First-principles study of boron speciation in calcite and aragonite

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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 $BO_2(OH)^{2-}$ species coexisting with a fraction of substituted $B(OH)_4^-$ groups. In aragonite, the $B(OH)_4^-$ substitution for CO_3^{2-} anions is dominant. Different species, including entrapped $B(OH)_3$ 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.
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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 CO_2 concentrations (Vengosh et al., 1991; Hemming and Hanson, 1992). A large number of studies have applied this idea to various biogenic carbonates, proposed paleo-CO_2 secular evolutions for the Earth's atmosphere and established the sensitivity of global climate to atmospheric CO_2 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.,

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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 $^{11}B/^{10}B$ 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 ^{11}B), and the tetragonal borate ion ($B(OH)_4^-$, preferentially enriched in ^{10}B), 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 coexisting in calcite and aragonite samples. Both partitioning and speciation of boron are polymorph dependent, aragonite incorporating tetragonal boron more easily than calcite (e.g. Sen et al., 1994; Branson et al., 2015; Mavromatis et al., 2015). Direct determination of the boron coordination state can be achieved using ^{11}B solid-state nuclear magnetic resonance (NMR) (Sen et al., 1994; Klochko et al., 2009; Rollion-Bard et al., 2011; Mavromatis et al., 2015), electron energy loss spectroscopy (EELS) (Rollion-Bard et al., 2011) and scanning transmission X-ray microscopy (STXM) (Branson et al., 2015). The observation of an often dominant contribution of trigonal B in calcite, and its occurrence in aragonite, has been interpreted as reflecting a coordination change of borate ions at the surface of growing crystals (Hemming et al., 1998; Klochko et al., 2009; Branson et al., 2015). This interpretation is consistent with in-situ Atomic Force Microscopy (AFM) observations of the morphology and dynamic of the surface of calcite crystals growing from B-bearing solutions (Ruiz-Agudo et al., 2012). According to this mechanism, the boron isotopic composition in the mineral phase still reflects that of the borate ions in the solution. This explains the success of the boron-isotope proxy for paleo-pH reconstitutions from mineral remains of extinct species. However, several studies have suggested that a fraction of incorporated B could correspond to boric acid molecules, directly scavenged from the solution (Xiao et al., 2008; Rollion-Bard et al., 2011; Noireaux et al., 2015). Consistently, higher than expected $^{11}B/^{10}B$ ratio have been determined on inorganically precipitated and biogenic calcium carbonate samples. Isotopic effects in biogenic carbonates have also been shown to depend upon the calcifying species. Although local variations of pH at the calcification site can surely contribute to the isotopic variability observed in biologically produced calcium 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 $B(OH)_2CO_3^-$ 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 $BO_2(OH)^{2-}$ and fully protonated tetragonal $B(OH)_4^-$ 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