First-principles study of boron speciation in calcite and aragonite

Etienne Balan, Fabio Pietrucci, Christel Gervais, Marc Blanchard, Jacques Schott, Jérôme Gaillardet

► To cite this version:

Etienne Balan, Fabio Pietrucci, Christel Gervais, Marc Blanchard, Jacques Schott, et al.. First-principles study of boron speciation in calcite and aragonite. *Geochimica et Cosmochimica Acta*, 2016, 193, pp.119-131. 10.1016/j.gca.2016.07.026 . hal-01371923

HAL Id: hal-01371923

<https://hal.sorbonne-universite.fr/hal-01371923>

Submitted on 26 Sep 2016

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

First-principles study of boron speciation in calcite and aragonite

Revision 1

Etienne Balan^{a,*}, Fabio Pietrucci^a, Christel Gervais^b, Marc Blanchard^a,
Jacques Schott^c, Jérôme Gaillardet^d

^aSorbonne Universités - Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie (IMPMC), UPMC Université Paris 06, UMR CNRS 7590, UMR IRD 206, MNHN, 4 place Jussieu, 75252 Paris cedex 05, France

^bSorbonne Universités - Laboratoire de Chimie de la Matière Condensée de Paris (LCMCP), UPMC Université Paris 06, UMR CNRS 7574, 4 place Jussieu, 75252 Paris cedex 05, France

^cGéosciences Environnement Toulouse, Observatoire Midi-Pyrénées, CNRS-Université de Toulouse, 14, avenue Edouard Belin 31400 Toulouse, France

^dInstitut de Physique du Globe de Paris, Sorbonne Paris Cité, Université Paris Diderot, CNRS, F-75005 Paris, France, and Institut Universitaire de France.

*Corresponding author: Prof. Etienne Balan, Institut de Minéralogie, Physique des Matériaux et Cosmochimie, Case 115, 4 Place Jussieu, 75252 Paris Cedex 05.
tel: 00.33.1.44.27.74.52 fax: 00.33.1.44.27.37.85 E-mail: Etienne.Balan@impmc.upmc.fr

Abstract

Despite the importance of boron as a proxy of past ocean pH, the crystal-chemical factors controlling its incorporation in the structure of calcium carbonates are still poorly understood. This is partly linked to an imperfect knowledge of the coordination, protonation state and local environment of boron species in these minerals. In the present study, we use first-principles quantum mechanical tools to model selected trigonal and tetragonal boron species in calcite and aragonite. The stable geometry of the models is obtained from standard energy minimization schemes or using a more advanced metadynamics exploration of their configurational space. The computation of ^{11}B NMR chemical shifts and quadrupolar coupling parameters enables a straightforward comparison of the models to existing experimental NMR data. The results show that B in calcium carbonates does occur as structural species substituted for CO_3^{2-} anions. The B speciation depends on the polymorph considered. In calcite, structural boron is present as partially deprotonated trigonal $\text{BO}_2(\text{OH})^{2-}$ species coexisting with a fraction of substituted $\text{B}(\text{OH})_4^-$ groups. In aragonite, the $\text{B}(\text{OH})_4^-$ substitution for CO_3^{2-} anions is dominant. Different species, including entrapped $\text{B}(\text{OH})_3$ molecules and substituted BO_3^{3-} groups also occur in biogenic samples. The diversity of B speciation reflects a diversity of B incorporation mechanisms and sheds light on previous studies confronting B isotopic composition determination with NMR observations. The mechanisms of boron incorporation in calcium carbonates are probably more complex than usually assumed in the literature using boron isotopes as a proxy of paleo-atmospheric CO_2 reconstructions. Although not invalidating the empirical paleo-pH proxy, these results call for a better understanding of the fundamental mechanisms of boron incorporation in carbonates.

1. INTRODUCTION

The isotopic composition of boron in biogenic calcite and aragonite has been proposed and successfully used as a proxy of the past ocean acidity, which in turn reflects past levels of atmospheric CO₂ concentrations (Vengosh et al. 1991; Hemming and Hanson 1992). A large number of studies have applied this idea to various biogenic carbonates, proposed paleo-CO₂ secular evolutions for the Earth's atmosphere and established the sensitivity of global climate to atmospheric CO₂ in the past (e.g., Spivack et al. 1993; Gaillardet and Allègre 1995; Sanyal et al. 1995; Palmer et al. 1998; Pearson and Palmer 1999; Lemarchand et al. 2002; Pagani et al. 2005; Pearson et al. 2009; Martinez-Boti et al. 2015). The use of boron isotopes as a paleo-pH meter is based on the large difference in ¹¹B/¹⁰B ratio (27.2 ‰ in delta notation of isotopic abundances; Klochko et al. 2006) occurring between the major dissolved forms of boron, the trigonal boric acid (B(OH)₃, preferentially enriched in ¹¹B), and the tetragonal borate ion (B(OH)₄⁻, preferentially enriched in ¹⁰B), under thermodynamic equilibrium conditions (Zeebe 2005; Liu and Tossell 2005; Klochko et al. 2006; Rustad et al. 2010; Nir et al. 2015). As the relative proportion of these aqueous species is strongly pH-dependent in the range of expected seawater pH, mass balance considerations require that their isotopic composition is also pH-dependent. Assuming that among the two major B species present in seawater only the borate ion (B(OH)₄⁻) is incorporated in the mineral structure during crystal growth and that no boron isotope fractionation occurs during uptake, the B isotopic composition in marine carbonate samples provides a straightforward record of the secular variations of seawater pH.

The assumption of sole B(OH)₄⁻ incorporation is challenged by spectroscopic studies reporting various proportions of both trigonal and tetragonal B species

77 coexisting in calcite and aragonite samples. Both boron partitioning and speciation are
78 polymorph dependent, aragonite incorporating tetragonal boron more easily than
79 calcite (e.g. Sen et al. 1994; Branson et al. 2015; Mavromatis et al. 2015). Direct
80 determination of the boron coordination state can be achieved using ^{11}B solid-state
81 nuclear magnetic resonance (NMR) (Sen et al. 1994; Klochko et al. 2006; Rollion-Bard et
82 al. 2011; Mavromatis et al. 2015), electron energy loss spectroscopy (EELS) (Rollion-
83 Bard et al. 2001) and scanning transmission X-ray microscopy (STXM) (Branson et al.
84 2015). The observation of an often dominant contribution of trigonal B in calcite, and its
85 occurrence in aragonite, has been interpreted as reflecting a coordination change of
86 borate ions at the surface of growing crystals (Hemming et al. 1998; Klochko et al. 2009;
87 Branson et al. 2015). This interpretation is consistent with in-situ Atomic Force
88 Microscopy (AFM) observations of the morphology and dynamic of the surface of calcite
89 crystals growing from B-bearing solutions (Ruiz-Agudo et al. 2012). According to this
90 mechanism, the boron isotopic composition in the mineral phase still reflects that of the
91 borate ions in the solution. This explains the success of the boron-isotope proxy for
92 paleo-pH reconstitutions from mineral remains of extinct species. However, several
93 studies have suggested that a fraction of incorporated B could correspond to boric acid
94 molecules, directly scavenged from the solution (Xiao et al. 2008, Rollion-Bard et al.
95 2011, Noireaux et al. 2015). Consistently, higher than expected $^{11}\text{B}/^{10}\text{B}$ ratio have been
96 determined on inorganically precipitated and biogenic calcium carbonate samples.
97 Isotopic effects in biogenic carbonates have also been shown to depend upon the
98 calcifying species. Although local variations of pH at the calcification site can surely
99 contribute to the isotopic variability observed in biologically produced calcium
100 carbonates, inorganic precipitation experiments under well-constrained pH conditions

cannot be reconciled with models based on the exclusive incorporation of borate ions, showing that the basis hypotheses of the paleo-pH theory are questionable.

Despite the importance of the boron-isotope pH proxy, the crystal-chemical factors controlling boron incorporation in carbonates are still elusive. Several factors impede a detailed understanding of its incorporation mechanisms. Differences between the geometry of the stiff molecular tetragonal B anions and that of the trigonal substitution sites can lead to substantial modifications of the medium-range structure around the B species. Various electrostatic charge compensation mechanisms (e.g. involving different protonation states, presence of vacancies, or incorporation of other trace elements) can also affect the B environment, which significantly increases the system complexity. These effects are difficult to determine from experiment because spectroscopic methods usually provide information restricted to the well-defined first coordination shell of boron. Complementary to experimental observations, theoretical approaches can bring important constraints to discuss molecular-scale aspects of B incorporation in calcium carbonates. Tossell (2005, 2006) has investigated the NMR spectroscopic and the thermodynamic properties of boron species using molecular modeling techniques. Although these studies mostly focused on B species in aqueous solutions and did not treat explicitly the role of the crystalline matrix, they provided quantitative relations between the geometry and protonation state of the boron complexes and their distinctive NMR parameters. In the light of the experimental data of Sen et al. (1994), Tossell (2005) suggested that the incorporation of trigonal B should occur via a distorted, partially deprotonated group instead of more symmetric fully protonated or deprotonated groups. Tossell (2006) and Klochko et al. (2009) also suggested that chemically more complex species such as $\text{B}(\text{OH})_2\text{CO}_3^-$ could account for the experimental observations of Sen et al. (1994).

In this article, we use first-principles quantum mechanical calculations to determine the most favorable coordination states and geometry of boron species in calcite and aragonite and discuss related incorporation mechanisms. We theoretically determine the stable configuration of atomic-scale models of boron in calcium carbonates, using an approach similar to that previously developed to study sulfate incorporation in carbonates (Balan et al. 2014). The computation of the related NMR parameters (Pickard and Mauri 2001; Charpentier 2011; Bonhomme et al. 2012) then enables a straightforward comparison of the theoretical models to existing NMR experimental data. The results attest to the diversity of B speciation in synthetic and biogenic calcium carbonates; among which the substitution of partially protonated trigonal $\text{BO}_2(\text{OH})^{2-}$ and fully protonated tetragonal $\text{B}(\text{OH})_4^-$ groups for CO_3^{2-} anions are dominant.

2. METHODS

2.1 Structural optimization of models of boron-bearing calcium carbonates

First-principles quantum mechanical calculations provide the electronic density and total energy of a system made of nuclei and electrons by solving the corresponding Schrödinger equation. Many properties of a system (e.g. equilibrium structure, elastic constants, vibrational modes, ...) are in fact determined by the total energy and its variations. These methods are considered as highly predictive because their ingredients are not fitted on experimental data. All of them are however characterized by a trade-off between computation time and accuracy. In the past twenty years, methods based on

the density functional theory (DFT) have reached a level of accuracy high enough to reproduce with an excellent agreement the static and dynamic properties of geochemically relevant systems (see, e.g., Cygan and Kubicki 2001). The present calculations were performed within the DFT framework, using periodic boundary conditions and the generalized gradient approximation (GGA) to the exchange-correlation functional as proposed by Perdew, Burke and Ernzerhof (PBE; Perdew et al. 1996). The ionic cores were described by ultra-soft pseudopotentials from the GBRV library (Garrity et al. 2014); which means that only the electrons contributing to chemical bonding are explicitly treated, while those occupying the core states are considered to be unaffected by variations in the atom environment. The electronic wave-functions and charge density were expanded using a finite basis sets of plane-waves with 40 and 200 Ry cutoffs, respectively, corresponding to a convergence of the total energy better than 1 mRy/atom.

Periodic models of boron-bearing calcium carbonates were built for the two common CaCO_3 polymorphs: calcite ($R\bar{3}c$, 10 atoms per rhombohedral primitive cell) and aragonite ($Pmcm$, 20 atoms per primitive cell). In order to minimize as much as possible spurious interactions between the periodic images of the boron defects, the unit-cell of the models was built from the 2x2x2 super-cells of calcite (rhombohedral cell, 80 atoms) and aragonite (160 atoms) previously used in Balan et al. (2014). The equilibrium geometry of these models was obtained by displacing the atoms up to a minimum energy state, characterized by the fact that the forces experienced by the atoms vanish. These structure relaxations were done using the PWscf code of the Quantum ESPRESSO package (Giannozzi et al. 2009; <http://www.quantum-espresso.org>) and forces on atoms were minimized to less than 10^{-4} Ry/a.u. The

Brillouin zone sampling was restricted to a single k -point; which is appropriate to treat such systems with large unit-cell.

A reference theoretical sassolite (boric acid; $\text{B}(\text{OH})_3$) structure was obtained using a $2 \times 2 \times 2$ k -points grid. The relaxed cell volume ($V = 285.28 \text{ \AA}^3$) and bond lengths ($d(\text{B-O}) = 1.378 \text{ \AA}$; $d(\text{O-H}) = 1.01 \text{ \AA}$) slightly overestimate their experimental counterparts ($V = 273.62 \text{ \AA}^3$; $d(\text{B-O}) = 1.36 \text{ \AA}$; $d(\text{O-H}) = 0.9 \text{ \AA}$; Zachariasen 1954), which is consistent with a previous DFT-GGA modeling study (Ferlat et al. 2006). A theoretical structure of takedaite ($\text{Ca}_3\text{B}_2\text{O}_6$) was also obtained with a $2 \times 2 \times 2$ k -points grid, leading to relaxed cell volume ($V = 785.23 \text{ \AA}^3$) and bond lengths ($d(\text{B-O}) = 1.391 \text{ \AA}$) slightly larger than experimental values ($V = 765.61 \text{ \AA}^3$, $d(\text{B-O}) = 1.384 \text{ \AA}$; Vegas et al. 1975).

2.2 First-principles metadynamics

First-principles metadynamics (Laio and Parrinello 2002) runs were used to determine the most stable configuration of $\text{B}(\text{OH})_4^-$ in its crystal host from an exploration of the free-energy landscape drawn by variations in the H-bonding pattern. This approach provides an efficient method to explore a free-energy landscape potentially displaying several relative minima separated by barriers higher than the relevant thermal energy. Usual molecular dynamics would require prohibitively high temperature and/or long simulation to achieve an adequate sampling of the corresponding phase space. In contrast, the metadynamics builds an history dependent bias potential which drives the system away from the previously explored configurations, thus accelerating the exploration of the phase space and providing an elegant way to pass the energy barriers. In practice, the bias potential is built in a space of reduced dimensionality depending on the properties under study and referred to as

collective variables space. For example, a chemical reaction can be described by selecting a specific inter-atomic distance reflecting the breaking or the formation of a chemical bond. In the present study, exploring the different possible configurations of a given tetragonal boron group with respect to the calcite/aragonite crystal host equates to exploring different topologies in the network of chemical interactions formed by covalent and hydrogen bonds in a boron-centered region.

Born-Oppenheimer metadynamics runs were performed in the NVT ensemble (i.e. the number of atoms, volume and average temperature were constant during the runs) using the same DFT framework and parameters as those used for the structural relaxations. The hydrogen mass was increased to two atomic mass units and the runs were carried out with a timestep of 0.4×10^{-15} s. Temperature was controlled to 300 K employing a stochastic velocity rescaling thermostat (Bussi et al. 2007). Both in aragonite and calcite, we employed SPRINT collective variables (Pietrucci and Andreoni 2011), as implemented in Plumed (Bonomi et al., 2009), including a total of 26 atoms, namely the 4 hydrogens belonging to B(OH)_4^- and 22 oxygens belonging to carbonates and lying within 4 Å of the oxygens belonging to B(OH)_4^- . The 26 collective variables were biased simultaneously adding every 100 molecular dynamics steps Gaussian hills of height 5.2 kJ/mol and width 0.9 or 1.1 (for aragonite or calcite, respectively).

To facilitate the identification of the different metastable configurations explored along the metadynamics trajectory, we performed a structural cluster analysis in the space of SPRINT collective variables, employing the k-medoids algorithm as implemented in the software piv-clustering (Gallet and Pietrucci 2013).

2.3 First-principles calculation of NMR parameters

The $I = 3/2$ nuclear spin of ^{11}B implies that its NMR properties involve both the Zeeman effect and the interaction of the nuclear quadrupolar moment with the electric field gradient at the nucleus. Accordingly, three parameters can be extracted from ^{11}B NMR spectra, namely the chemical shift δ_{iso} , the quadrupolar coupling constant C_Q and the asymmetry parameter η .

The NMR chemical shift describes the difference between the applied external magnetic field and the magnetic field at the nucleus positions. It can be obtained from the structural models by calculating the shielding of the nuclei relative to the electronic current induced by the external magnetic field. This current was calculated by using the GIPAW approach, which allows reconstructing the all-electron magnetic response from the pseudo-wave-functions (Pickard and Mauri 2001; Charpentier 2011; Bonhomme et al. 2012). The calculations were performed using the PWscf and GIPAW codes of the Quantum ESPRESSO package (Giannozzi et al. 2009). Norm-conserving pseudo-potentials were used and the wave functions kinetic energy cutoff was increased to 80 Ry. The integral over the Brillouin zone was done using a Monkhorst-Pack $1 \times 1 \times 1$ k -point grid for the different models and $2 \times 2 \times 2$ for sassolite ($\text{B}(\text{OH})_3$) used as a reference. The isotropic chemical shift δ_{iso} is defined as $\delta_{\text{iso}} = -(\sigma - \sigma^{\text{ref}})$, where σ is the isotropic shielding (one-third of the trace of the NMR shielding tensor) and σ^{ref} is the isotropic shielding of the same nucleus in a reference system. In our calculations, absolute shielding tensors are obtained. To fix the scales, σ^{ref} was chosen by comparing experimental (19.2 ppm, Soraru et al. 1999) and calculated δ_{iso} values in $\text{B}(\text{OH})_3$.

The C_Q and η parameters are related to the eigenvalues of the electric field gradient tensor and reflect the symmetry of the B environment. The $C_Q = 2.49$ MHz and $\eta = 0.0$ parameters computed for sassolite ($\text{B}(\text{OH})_3$) are consistent with experimental

values (2.47 MHz and 0.0; Klochko et al. 2009). It should be noted that for the $C_Q(^{11}\text{B})$ calculation, a quadrupole moment of 35 mb was used: this value is smaller than the theoretical value of 40 mb (Pyykkö, 2008) as recommended by Soleilhavoip et al. (2010) in borosilicate glasses. Estimated precision is ± 0.5 ppm, ± 0.1 MHz and ± 0.1 for δ_{iso} , C_Q and η , respectively.

3. RESULTS

3.1 Trigonal boron incorporation at the carbonate site

We first consider the incorporation of trigonal boron species. The simplest model is obtained by substituting a B^{3+} for a C^{4+} (Table 1). The charge balance is obtained by spreading homogeneously an electrostatic counter-charge over the unit-cell. The crystal site symmetry is preserved. The three equivalent B-O bonds in calcite have a length of 1.388 Å. The BO_3^{3-} group in aragonite displays a mirror symmetry with a shorter B-O distance of 1.380 Å on the mirror plane and two symmetric B-O distances of 1.383 Å. The high symmetry of BO_3^{3-} groups in the homogeneously compensated models leads to very small η parameters. Compared to calcite, the aragonite ^{11}B chemical shift is higher and similar to that of the calcium orthoborate, takedaite.

A more realistic charge compensation mechanism consists in adding one H atom to the previous system, forming a $\text{BO}_2(\text{OH})^{2-}$ group (Fig. 1). For the 3-fold calcite site, the three oxygen atoms are symmetrically equivalent and only one protonation scheme was considered. Two different protonation schemes are considered for aragonite, affecting the oxygen on the mirror plane of the BO_3 triangle (scheme A) or one of the other two symmetric oxygen atoms (scheme B). Scheme A is more stable than B by 16.8 kJ/mol

and should be thermodynamically dominant at room temperature. The $\text{BO}_2(\text{OH})^{2-}$ species in calcite and aragonite display similar structural characteristics. The OH group points out of the BO_3 triangle sharing a H-bond of moderate strength with an oxygen belonging to an adjacent carbonate group. A significant distortion of the trigonal geometry is observed with the B-O(H) distance increasing by $\sim 0.1 \text{ \AA}$; whereas the two other B-O distances decrease by 0.03 to 0.04 $\text{\AA}$. Compared to the models with an homogeneous charge compensation, the ^{11}B δ_{iso} decreases by 1.5 and by 3 to 4 ppm in calcite and aragonite, respectively; whereas the quadrupolar coupling parameter C_Q is weakly affected. The asymmetry parameter η increases to 0.8 indicating a strong departure from the revolution symmetry, consistent with the in-plane distortion of the BO_3 triangle.

3.2 Tetragonal boron incorporation at the carbonate site

Following an approach similar to that applied to the trigonal B species, $\text{B}(\text{OH})_4^-$ for CO_3^{2-} substitution was modeled by using a homogeneous electrostatic background to compensate the charge imbalance. Previous calculations on sulfate incorporation in carbonate (Balan et al. 2014) provided a suitable starting guess for the structural optimization. However, the large number of potential H-bond acceptors around the impurity increases the probability to drive the system to a metastable configuration. This difficulty was circumvented by performing first-principles metadynamics (FPM) runs (Laio and Parrinello 2002; Pietrucci and Andreoni 2011) to explore the free energy landscape of the borate group conformation and to isolate the most favorable one.

The aragonite FPM run lasted $\sim 6 \times 10^{-12} \text{ s}$ (Fig. 2, video file in electronic annex). In an initial phase of $\sim 3 \times 10^{-12} \text{ s}$ the instantaneous bias potential fluctuates between

zero and less than 10 kJ/mol, indicating that different configurations are being explored (zero bias corresponds to an unexplored region of the configuration space). In a second phase, the bias potential starts to grow more consistently to few tens of kJ/mol without coming back to zero. This indicates that the available low-energy configurations have been exhausted and that higher-energy configurations have been explored. Concomitantly, the fluctuations of the SPRINT topological variables related to H and O atoms (Fig. 2) attest to the changes of configuration of the B(OH)_4^- species, by reorienting the OH groups to engage in different patterns of hydrogen bonds with the carbonates. The trajectory analysis leads to 8 maximally distinct instantaneous configurations. After structural optimization, two classes of configurations differing by the orientation of the O3-H bond (almost parallel to the b- axis or to the c-axis), could be defined. In the following, only the most stable configuration will be considered since the energy difference between the two (19 kJ/mol) is significantly larger than the typical thermal energy at ambient temperature (2.5 kJ/mol). In this configuration (Fig. 1), the O3-H bond is almost parallel to the c-axis and the borate group is slightly distorted with an average B-O length of 1.481 Å (Table 1). As for sulfate (Balan et al. 2014), the borate group is tilted with respect to the (a,b) plane and a significant displacement of the neighboring carbonate groups is observed. The four H-bonds display quite regular characteristics with O-H distances ranging from 0.989 to 1.008 Å and O(H)...O distances from 2.62 to 2.65 Å. Few relative energy minima were however observed in each configuration class due to moderate displacements of the surrounding carbonates, leading to energy differences ranging between 5 and 13 kJ/mol. These configurations can be envisioned as intermediate states in the transition from one H-bonding geometry to the other. A longer FPM run (15×10^{-12} s, Fig. 3, video file in electronic annex) was performed on calcite but only two different instantaneous configurations were

identified, leading to a single relaxed structure. As observed for other tetrahedral anions in calcite (Reeder et al. 1994; Fernandez-Diaz et al. 2010; Balan et al. 2014), the B(OH)_4^- anion is slightly tilted with the apical B-O bond forming an angle of 13° with respect to the ternary axis of calcite. Although the structural environment is different, only slight differences in the B-O and H-bond distances are observed between calcite and aragonite (Table 1). The theoretical ^{11}B NMR parameters of B(OH)_4^- in calcite and aragonite are similar, with δ_{iso} close to 1 ppm and small quadrupolar coupling parameters (Table 1).

As for the trigonal B species, alternative models of tetragonal borate in calcium carbonates were explored by assuming local charge compensation mechanisms. Removing a proton from the B(OH)_4^- group, modifies its charge to -2 (equivalent to that of the CO_3^{2-} group). Starting from the tetrahedral geometries obtained from FPM runs, four relaxed schemes (matching the four different H atoms of the borate group) are obtained for each calcium carbonate polymorph. The deprotonation of the O3-H group (Table 1) is favored in aragonite by more than 27 kJ/mol. In calcite, the most stable (by more than 7 kJ/mol) configuration is obtained by deprotonation of the O2-H group (Table 1). All the BO(OH)_3^{2-} species display a significant distortion of the boron coordination shell. Consistently, the C_Q values increase, ranging between 1.01 and 1.53 MHz.

A different mechanism ensuring the neutrality of B(OH)_4^- for CO_3^{2-} substitution corresponds to the coupled substitution of a monovalent cation for Ca^{2+} . Sodium is the most relevant one both in terms of seawater abundance and ionic radii similarity. Two configurations have been selected by assuming that the Na^+ for Ca^{2+} substitution affects the site closest to the central boron atom (Fig. 1). In both configurations, the structure of the B(OH)_4^- group and the H-bonding pattern is weakly affected by the Na^+ for Ca^{2+} substitution. The Na to B distances increase by $\sim 0.05 \text{ \AA}$ compared to Ca to B distances.

Compared with the homogeneously compensated models, only weak variations of the ^{11}B NMR parameters are observed (Table 1).

4. DISCUSSION

4.1 Boron in calcium carbonates: Comparing theory and experiment

4.1.1 Trigonal boron speciation

Although only few studies report experimentally determined NMR parameters of boron in calcite and aragonite, they reveal a significant variability of the trigonal boron environment (Table 2, Fig. 4). The chemical shift of trigonal boron ranges from 16 ppm (calcite) to 22 ppm (heated aragonite) and strong differences are observed on the rhombic η parameter. The trigonal boron species in the calcite samples investigated by Sen et al. (1994) is rhombically distorted, with η values of 0.67 and 0.5 in the synthetic and biogenic sample, respectively. In contrast, the nil η values reported by Klochko et al. (2009) in biogenic calcite and aragonite samples correspond to a radially symmetric environment of boron. A similarly low value of η is reported by Rollion-Bard et al. (2011) for a biogenic aragonitic coral sample. As already highlighted by Klochko et al. (2009), these variations in η values are highly significant because η is only defined between 0 and 1.

The theoretical parameters determined for the $\text{BO}_2(\text{OH})^{2-}$ species in calcite are consistent with those reported by Sen et al. (1994) for synthetic calcite. The chemical shift and quadrupolar coupling of $\text{BO}_2(\text{OH})^{2-}$ in aragonite also match the experimental values reported by Mavromatis et al. (2015) for synthetic aragonite. Unfortunately, the η

parameter was not reported for this sample, likely because of its low trigonal B content. From the comparison of theoretical and experimental NMR parameters, singly protonated $\text{BO}_2(\text{OH})^{2-}$ groups appear as the dominant speciation of trigonal boron in the synthetic calcium carbonates precipitated from solutions. This confirms the previous suggestions that trigonal boron in carbonates should be distorted and partially deprotonated (Hemming and Hanson 1992; Tossell 2005). This speciation is favored by the electrostatic balance requirements. An overall preference for local electrostatic charge compensation in minerals is attested by the observation of chemically complex defects, associating different trace elements in the same crystal site. For example, clumped-defects associating fluoride ions with carbonate groups have been observed in apatite (Yi et al. 2013). Note however that, in absence of C_Q and η values, some uncertainty affects the interpretation of the NMR parameters reported by Mavromatis et al. (2015) for synthetic calcite samples. Their chemical shift is only slightly lower than that of $\text{BO}_2(\text{OH})^{2-}$ species and consistent with the value reported by Sen et al. (1994) for a synthetic calcite sample (Fig. 4). Isotopic compositions (Noireaux et al. 2015) indicate (under the assumption that no isotope fractionation occurs during incorporation) that between 20% and 40% of boron in these samples results from the incorporation of aqueous boric acid and that this proportion is linearly correlated with the pH-dependent amount of boric acid in solution. The proportion of trigonal B detected by NMR is however higher than that inferred from isotopic composition (Noireaux et al., 2015). Thus, both borate anions and boric acid molecules could contribute to the incorporation of $\text{BO}_2(\text{OH})^{2-}$ species in the bulk of calcite particles. This implies a coordination change of tetragonal borate as well as several deprotonation steps affecting the tetragonal and trigonal boron species in the interfacial region of growing calcite crystals.

Concerning the biogenic calcium carbonates, the algal calcite investigated by Sen et al. (1994) displays NMR parameters consistent with $\text{BO}_2(\text{OH})^{2-}$ groups. In contrast, the parameters reported by Klochko et al. (2009) for a foram calcite correspond to fully deprotonated BO_3^{3-} groups substituted in the calcite structure (Fig. 4, Table 1). The sensitivity of ^{11}B NMR to the trigonal boron protonation state is further confirmed by the higher δ_{iso} , and weak η , indicative of a more symmetric boron environment in a calcite sample produced by the high-temperature (500 °C) transformation of biogenic aragonite. These parameters are close to those computed for BO_3^{3-} groups in aragonite (Fig. 4) and in the calcium orthoborate takedaite (Table 1). They indicate that the thermally driven aragonite to calcite transformation leads to a full deprotonation of borate groups. They however suggest that the local environment of BO_3^{3-} groups in the heated aragonite differs from that in crystalline calcite.

The ^{11}B NMR parameters of trigonal boron in coral aragonitic samples combine comparatively low δ_{iso} value and weak η (Klochko et al. 2009; Rollion-Bard et al. 2011). The weak η is indicative of a regular coordination shell, but the δ_{iso} values are too low to correspond to fully deprotonated BO_3^{3-} groups (Fig. 4; Table 1). Accordingly, these parameters are interpreted as related to fully protonated $\text{B}(\text{OH})_3$ molecules. The incorporation of boric acid molecules in crystallographic sites is unrealistic because of the corresponding strong electrostatic charge imbalance. It is more likely that $\text{B}(\text{OH})_3$ molecules are directly scavenged from the solution and encapsulated by the solid phase. Such step can involve their incorporation in the amorphous and hydrous calcium carbonate phases, observed under high supersaturation and elevated growth rate conditions and identified as intermediate phases in the growth of biogenic calcium carbonates (e.g. Gower 2008; Purgstaller et al., 2016). The $\text{B}(\text{OH})_3$ molecules could also occur in interfacial or porous regions separating ordered CaCO_3 nanodomains, such as

those observed in calcitic red coral (Vielzeuf et al. 2008). The preserved coordination state and isotopic composition can lead to higher than expected $\delta^{11}\text{B}$, depending on the proportion of $\text{B}(\text{OH})_3$ molecules relative to the total B content. This interpretation is consistent with the concomitant observation of elevated $\delta^{11}\text{B}$ and higher trigonal boron concentration at the center of calcification of an aragonitic coral sample by Rollion-Bard et al. (2011). Note however that trigonal B usually is a minority species in aragonitic samples, which tempers the isotopic effect related to $\text{B}(\text{OH})_3$ incorporation.

4.1.2 Tetragonal boron speciation

The experimental chemical shift of tetragonal B species displays a range of variation between -2.4 and 3 ppm, considering both calcite and aragonite (Fig. 5). Except two samples with δ_{iso} above 2 ppm and two signals with negative chemical shifts ascribed to non-structural species in calcitic samples (Mavromatis et al. 2015), the NMR parameters are consistent with those obtained for the $\text{B}(\text{OH})_4^-$ models. The systematically nil values of experimental quadrupolar coupling parameters (Table 2) attest to a highly symmetric B environment. They rule out the partially deprotonated tetragonal species, which are characterized by theoretical C_Q values larger than 1 MHz. Accordingly, tetragonal B should mostly occur in the calcium carbonate samples as fully protonated $\text{B}(\text{OH})_4^-$ groups. A high protonation state of tetragonal B was suggested by Klochko et al. (2009) from ^1H decoupling experiments.

The substitution of $\text{B}(\text{OH})_4^-$ for CO_3^{2-} implies that more remote mechanisms ensure the charge compensation, among which the Na^+ for Ca^{2+} substitution is the most probable one. As a matter of fact, the Na-bearing models also display NMR parameters consistent with the experimental observations. This coupled substitution could be

responsible, at least in part, for the dependence of B/Ca ratio on salinity reported for biogenic calcium carbonates (Allen et al. 2011, 2012; Allen and Hönisch 2012; Henehan et al. 2015). Inorganic co-precipitation experiments of Kitano et al. (1978) have also shown a significant increase in B incorporation in calcite with increasing NaCl concentration in the parent solution. For aragonite, the observed dependence was in the opposite direction but with a comparatively weaker magnitude. We note however that an aragonitic coral sample and an hydrothermal calcitic sample investigated by Klochko et al. (2009) display higher δ_{iso} values of 2.54 and 2.87 ppm, respectively, and likely correspond to B(OH)_4^- groups in a different environment or involving a charge compensation mechanism differing from that prevailing in the other samples. The potential presence of contaminant phases cannot be fully excluded for these natural samples. Beside Na^+ for Ca^{2+} substitution, different charge compensation mechanisms could occur, as shown by the Na-free synthesis experiments of Hemming et al. (1995) and Sen et al. (1994). For example, HCO_3^- groups associated with Ca vacancies could play such compensation role. A potential role of phosphate anions substituted for carbonate groups has also been suggested by Henehan et al. (2015). Variations in the borate group environment are also attested by the broad signals with slightly negative chemical shifts observed by Mavromatis et al. (2015), interpreted as corresponding to a fraction of borate groups occurring in defective domains of the calcite samples.

4.2 Boron speciation in calcium carbonates: Implications for the paleo-pH proxy

The present results show that B in calcium carbonates does occur as substituted species for CO_3^{2-} anions, thus confirming its structural nature. They further show that its speciation depends on the polymorph considered. This is fully consistent with a number

of previous studies on boron incorporation in biogenic and abiotic carbonates (e.g. Klochko et al. 2009; Mavromatis et al. 2015; Noireaux et al. 2015) and strongly challenge the hypothesis on which the use of boron isotopes to reconstruct paleo ocean pH has been used (i.e. sole incorporation of the aqueous borate ion). In calcite, structural boron is present as partially deprotonated trigonal $\text{BO}_2(\text{OH})^{2-}$ species, coexisting with substituted $\text{B}(\text{OH})_4^-$ groups in a proportion depending on the crystal growth parameters. In aragonite, the $\text{B}(\text{OH})_4^-$ substitution for CO_3^{2-} anions is dominant. The theoretical modeling of NMR spectra also indicates that different B species, including entrapped $\text{B}(\text{OH})_3$ molecules and substituted BO_3^{3-} groups can occur in biogenic samples. The diversity of B speciation indirectly confirms the importance of out-of-equilibrium parameters and interfacial properties in determining the chemical form and abundance of boron in calcium carbonate (e.g., Hemming et al. 1998; Hobbs and Reardon 1999; Ruiz-Agudo et al. 2012; Gabitov et al. 2014; Branson et al. 2015; Noireaux et al. 2015; Uchikawa et al. 2015; Kaczmarek et al. 2016). Although the $\text{B}(\text{OH})_3$ molecules in biogenic aragonitic samples might have been directly scavenged from the solution, the other trigonal $\text{BO}_2(\text{OH})^{2-}$ and BO_3^{3-} species most probably result from a coordination change and deprotonation of boron species adsorbed at the mineral surface.

An important implication of the observed diversity of B speciation in calcium carbonates is that the ratio of trigonal to tetragonal species determined by NMR spectroscopy is not a sufficient parameter to infer its incorporation mechanism. This ratio is not simply related to the trigonal to tetragonal proportion in the solution nor solely results from a coordination decrease affecting the adsorbed borate ion during its incorporation in the crystal structure. The environment and protonation state of trigonal B however appears as more variable than that of the tetragonal species. In this latter case, the variations are most likely related to more remote charge compensation

mechanisms and do not affect the first coordination shell of boron. In addition, the high sodium concentration of seawater could favor the Na^+ for Ca^{2+} substitution in the charge compensation of B(OH)_4^- species. The prevalence of a specific charge compensation mechanism would reduce the crystal-chemical complexity of the B(OH)_4^- incorporation mechanism. Interestingly, the affinity of aragonite is higher than that of calcite for both B and Na. In the case of Na, this has been interpreted as reflecting its incorporation in interstitial sites of calcite, instead of structural Ca site as in aragonite (Ishikawa and Ichikuni 1984; Okumura et al. 1986). As a consequence, aragonitic samples in which tetragonal B is dominant should faithfully reflect the pH of past oceans, as proposed by Noireaux et al. (2015), provided that sampling strategies taking into account the growth mechanism of biogenic aragonite are developed (Rollion-Bard et al. 2011).

In the case of calcitic samples, the more diverse boron speciation could be considered as a fingerprint of the growth mechanism and could serve as an indicator to extrapolate the laboratory calibrations to the geologic samples. The recent spatially-resolved study of Branson et al. (2015) indicates a dominantly trigonal (>85%) coordination and a heterogeneous distribution of boron in foraminiferal calcite; whereas NMR studies revealed a fraction of tetragonal B in biogenic calcite (~20%, Sen et al. 1994; ~54%, Klochko et al. 2009). Thus, the occurrence of differently coordinated species, with potentially distinct isotopic compositions, in spatially different domains of the composite biogenic samples cannot be excluded. As diagenesis and alteration may differently affect these domains, the boron isotopic composition of geological samples would then depend on their preservation state (Wara et al. 2003). We note however that the observations of Edgar et al. (2015) suggest that the boron isotopic composition of fossil planktonic foraminiferal calcite is resistant to diagenetic transformations. This

calls for further experimental studies focusing on the effects of diagenesis on boron speciation in carbonates.

Finally, we highlight that the approach developed in the present study, which combines a metadynamics determination of stable configurations of polyatomic groups with the first-principles calculation of related spectroscopic parameters, represents a general tool to explore the speciation of molecular anions in host crystalline matrices, readily applicable to a larger range of geochemical proxies in minerals.

ACKNOWLEDGMENTS

This work has been supported by the French National Research Agency through the CARBORIC (ANR-13-BS06-0013-06) project. This work was performed using HPC resources from GENCI-IDRIS (Grants i2016041519 and i2016097535). We thank M. Henehan and two anonymous reviewers for their constructive comments and suggestions.

REFERENCES

- Allen K. A. and Hoenisch B. (2012) The planktic foraminiferal B/Ca proxy for seawater carbonate chemistry: A critical evaluation, *Earth Planet. Sci. Lett.* **345–348**, 203–21.
- Allen K. A., Hoenisch B., Eggins S. M., Yu J., Spero H. J. and Elderfield H. (2011) Controls on boron incorporation in cultured tests of the planktic foraminifer *Orbulina universa*, *Earth Planet. Sci. Lett.* **309**, 291–30.

545 Allen K. A., Hoenisch B., Eggins S. M. and Rosenthal Y. (2012) Environmental controls on
 546 B/Ca in calcite tests of the tropical planktic foraminifer species *Globigerinoides*
 547 *ruber* and *Globigerinoides sacculifer*, *Earth Planet. Sci. Lett.* **351–352**, 270–280,
 548 Balan E., Blanchard M., Pinilla C. and Lazzeri M. (2014) First-principles modeling of
 549 sulfate incorporation and $^{34}\text{S}/^{32}\text{S}$ isotopic fractionation in different calcium
 550 carbonates. *Chem. Geol.* **374–375**, 84–91.
 551 Bonhomme C., Gervais C., Babonneau F., Coelho C., Pourpoint F., Azaïs T., Ashbrook S.E.,
 552 Griffin J.M., Yates J.R., Mauri F. and Pickard C.I. (2012) First-Principles Calculation
 553 of NMR Parameters using the gauge including projector augmented wave method:
 554 A chemist's point of view. *Chemical reviews* **112**, 5733–5779.
 555 Bonomi M., Branduardi D., Bussi G., Camilloni C., Provasi D., Raiteri P., Donadio D.,
 556 Marinelli F., Pietrucci F., Broglia R.A. and Parrinello M. (2009) PLUMED: a portable
 557 plugin for free-energy calculations with molecular dynamics. *Comp. Phys. Comm.*
 558 **180**, 1961.
 559 Branson O., Kaczmarek K., Refern S. A. T., Misra, S., Langer G., Tylliszczak T., Bijma J. and
 560 Elderfield H. (2015) The coordination and distribution of B in foraminiferal calcite.
 561 *Earth Planet. Sci. Lett.* **416**, 67–72.
 562 Bussi G., Donadio D. and Parrinello M. (2007) Canonical sampling through velocity
 563 rescaling. *J. Chem. Phys.* **126**, 014101.
 564 Charpentier T. (2011) The PAW/GIPAW approach for computing NMR parameters: A
 565 new dimension added to NMR study of solids. *Solid State NMR* **40**, 1–20.
 566 Cygan, R.T. and Kubicki, J.D. (2001) Reviews in Mineralogy and Geochemistry: Molecular
 567 Modeling Theory: Applications in the Geosciences. 531 p. The Mineralogical
 568 Society of America, Washington, D.C.

569 Edgar K., Anagnostou E., Pearson P. and Foster G. (2015) Assessing the impact of
570 diagenesis on 11B, 13C, 18O, Sr/Ca and B/Ca values in fossil planktic foraminiferal
571 calcite. *Geochim. Cosmochim. Acta* **166**, 189- 209.

572 Ferlat G., Cormier L., Mauri F., Balan E., Charpentier T., Anglada E. and Calas G. (2006)
573 Ab initio calculations on borate systems. *Eur. J. Glass Sci. Techno. B* **4**, 441-444.

574 Fernández-Díaz L., Fernández-González A. and Prieto M. (2010) The role of sulfate
575 groups in controlling CaCO₃ polymorphism. *Geochim. Cosmochim. Acta* **74**, 6064-
576 6076.

577 Gabitov R. I., Rollion-Bard C., Tripathi A. and Sadekov A. (2014) In situ study of boron
578 partitioning between calcite and fluid at different crystal growth rates. *Geochim.*
579 *Cosmochim. Acta* **137**, 81-92.

580 Gaillardet J. and Allègre C.J. (1995) Boron isotopic compositions of corals: Seawater or
581 diagenesis record? *Earth Planet. Sci. Lett.* **136**, 665-676.

582 Gallet G. A. and Pietrucci F. (2013) Structural cluster analysis of chemical reactions in
583 solution. *J. Chem. Phys.* **139**, 074101.

584 Garrity K. F., Bennett J. W., Rabe K. M. and Vanderbilt D. (2014) Pseudopotentials for
585 high-throughput DFT calculations. *Comput. Mat. Sci.* **81**, 446-452.

586 Giannozzi P., Baroni S., Bonini N., Calandra M., Car R., Cavazzoni C., Ceresoli D., Chiarotti
587 G.L., Cococcioni M., Dabo I., Dal Corso A., de Gironcoli S., Fabris S., Fratesi G.,
588 Gebauer R., Gerstmann U., Gougoussis C., Kokalj A., Lazzeri M., Martin-Samos L.,
589 Marzari N., Mauri F., Mazzarello R., Paolini S., Pasquarello A., Paulatto L., Sbraccia
590 C., Scandolo S., Sclauzero G., Seitsonen A.P., Smogunov A., Umari P. and
591 Wentzcovitch R.M. (2009) Quantum ESPRESSO: a modular and open-source
592 software project for quantum simulations of materials. *J. Phys.: Cond. Matt.* **21**,
593 395502.

594 Gower L. B. (2008) Biomimetic model systems for investigating the amorphous
 595 precursor pathway and its role in biomineralization. *Chem. Rev.* **108**, 4551–4627.

596 Hennehan M. J., Foster G. L., Rae J. W. B., Prentice K. C., Erez J., Bostock H. C.,
 597 Marshall B. J. and Wilson P. A. (2015) Evaluating the utility of B/Ca ratios in
 598 planktic foraminifera as a proxy for the carbonate system: A case study of
 599 *Globigerinoides ruber*. *Geochem. Geophys. Geosyst.* **16**, 1052–1069

600 Hemming N. G. and Hanson G. N. (1992) Boron isotopic composition and concentration
 601 in modern marine carbonates. *Geochim. Cosmochim. Acta* **56**, 537-543.

602 Hemming N. G., Reeder R. J. and Hanson G. N. (1995) Mineral-fluid partitioning and
 603 isotopic fractionation of boron in synthetic calcium carbonates. *Geochim.*
 604 *Cosmochim. Acta* **59**, 371-379.

605 Hemming N. G., Reeder R. J. and Hart S. R. (1998) Growth-step-selective incorporation of
 606 boron on the calcite surface. *Geochim. Cosmochim. Acta* **62**, 2915-2922.

607 Hobbs M. Y. and Reardon E. J. (1999) Effect of pH on boron coprecipitation by calcite:
 608 Further evidence for nonequilibrium partitioning of trace elements. *Geochim.*
 609 *Cosmochim. Acta* **63**, 1013-1021.

610 Ishikawa M. and Ichikuni M. (1984) Uptake of sodium and potassium by calcite. *Chem.*
 611 *Geol.* **42**, 137-146

612 Kaczmarek K., Nehrke G., Misra S., Bijma J. and Elderfield H. (2016) Investigating the
 613 effects of growth rate and temperature on the B/Ca ratio and $\delta^{11}\text{B}$ during inorganic
 614 calcite formation. *Chem. Geol.* **421**, 81-92.

615 Kitano Y., Okumura M. and Idogaki (1978) Coprecipitation of borate-born with calcium
 616 carbonate. *Geochemical Journal* **12**, 183-189.

617 Klochko K., Kaufman A. J., Yao W., Byrne R. H. and Tossell J. A. (2006) Experimental
 618 measurement of boron isotope fractionation in seawater. *Earth Planet. Sci. Lett.*

619 **248**, 276-285.

620 Laio A. and Parrinello M. (2002) Escaping free-energy minima. *Proc. Nat. Acad. Sci.* **99**,
621 12562-12566.

622 Liu Y. and Tossell J. A. (2005) Ab initio molecular orbital calculations for boron isotope
623 fractionations on boric acids and borates. *Geochim. Cosmochim. Acta* **69**, 3995-
624 4006.

625 Lemarchand D., Gaillardet J., Lewin E. and Allègre C. J. (2002) Boron isotope systematics
626 in large rivers: implications for the marine boron budget and paleo-pH
627 reconstruction over the Cenozoic. *Nature* **408**, 951-954.

628 Martinez-Boti M. A., Marino G., Foster G. L., Ziveri P., Henehan M.J., Rae J. W. B., Mortyn P.
629 G. and Vance D. (2015) Boron isotope evidence for oceanic carbon dioxide leakage
630 during the last deglaciation. *Nature* **518**, 219-222.

631 Mavromatis V., Montouillout V., Noireaux J., Gaillardet J. and Schott J. (2015)
632 Characterization of boron incorporation and speciation in calcite and aragonite
633 from co-precipitation experiments under controlled pH, temperature and
634 precipitation rate *Geochim. Cosmochim. Acta* **150**, 299-313.

635 Nir O., Vengosh A., Harkness J. S., Dwyer G. S. and Lahav O. (2015) Direct measurement
636 of the boron isotope fractionation factor: Reducing the uncertainty in
637 reconstructing ocean paleo-pH. *Earth Planet. Sci. Lett.* **414**, 1-5.

638 Noireaux J., Mavromatis V., Gaillardet J., Schott J., Montouillout V., Louvat P., Rollion-Bard
639 C. and Neuville D. R. (2015) Crystallographic control on the boron isotope paleo-
640 pH proxy. *Earth Planet. Sci. Lett.* **430**, 398-407.

641 Okumura M. and Kitano Y. (1986) Coprecipitation of alkali metal ions with calcium
642 carbonate. *Geochim. Cosmochim. Acta* **50**, 49-58.

643 Pagani M., Lemarchand D., Spivack A and Gaillardet J. (2005) A critical evaluation of the
 644 boron isotope-pH proxy: the accuracy of ancient ocean pH estimates. *Geochim.*
 645 *Cosmochim. Acta* **69**, 953–961.

646 Palmer M. R., Pearson P. N. and Cobb S. J. (1998) Reconstructing past ocean pH-depth
 647 profiles. *Science* **282**, 1468-1471.

648 Pearson P. N. and Palmer M. R. (1999) Middle eocene seawater pH and atmospheric
 649 carbon dioxide concentrations. *Science* **284**, 1824-1826.

650 Pearson P. N., Foster G. L. and Wade B. S. (2009) Atmospheric carbon dioxide through
 651 the Eocene-Oligocene climate transition. *Nature* **461**, 1110–1113.

652 Perdew J. P., Burke K. and Ernzerhof M. (1996) Generalized gradient approximation
 653 made simple. *Phys. Rev. Lett.* **77**, 3865–3868.

654 Pickard C. and Mauri F. (2001) All-electron magnetic response with pseudopotentials:
 655 NMR chemical shifts. *Phys. Rev. B* **63**, 245101.

656 Pietrucci F. and Andreoni W. (2011) Graph theory meets ab initio molecular dynamics:
 657 atomic structures and transformations at the nanoscale. *Phys. Rev. Lett.* **107**,
 658 085504.

659 Purgstaller B., Mavromatis V., Immenhauser A. and Dietzel M. (2016) Transformation of
 660 Mg bearing amorphous calcium carbonate to Mg-calcite - In situ monitoring.
 661 *Geochim. Cosmochim. Acta* **174**, 180-195.

662 Pyykkö P. (2008) Year-2008 nuclear quadrupole moments. *Mol. Phys.* **106**, 1065.

663 Reeder R. J., Lamble G. M., Lee J.-F. and Staudt W. J. (1994) Mechanism of SeO_4^{2-}
 664 substitution in calcite: An XAFS study. *Geochim. Cosmochim. Acta* **58**, 5639-5646.

665 Rollion-Bard C., Blamart D., Trebosc J., Tricot G., Mussi A. and Cuif J.-P. (2011) Boron
 666 isotopes as a pH proxy: A new look at boron speciation in deep-sea corals using ^{11}B
 667 MAS NMR and EELS. *Geochim. Cosmochim. Acta* **75**, 1003-1012.

668 Ruiz-Agudo E., Putnis C. V., Kowacz M., Ortega-Huertas M. and Putnis A. (2012) Boron
 669 incorporation into calcite during growth: Implications for the use of boron in
 670 carbonates as a pH proxy. *Earth Planet. Sci. Lett.* **345-348**, 9-17.

671 Rustad J. R., Bylaska E. J., Jackson V. E. and Dixon D. A. (2010) Calculation of boron-
 672 isotope fractionation between $\text{B}(\text{OH})_{3(\text{aq})}$ and $\text{B}(\text{OH})_{4^{-}(\text{aq})}$. *Geochim. Cosmochim. Acta*
 673 **74**, 2843-2850.

674 Sanyal A., Hemming N. G., Hanson G. N. and Broecker W. S. (1995) Evidence for a higher
 675 pH in the glacial ocean from boron isotopes in foraminifera. *Nature* **373**, 234-236.

676 Sen S., Stebbins J. F., Hemming N. G. and Ghosh B. (1994) Coordination environments of
 677 B impurities in calcite and aragonite polymorphs: A ^{11}B MAS NMR study. *Am.*
 678 *Mineral.* **79**, 819-825.

679 Soleilhavoup A., Delaye J.-M., Angeli F., Caurant D. and Charpentier T. (2010)
 680 Contribution of first-principles calculations to multinuclear NMR analysis of
 681 borosilicate glasses. *Magn. Reson. Chem.* **48**, S159-S170.

682 Soraru G.D., Babonneau F., Gervais C. and Dallabona N. (2000) Hybrid $\text{RSiO}_{1.5}/\text{B}_2\text{O}_3$ gels
 683 from modified silicon alkoxides and boric acid. *J. Sol-Gel Sci. and Techno.* **18**, 11-19.

684 Spivack A. J., You C. and Smith H. J. (1993) Foraminiferal boron isotope ratios as a proxy
 685 for surface ocean pH over the past 21 Myr. *Nature* **363**, 149-151.

686 Tossell J. A. (2005) Boric acid, "carbonic" acid, and N-containing oxyacids in aqueous
 687 solution: Ab initio studies of structure, pKa, NMR shifts, and isotopic fractionations.
 688 *Geochim. Cosmochim. Acta* **69**, 5647-5658.

689 Tossell J. A. (2006) Boric acid adsorption on humic acids: Ab initio calculation of
 690 structures, stabilities, ^{11}B NMR and $^{11}\text{B},^{10}\text{B}$ isotopic fractionations of surface
 691 complexes. *Geochim. Cosmochim. Acta* **70**, 5089-5103.

692 Uchikawa J., Penman D. E., Zachos J. C. and Zeebe R. E. (2015) Experimental evidence of
 693 kinetic effects on B/Ca in synthetic calcite: Implications for potential B(OH)_4^- and
 694 B(OH)_3 incorporation. *Geochim. Cosmochim. Acta* **150**, 171-191.

695 Vegas A., Cano F. H. and Garcia-Blanco S. (1975) The crystal structure of calcium
 696 orthoborate: a redetermination. *Acta Crystallogr B* **31**, 1416-1419.

697 Vengosh A., Kolodny Y., Starinsky A., Chivas A. R. and McCulloch M. T. (1991) Copre-
 698 cipitation and isotopic fractionation of boron in modern biogenic carbonates.
 699 *Geochim. Cosmochim. Acta* **55**, 2901-2910.

700 Vielzeuf D., Garrabou J., Baronnet A., Grauby O. and Marschal C. (2008) Nano to
 701 macroscale biomineral architecture of red coral (*Corallium rubrum*). *Amer.*
 702 *Mineral.* **93**, 1799-1815.

703 Wara M. W., Delaney M. L., Bullen T. D. and Ravelo A. C. (2003) Possible roles of pH,
 704 temperature, and partial dissolution in determining boron concentration and
 705 isotopic composition in planktonic foraminifera. *Paleoceanography* **18(4)**, 1100,
 706 doi:10.1029/2002PA000797

707 Xiao Y. K., Li H. L., Liu W. G., Wang X. F. and Jiang S. Y. (2008) Boron isotopic fractionation
 708 in laboratory inorganic carbonate precipitation: Evidence for the incorporation of
 709 B(OH)_3 into carbonate. *Sci. China Ser. D* **51**, 1776-1785.

710 Yi H., Balan E., Gervais C., Segalen L., Fayon F., Roche D., Person A., Morin G., Guillaumet
 711 M., Blanchard M., Lazzeri M. and Babonneau F. (2013) A carbonate-fluoride defect
 712 model for carbonate-rich fluorapatite. *Amer. Mineral.* **98**, 1066-1069.

713 Zachariasen W. H. (1954) The precise structure of orthoboric acid. *Acta Crystallogr.* **7**,
 714 305-310.

715 Zeebe R. E. (2005) Stable boron isotope fractionation between dissolved B(OH)_3 and B(OH)_4^-
 716 *Geochim. Cosmochim. Acta* **69**, 2753-2766.

718 Table 1: Structural and ^{11}B NMR parameters of boron-bearing calcium carbonate models

B coordinence	mineral	model	B-O bond length (Å)	O-H bond length (Å)	δ_{iso} (ppm)	C_Q (MHz)	η
trigonal	calcite	BO_3^{3-}	1.388 (x3)	-	19.10	2.73	0.00
		$\text{BO}_2(\text{OH})^{2-}$	1.345	-	17.51	2.59	0.84
			1.350	-			
	aragonite	BO_3^{3-}	O(H) 1.491	0.995	22.04	2.74	0.04
			1.380	-			
		$\text{BO}_2(\text{OH})^{2-}$ (A)	1.383 (x2)	-	19.11	2.59	0.81
			1.343	-			
		$\text{BO}_2(\text{OH})^{2-}$ (B)	1.350	-	18.14	2.57	0.82
			O(H) 1.472	0.988			
tetragonal	takedaite	BO_3^{3-}	1.347	-	22.11	2.74	0.00
	calcite	$\text{B}(\text{OH})_4^-$	1.349	-	1.05	0.43	0.57
			O(H) 1.472	0.991			
			1.391	-			
			1.391	-			
	aragonite	$\text{BO}(\text{OH})_3^{2-}$	O1 1.438	1.005	1.29	1.09	0.34
			O3 1.477	1.002			
			O4 1.489	0.997			
			O2 1.510	0.996			
		$\text{B}(\text{OH})_4^-, \text{Na}^+$	O2 1.402	-	1.15	0.56	0.67
			O1 1.494	0.996			
			O3 1.524	0.996			
			O4 1.532	0.994			
		$\text{B}(\text{OH})_4^-$	O1 1.434	1.006	0.81	0.22	0.50
			O3 1.470	0.993			
			O4 1.499	0.997			
			O2 1.522	0.992			
		$\text{BO}(\text{OH})_3^{2-}$	O2 1.455	0.992	1.02	1.15	0.26
			O1 1.476	1.008			
			O4 1.497	0.989			
			O3 1.497	1.003			
		$\text{B}(\text{OH})_4^-, \text{Na}^+$	O3 1.402	-	0.88	0.38	0.58
			O2 1.492	0.987			
			O1 1.530	1.001			
			O4 1.543	0.985			
		$\text{B}(\text{OH})_4^-, \text{Na}^+$	O2 1.457	0.990	0.88	0.38	0.58
			O1 1.455	1.005			
			O3 1.501	0.992			
			O4 1.514	0.989			

723 Table 2: Experimental ^{11}B NMR parameters of synthetic and natural calcium carbonates

B coordinence		sample	δ_{iso} (ppm)	C_Q (MHz)	η	ref.*	present interpretation	
trigonal	synthetic	calcite	17.1 $\pm$ 1	3.0 $\pm$ 0.3	0.67 $\pm$ 0.05	1	BO ₂ (OH) ²⁻	
		heated aragonite	22.0 $\pm$ 1	2.7 $\pm$ 0.3	0.2 $\pm$ 0.05	1	BO ₃ ³⁻	
		calcite	16.6 $\pm$ 0.5	n.d.	n.d.	2	BO ₂ (OH) ²⁻	
		Mg-calcite	16.5 $\pm$ 0.5	n.d.	n.d.	2	"	
		aragonite	18.9 $\pm$ 0.5	2.8 $\pm$ 0.1	n.d.	2	"	
	natural	biogenic calcite	18.9 $\pm$ 1	2.8 $\pm$ 0.3	0.5 $\pm$ 0.05	1	BO ₂ (OH) ²⁻	
			19.3	2.6	0	3	BO ₃ ³⁻	
		biogenic aragonite	16.8	2.5	0	3	B(OH) ₃	
			18.3	2.5	0	3	"	
		coral CoC	17.5	2.3	0.2	4	"	
	tetragonal	synthetic	calcite	0.5 $\pm$ 1	0.0 $\pm$ 0.3	-	1	B(OH) ₄ ⁻
				1.9 $\pm$ 0.5	n.d.	-	2	"
			calcite ("interstitial")	-0.3 $\pm$ 0.5				?
			calcite ("interstitial")	-2.4 $\pm$ 0.5				?
Mg-calcite			1.2 $\pm$ 0.5	n.d.	-	2	B(OH) ₄ ⁻	
aragonite			1.6 $\pm$ 0.5	0.0 $\pm$ 0.3	-	1	"	
			1.6 $\pm$ 0.5	n.d.	-	2	"	
natural		biogenic calcite	1.1 $\pm$ 1	0.0 $\pm$ 0.3	-	1	B(OH) ₄ ⁻	
			1.67	0.0	-	3	"	
		hydrothermal calcite	2.85	0.0		3	?	
		biogenic aragonite	1.2 $\pm$ 0.5	0.0 $\pm$ 0.3	-	1	B(OH) ₄ ⁻	
			2.54	0.0	-	3	?	
			2.0	0.0	-	3	B(OH) ₄ ⁻	
		coral CoC	1.5	0.1	-	4	"	

*references: ¹Sen et al. (1994), ²Mavromatis et al. (2015), ³Klochko et al. (2009), ⁴Rollion-Bard et al. (2011)

Figure captions

Figure 1: Theoretical structure of B-bearing calcite and aragonite obtained from first-principles modeling. The H-bond with an oxygen atom of a neighboring carbonate group is indicated by a dotted line. The star in the tetragonal models indicates the Ca atom closest to boron, which has been selected to test the effect of Na^+ for Ca^{2+} substitution. This atom is located at a distance of 3.09 Å and 3.05 Å from the boron atom in calcite and aragonite, respectively.

Red: oxygen, blue: calcium, black: hydrogen, purple: carbon, green: boron.

Figure 2: Summary of first-principles metadynamic run on aragonite. The fluctuations of SPRINT coordinates (top and middle panel) reflect the geometrical changes affecting the H-bonding pattern of OH groups with O atoms belonging to surrounding carbonate groups. The bottom panel reports the history dependent bias potential which drives the system away from the previously explored configurations (see text). SPRINT coordinates are defined through the product of the principal eigenvalue of the (real valued) adjacency matrix with its corresponding eigenvector. To enforce invariance under permutation of identical atoms, the resulting values are sorted in ascending order within the oxygen and hydrogen subsets, and are shown with a color gradient ranging from the lowest to the highest components.

Figure 3: Summary of first-principles metadynamic run on calcite. Legend as in Figure 2.

751 Figure 4: Theoretical and experimental ^{11}B NMR chemical shifts of trigonal boron. Full
752 symbols: theoretical values from Table 1, open symbols: experimental values from Table
753 2. The circles correspond to nil or weak η parameters; whereas the squares correspond
754 to high η values indicating in-plane distortion of the trigonal group. The triangles
755 correspond to experimental data for which the η parameter is lacking.

756

757 Figure 5: Theoretical and experimental ^{11}B NMR chemical shifts of tetragonal boron. Full
758 symbols: theoretical values from Table 1, open symbols: experimental values from Table
759 2.

760

761

762

763

trigonal

calcite

tetragonal

Summary of first-principles metadynamic run on aragonite.

[Click here to download high resolution image](#)

Summary of first-principles metadynamic run on calcite.

[Click here to download high resolution image](#)