1	First-principles study of boron speciation in calcite and
2	aragonite
3	Revision 1
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Abstract

28 Despite the importance of boron as a proxy of past ocean pH, the crystal-chemical 29 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, 30 31 protonation state and local environment of boron species in these minerals. In the 32 present study, we use first-principles quantum mechanical tools to model selected 33 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 34 35 advanced metadynamics exploration of their configurational space. The computation of ¹¹B NMR chemical shifts and quadrupolar coupling parameters enables a 36 37 straightforward comparison of the models to existing experimental NMR data. The 38 results show that B in calcium carbonates does occur as structural species substituted for CO₃²⁻ anions. The B speciation depends on the polymorph considered. In calcite, 39 40 structural boron is present as partially deprotonated trigonal BO₂(OH)²⁻ species 41 coexisting with a fraction of substituted $B(OH)_{4}$ groups. In aragonite, the $B(OH)_{4}$ 42 substitution for CO_3^{2-} anions is dominant. Different species, including entrapped B(OH)₃ 43 molecules and substituted BO₃³⁻ groups also occur in biogenic samples. The diversity of 44 B speciation reflects a diversity of B incorporation mechanisms and sheds light on 45 previous studies confronting B isotopic composition determination with NMR 46 observations. The mechanisms of boron incorporation in calcium carbonates are 47 probably more complex than usually assumed in the literature using boron isotopes as a 48 proxy of paleo-atmospheric CO₂ reconstructions. Although not invalidating the empirical 49 paleo-pH proxy, these results call for a better understanding of the fundamental 50 mechanisms of boron incorporation in carbonates.

52 **1. INTRODUCTION**

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54 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 55 56 reflects past levels of atmospheric CO₂ concentrations (Vengosh et al. 1991; Hemming 57 and Hanson 1992). A large number of studies have applied this idea to various biogenic 58 carbonates, proposed paleo-CO₂ secular evolutions for the Earth's atmosphere and 59 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 60 61 and Palmer 1999; Lemarchand et al. 2002; Pagani et al. 2005; Pearson et al. 2009; 62 Martinez-Boti et al. 2015). The use of boron isotopes as a paleo-pH meter is based on the 63 large difference in ¹¹B/¹⁰B ratio (27.2 % in delta notation of isotopic abundances; 64 Klochko et al. 2006) occurring between the major dissolved forms of boron, the trigonal 65 boric acid (B(OH)₃, preferentially enriched in ¹¹B), and the tetragonal borate ion 66 (B(OH)₄⁻, preferentially enriched in ¹⁰B), under thermodynamic equilibrium conditions 67 (Zeebe 2005; Liu and Tossell 2005; Klochko et al. 2006; Rustad et al. 2010; Nir et al. 68 2015). As the relative proportion of these aqueous species is strongly pH-dependent in 69 the range of expected seawater pH, mass balance considerations require that their 70 isotopic composition is also pH-dependent. Assuming that among the two major B 71 species present in seawater only the borate ion $(B(OH)_{4})$ is incorporated in the mineral 72 structure during crystal growth and that no boron isotope fractionation occurs during 73 uptake, the B isotopic composition in marine carbonate samples provides a 74 straightforward record of the secular variations of seawater pH.

75 The assumption of sole $B(OH)_{4}$ incorporation is challenged by spectroscopic 76 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 ¹¹B 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 ¹¹B/¹⁰B 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

101 cannot be reconciled with models based on the exclusive incorporation of borate ions,102 showing that the basis hypotheses of the paleo-pH theory are questionable.

103 Despite the importance of the boron-isotope pH proxy, the crystal-chemical 104 factors controlling boron incorporation in carbonates are still elusive. Several factors 105 impede a detailed understanding of its incorporation mechanisms. Differences between 106 the geometry of the stiff molecular tetragonal B anions and that of the trigonal 107 substitution sites can lead to substantial modifications of the medium-range structure 108 around the B species. Various electrostatic charge compensation mechanisms (e.g. 109 involving different protonation states, presence of vacancies, or incorporation of other 110 trace elements) can also affect the B environment, which significantly increases the 111 system complexity. These effects are difficult to determine from experiment because 112 spectroscopic methods usually provide information restricted to the well-defined first 113 coordination shell of boron. Complementary to experimental observations, theoretical 114 approaches can bring important constraints to discuss molecular-scale aspects of B 115 incorporation in calcium carbonates. Tossell (2005, 2006) has investigated the NMR spectroscopic and the thermodynamic properties of boron species using molecular 116 117 modeling techniques. Although these studies mostly focused on B species in aqueous 118 solutions and did not treat explicitly the role of the crystalline matrix, they provided 119 quantitative relations between the geometry and protonation state of the boron 120 complexes and their distinctive NMR parameters. In the light of the experimental data of 121 Sen et al. (1994), Tossell (2005) suggested that the incorporation of trigonal B should 122 occur via a distorted, partially deprotonated group instead of more symmetric fully 123 protonated or deprotonated groups. Tossell (2006) and Klochko et al. (2009) also 124 suggested that chemically more complex species such as B(OH)₂CO₃- could account for 125 the experimental observations of Sen et al. (1994).

126 In this article, we use first-principles quantum mechanical calculations to 127 determine the most favorable coordination states and geometry of boron species in 128 calcite and aragonite and discuss related incorporation mechanisms. We theoretically 129 determine the stable configuration of atomic-scale models of boron in calcium 130 carbonates, using an approach similar to that previously developed to study sulfate 131 incorporation in carbonates (Balan et al. 2014). The computation of the related NMR 132 parameters (Pickard and Mauri 2001; Charpentier 2011; Bonhomme et al. 2012) then 133 enables a straightforward comparison of the theoretical models to existing NMR 134 experimental data. The results attest to the diversity of B speciation in synthetic and 135 biogenic calcium carbonates; among which the substitution of partially protonated 136 trigonal $BO_2(OH)^{2-}$ and fully protonated tetragonal $B(OH)_{4^-}$ groups for CO_3^{2-} anions are 137 dominant. 138

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140 **2. METHODS**

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142 **2.1 Structural optimization of models of boron-bearing calcium carbonates**

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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

151 the density functional theory (DFT) have reached a level of accuracy high enough to 152 reproduce with an excellent agreement the static and dynamic properties of 153 geochemically relevant systems (see, e.g., Cygan and Kubicki 2001). The present 154 calculations were performed within the DFT framework, using periodic boundary 155 conditions and the generalized gradient approximation (GGA) to the exchange-156 correlation functional as proposed by Perdew, Burke and Ernzerhof (PBE; Perdew et al. 157 1996). The ionic cores were described by ultra-soft pseudopotentials from the GBRV 158 library (Garrity et al. 2014); which means that only the electrons contributing to 159 chemical bonding are explicitly treated, while those occupying the core states are 160 considered to be unaffected by variations in the atom environment. The electronic 161 wave-functions and charge density were expanded using a finite basis sets of plane-162 waves with 40 and 200 Ry cutoffs, respectively, corresponding to a convergence of the 163 total energy better than 1 mRy/atom.

164 Periodic models of boron-bearing calcium carbonates were built for the two 165 common CaCO₃ polymorphs: calcite ($R\overline{3}c$, 10 atoms per rhombohedral primitive cell) 166 and aragonite (*Pmcm*, 20 atoms per primitive cell). In order to minimize as much as 167 possible spurious interactions between the periodic images of the boron defects, the 168 unit-cell of the models was built from the 2x2x2 super-cells of calcite (rhombohedral 169 cell, 80 atoms) and aragonite (160 atoms) previously used in Balan et al. (2014). The 170 equilibrium geometry of these models was obtained by displacing the atoms up to a 171 minimum energy state, characterized by the fact that the forces experienced by the 172 atoms vanish. These structure relaxations were done using the PWscf code of the 173 Quantum ESPRESSO package (Giannozzi et al. 2009; http://www.quantum-174 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 treatsuch systems with large unit-cell.

177 A reference theoretical sassolite (boric acid; B(OH)₃) structure was obtained using a 2x2x2 *k*-points grid. The relaxed cell volume (V = 285.28 Å³) and bond lengths 178 179 (d(B-0) = 1.378 Å; d(0-H) = 1.01 Å) slightly overestimate their experimental 180 counterparts (V = 273.62 Å³; d(B-O) = 1.36 Å; d(O-H) = 0.9 Å; Zachariasen 1954), which 181 is consistent with a previous DFT-GGA modeling study (Ferlat et al. 2006). A theoretical 182 structure of takedaite (Ca₃B₂O₆) was also obtained with a 2x2x2 k-points grid, leading to relaxed cell volume (V = 785.23 Å³) and bond lengths (d(B-O) = 1.391 Å) slightly larger 183 than experimental values (V = 765.61 Å^3 , d(B-O) = 1.384 Å; Vegas et al. 1975). 184

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186 **2.2 First-principles metadynamics**

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188 First-principles metadynamics (Laio and Parrinello 2002) runs were used to 189 determine the most stable configuration of $B(OH)_{4}$ in its crystal host from an 190 exploration of the free-energy landscape drawn by variations in the H-bonding pattern. 191 This approach provides an efficient method to explore a free-energy landscape 192 potentially displaying several relative minima separated by barriers higher than the 193 relevant thermal energy. Usual molecular dynamics would require prohibitively high 194 temperature and/or long simulation to achieve an adequate sampling of the 195 corresponding phase space. In contrast, the metadynamics builds an history dependent 196 bias potential which drives the system away from the previously explored 197 configurations, thus accelerating the exploration of the phase space and providing an 198 elegant way to pass the energy barriers. In practice, the bias potential is built in a space 199 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.

206 Born-Oppenheimer metadynamics runs were performed in the NVT ensemble 207 (i.e. the number of atoms, volume and average temperature were constant during the 208 runs) using the same DFT framework and parameters as those used for the structural 209 relaxations. The hydrogen mass was increased to two atomic mass units and the runs were carried out with a timestep of 0.4 x 10⁻¹⁵ s. Temperature was controlled to 300 K 210 211 employing a stochastic velocity rescaling thermostat (Bussi et al. 2007). Both in 212 aragonite and calcite, we employed SPRINT collective variables (Pietrucci and Andreoni 213 2011), as implemented in Plumed (Bonomi et al., 2009), including a total of 26 atoms, 214 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 215 216 were biased simultaneously adding every 100 molecular dynamics steps Gaussian hills 217 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).

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223 **2.3 First-principles calculation of NMR parameters**

The I = 3/2 nuclear spin of ¹¹B 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 ¹¹B NMR spectra, namely the chemical shift δ_{iso} , the quadrupolar coupling constant C_Q and the asymmetry parameter η .

230 The NMR chemical shift describes the difference between the applied external 231 magnetic field and the magnetic field at the nucleus positions. It can be obtained from 232 the structural models by calculating the shielding of the nuclei relative to the electronic 233 current induced by the external magnetic field. This current was calculated by using the 234 GIPAW approach, which allows reconstructing the all-electron magnetic response from 235 the pseudo-wave-functions (Pickard and Mauri 2001; Charpentier 2011; Bonhomme et 236 al. 2012). The calculations were performed using the PWscf and GIPAW codes of the 237 Quantum ESPRESSO package (Giannozzi et al. 2009). Norm-conserving pseudo-238 potentials were used and the wave functions kinetic energy cutoff was increased to 80 239 Ry. The integral over the Brillouin zone was done using a Monkhorst-Pack $1 \times 1 \times 1 k$ -240 point grid for the different models and $2 \times 2 \times 2$ for sassolite (B(OH)₃) used as a reference. The isotropic chemical shift δ_{iso} is defined as $\delta_{iso} = -(\sigma - \sigma^{ref})$, where σ is the isotropic 241 242 shielding (one-third of the trace of the NMR shielding tensor) and σ^{ref} is the isotropic 243 shielding of the same nucleus in a reference system. In our calculations, absolute 244 shielding tensors are obtained. To fix the scales, σ^{ref} was chosen by comparing 245 experimental (19.2 ppm, Soraru et al. 1999) and calculated δ_{iso} values in B(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 η = 0.0 parameters computed for sassolite (B(OH)₃) are consistent with experimental

249	values (2.47 MHz and 0.0; Klochko et al. 2009). It should be noted that for the $C_Q(^{11}B)$
250	calculation, a quadrupole moment of 35 mb was used: this value is smaller than the
251	theoretical value of 40 mb (Pyykkö, 2008) as recommended by Soleilhavoup et al.
252	(2010) in borosilicate glasses. Estimated precision is ± 0.5 ppm, ± 0.1 MHz and ± 0.1 for
253	δ_{iso} , C_Q and η , respectively.

- 254
- 255 **3. RESULTS**
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257 **3.1 Trigonal boron incorporation at the carbonate site**

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259 We first consider the incorporation of trigonal boron species. The simplest model 260 is obtained by substituting a B^{3+} for a C^{4+} (Table 1). The charge balance is obtained by 261 spreading homogeneously an electrostatic counter-charge over the unit-cell. The crystal 262 site symmetry is preserved. The three equivalent B-O bonds in calcite have a length of 263 1.388 Å. The BO_{3³⁻} group in aragonite displays a mirror symmetry with a shorter B-O 264 distance of 1.380 Å on the mirror plane and two symmetric B-O distances of 1.383 Å. The high symmetry of BO₃³⁻ groups in the homogeneously compensated models leads to 265 266 very small η parameters. Compared to calcite, the aragonite ¹¹B chemical shift is higher 267 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 $BO_2(OH)^{2-}$ 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 274 and should be thermodynamically dominant at room temperature. The BO₂(OH)²⁻ 275 species in calcite and aragonite display similar structural characteristics. The OH group 276 points out of the BO₃ triangle sharing a H-bond of moderate strength with an oxygen 277 belonging to an adjacent carbonate group. A significant distortion of the trigonal geometry is observed with the B-O(H) distance increasing by ~ 0.1 Å; whereas the two 278 other B-O distances decrease by 0.03 to 0.04 Å. Compared to the models with an 279 280 homogeneous charge compensation, the ¹¹B δ_{iso} decreases by 1.5 and by 3 to 4 ppm in calcite and aragonite, respectively; whereas the quadrupolar coupling parameter C₀ is 281 weakly affected. The asymmetry parameter η increases to 0.8 indicating a strong 282 283 departure from the revolution symmetry, consistent with the in-plane distortion of the 284 BO_3 triangle.

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286 **3.2 Tetragonal boron incorporation at the carbonate site**

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288 Following an approach similar to that applied to the trigonal B species, $B(OH)_{4}$ -289 for CO_3^{2-} substitution was modeled by using a homogeneous electrostatic background to 290 compensate the charge imbalance. Previous calculations on sulfate incorporation in 291 carbonate (Balan et al. 2014) provided a suitable starting guess for the structural 292 optimization. However, the large number of potential H-bond acceptors around the 293 impurity increases the probability to drive the system to a metastable configuration. 294 This difficulty was circumvented by performing first-principles metadynamics (FPM) 295 runs (Laio and Parrinello 2002; Pietrucci and Andreoni 2011) to explore the free energy 296 landscape of the borate group conformation and to isolate the most favorable one.

297 The aragonite FPM run lasted ~ $6 \ge 10^{-12}$ s (Fig. 2, video file in electronic annex). 298 In an initial phase of ~3 $\ge 10^{-12}$ s the instantaneous bias potential fluctuates between

299 zero and less than 10 kJ/mol, indicating that different configurations are being explored 300 (zero bias corresponds to an unexplored region of the configuration space). In a second 301 phase, the bias potential starts to grow more consistently to few tens of kJ/mol without 302 coming back to zero. This indicates that the available low-energy configurations have been exhausted and that higher-energy configurations have been explored. 303 304 Concomitantly, the fluctuations of the SPRINT topological variables related to H and O 305 atoms (Fig. 2) attest to the changes of configuration of the $B(OH)_{4}$ species, by 306 reorienting the OH groups to engage in different patterns of hydrogen bonds with the 307 carbonates. The trajectory analysis leads to 8 maximally distinct instantaneous 308 configurations. After structural optimization, two classes of configurations differing by 309 the orientation of the O3-H bond (almost parallel to the b- axis or to the c-axis), could be 310 defined. In the following, only the most stable configuration will be considered since the 311 energy difference between the two (19 kJ/mol) is significantly larger than the typical 312 thermal energy at ambient temperature (2.5 kJ/mol). In this configuration (Fig. 1), the 313 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 314 315 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 316 characteristics with O-H distances ranging from 0.989 to 1.008 Å and O(H)...O distances 317 318 from 2.62 to 2.65 Å. Few relative energy minima were however observed in each 319 configuration class due to moderate displacements of the surrounding carbonates, 320 leading to energy differences ranging between 5 and 13 kJ/mol. These configurations 321 can be envisioned as intermediate states in the transition from one H-bonding geometry 322 to the other. A longer FPM run (15 x 10^{-12} s, Fig. 3, video file in electronic annex) was 323 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)₄anion 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 ¹¹B 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).

331 As for the trigonal B species, alternative models of tetragonal borate in calcium 332 carbonates were explored by assuming local charge compensation mechanisms. 333 Removing a proton from the $B(OH)_{4}$ group, modifies its charge to -2 (equivalent to that 334 of the CO₃²⁻ group). Starting from the tetrahedral geometries obtained from FPM runs, 335 four relaxed schemes (matching the four different H atoms of the borate group) are 336 obtained for each calcium carbonate polymorph. The deprotonation of the O3-H group 337 (Table 1) is favored in aragonite by more than 27 kJ/mol. In calcite, the most stable (by 338 more than 7 kJ/mol) configuration is obtained by deprotonation of the 02-H group 339 (Table 1). All the $BO(OH)_{3^{2}}$ species display a significant distortion of the boron 340 coordination shell. Consistently, the C_Q values increase, ranging between 1.01 and 1.53 341 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 Ca²⁺ 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 Ca²⁺ substitution. The Na to B distances increase by ~0.05 Å compared to Ca to B distances. Compared with the homogeneously compensated models, only weak variations of the
 ¹¹B NMR parameters are observed (Table 1).

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352 4. DISCUSSION

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4.1 Boron in calcium carbonates: Comparing theory and experiment

- 355
- 356 4.1.1 Trigonal boron speciation
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358 Although only few studies report experimentally determined NMR parameters of 359 boron in calcite and aragonite, they reveal a significant variability of the trigonal boron 360 environment (Table 2, Fig. 4). The chemical shift of trigonal boron ranges from 16 ppm 361 (calcite) to 22 ppm (heated aragonite) and strong differences are observed on the 362 rhombic n parameter. The trigonal boron species in the calcite samples investigated by 363 Sen et al. (1994) is rhombically distorted, with η values of 0.67 and 0.5 in the synthetic 364 and biogenic sample, respectively. In contrast, the nil η values reported by Klochko et al. 365 (2009) in biogenic calcite and aragonite samples correspond to a radially symmetric 366 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. 367 368 (2009), these variations in η values are highly significant because η is only defined 369 between 0 and 1.

The theoretical parameters determined for the $BO_2(OH)^{2-}$ species in calcite are consistent with those reported by Sen et al. (1994) for synthetic calcite. The chemical shift and quadrupolar coupling of $BO_2(OH)^{2-}$ in aragonite also match the experimental values reported by Mavromatis et al. (2015) for synthetic aragonite. Unfortunately, the η 374 parameter was not reported for this sample, likely because of its low trigonal B content. 375 From the comparison of theoretical and experimental NMR parameters, singly 376 protonated $BO_2(OH)^{2-}$ groups appear as the dominant speciation of trigonal boron in the 377 synthetic calcium carbonates precipitated from solutions. This confirms the previous 378 suggestions that trigonal boron in carbonates should be distorted and partially 379 deprotonated (Hemming and Hanson 1992; Tossell 2005). This speciation is favored by 380 the electrostatic balance requirements. An overall preference for local electrostatic 381 charge compensation in minerals is attested by the observation of chemically complex 382 defects, associating different trace elements in the same crystal site. For example, 383 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 384 385 uncertainty affects the interpretation of the NMR parameters reported by Mavromatis et 386 al. (2015) for synthetic calcite samples. Their chemical shift is only slightly lower than 387 that of $BO_2(OH)^{2-}$ species and consistent with the value reported by Sen et al. (1994) for 388 a synthetic calcite sample (Fig. 4). Isotopic compositions (Noireaux et al. 2015) indicate 389 (under the assumption that no isotope fractionation occurs during incorporation) that 390 between 20% and 40% of boron in these samples results from the incorporation of 391 aqueous boric acid and that this proportion is linearly correlated with the pH-dependent 392 amount of boric acid in solution. The proportion of trigonal B detected by NMR is 393 however higher than that inferred from isotopic composition (Noireaux et al., 2015). 394 Thus, both borate anions and boric acid molecules could contribute to the incorporation 395 of BO₂(OH)²⁻ species in the bulk of calcite particles. This implies a coordination change 396 of tetragonal borate as well as several deprotonation steps affecting the tetragonal and 397 trigonal boron species in the interfacial region of growing calcite crystals.

398 Concerning the biogenic calcium carbonates, the algal calcite investigated by Sen 399 et al. (1994) displays NMR parameters consistent with BO₂(OH)²⁻ groups. In contrast, 400 the parameters reported by Klochko et al. (2009) for a foram calcite correspond to fully 401 deprotonated BO₃³⁻ groups substituted in the calcite structure (Fig. 4, Table 1). The 402 sensitivity of ¹¹B NMR to the trigonal boron protonation state is further confirmed by 403 the higher δ_{iso} , and weak η , indicative of a more symmetric boron environment in a 404 calcite sample produced by the high-temperature (500 °C) transformation of biogenic 405 aragonite. These parameters are close to those computed for BO_3^{3-} groups in aragonite 406 (Fig. 4) and in the calcium orthoborate takedaite (Table 1). They indicate that the 407 thermally driven aragonite to calcite transformation leads to a full deprotonation of 408 borate groups. They however suggest that the local environment of BO₃³⁻ groups in the 409 heated aragonite differs from that in crystalline calcite.

410 The ¹¹B NMR parameters of trigonal boron in coral aragonitic samples combine 411 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 412 413 correspond to fully deprotonated BO_3^{3-} groups (Fig. 4; Table 1). Accordingly, these 414 parameters are interpreted as related to fully protonated B(OH)₃ molecules. The 415 incorporation of boric acid molecules in crystallographic sites is unrealistic because of 416 the corresponding strong electrostatic charge imbalance. It is more likely that B(OH)₃ 417 molecules are directly scavenged from the solution and encapsulated by the solid phase. 418 Such step can involve their incorporation in the amorphous and hydrous calcium 419 carbonate phases, observed under high supersaturation and elevated growth rate 420 conditions and identified as intermediate phases in the growth of biogenic calcium 421 carbonates (e.g. Gower 2008; Purgstaller et al., 2016). The B(OH)₃ molecules could also 422 occur in interfacial or porous regions separating ordered CaCO₃ 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 δ^{11} B, depending on the proportion of B(OH)₃ molecules relative to the total B content. This interpretation is consistent with the concomitant observation of elevated δ^{11} 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 B(OH)₃ incorporation.

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431 4.1.2 Tetragonal boron speciation

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433 The experimental chemical shift of tetragonal B species displays a range of 434 variation between -2.4 and 3 ppm, considering both calcite and aragonite (Fig. 5). Except 435 two samples with δ_{iso} above 2 ppm and two signals with negative chemical shifts 436 ascribed to non-structural species in calcitic samples (Mavromatis et al. 2015), the NMR 437 parameters are consistent with those obtained for the B(OH)₄- models. The 438 systematically nil values of experimental quadrupolar coupling parameters (Table 2) 439 attest to a highly symmetric B environment. They rule out the partially deprotonated 440 tetragonal species, which are characterized by theoretical C_Q values larger than 1 MHz. 441 Accordingly, tetragonal B should mostly occur in the calcium carbonate samples as fully 442 protonated B(OH)₄- groups. A high protonation state of tetragonal B was suggested by 443 Klochko et al. (2009) from ¹H decoupling experiments.

The substitution of $B(OH)_{4^-}$ for $CO_{3^{2^-}}$ implies that more remote mechanisms ensure the charge compensation, among which the Na⁺ for Ca²⁺ 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

448 responsible, at least in part, for the dependence of B/Ca ratio on salinity reported for 449 biogenic calcium carbonates (Allen et al. 2011, 2012; Allen and Hönisch 2012; Henehan 450 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 451 452 concentration in the parent solution. For aragonite, the observed dependence was in the 453 opposite direction but with a comparatively weaker magnitude. We note however that 454 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 455 456 correspond to $B(OH)_{4}$ groups in a different environment or involving a charge 457 compensation mechanism differing from that prevailing in the other samples. The 458 potential presence of contaminant phases cannot be fully excluded for these natural 459 samples. Beside Na⁺ for Ca²⁺ substitution, different charge compensation mechanisms 460 could occur, as shown by the Na-free synthesis experiments of Hemming et al. (1995) 461 and Sen et al. (1994). For example, HCO_3^{-1} groups associated with Ca vacancies could play 462 such compensation role. A potential role of phosphate anions substituted for carbonate 463 groups has also been suggested by Henehan et al. (2015). Variations in the borate group 464 environment are also attested by the broad signals with slightly negative chemical shifts 465 observed by Mavromatis et al. (2015), interpreted as corresponding to a fraction of 466 borate groups occurring in defective domains of the calcite samples.

467

468 **4.2 Boron speciation in calcium carbonates: Implications for the paleo-pH proxy**

469

470 The present results show that B in calcium carbonates does occur as substituted 471 species for CO_3^{2-} anions, thus confirming its structural nature. They further show that its 472 speciation depends on the polymorph considered. This is fully consistent with a number

473 of previous studies on boron incorporation in biogenic and abiotic carbonates (e.g. 474 Klochko et al. 2009; Mavromatis et al. 2015; Noireaux et al. 2015) and strongly challenge 475 the hypothesis on which the use of boron isotopes to reconstruct paleo ocean pH has 476 been used (i.e. sole incorporation of the aqueous borate ion). In calcite, structural boron is present as partially deprotonated trigonal $BO_2(OH)^{2-}$ species, coexisting with 477 478 substituted B(OH)₄⁻ groups in a proportion depending on the crystal growth parameters. 479 In aragonite, the $B(OH)_{4}$ substitution for CO_{3}^{2} anions is dominant. The theoretical 480 modeling of NMR spectra also indicates that different B species, including entrapped 481 B(OH)₃ molecules and substituted BO₃³⁻ groups can occur in biogenic samples. The 482 diversity of B speciation indirectly confirms the importance of out-of-equilibrium 483 parameters and interfacial properties in determining the chemical form and abundance 484 of boron in calcium carbonate (e.g., Hemming et al. 1998; Hobbs and Reardon 1999; 485 Ruiz-Agudo et al. 2012; Gabitov et al. 2014; Branson et al. 2015; Noireaux et al. 2015; 486 Uchikawa et al. 2015; Kaczmarek et al. 2016). Although the B(OH)₃ molecules in 487 biogenic aragonitic samples might have been directly scavenged from the solution, the 488 other trigonal $BO_2(OH)^{2-}$ and BO_3^{3-} species most probably result from a coordination 489 change and deprotonation of boron species adsorbed at the mineral surface.

490 An important implication of the observed diversity of B speciation in calcium 491 carbonates is that the ratio of trigonal to tetragonal species determined by NMR 492 spectroscopy is not a sufficient parameter to infer its incorporation mechanism. This 493 ratio is not simply related to the trigonal to tetragonal proportion in the solution nor 494 solely results from a coordination decrease affecting the adsorbed borate ion during its 495 incorporation in the crystal structure. The environment and protonation state of 496 trigonal B however appears as more variable than that of the tetragonal species. In this 497 latter case, the variations are most likely related to more remote charge compensation

498 mechanisms and do not affect the first coordination shell of boron. In addition, the high 499 sodium concentration of seawater could favor the Na⁺ for Ca²⁺ substitution in the charge 500 compensation of $B(OH)_{4^{-}}$ species. The prevalence of a specific charge compensation 501 mechanism would reduce the crystal-chemical complexity of the B(OH)₄- incorporation 502 mechanism. Interestingly, the affinity of aragonite is higher than that of calcite for both B 503 and Na. In the case of Na, this has been interpreted as reflecting its incorporation in 504 interstitial sites of calcite, instead of structural Ca site as in aragonite (Ishikawa and 505 Ichikuni 1984; Okumura et al. 1986). As a consequence, aragonitic samples in which 506 tetragonal B is dominant should faithfully reflect the pH of past oceans, as proposed by 507 Noireaux et al. (2015), provided that sampling strategies taking into account the growth 508 mechanism of biologic aragonite are developed (Rollion-Bard et al. 2011).

509 In the case of calcitic samples, the more diverse boron speciation could be 510 considered as a fingerprint of the growth mechanism and could serve as an indicator to 511 extrapolate the laboratory calibrations to the geologic samples. The recent spatially-512 resolved study of Branson et al. (2015) indicates a dominantly trigonal (>85%) coordination and a heterogeneous distribution of boron in foraminiferal calcite; 513 514 whereas NMR studies revealed a fraction of tetragonal B in biogenic calcite ($\sim 20\%$, Sen 515 et al. 1994; ~54%, Klochko et al. 2009). Thus, the occurrence of differently coordinated 516 species, with potentially distinct isotopic compositions, in spatially different domains of 517 the composite biogenic samples cannot be excluded. As diagenesis and alteration may 518 differently affect these domains, the boron isotopic composition of geological samples 519 would then depend on their preservation state (Wara et al. 2003). We note however that 520 the observations of Edgar et al. (2015) suggest that the boron isotopic composition of 521 fossil planktonic foraminiferal calcite is resistant to diagenetic transformations. This

522 calls for further experimental studies focusing on the effects of diagenesis on boron523 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.

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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
		BO ₂ (OH) ²⁻	1.345 1.350 O(H) 1.491	- - 0.995	17.51	2.59	0.84
	aragonite	BO ₃ ³⁻	1.380 1.383 (x2)	-	22.04	2.74	0.04
		BO ₂ (OH) ²⁻ (A)	1.343 1.350 O(H) 1.472	- - 0.988	19.11	2.59	0.81
		BO ₂ (OH) ²⁻ (B)	1.347 1.349 O(H) 1.472	- - 0.991	18.14	2.57	0.82
	takedaite	BO33-	1.391	-	22.11	2.74	0.00
tetragonal	calcite	B(OH) ₄ ⁻	O1 1.438 O3 1.477 O4 1.489 O2 1.510	1.005 1.002 0.997 0.996	1.05	0.43	0.57
		BO(OH)3 ²⁻	O2 1.402 O1 1.494 O3 1.524 O4 1.532	0.996 0.996 0.994	1.29	1.09	0.34
		B(OH)₄ ⁻ ,Na ⁺	O1 1.434 O3 1.470 O4 1.499 O2 1.522	1.006 0.993 0.997 0.992	1.15	0.56	0.67
	aragonite	B(OH)4 ⁻	O2 1.455 O1 1.476 O4 1.497 O3 1.497	0.992 1.008 0.989 1.003	0.81	0.22	0.50
		BO(OH) ₃ ²⁻	O3 1.402 O2 1.492 O1 1.530 O4 1.543	0.987 1.001 0.985	1.02	1.15	0.26
		B(OH)₄ ⁻ ,Na ⁺	O2 1.457 O1 1.455 O3 1.501 O4 1.514	0.990 1.005 0.992 0.989	0.88	0.38	0.58

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

B coordinence		sample	δ_{iso} (ppm)	C _Q (MHz)	η	ref.*	present interpretation
trigonal	synthetic	calcite	17.1 ±1	3.0 ±0.3	0.67 ±0.05	1	BO ₂ (OH) ²⁻
0.	-,	heated aragonite	22 0 +1	27+03	0 2 +0 05	1	BO ₃ ³
		calcite	16.6 +0.5	n d	n d	2	BO ₂ (OH) ²⁻
		Ma_calcite	16.5 ± 0.5	n.d.	n.d.	2	"
		Nig-calcile	10.5 ±0.5	11.U.	n.u.	2	
		aragonite	16.9 ±0.5	2.6 ±0.1	n.a.	2	
	natural	biogenic calcite	18.9 ±1	2.8 ±0.3	0.5 ±0.05	1	BO ₂ (OH) ²⁻
		0	19.3	2.6	0	3	BO3 ³⁻
		biogenic aragonite	16.8	2.5	0	3	B(OH)
		biogenie aragenie	18.3	2.5	Õ	3 3	"
		coral CoC	17.5	2.3	02	1	
			17.5	2.5	0.2	4	
tetragonal	synthetic	calcite	0.5 ±1	0.0 ±0.3	-	1	B(OH)4 ⁻
U U	2		1.9 ±0.5	n.d.	-	2	"`´
		calcite	-03+05				2
		("interstitial")	0.0 20.0				•
		calcite	-2.4 ± 0.5				2
		("interatitiel")	-2.4 10.5				:
			40.05			~	
		Mg-calcite	1.2 ±0.5	n.a.	-	2	B(OH) ₄
		aragonite	1.6 ±0.5	0.0 ± 0.3	-	1	
			1.6 ±0.5	n.d.	-	2	"
	natural	biogenic calcite	11+1	00+03	-	1	B(OH)₄ ⁻
		2.090110 001010	1.67	0.0	_	3	"
		bydrothormal	2.95	0.0	-	3	2
		calcite	2.00	0.0		3	1
		biogenic aragonite	1.2 ±0.5	0.0 ±0.3	-	1	B(OH)₄⁻
			2 54	0.0	-	3	?``
			2.0	0.0	_	3 3	
		coral CoC	1.5	0.0	_	1	"
1-			1.0	<u>v.</u>	-		

Table 2: Experimental ¹¹B NMR parameters of synthetic and natural calcium carbonates

al. (1994), ²Mavromatis et al. (2015), ³Klochko et al. (2009), ⁴Rollion-Bard et al. (2011)

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727 Figure captions

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Figure 1: Theoretical structure of B-bearing calcite and aragonite obtained from firstprinciples 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 Ca²⁺ 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.

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

736

737 Figure 2: Summary of first-principles metadynamic run on aragonite. The fluctuations of 738 SPRINT coordinates (top and middle panel) reflect the geometrical changes affecting the 739 H-bonding pattern of OH groups with O atoms belonging to surrounding carbonate 740 groups. The bottom panel reports the history dependent bias potential which drives the 741 system away from the previously explored configurations (see text). SPRINT 742 coordinates are defined through the product of the principal eigenvalue of the (real 743 valued) adjacency matrix with its corresponding eigenvector. To enforce invariance 744 under permutation of identical atoms, the resulting values are sorted in ascending order 745 within the oxygen and hydrogen subsets, and are shown with a color gradient ranging 746 from the lowest to the highest components.

747

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

749

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 $\boldsymbol{\eta}$ parameters; whereas the squares correspond
754	to high $\boldsymbol{\eta}$ values indicating in-plane distortion of the trigonal group. The triangles
755	correspond to experimental data for which the $\boldsymbol{\eta}$ 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.
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Theoretical structure of B-bearing calcite and aragonite Click here to download high resolution image







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