for the solution chemistry of these experiments. Solid line is calculated using $\alpha_B = 1.026$ (Nir et al., 2015); dashed line is calculated using $\alpha_B = 1.0272$ (Klochko et al., 2006). Black lines in (d) and (f) are least-squares best fits to $\delta^{11}B_{calcite}$ versus [Ca²⁺] and [DIC], respectively, with regression parameters given in each panel. $\delta^{11}B_{borate}$ is constant at -33.3% for the [Ca²⁺] and [DIC] experiments (e-f). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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Uchikawa et al. (2015) found significant scatter in K_D as a function of R_p , particularly at higher R_p (Fig. 3a), implying that this expression of K_D does not adequately capture the processes of B incorporation. Instead, Uchikawa et al. (2015) found that data scatter with R_p is minimized by a partitioning parameter (λ_B) that relates inorganic calcite B/Ca to solution B_T/DIC (Fig. 3b):

$$\lambda_B = \frac{(B/Ca)_{CaCO_3}}{\left(\frac{|B_T|}{|DIC|}\right)_{fluid}} \tag{5}$$

The correlation between $\lambda_{\rm B}$ and R_p is significantly better than the correlation between K_D and R_p at higher R_p (Fig. 3a-b). This observation also holds for the B/Ca data from a follow-up study using Mg-free synthetic seawater for calcite precipitation (Uchikawa et al., 2017). If the strength of correlation between $\lambda_{\rm B}$ and R_p reflects mechanisms of B incorporation, then the above relationships imply that inorganic calcite B content may reflect involvement of both $B(OH)_3$ and $B(OH)_4^-$ during B incorporation. Specifically, Fig. 3b would imply that a contribution of $B(OH)_3$ to the total B hosted in inorganic calcite may be particularly relevant at higher R_p (Uchikawa et al., 2015).

Our $\delta^{11}B_{\text{calcite}}$ data provide an additional constraint for evaluating existing partition definitions, and the incorporation mechanisms they imply. Because of the large isotopic fractionation between $B(OH)_3$ and $B(OH)_4^-$ (i.e., 26–27‰; Klochko et al., 2006; Nir et al., 2015), as long as there is no kinetic B isotope fractionation during incorporation (e.g., Zeebe et al., 2001; see below), even small proportions of $B(OH)_3$ incorporation would significantly increase $\delta^{11}B_{calcite}$ relative to $\delta^{11}B_{borate}$. We observe higher $\delta^{11}B_{calcite}$ than $\delta^{11}B_{\text{borate}}$ for all experiments (see Fig. 2 and Table 2), which can be interpreted as either that some fraction of B in calcite is derived from aqueous B(OH)₃, or alternatively that B incorporation occurs exclusively via aqueous $B(OH)_4^-$ but with a significant and variable isotope fractionation (Balan et al., 2018; Saldi et al., 2018).

If there is no kinetic isotope fractionation during B incorporation (e.g., Zeebe et al., 2001), the inference of greater B incorporation derived from aqueous B(OH)₃ at higher R_p drawn from the partitioning data of Uchikawa et al. (2015) would predict systematically heavier $\delta^{11}B_{calcite}$ than $\delta^{11}B_{\text{borate}}$ at higher R_p . Instead, we observe the opposite - a significant, linearly decreasing offset between $\delta^{\bar{1}1}B_{\text{calcite}}$ and $\bar{\delta^{1}1}B_{\text{borate}}$ (expressed as ε_{c-b} ; Fig. 3d) at higher

d) С -30 3 -6.5 -6 -5.5 -5 -6.5 -6 -5.5 -5 $\log_{10}R_{p}$ (mol/m²/sec) $\log_{10}R_{p}$ (mol/m²/sec) Fig. 3. Variations in calcite B/Ca and δ^{11} B as a function of precipitation rate. (a-b) R_p versus boron incorporation parameters (K_D in a, λ_B in b) for the full dataset of Uchikawa et al. (2015). (c) R_p versus $\delta^{11}B_{\text{calcite}}$ for all measured experiments. (d) R_p versus $\varepsilon_{c-b} = \delta^{11}B_{\text{calcite}}$ $\delta^{11}B_{borate}$) for all measured experiments. Symbols are the same as Fig. 2. Grayed out symbols in (a-b) indicate experiments of Uchikawa et al. (2015) not measured for $\delta^{11}B_{calcite}$. Black curves in a, b, and d indicate least-squares best fits.



 R_p . We note that one sample from the $10x[B_T]_{ctrl}$ experiment (Sample 4B, Table 2) has a much lower R_p than other experiments (Fig. 4d). This relationship is not driven by Sample 4B because the slope and intercept of this relationship and its significance (evaluated via *F*-test at $\alpha = 0.05$) are not altered when Sample 4B is excluded from the regression. This relationship suggests that, even if aqueous B(OH)₃ is involved during B incorporation, our new isotopic constraints are not in line with a rather simplistic view of increased B(OH)₃ contribution at higher R_p proposed by Uchikawa et al. (2015, 2017). Thus, the inconsistency between the B incorporation mechanisms inferred from B/Ca data and those inferred from δ^{11} B highlights the fact that the actual processes of B incorporation are more complex than what can be portrayed by partitioning expressions (e.g., K_D versus λ_B). Specifically, when both B species are considered, simple partitioning expressions cannot fully capture the independent interaction of each B species with the growing crystal.

An alternative possibility is that the assumption of no isotopic fractionation during B incorporation is invalid. Based on isotopic equilibration times between dissolved $B(OH)_3$ and $B(OH)_4^-$ in solution, Zeebe et al. (2001) suggested that kinetic isotope effects during coprecipitation of boron are unlikely, but did not rule out other effects. Recent computational studies suggest a strong isotopic fractionation associated with $B(OH)_4^-$ hosted in structural

sites within the calcite lattice (\sim +11% relative to aqueous $B(OH)_{4}^{-}$; Balan et al., 2018). A weaker fractionation during $B(OH)_{4}^{-}$ adsorption onto calcite has been observed experimentally ($\sim+2-5\%$; Saldi et al., 2018). The existence of fractionation associated with the adsorption and/or incorporation of B into calcite may provide a mechanism to explain the observed offsets between $\delta^{11}B_{calcite}$ and δ^{11} B_{borate}, without the need to consider B(OH)₃. However, we highlight that both the recent computational (Balan et al., 2018) and experimental work (Saldi et al., 2018) investigate systems that are at or near thermodynamic equilibrium (i.e., $R_p \approx 0$; DePaolo, 2011). In contrast, the majority of natural and synthetic carbonates (including ours) precipitate far from equilibrium conditions, and are more likely to be dominated by kinetically controlled processes (DePaolo, 2011), hence fractionation factors observed in near-equilibrium conditions may not be applicable to our inorganic calcite samples.

There appear to be three key features in our paired B/Ca and $\delta^{11}B$ data that cannot be adequately explained by the scenario of sole B(OH)₄⁻ incorporation, even with or without taking the aforementioned (presumably equilibrium) fractionations into consideration. First, the inability of K_D to explain patterns in the partitioning data (Fig. 3a) implies that B(OH)₄⁻ alone is insufficient to explain B incorporation into inorganic calcite. Second, the variability of $\delta^{11}B_{calcite}$ with [DIC] and [Ca] (Fig. 2) at precipitation rates



Fig. 4. Schematic illustration of boron incorporation into carbonates tested by our SKM. Arrow thickness indicates relative magnitude of attachment (K_f), detachment (K_b), and bulk crystal incorporation fluxes (straight arrows). Detachment and incorporation arrows are specific for mineralogy: blue arrows indicate calcite, and red arrows indicate hypothesized detachment and incorporation for aragonite. Based on the tetrahedral coordination of the anion site in aragonite, we predict that B(OH)⁴ detachment (${}^{4}K_{b}$) is lower, and B(OH)₃ detachment (${}^{3}K_{b}$) is higher in aragonite versus calcite. This would tend to favor some B(OH)₃ incorporation in calcite, versus dominantly B(OH)⁴ incorporation in aragonite. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

far from equilibrium (Fig. 3c) suggest that non-equilibrium processes play a significant role in B incorporation. And third, the systematic trend in ε_{c-b} with R_p (Fig. 3d) highlights precipitation rate as a unifying controlling parameter which exerts a primary influence on both B elemental and isotopic partitioning, irrespective of which solution chemical parameter is causing the change in R_p . Moreover, the lowest precipitation rates considered in our study exceed the ranges of R_n where equilibrium fluid-calcite Ca isotope fractionation and Sr partitioning can be expected (Tang et al., 2008; DePaolo, 2011) by 1-2 orders of magnitude, suggesting that the calcite samples analyzed here were grown in a kinetically-dominated regime. We therefore focus our discussion on the kinetic processes that might drive these patterns of B elemental and isotopic partitioning as a function of precipitation rate, but offer a more detailed exploration of the influence of B fractionation during incorporation in Section 4.2.6 below and in Electronic Annex 2.

We have developed a model of B incorporation that explicitly considers the incorporation of each B species independently, and is able to simultaneously explain patterns in both B/Ca and $\delta^{11}B_{\text{calcite}}$ as a function of R_p , solution chemistry, and kinetic partitioning coefficients.

4.2. Surface kinetic modeling of boron incorporation

4.2.1. Model description

Our B incorporation model is an adaptation of the kinetic model proposed by Branson (2018), which itself is based on DePaolo's (2011) surface kinetic model (SKM). The SKM parameterizes crystal precipitation in terms of the rates of forward 'attachment' $({}^{C}R_{f})$ and backward 'detachment' $({}^{C}R_{b})$ of constituent ions to and from the crystal surface, where precipitation rate $({}^{C}R_{p})$ is defined as ${}^{C}R_{f} - {}^{C}R_{b}$. Trace element (TE) incorporation is then defined relative to the attachment and detachment fluxes of host constituent ions:

$${}^{TE}R_p = {}^{TE}R_f - {}^{TE}R_b$$

= $K_f r_L^C R_f - K_b r_s^C R_b$ (6)

where K is a fractionation factor for the TE attachment (K_f) or detachment (K_b) , and r is the ratio of TE to the host constituent in the liquid (r_L) or solid (r_S) . Following DePaolo (2011), Eq. (6) can be solved for a steady state where the TE content of the bulk crystal and the crystal growth surface are the same:

$$\frac{\partial r_s}{\partial t} = 0 = \frac{1}{N_C} \left(\frac{\partial N_{TE}}{\partial t} - r_s \frac{\partial N_C}{\partial t} \right)$$

$$= {^{TE}} R_P - r_s^C R_P$$
(7)

$$r_s = \frac{K_f r_L^C R_f}{K_b^C R_b + {}^C R_p} \tag{8}$$

For the steady-state case (Eq. (8)), the TE ratio of the solid (r_s) is a function of r_L , the forward and backward TE kinetic fractionation factors (K_f, K_b) , the rates of host ion attachment $({}^{c}R_f)$ and detachment $({}^{c}R_b)$, and the net precipitation rate $({}^{c}R_p = {}^{c}R_f - {}^{c}R_b)$.

DePaolo's (2011) SKM was developed to describe the incorporation of cationic trace elements into calcite, relative to the attachment/detachment of Ca to/from the calcite

surface. Because B exists primarily in two aqueous species with different structures and charges, and most likely substitutes into the CO_3^{2-} site in the calcite structure (Balan et al., 2016), the SKM for cationic trace elements cannot be directly applied to B (Watkins et al., 2017). It is therefore appropriate to describe B incorporation as a combination of two separate SKMs, which parameterize the independent interactions of B(OH)₃ and B(OH)₄ (which are abbreviated as 3 and 4, respectively, in the following expressions) with the growing crystal (Branson, 2018):

$${}^{B}r_{s} = {}^{3}r_{s} + {}^{4}r_{s} = \frac{{}^{3}K_{s}^{2}r_{L}^{C}R_{f}}{{}^{3}K_{b}^{C}R_{b} + {}^{C}R_{p}} + \frac{{}^{4}K_{b}^{A}r_{L}^{C}R_{f}}{{}^{4}K_{b}^{C}R_{b} + {}^{C}R_{p}}$$
(9)

This allows the B isotopic content of the mineral to be calculated as a mixture of each B species:

$${}^{11}A_s = \frac{{}^{11}A_{B3}^3r_s + {}^{11}A_{B4}^4r_s}{{}^3r_s + {}^4r_s}$$
(10)

where ${}^{II}A = [{}^{11}B]/([{}^{10}B] + [{}^{11}B])$ is the fractional abundance of ${}^{11}B$. This is applied here to avoid non-linear ratio mixing effects inherent in $\delta^{11}B$ notation (Rae, 2018; see Section 3.1.5 in Zeebe and Wolf-Gladrow, 2001).

Within this parameterization, the B content of calcite is a function of the attachment/detachment rates ($^{C}R_{f}$ and ${}^{C}R_{b}$) of carbon species to/from the calcite surface (and therefore the net precipitation rate, ${}^{C}R_{p}$), the ratios of aqueous B(OH)₃ and B(OH)⁻₄ to C species $({}^{3}r_{L}, {}^{4}r_{L})$, and four kinetic fractionation factors that describe the interaction of each B species with the attachment and detachment of C from the surface $({}^{3}K_{f}, {}^{3}K_{b}, {}^{4}K_{f} \text{ and } {}^{4}K_{b})$ (Eq. (9)). These four fractionation factors and the detachment rate of C $({}^{C}R_{b})$ are unknown, but can be solved by optimization, fitting the model to data where the solution chemistry and precipitation rate are well constrained. However, B concentration data alone are insufficient to constrain all four kinetic coefficients, as the two forward (K_t) and backward (K_b) coefficients will covary. To isolate these parameters, we require an additional constraint on the relative abundance of B derived from $B(OH)_3$ and $B(OH)_4^-$ within the solid $({}^{3}r_{S}, {}^{4}r_{S})$. This is provided by paired measurements of δ^{11} B_{calcite}, which is a function of both the relative abundance of each B species in the mineral, and their isotopic content (Eq. (10)). Thus, it is possible to constrain the entire SKM for B with paired measurements of B/Ca and δ^{11} B in calcite produced at known precipitation rates from solutions of known compositions.

4.2.2. Conceptual framework

Our B SKM contains four free parameters $({}^{3}K_{f}, {}^{3}K_{b}, {}^{4}K_{f}$ and ${}^{4}K_{b})$, which describe the partitioning associated with the attachment/detachment rates of each B species to/from the crystal surface. Conceptually, the forward partitioning parameters (${}^{4}K_{f}$ and ${}^{3}K_{f}$) can be considered as the 'affinity' for each species for the crystal surface, while the backward partitioning parameters (${}^{4}K_{b}$ and ${}^{3}K_{b}$) approximate the 'stability' of each species once attached to the surface, which is inversely proportional to the likelihood of each species being incorporated into the mineral structure. This framework does not depend on the final chemical state of the incorporated B species in the mineral, and the backward reaction rate implicitly includes all energy barriers to recoordination or deprotonation that must occur to incorporate B into the calcite structure. Within this framework, it is possible to form an initial hypothesis of the relative magnitude of these parameters based on past studies of B incorporation in calcite.

Measurements (Sen et al., 1994; Branson et al., 2015) and modeling (Balan et al., 2016) of B coordination in calcite have shown that trigonal B is most stable in the calcite lattice as $B(O_2)OH^{2-}$. While other studies have shown much more variable B coordination states (Klochko et al., 2009; Noireaux et al., 2015), this variability is likely attributable to varying amounts of non-structurally hosted B within the solid (Balan et al., 2016). We consider the combination of first-principles modeling work (Balan et al., 2016), and the observation of tetrahedral to trigonal recoordination on transition from aragonite to calcite (Sen et al., 1994) to be conclusive evidence for a link between crystal structure and the preferential stability of specific B species within the crystal.

If the detachment partitioning (K_b) is related to the stability of the ion within the calcite structure, trigonallycoordinated B will be more stable than tetrahedrallycoordinated B on the calcite surface, and less likely to detach (i.e., ${}^{4}K_{b} > {}^{3}K_{b}$; Fig. 4). Conversely, in aragonite tetrahedrally-coordinated B is most stable (Sen et al., 1994; Balan et al., 2016), and would be less likely to detach (i.e., ${}^{4}K_{b} < {}^{3}K_{b}$; Fig. 4). The relative sizes of the attachment fluxes may be considered in terms of the surface charge (or, more precisely, the anion binding-site availability; Nielsen et al., 2012, 2013) of the crystal. If the crystal surface is positively charged, aqueous $B(OH)_4^-$ will be much more likely to interact with the surface than the uncharged aqueous B(OH)₃ (i.e., ${}^{4}K_{f} > {}^{3}K_{f}$; Fig. 4), and conversely we would expect ${}^{4}K_{f} < {}^{3}K_{f}$ if the surface is negatively charged. Studies of the surface charge of calcite have produced a wide range of results (Wolthers et al., 2008), so it is difficult to have an a priori estimate for these parameters. However, the greater similarity of inorganic calcite δ^{11} B to solution δ^{11} B_{borate} than $\delta^{11}B_{\text{boric acid}}$ (e.g., Hemming et al., 1995; Sanyal et al., 2000; Noireaux et al., 2015; Farmer et al., 2016) strongly suggests that aqueous $B(OH)_4^-$ is the primary B species incorporated into calcite, implying ${}^{4}K_{f} > {}^{3}K_{f}$, and a positively charged calcite surface. Finally, given that the overall partitioning of B into inorganic calcite is much less than 1 (e.g., Hemming et al., 1995; Mavromatis et al., 2015; Uchikawa et al., 2015), it follows that $K_b > K_f$ for total B species at CaCO₃ crystal surfaces.

In summary, our modeling approach describes B incorporation in calcite as a competition between attachment fluxes, which are likely to favor the attachment of charged, tetrahedrally-coordinated $B(OH)_{4}^{-}$, and detachment fluxes, which are likely to favor the retention of both trigonallycoordinated $B(OH)_{3}$ and $B(OH)_{4}^{-}$ transformed to trigonal coordination ($BO_{2}(OH)^{2-}$ groups, Balan et al., 2016) during incorporation (Fig. 4). The relative magnitude of these fluxes, and therefore the partitioning and isotopic content of B in the mineral, will be sensitive to both the abundance and isotopic content of each B species in solution, and the mineral precipitation rate. The dataset compiled in this study constrains all parameters necessary to test whether our B SKM is sufficient to explain the patterns of B incorporation in calcite.

4.2.3. Model fitting

The values of ${}^{3}K_{f}$, ${}^{3}K_{b}$, ${}^{4}K_{f}$, ${}^{4}K_{b}$ and ${}^{C}R_{b}$ are solved through an optimization approach that minimizes the difference between observed and predicted $\lambda_{\rm B}$ and δ^{11} B, based on the known solution chemistry and precipitation rate parameters. The value of ${}^{c}R_{b}$ has been estimated from calcite dissolution experiments as $\sim 6 \times 10^{-7}$ mol/m²/s $(\log_{10}R_p = -6)$, and is relatively constant across the pH and precipitation ranges considered in our study (DePaolo, 2011). We therefore apply the same ${}^{C}R_{h}$ to all our precipitates. However, because calculation of precipitation rates $({}^{c}R_{n})$ for our calcite require several assumptions (Uchikawa et al., 2015), we allow the value of $^{C}R_{b}$ to vary during model fitting to account for uncertainties in the accuracy of ${}^{C}R_{p}$, but note that its value should fall within a similar range to those explored by DePaolo (2011) (i.e., ± 2 orders of magnitude). The starting values for ${}^{3}K_{f}$, ${}^{3}K_{h}$, ${}^{4}K_{f}$ and ${}^{4}K_{h}$ during optimization are constrained only in their approximate relative magnitudes by the basic principles discussed above.

Model optimization was performed in Python (v3.6) using an unconstrained non-linear-least-squares optimizer (Powell, 1964) via the 'minimize' function of SciPy's 'optimize' module (v0.19; Jones et al., 2001). Sensitivity of the model fit to analytical uncertainties in the data was estimated by Bootstrap error resampling. In each bootstrap iteration, the model is refit to data that are modified within their analytical uncertainties, using the best-fit parameters from the original data modified randomly to $\pm 25\%$ as a starting point for the optimization. Confidence intervals for the fitted parameters are estimated from the 95% quantiles of the bootstrap fitted parameters. All data and code required to reproduce the model fit are available in Electronic Annex 2.

4.2.4. Optimized SKM model

The optimal values of R_b , 4K_f , 4K_b , 3K_f and 3K_b are shown versus partitioning (λ_B) and isotope (ε_{c-b}) data in Fig. 5. In fitting, the attachment partition coefficients are defined relative to ratios of B to carbon species in solution. The best fit to the data is achieved when considering aqueous B(OH)₄ partitioning relative to CO_3^{2-} (i.e., $[B(OH)_4^{-}]/$ $[CO_3^{2-}]$), and aqueous B(OH)₃ relative to DIC (i.e., [B(OH)₃]/[DIC]). Using the same carbon species as the denominator for both $B(OH)_3$ and $B(OH)_4^-$ produces systematic divergences in the model residuals, highlighting that the model does not adequately describe the processes underlying the data. Conceptually, this may be considered in terms of what each aqueous B species competes with for surface binding sites. If the calcite surface is positively charged, $B(OH)_4^-$ will be attracted to the surface, and compete for attachment sites with CO_3^{2-} . Conversely, the interaction of the uncharged B(OH)₃ species with the surface



Fig. 5. Comparison of B elemental (expressed as λ_B , Eq. (2); panel a) and isotopic partitioning (expressed as ε_{c-b} , panel c) patterns versus precipitation rate between original data (blue circles) and SKM model (orange circles). Right panels (b and d) show model minus data residuals, with gray band indicating model 95% confidence interval. See text for discussion. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

will be purely stochastic, and thus a function of its abundance relative to total carbon in solution.

Our B SKM reproduces the observed patterns in both B partitioning and isotope fractionation as a function of R_n . For isotope partitioning (Fig. 5c-d), ε_{c-b} is predicted to within uncertainty for twelve of thirteen data points, and the SKM recovers the trend of decreasing ε_{c-b} with increasing R_p (Fig. 5c). For element partitioning (Fig. 5a-b), the SKM predicts nonlinear relationship between $\lambda_{\rm B}$ and R_p that has a similar form to the data (Fig. 5a), although the observed trend is slightly larger than the model prediction (Fig. 5b). The fitted parameters describing the fluxes of B species to and from the crystal surface are consistent with the relative magnitudes predicted by consideration of previously reported B geochemistry (Section 4.2.2), with ${}^{4}K_{f} > {}^{3}K_{f}$ and ${}^{4}K_{b} > {}^{3}K_{b}$, and detachment partitioning coefficients (K_b) substantially larger than attachment coefficients (K_f) (Table 3). The optimal R_b required by the model is consistent with previous estimates (DePaolo, 2011).

Table 3 Optimized model parameters with 95% confidence intervals.

Parameter	Median	95% CI
$^{3}K_{f}$	0.48	0.34-0.77
${}^{4}K_{f}$	5.49	2.85-8.26
${}^{3}K_{b}$	316.6	92.5-793.7
${}^{4}K_{b}$	7472	1774-14,560
$\log_{10}(R_b)$	-7.8	-7.2 to -8.2

4.2.5. Application to other precipitation experiments

Fitting our model to data from previously published inorganic precipitation studies is complicated by a lack of quantitative, surface-normalized precipitation rates and the diversity of solution speciation calculation methods used in previous studies (Section 2.2). However, some progress can be made by re-calculating solution chemistry using a single method (PHREEQC with PITZER database, see Electronic Annex 2) and exploiting the well-established relationship between saturation index (SI) and precipitation rate (e.g., Zhang and Nancollas, 1998) to investigate trends in all published studies that report paired B/Ca and δ^{11} B measurements with sufficiently detailed solution chemistry data (Noireaux et al., 2015; Kaczmarek et al., 2016). This exercise reveals that SI and estimated precipitation rate in past studies are poorly correlated. This poor correlation may reflect R_p measurement errors and contribute to a lack of robust patterns in these data (Supplementary Fig. 2; Electronic Annex 3). Considering $\lambda_{\rm B}$ and $\varepsilon_{\rm c-b}$ as a function of SI (Fig. 6a, c) reveals broadly consistent trends in the present and previous calcite precipitation experiments. In particular, the data of Mavromatis et al. (2015) and Noireaux et al. (2015), while considerably scattered, appear to form a continuation of the λ_B and ε_{c-b} relationships with R_p observed in this study. Our $\lambda_{\rm B}$ and $\varepsilon_{\rm c-b}$ data are notably offset from those of Kaczmarek et al. (2016) at similar SI, although similar trends of increasing $\lambda_{\rm B}$ and decreasing ε_{c-b} with increasing SI are evident in both datasets.

The B SKM is able to fit both λ_B and ε_{c-b} of the Kaczmarek et al. (2016) experiments largely to within the analytical uncertainty of the data (Fig. 6b, d). The B



Fig. 6. Boron elemental (λ_B , panel a) and isotopic partitioning (ϵ_{c-b} , panel c) plotted against calcite Saturation Index (SI_{cal}) for all paired B/Ca and $\delta^{11}B$ measurements on inorganic calcite from the literature. B speciation for literature studies was recalculated using the PITZER speciation database in PHREEQC, and $\delta^{11}B_{\text{borate}}$ recalculated using $\alpha_B = 1.026$ (Nir et al., 2015). Note that consistent patterns with precipitation rate were difficult to discern from previous studies because these studies either covered narrow SI ranges, or covered saturation conditions where B elemental and isotopic partitioning are relatively insensitive to changes in SI. Right panels show the observations versus calculated λ_B (b) and ϵ_{c-b} (d) from the SKM model using solution chemistries recalculated as above. Dashed lines in b and d are 1-to-1 lines.

SKM fits $\lambda_{\rm B}$ of, but underestimates the $\varepsilon_{\rm c-b}$ variability within, the Noireaux et al. (2015) experiments. The optimized parameters (${}^{4}K_{f}$, ${}^{4}K_{b}$, ${}^{3}K_{f}$ and ${}^{3}K_{b}$) vary between studies (Table 4), although the relative parameter magnitudes (i.e., ${}^{4}K_{f} > {}^{3}K_{f}$ and ${}^{4}K_{b} > {}^{3}K_{b}$) are similar between studies. This has three implications for our understanding of B incorporation across different precipitation experiments: First, differences in $\lambda_{\rm B}$ and $\varepsilon_{\rm c-b}$ between inorganic precipitation experiments likely indicate the role of solution chemistry on surface kinetics, which affects the ${}^{4}K_{f}$, ${}^{4}K_{b}$, ${}^{3}K_{f}$ and ${}^{3}K_{b}$ values of each experiment. Thus, the scatter observed in Fig. 6a and c reflects how different solution chemistries (ionic strength and ion composition) influence the attachment and detachment of aqueous B species to the growing crystal (e.g., compare results of Uchikawa et al., 2015, 2017). Second, the similar relative magnitudes of ${}^{4}K_{f}$, ${}^{4}K_{b}$, ${}^{3}K_{f}$ and ${}^{3}K_{b}$ between studies imply that the overall mechanism of B incorporation remains the same for all studies. Finally, this comparison demonstrates the vital importance of consistent methods for calculating solution chemistry, and accurate estimates of precipitation rate, in inorganic precipitation experiments seeking to understand

Table 4

Optimized model parameters for inorganic calcite precipitation experiments.

Study	${}^{3}K_{f}$	${}^{4}K_{f}$	${}^{3}K_{b}$	${}^{4}K_{b}$	$\log_{10}(R_b)$	
This study	0.49	5.42	317	7470	-7.76	
This study, B3 and B4 fractionation during incorporation	0.08	5.95	113	13,500	-8.07	
This study, B4 fractionation during incorporation	0.09	2.86	193	9330	-8.25	
Kaczmarek et al. (2016)	0.26	5.54	155	9590	-7.78	
Noireaux et al. (2015)	0.23	5.62	23.3	7710	-8.52	

B incorporation. When the same speciation calculation and precipitation rate estimation methods are applied to all data, first-order patterns emerge, which suggest that the SKM model developed here is able to explain trends across

all recent published data. In summary, our two-component boron SKM is able to predict observed patterns in both B partitioning and isotope fractionation in inorganic calcite by explicitly considering the contribution of both aqueous $B(OH)_3$ and B $(OH)_{4}^{-}$ during B incorporation into inorganic calcite (Fig. 4). Application of the B SKM reveals that the elemental and isotopic partitioning of B into synthetic calcite depends upon precipitation rate, solution C and B chemistry, and specific interactions between aqueous B species and the crystal growth surface. By considering these parameters, the $\lambda_{\rm B}$ and $\varepsilon_{\rm c-b}$ patterns with precipitation rate (Fig. 3) can be explained under a single B incorporation framework. We have also highlighted the presence of an additional and as yet unidentified process, which is not captured by our model, but depends on precipitation rate and aspects of solution chemistry, suggestive of a relationship to binding site availability or the incorporation of non-structurallybound B. Crucially, the specific interactions of B species with the crystal surface will be sensitive to any change in the structure, charge or chemistry of that surface. The incorporation of B is therefore likely to depend significantly on both the ionic composition of the solution (e.g., Uchikawa et al., 2017) and the geometry of the growing crystal. Additional studies are needed to elucidate these effects.

4.2.6. Caveats to the SKM

Distilling B incorporation to the simple concepts encapsulated in our B SKM is illustratively useful and mechanistically informative, but necessarily oversimplifies mineral precipitation and B incorporation. This is evident in the model's ability to predict the main effects in our data, but its inability to quantitatively match our observations; there are trends in the residuals that suggest the presence of other, secondary influences over B incorporation. The most notable deviation between model and data is evident in the $\lambda_{\rm B}$ residuals (Fig. 5b), which show a systematic trend outside the 95% confidence interval. This trend exhibits a parabolic relationship with $\log_{10}R_p$, $[CO_3^{2-}]$, $[CO_3^{2-}]/[Ca^{2+}]$ and Saturation Index (SI = Ω -1; where Ω = ([Ca²⁺]* $[CO_3^{2-}]$ solution/ $K_{sp calcite}^*$; Supplementary Figs. 3 and 4; Electronic Annex), indicating that it is most likely caused by an aspect of calcite precipitation that is not parameterized in the B SKM, such as differences in specific binding site availability driven by solution $[CO_3^{2-}]/[Ca^{2+}]$ (Nielsen et al., 2012, 2013). A more complete approach may eventually be provided by ion-by-ion growth models, which explicitly consider the interaction between impurity incorporation and binding site availability on the mineral surface (Nielsen et al., 2012, 2013). These models have been applied to cation incorporation in calcite (Nielsen et al., 2013), and highlight the importance of solution Ca^{2+}/CO_3^{2-} and binding site availability on the crystal surface as primary controlling factors of trace element incorporation. However, it is not yet practical to apply these models to

B incorporation, as it would require detailed knowledge of the interaction of each independent B species with the mineral surface, which does not currently exist.

A number of processes that could be explicitly parameterized in an ion-by-ion model are already implicitly included in our model parameters. For example, the energy barrier to recoordination of B to a structurally-stable BO₂(OH)²⁻ state (Balan et al., 2016, 2018) will be higher for $B(OH)_4^-$ (breaking a B-O bond) than $B(OH)_3$ (deprotonation). This is implicitly included in the backward fractionation factor, which is higher for $B(OH)_4^-$ than B(OH)₃. Similarly, differences in surface charge and hydration structure driven by aqueous chemistry are included by using distinct sets of fractionation factors for experiments grown under different conditions (Table 4). Other potentially important secondary processes that are not implicitly embedded in our parameters include the incorporation of B in non-structural sites, the entrapment of B by kink collision, and the role of surface entrapment processes or involvement of non-classical crystallization pathways (Branson, 2018). These processes may reconcile differences between our model and the data, but are not currently sufficiently constrained to be usefully parameterized.

A potential limitation of our B SKM is the ability of the Surface Entrapment Model (SEMO; Watson, 2004) to explain patterns in our data with similar skill. The SEMO model is functionally identical to the SKM, predicting a sigmoidal change in trace element partitioning as a function of $\log_{10}R_p$, but describes this pattern based on fundamentally different mechanisms. The SEMO model describes the 'entrapment' of impurities in the surface of a growing crystal, as precipitation rate outstrips the ability of impurities to diffuse out of a surface boundary layer that is depleted in the crystal's main constituents (i.e., Ca^{2+} and CO_3^{2-}). Our data could be equivalently well explained by a SEMO model where aqueous $B(OH)_3$ and $B(OH)_4^-$ have different diffusion rates in the surface boundary layer, which is plausible given their electrochemical differences. The SKM and SEMO both have strengths, and rely on significant assumptions (DePaolo, 2011; Watson, 2004). Our choice of the SKM over SEMO was based primarily on the nature of our precipitates, which were grown in well-mixed solutions at relatively slow precipitation rates. Under these conditions, the surface boundary layer thickness should never exceed the critical diffusion length of trace elements in solution, and the influence of surface entrapment should therefore be negligible (DePaolo, 2011). Importantly, whichever of these models is employed, the mechanistic implication is the same – that B incorporation and isotope fractionation in calcite can be explained by the rate-dependent contribution of both aqueous $B(OH)_3$ and $B(OH)_4^-$. It is not possible to conclusively distinguish between SKM and SEMO based on currently available data.

Finally, our B SKM neglects possible isotope fractionation during the incorporation of either aqueous B species into calcite. As stated above, our rationale is that both predictions of isotope fractionation during structural B incorporation from *ab-initio* calculations (Balan et al., 2018) and experimental observations of fractionation during $B(OH)_4^$ adsorption (Saldi et al., 2018) are based on systems that are at or near thermodynamic equilibrium. A precipitating crystal is, by definition, not at thermodynamic equilibrium, so our model assumes that kinetic interactions at the surface will dominantly control the B/Ca and δ^{11} B of our calcite samples. Nevertheless, we have explored the potential influence of rate-dependent and -independent fractionation of both B species on our SKM result (Electronic Annex). The key outcome of this analysis is that a B SKM forced with sole $B(OH)_4^-$ incorporation and rate-dependent isotope fractionation can also explain the patterns in our data, but only with equilibrium $B(OH)_4^-$ fractionation = +9.5% and kinetic $B(OH)_4^-$ fractionation = +4.2% (Supplementary Fig. 5). These values are similar to the theoretical structural fractionation of $\sim 11\%$ (Balan et al., 2018), and the range of measured adsorption fractionations of $\sim +2.5$ to +5% (Saldi et al., 2018).

At first sight, the similarity of these optimal parameters to literature values makes sole $B(OH)_4^-$ incorporation with rate-dependent isotope fractionation a viable alternative mechanism to our two-component B SKM. The alignment of equilibrium partitioning with the calculations of Balan et al. (2018) is particularly convincing, as at low precipitation rates the kinetic system moves towards thermodynamic equilibrium. However, the similarity of the kinetic fractionation to the measured adsorption fractionation of Saldi et al. (2018) is more complex. Their adsorption experiments were conducted in solutions with significantly lower ionic strength (I = 0.01 and 0.1) under near-equilibrium conditions, so it is likely that the convergence of our kinetic fractionation with this value is coincidental rather than meaningful. Furthermore, the magnitude of the ratedependent fractionation of a single species ($\sim 4.2\%$) is unprecedented within an SKM framework, given that isotope fractionation should follow mass-dependent laws. For instance, calcium isotopes (δ^{44} Ca) exhibit a total ratedependent fractionation of $\sim 1\%$, with a mass difference of ~10% (DePaolo, 2011; Tang et al., 2008). It is reasonable to expect a rate-dependent single species δ^{11} B change of <1%, given the $\sim10\%$ mass difference in B isotopes in isolation, and an even smaller mass difference between B complexes with oxyanions (e.g., ¹⁰BO₂(OH)²⁻ versus ¹¹BO₂(OH)^{2–}). This is \sim 4x lower than the observed kinetic range required to describe patterns in our data. Therefore, we consider that rate-dependent fractionation of $B(OH)_4^-$ is unlikely to be a primary driver of δ^{11} B patterns in inorganic calcites.

4.3. Considerations for the δ^{11} B-pH proxy

Our study shows that kinetic processes can exert significant control on B incorporation into inorganic calcite, implying that $\delta^{11}B_{\text{calcite}}$ is affected by precipitation rate (R_p) and solution chemistry. A key question for applications of the $\delta^{11}B$ -pH proxy is, to what extent does solution composition and R_p influence $\delta^{11}B$ of biogenic calcite used for paleo-pH reconstruction? Here we assess this by compiling available constraints on foraminifera calcifying microenvironment chemistry and R_p . We focus on foraminifera because of the relative abundance of information for these calcifiers, although we note that our discussion

is necessarily speculative due to very limited constraints for either parameter, even for foraminifera.

Foraminifera calcify from seawater modified by ion transport mechanisms and/or internal ion reservoirs that supply Ca^{2+} and CO_3^{2-} needed for calcification (Erez, 2003; de Nooijer et al., 2014). Based on the differences we observe between inorganic experiments with different major-ion chemistry (Fig. 6; Section 2.2), we would expect the chemistry of the calcifying microenvironment to exert a first-order control over the kinetics of ion attachment and detachment during calcification, and thus influence δ^{11} B. Unfortunately, given relatively limited constraints on the composition of foraminiferal calcifying fluids (e.g., Jørgensen et al., 1985; Rink et al., 1998; Köhler-Rink and Kühl, 2001, 2005), assessing the influence of microenvironment chemistry on foraminiferal δ^{11} B is not currently feasi-However, given that the foraminiferal ble. microenvironment is ultimately derived from seawater, it appears unlikely that its chemistry would vary to the degree employed in inorganic precipitation experiments. We therefore consider microenvironment chemistry to be a relatively constant control on B incorporation within single foraminiferal species growing at constant seawater chemistry.

In contrast to microenvironment chemistry, measurements of foraminiferal precipitation rates are available, and known to vary significantly. In laboratory culturing experiments of planktic foraminifera, measured calcification rates range from -8.9 to -6.1 ($\log_{10}R_p$ units), with the majority falling between -8.9 and -7.5 (Allen et al., 2016; Haynes et al., 2017; Holland et al., 2017). Notably, these precipitation rates are multi-day 'CaCO₃ accretion rate' averages and could encompass intervals of episodic, more rapid calcification (Allen et al., 2016; Uchikawa et al., 2017). Because R_p variations influence B incorporation in inorganic calcite, it is possible that R_p variations in foraminifera influence foraminiferal δ^{11} B.

Do any features of foraminiferal δ^{11} B suggest influence from R_p ? As noted in Section 1, empirical calibrations of for aminiferal δ^{11} B to δ^{11} B_{borate}, which take the form δ^{11} B_{calcite} = $m^* \delta^{11}$ B_{borate} + c, show small but non-negligible offsets between δ^{11} B_{calcite} and δ^{11} B_{borate} (e.g., $m \neq 1$, $c \neq 0$, or both; see Fig. 7). In field calibrations of benthic and planktic foraminifera (open symbols, Fig. 7), δ^{11} B_{calcite} generally scales with δ^{11} B_{borate} ($m \sim 1$) although with large uncertainty due to the difficulty in precisely constraining $\delta^{11}B_{borate}$ for the foraminifera's growth environment and the small $\delta^{11}B_{borate}$ ranges covered by these studies. In contrast, laboratory calibrations minimize $\delta^{11}B_{borate}$ uncertainty by growing calcites (inorganic and biogenic) under controlled conditions and broader ranges of $\delta^{11}B_{borate}$. All published laboratory calibrations of calcite, including this and previous inorganic calcite precipitation experiments, and foraminifera culturing experiments, show m < 1 (filled symbols, Fig. 7). Consequently, $\delta^{11}B_{\text{calcite}}$ is elevated above $\delta^{11}B_{\text{borate}}$ at lower pH (lower $\delta^{11}B_{\text{borate}}$), and becomes progressively closer to δ^{11} B_{borate} at higher pH (higher δ^{11} B_{borate}).

Numerous hypotheses have been proposed to explain the offsets between foraminiferal δ^{11} B and δ^{11} B_{borate} (see review in Foster and Rae, 2016), including overprinting of



Fig. 7. $\delta^{11}B_{calcite}$ versus $\delta^{11}B_{borate}$ relationships for laboratory grown foraminifera (*O. universa*: Sanyal et al., 1996; Hönisch et al., 2009; *G. ruber*: Henehan et al., 2013; *T. sacculifer*: Sanyal et al., 2001; Hönisch et al., 2009), field calibrations of foraminifera (*O. universa*, Henehan et al., 2016; *G. bulloides*, Martínez-Botí et al., 2015; *C. wuellerstorfi*, Hönisch et al., 2008; Rae et al., 2011), and laboratory grown inorganic calcites (squares; orange from Noireaux et al., 2015; blue from pH experiment at [B]_{ctr1}, this study; gray from Sanyal et al., 2000). To facilitate comparison, $\delta^{11}B_{calcite}$ and $\delta^{11}B_{borate}$ values for inorganic calcites are scaled from their respective solution $\delta^{11}B$ values to $\delta^{11}B_{sw}$ (39.61%; Foster et al., 2010) using the fractionation factor between $\delta^{11}B$ of two solutions (Equation 3.1.6 in Zeebe and Wolf-Gladrow, 2001). The dotted black line shows derived values of $\delta^{11}B_{calcite}$ as a function of $\delta^{11}B_{borate}$ calculated in the SKM using the best-fit parameters (Table 2). Slopes for $\delta^{11}B_{calcite}$ versus $\delta^{11}B_{borate}$ (*m*) for each calibration are from Hönisch et al. (2015) data (yellow squares) is recalculated using new $\delta^{11}B_{borate}$ values derived from PITZER speciation (Section 2.2). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

aqueous B(OH)₄⁻ incorporation by alterations in microenvironment pH due to respiration, calcification rate, or symbiont photosynthesis when symbionts are present (Hönisch et al., 2003; Henehan et al., 2016; Rae, 2018). Rae (2018) recently proposed that the shallower slopes (m < 1) in calibrations of cultured foraminifera might reflect greater ranges of calcification rates in these laboratory grown foraminifera as opposed to wild foraminifera. Rae (2018) hypothesized that foraminifera grown under higher pH conditions (and thus higher $\delta^{11}B_{\text{borate}}$) would exhibit higher calcification rates than foraminifera grown under lower pH conditions. Because calcification releases protons, higher foraminiferal calcification rates would actually reduce microenvironment pH relative to ambient pH, thus lowering $\delta^{11}B_{\text{calcite}}$ of these specimens and reducing the slope of $\delta^{11}B_{\text{calcite}}$ to $\delta^{11}B_{\text{borate}}$ relationships.

Our B SKM provides an alternative explanation for patterns of $\delta^{11}B_{calcite}$ with $\delta^{11}B_{borate}$ observed in laboratory experiments as a function of R_p . The B SKM predicts the observed pattern of a greater positive offset between $\delta^{11}B_{\text{calcite}}$ and $\delta^{11}B_{\text{borate}}$ at lower pH (lower $\delta^{11}B_{\text{borate}}$) (Fig. 5; dotted black line in Fig. 7) observed in inorganic calcite. This is because pH correlates with the calcite precipitation rate in our experiments, such that R_p unequivocally increases with pH (Fig. 3; Uchikawa et al., 2015). At lower pH, lower R_p will drive greater detachment of aqueous $B(OH)_4^-$ (⁴K_b arrow in Fig. 4), leading to a correspondingly greater fraction of aqueous B(OH)₃ comprising B incorporated into the calcite and higher $\delta^{11}B_{\text{calcite.}}$ Conversely, at higher pH, higher R_p will limit B(OH)⁻₄ detachment, leading to correspondingly more aqueous $B(OH)_4^-$ being incorporated into the calcite and consequently lower $\delta^{11}B_{calcite}$.

Although calling upon different mechanisms, both our and Rae's (2018) explanations for m < 1 in laboratory experiments of foraminifera rely on precipitation rate changes as a function of pH. While measurements of surface area-normalized precipitation rates in foraminifera cultured over broad pH ranges are limited, available evidence suggest that foraminifera precipitation rates may be relatively insensitive to variations in solution chemistry. Holland et al. (2017) report a narrow range of R_n for the symbiont-bearing planktic foraminifera Orbulina universa $(\log_{10}R_p \text{ of } -6.5 \text{ to } -6.1 \text{ mol/m}^2/\text{sec})$ grown under dramatic modifications of seawater chemistry ($\Omega_{calcite} = 1.5$ -10.7). The relationship between ε_{c-b} and R_p for our data (Fig. 3d) suggests the R_p range observed by Holland et al. (2017) would only change ε_{c-b} by ~0.8‰. In contrast, our inorganic precipitates appear much more sensitive to solution chemistry: our experimental solutions cover less than one SI unit (approximately one $\Omega_{calcite}$ unit) yet exhibit an ε_{c-b} range of about 4% (Fig. 3d, Fig. 6). Studies of B elemental partitioning in foraminifera similarly imply low sensitivity of foraminiferal B/Ca to R_p ; the B content of cultured for a best reflects solution $[B(OH)_4]/$ $[HCO_3^-]$ or $[B(OH)_4^-]/DIC$ (Allen et al., 2012, 2016; Haynes et al., 2017; Holland et al., 2017). The limited contribution of aqueous B(OH)₃ to foraminiferal B inferred by these studies may reflect limited R_p ranges in foraminifera. In contrast, the B content of inorganic calcites is strongly affected by precipitation rate (Gabitov et al., 2014; Mavromatis et al., 2015; Uchikawa et al., 2015, 2017; this study). Provided that existing planktic foraminiferal R_p estimates are accurate, it seems possible that planktic foraminiferal R_p is tightly controlled, and relatively independent of changes in the chemistry of ambient seawater (Allen et al., 2016; Haynes et al., 2017; Holland et al., 2017). In contrast, inorganic calcite B content and δ^{11} B are more sensitive to solution chemistry and R_p (Uchikawa et al., 2017). If true, then neither changes in B incorporation nor calcification rate-driven changes in microenvironment pH (Rae, 2018) can explain the observed discrepancies between δ^{11} -B_{calcite} and δ^{11} B_{borate} in cultured planktic foraminifera.

However, the above discussion must be cautiously considered as it hinges on sound knowledge of factors affecting field calibrations and for a miniferal R_p . The assumption that $m \sim 1$ in field calibrations reflects limited variability in kinetically-driven changes in aqueous B(OH)₃ contribution to B incorporation requires independent constraints on potentially important controls on these calibrations, such as microenvironment pH alteration from variable symbiont photosynthesis and foraminiferal respiration (Hönisch et al., 2003; Henehan et al., 2016), and a possible temperature influence on the B isotope fractionation (Zeebe, 2005; Hönisch et al., 2008; Rae et al., 2011; Farmer et al., 2015; Hönisch et al., 2019). For instance, while observations of δ^{11} B_{calcite} equaling δ^{11} B_{borate} (e.g. m = 1, c = 0) in benthic for a minifera have been used to argue for sole $B(OH)_4^$ incorporation (Rae et al., 2011; Rae, 2018), our study cautions that it is not possible to exclude variable $B(OH)_3$ incorporation in these specimens absent knowledge of precipitation rates. Thus, it is uncertain whether m = 1 in field calibrations represents sole $B(OH)_4^-$ incorporation or a fortuitous combination of biological and abiotic processes. Accurate determinations of foraminiferal calcification rates will provide important insights on B proxies. Future studies that directly measure for aminiferal calcification rates. B/Ca and δ^{11} B may be able to apply the B SKM to better understand B isotopic and elemental incorporation pathways in biogenic calcite.

5. CONCLUSIONS

In inorganic calcite precipitation experiments, calcite δ^{11} B increases with increasing solution pH but decreases with increasing solution calcium and DIC concentration. These observations demonstrate a precipitation rate effect on inorganic calcite δ^{11} B, where the B isotopic difference between inorganic calcite and solution $B(OH)_4^-$ (termed ϵ_{c-b}) linearly decreases over the $\log_{10}R_p$ range of -6.5 to -5. While previous measurements of inorganic calcite B/Ca suggested enhanced B(OH)₃ contribution to B incorporation at higher precipitation rates, our δ^{11} B data indicate enhanced $B(OH)_4^-$ contribution to B incorporation at higher precipitation rates. These disparate observations are reconciled with the first application of surface kinetic modeling to B incorporation. The B SKM is able to reproduce both B elemental and isotopic partitioning patterns as a function of precipitation rate in this and previous inorganic precipitation experiments. This model suggests that B incorporation is a function of the relative attachment and detachment partitioning of aqueous B(OH)3 and $B(OH)_4^-$. For attachment, negatively charged $B(OH)_4^-$ is more likely to attach to the presumably positively charged calcite surface than neutral B(OH)₃, while B(OH)₃ attachment should be purely stochastic. For detachment, B $(OH)_4^-$ is likely more prone to detachment due to its tetrahedral coordination, whereas trigonally coordinated $B(OH)_3$ is more compatible with the trigonally configured calcite anion site. At higher precipitation rates, calcite composition more closely follows attachment partitioning, and thus $B(OH)_4^-$ dominates B incorporation into calcite, leading to better agreement between $\delta^{11}B_{\text{calcite}}$ and $\delta^{11}B_{\text{borate}}$. On the contrary, detachment partitioning becomes a stronger determinant of inorganic calcite composition at lower precipitation rates, increasing the contribution of aqueous $B(OH)_3$ to calcite and a larger positive offset between $\delta^{11}B_{\text{calcite}}$ and $\delta^{11}B_{\text{borate}}$. The implications of this incorporation scheme for biogenic calcite hinge on better knowledge of biogenic calcite precipitation mechanisms and rates, the B isotopic composition of the calcification fluid, and the influence of solution chemistry and temperature on the kinetics at mineral growth surface. Future application of the B SKM to biogenic calcite is feasible given knowledge of starting solution chemistry, precipitation rate, B/Ca, and δ^{11} B, and may provide important insights on B incorporation in biogenic calcite.

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ELECTRONIC ANNEXES

All electronic information for this publication may be accessed by the following link: https://github.com/oscar-branson/Farmer_2018_Supplement/tree/publication.

Individual Electronic Annexes referenced in the text are accessible via the following direct links.

Annex #1 Solution Carbon Chemistry: https://nbviewer. jupyter.org/github/oscarbranson/Farmer_2018_Supplement/blob/master/Solution%20Speciation.ipynb.

Annex #2 Model Optimization: https://nbviewer.jupyter.org/github/oscarbranson/Farmer_2018_Supplement/ blob/master/Model%20Fitting.jpynb.

Annex #3 Previously Published Data: https://nbviewer. jupyter.org/github/oscarbranson/Farmer_2018_Supplement/blob/master/Model%20Application%20to%20Other %20Precipitates.ipynb.

APPENDIX A. SUPPLEMENTARY MATERIAL

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gca.2018.10.008.

REFERENCES

Allen K. A., Hönisch B., Eggins S. M. and Rosenthal Y. (2012) Environmental controls on B/Ca in calcite tests of the tropical planktic foraminifer species *Globigerinoides ruber* and *Globigerinoides sacculifer*. *Earth Planet*. *Sci. Lett.* **351–352**, 270–280. https://doi.org/10.1016/j.epsl.2012.07.004.

- Allen K. A., Hönisch B., Eggins S. M., Haynes L. L., Rosenthal Y. and Yu J. (2016) Trace element proxies for surface ocean conditions: A synthesis of culture calibrations with planktic foraminifera. *Geochim. Cosmochim. Acta* 193, 197–221. https:// doi.org/10.1016/j.gca.2016.08.015.
- Allison J.D., Brown D.S. and Novo-Gradac K.J. (1991) MINTE-QA2/PRODEFA2, A geochemical assessment model for environmental systems: Version 3.0 User's Manual. U.S. Environmental Protection Agency, Athens, GA.
- Balan E., Pietrucci F., Gervais C., Blanchard M., Schott J. and Gaillardet J. (2016) First-principles study of boron speciation in calcite and aragonite. *Geochim. Cosmochim. Acta* 193, 119–131. https://doi.org/10.1016/j.gca.2016.07.026.
- Balan E., Noireaux J., Mavromatis V., Saldi G. D., Montouillout V., Blanchard M., Pietrucci F., Gervais C., Rustad J. R., Schott J. and Gaillardet J. (2018) Theoretical isotopic fractionation between structural boron in carbonates and aqueous boric acid and borate ion. *Geochim. Cosmochim. Acta* 222, 117–129. https://doi.org/10.1016/j.gca.2017.10.017.
- Ball J. W. and Nordstrom D. K. (1991) User's manual for WATEQ4F, with revised thermodynamic database and test cases for calculation speciation of major, trace, and redox elements in natural waters. U.S. Geological Survey Open-File Report, 91–183.
- Branson O., Kaczmarek K., Redfern S. A. T., Misra S., Langer G., Tyliszczak T., Bijma J. and Elderfield H. (2015) The coordination and distribution of B in foraminiferal calcite. *Earth Planet. Sci. Lett.* **416**, 67–72. https://doi.org/10.1016/j. epsl.2015.02.006.
- Branson O. (2018) Chapter 4: boron incorporation into marine CaCO₃. In *Boron Isotopes. Advances in Isotope Geochemistry* (eds. H. Marschall and G. Foster). Springer, Cham. https://doi. org/10.1007/978-3-319-64666-4 4.
- Caldeira K. and Wickett M. E. (2003) Anthropogenic carbon and ocean pH. Nature 425, 365. https://doi.org/10.1038/425365a.
- Catanzaro E., Champion C., Garner E., Marinenko G., Sappenfield K. and Shields W. (1970) Boric acid: isotopic and assay standard references materials. *Natl. Bureau Standards (USA) Spec. Publ.* 260–17, 1–70.
- Cusack M., Kamenos N. A., Rollion-Bard C. and Tricot G. (2015) Red coralline algae assessed as marine pH proxies using ¹¹B MAS NMR. *Sci. Rep.* 5, 8175. https://doi.org/10.1038/ srep08175.
- Davies C. W. (1962) Ion Association. Butteworths, London, p. 190.
- de Nooijer L. J., Spero H. J., Erez J., Bijma J. and Reichart G. J. (2014) Biomineralization in perforate foraminifera. *Earth-Sci. Rev.* 135, 48–58. https://doi.org/10.1016/j. earscirev.2014.03.013.
- DePaolo D. J. (2011) Surface kinetic model for isotopic and trace element fractionation during precipitation of calcite from aqueous solutions. *Geochim. Cosmochim. Acta* 75, 1039–1056. https://doi.org/10.1016/j.gca.2010.11.020.
- Dickson A. G. (1990) Thermodynamics of the dissociation of boric acid in synthetic seawater from 273.15 to 318.15 K. *Deep Sea Res. Part A* 37(5), 755–766.
- Erez J. (2003) The source of ions for biomineralization in foraminifera and their implications for paleoceanographic proxies. *Rev. Mineral. Geochem.* 54(1), 115–149.
- Farmer J. R., Hönisch B., Robinson L. F. and Hill T. M. (2015) Effects of seawater-pH and biomineralization on the boron isotopic composition of deep-sea bamboo corals. *Geochim. Cosmochim. Acta* 155, 86–106. https://doi.org/10.1016/j. gca.2015.01.018.

- Farmer J. R., Hönisch B. and Uchikawa J. (2016) Single laboratory comparison of MC-ICP-MS and N-TIMS boron isotope analyses in marine carbonates. *Chem. Geol.* 447, 173–182. https://doi.org/10.1016/j.chemgeo.2016.11.008.
- Foster G. L., Pogge von Strandmann P. A. E. and Rae J. W. B. (2010) Boron and magnesium isotopic composition of seawater. *Geochem. Geophys. Geosyst.* 11, Q08015. https://doi.org/ 10.1029/2010GC003201.
- Foster G. L. and Rae J. W. B. (2016) Reconstructing ocean pH with boron isotopes in foraminifera. *Annu. Rev. Earth Planet. Sci.* 44, 207–237. https://doi.org/10.1146/annurev-earth-060115-012226.
- Gabitov R. I., Rollion-Bard C., Tripati A. and Sadekov A. (2014) In situ study of boron partitioning between calcite and fluid at different crystal growth rates. Geochim. Cosmochim. Acta 137, 81–92. https://doi.org/10.1016/j.gca.2014.04.014.
- Gustafsson J.P. (2008) Visual MINTEQ Version 3.0, https:// vminteq.lwr.kth.se/.
- Hain M. P., Sigman D. M., Higgins J. A. and Haug G. H. (2015) The effects of secular calcium and magnesium concentration changes on the thermodynamics of seawater acid/base chemistry: Implications for Eocene and Cretaceous ocean carbon chemistry and buffering. *Global Biogeochem. Cycles* 29, 517– 533. https://doi.org/10.1002/2014GB004986.
- Haynes L. L., Hönisch B., Dyez K. A., Holland K., Rosenthal Y., Fish C. R., Subhas A. V. and Rae J. W. B. (2017) Calibration of the B/Ca proxy in the planktic foraminifer *Orbulina universa* to Paleocene seawater conditions. *Paleoceanography* 32, 580–599. https://doi.org/10.1002/2016PA003069.
- Hemming N. G. and Hanson G. N. (1992) Boron isotopic composition and concentration in modern marine carbonates. *Geochim. Cosmochim. Acta* 56, 537–543.
- Hemming N. G., Reeder R. J. and Hanson G. N. (1995) Mineralfluid partitioning and isotopic fractionation of boron in synthetic calcium carbonate. *Geochim. Cosmochi. Acta* 59, 371–379.
- Henehan M. J., Rae J. W. B., Foster G. L., Erez J., Prentice K. C., Kucera M., Bostock H. C., Martínez-Botí M. A., Milton J. A., Wilson P. A., Marshall B. J. and Elliott T. (2013) Calibration of the boron isotope proxy in the planktonic foraminifera *Globigerinoides ruber* for use in palaeo-CO₂ reconstruction. *Earth Planet. Sci. Lett.* **364**, 111–122. https://doi.org/10.1016/j. epsl.2012.12.029.
- Henehan M. J., Foster G. L., Bostock H. C., Greenop R., Marshall B. J. and Wilson P. A. (2016) A new boron isotope-pH calibration for *Orbulina universa*, with implications for understanding and account for "vital effects". *Earth Planet. Sci. Lett.* **454**, 282–292. https://doi.org/10.1016/j.epsl.2016.09.024.
- Hershey J. P., Fernandez M., Milne P. J. and Millero F. J. (1986) The ionization of boric acid in NaCl, Na-Ca-Cl, and Na-Mg-Cl solutions at 25°C. *Geochim. Cosmochim. Acta* **50**, 143–148.
- Hobbs M. Y. and Reardon E. J. (1999) Effect of pH on boron coprecipitation by calcite: further evidence for nonequilibrium partitioning of trace elements. *Geochim. Cosmochim. Acta* 63, 1013–1021.
- Holland K., Eggins S. M., Hönisch B., Haynes L. L. and Branson O. (2017) Calcification rate and shell chemistry response of the planktic foraminifer *Orbulina universa* to changes in microenvironment seawater carbonate chemistry. *Earth Planet. Sci. Lett.* 464, 124–134. https://doi.org/10.1016/j.epsl.2017.02.018.
- Hönisch B., Bijma J., Russell A. D., Spero H. J., Palmer M. R., Zeebe R. E. and Eisenhaur A. (2003) The influence of symbiont photosynthesis on the boron isotopic composition of foraminifera shells. *Mar. Micropaleontol.* **49**, 87–96.
- Hönisch B., Bickert T. and Hemming N. G. (2008) Modern and Pleistocene boron isotope composition of the benthic forami-

nifer Cibicidoides wuellerstorfi. Earth Planet. Sci. Lett. 272, 309–318. https://doi.org/10.1016/j.epsl.2008.04.047.

- Hönisch B., Hemming N. G., Archer D., Siddall M. and McManus J. F. (2009) Atmospheric carbon dioxide concentration across the Mid-Pleistocene transition. *Science* 324, 1551–1554. https:// doi.org/10.1126/science.1171477.
- Hönisch B., Eggins S. M., Haynes L. L., Allen K. A., Holland K. D. and Lorbacher K. (2019) *Boron Proxies in Paleoceanography* and *Paleoclimatology*. Analytical Methods in Earth And Environmental Science Series, Wiley-Blackwell, p. 264.
- Jones E., Oliphant T., Peterson P. et al. (2001) SciPy: Open Source Scientific Tools for Python, http://www.scipy.org (online).
- Jørgensen B. B., Erez J., Revsbech P. and Cohen Y. (1985) Symbiotic photosynthesis in a planktonic foraminiferan, *Globigerinoides sacculifer* (Brady), studied with microelectrodes. *Limnol. Oceanogr.* **30**, 1253–1267.
- Kaczmarek K., Nehrke G., Misra S. and Bijma J. (2016) Investigating the effects of growth rate and temperature on the B/Ca ratio and δ^{11} B during inorganic calcite formation. *Chem. Geol.* **421**, 81–92. https://doi.org/10.1016/j. chemgeo.2015.12.002.
- Klochko K., Kaufman A. J., Yao W., Byrne R. H. and Tossell J. A. (2006) Experimental measurement of boron isotope fractionation in seawater. *Earth Planet. Sci. Lett.* 248, 276–285. https://doi.org/10.1016/j.epsl.2006.05.034.
- Klochko K., Cody G. D., Tossell J. A., Dera P. and Kaufman A. J. (2009) Re-evaluating boron speciation in biogenic calcite and aragonite using ¹¹B MAS NMR. *Geochim. Cosmochim. Acta* 73, 1890–1900. https://doi.org/10.1016/j.gca.209.01.002.
- Köhler-Rink S. and Kühl M. (2001) Microsensor studies of photosynthesis and respiration in the larger symbiont bearing foraminifera *Amphistegina lobifera*, and *Amphisorus hemprichii*. *Ophelia* 2, 111–122. https://doi.org/10.1080/ 00785236.2001.10409478.
- Köhler-Rink S. and Kühl M. (2005) The chemical microenvironment of the symbiotic planktonic foraminifer *Orbulina universa*. *Mar. Biol. Res.* 1, 68–78. https://doi.org/10.1080/ 17451000510019015.
- Lee K., Kim T.-W., Byrne R. H., Millero F. J., Feely R. A. and Liu Y.-M. (2010) The universal ratio of boron to chlorinity for the North Pacific and North Atlantic oceans. *Geochim. Cosmochim. Acta* 74, 1801–1811. https://doi.org/10.1016/j.gca.2009.12.027.
- Le Quéré C. et al. (2016) Global carbon budget 2016. *Earth Syst. Sci. Data* **8**, 605–649. https://doi.org/10.5194/essd-8-605-2016.
- Martínez-Botí M., Marino G., Foster G. L., Ziveri P., Henehan M. J., Rae J. W. B., Mortyn P. G. and Vance D. (2015) Boron isotope evidence for oceanic carbon dioxide leakage during the last deglaciation. *Nature* 518, 219–222. https://doi.org/ 10.1038/nature14155.
- Mavromatis V., Montouillout V., Noireaux J., Gaillardet J. and Schott J. (2015) Characterization of boron incorporation and speciation in calcite and aragonite from co-precipitation experiments under controlled pH, temperature and precipitation rate. *Geochim. Cosmochim. Acta* 150, 299–313. https://doi.org/ 10.1016/j.gca.2014.10.024.
- Nielsen L. C., DePaolo D. J. and De Yoreo J. J. (2012) Selfconsistent ion-by-ion growth model for kinetic isotopic fractionation during calcite precipitation. *Geochim. Cosmochim. Acta* 86, 166–181. https://doi.org/10.1016/j.gca.2012.02.009.
- Nielsen L. C., De Yoreo J. J. and DePaolo D. J. (2013) General model for calcite growth kinetics in the presence of impurity ions. *Geochim. Cosmochim. Acta* **115**, 100–114. https://doi.org/ 10.1016/j.gca.2013.04.001.
- Nir O., Vengosh A., Harkness J. S., Dwyer G. S. and Lahav O. (2015) Direct measurement of the boron isotope fractionation factor: Reducing the uncertainty in reconstructing ocean paleo-

pH. Earth Planet. Sci. Lett. 414, 1–5. https://doi.org/10.101/j. epsl.2015.01.006.

- Noireaux J., Mavromatis V., Gaillardet J., Schott J., Montouillout V., Louvat P., Rollion-Bard C. and Neuville D. R. (2015) Crystallographic control on the boron isotope paleo-pH proxy. *Earth Planet. Sci. Lett.* **430**, 398–407. https://doi.org/10.1016/j. epsl.2015.07.063.
- Parkhurst D.L. and Appelo C.A.J. (2013) Description of Input and Examples for PHREEQC version 3—A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations: U.S. Geological Survey Techniques and Methods. Book 6: p. 497 (chap. A43 available only at http://pubs.usgs.gov/tm/06/a43/).
- Plummer L. N., Parkhurst D. K., Fleming G. W. and Dunkle S. A. (1988) A computer program incorporating Pitzer's equations for calculation of geochemical reactions in brines. U.S. Geological Society Water-Resources Investigations Report 88– 4153, 310 p.
- Powell M. J. D. (1964) An efficient method for finding the minimum of a function of several variables without calculating derivatives. *Comput. J.* 7, 155–162. https://doi.org/ 10.1093/comjnl/7.2.155.
- Rae J. W., Foster G. L., Schmidt D. N. and Elliott T. (2011) Boron isotopes in B/Ca in benthic foraminifera: Proxies for the deep ocean carbonate system. *Earth Planet. Sci. Lett.* **302**, 403–413. https://doi.org/10.1016/j.epsl.2010.12.034.
- Rae J. W. (2018) Chapter 5: boron isotopes in foraminfiera: systematics, biomineralisation, and CO₂ reconstruction. In *Boron Isotopes. Advances in Isotope Geochemistry* (eds. H. Marschall and G. Foster). Springer, Cham. https://doi.org/ 10.1007/978-3-319-64666-4_5.
- Rink S., Kühl M., Bijma J. and Spero H. J. (1998) Microsensor studies of photosynthesis and respiration in the symbiotic foraminifer *Orbulina universa*. *Mar. Biol.* **131**, 583–595.
- Rollion-Bard C. and Erez J. (2010) Intra-shell boron isotope ratios in the symbiont-bearing benthic foraminiferan *Amphistegina lobifera*: Implications for δ^{11} B vital effects and paleo-pH reconstructions. *Geochim. Cosmochim. Acta* **74**, 1530–1536. https://doi.org/10.1016/j.gca.2009.11.017.
- Rollion-Bard C., Blamart D., Trebosc J., Tricot G., Mussi A. and Cuif J.-P. (2011) Boron isotopes as pH proxy: A new look at boron speciation in deep-sea corals using ¹¹B MAS NMR and EELS. *Geochim. Cosmochim. Acta* 75, 1003–1012. https://doi. org/10.1016/j.gca.2010.11.023.
- Saldi G. D., Noireaux J., Louvat P., Faure L., Balan E., Schott J. and Gaillardet J. (2018) Boron isotopic fractionation during adsorption by calcite—Implication for the seawater pH proxy. *Geochim. Cosmochim. Acta* 240, 255–273. https://doi.org/ 10.1016/j.gca.2018.08.025.
- Sanyal A., Hemming N. G., Broecker W. S., Lea D. W., Spero H. J. and Hanson G. N. (1996) Oceanic pH control on the boron isotopic composition of foraminifera: Evidence from culture experiments. *Paleoceanography* **11**, 513–517.
- Sanyal A., Nugent M., Reeder R. J. and Bijma J. (2000) Seawater pH control on the boron isotopic composition of calcite: Evidence from inorganic calcite precipitation experiments. *Geochim. Cosmochim. Acta* 64, 1551–1555.
- Sanyal A., Bijma J., Spero H. and Lea D. W. (2001) Empirical relationship between pH and the boron isotopic composition of *Globigerinoides sacculifer*: Implications for the boron isotope paleo-pH proxy. *Paleoceanography* 16, 515–519.
- Sen S., Stebbins J. F., Hemming N. G. and Ghosh B. (1994) Coordination environments of B impurities in calcite and aragonite polymorphs: A ¹¹B MAS NMR study. *Am. Mineral.* 79, 819–825.

- Simonson J. M., Roy R. N., Mrad D., Lord P., Roy L. N. and Johnson D. A. (1988) The thermodynamics of aqueous borate solutions. II. Mixtures of boric acid with calcium or magnesium borate and chloride. *J. Solution Chem.* 17, 435–446.
- Spivack A. J., You C.-F. and Smith H. J. (1993) Foraminiferal boron isotope ratios as a proxy for surface ocean pH over the past 21 Myr. *Nature* 363, 149–151.
- Tang J., Dietzel M., Böhm F., Köhler S. J. and Eisenhauer A. (2008) Sr²⁺/Ca²⁺ and ⁴⁴Ca/⁴⁰Ca fractionation during inorganic calcite formation: II. Ca isotopes. *Geochim. Cosmochim. Acta* 72, 3733–3745.
- Trotter J., Montagna P., McCulloch M., Silenzi S., Reynaud S., Mortimer G., Martin S., Ferrier-Pagès C., Gattuso J.-P. and Rodolfo-Metalpa R. (2011) Quantifying the pH 'vital effect' in the temperate zooxanthellate coral *Cladocora caespitosa*: Validation of the boron seawater pH proxy. *Earth Planet. Sci. Lett.* **303**, 163–173. https://doi.org/10.1016/j.epsl.2011.01.030.
- Uchikawa J., Penman D. E., Zachos J. C. and Zeebe R. E. (2015) Experimental evidence for kinetic effects on B/Ca in synthetic calcite: Implications for potential B(OH)₄ and B(OH)₃ incorporation. *Geochim. Cosmochim. Acta* **150**, 171–191. https://doi. org/10.1016/j.gca.2014.11.022.
- Uchikawa J., Harper D. T., Penman D. E., Zachos J. C. and Zeebe R. E. (2017) Influence of solution chemistry on the boron content in inorganic calcite grown in artificial seawater. *Geochim. Cosmochim. Acta* 218, 291–307. https://doi.org/ 10.1016/j.gca.2017.09.016.
- Vengosh A., Kolodny Y., Starinsky A., Chivas A. R. and McCulloch M. T. (1991) Coprecipitation and isotopic fractionation of boron in modern biogenic carbonates. *Geochim. Cosmochim. Acta* 55, 2901–2910.

- Watkins J. M., DePaolo D. J. and Watson E. B. (2017) Kinetic fractionation of non-traditional stable isotopes by diffusion and crystal growth reactions. *Rev. Mineral. Geochem.* 82, 85–125. https://doi.org/10.2138/rmg.2017.82.4.
- Watson E. B. (2004) A conceptual model for near-surface kinetic controls on the trace-element and stable isotope composition of abiogenic calcite crystals. *Geochim. Cosmochim. Acta* 68, 1473– 1488. https://doi.org/10.1016/j.gca.2003.10.003.
- Wolthers M., Charlet L. and Van Cappellen P. (2008) The surface chemistry of divalent metal carbonate minerals; a critical assessment of surface charge and potential data using the charge distribution multi-site ion complexation model. *Am. J. Sci.* 308, 905–941.
- Zeebe R. E. (2005) Stable boron isotope fractionation between dissolved B(OH)₃ and B(OH)₄. *Geochim. Cosmochim. Acta* **69** (11), 2753–2766. https://doi.org/10.1016/j.gca.2004.12.011.
- Zeebe R. E. and Wolf-Gladrow D. A. (2001) CO₂ in Seawater: Equilibrium, Kinetics, Isotopes. Elsevier Oceanography Series, v. 65, Elsevier, Amsterdam.
- Zeebe R. E., Sanyal A., Ortiz J. D. and Wolf-Gladrow D. A. (2001) A theoretical study of the kinetics of the boric acid-borate equilibrium in seawater. *Mar. Chem.* 73, 113–124.
- Zhang J. and Nancollas G. H. (1998) Kink density and rate of step movement during growth and dissolution of an *AB* crystal in a nonstoichiometric solution. *J. Colloid Interface Sci.* 200, 131– 145.

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