

Coordination environments of B impurities in calcite and aragonite polymorphs: A ^{11}B MAS NMR study

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ABSTRACT

Coordination environments of B impurities in concentration levels on the order of parts per million in calcite and aragonite have been studied by ^{11}B MAS NMR spectroscopy. B-O coordination in these polymorphs of CaCO_3 has been found to be very sensitive to the carbonate crystal structure. In calcite, B occurs principally in trigonal coordination, whereas it occurs in tetrahedral coordination in aragonite. On phase transformation from aragonite to calcite, B changes its coordination accordingly. Thus, B impurities reside in the CaCO_3 crystal structure rather than in fluid inclusions or trace mineral phases. Isolated BO_3^{3-} anions are most likely to replace CO_3^{2-} anions in the calcite structure, through a process of coupled substitution in order to maintain the electrical neutrality. On the other hand, the structural role of BO_4^{3-} tetrahedra in the aragonite structure is not clear. The similarity in B isotopic composition between the two CaCO_3 polymorphs, in spite of the difference in the B coordination states, implies disequilibrium between B in the CaCO_3 structure and that in the parent solution. Different coordination states of B in calcite and aragonite are the likely controlling factor behind the stronger partitioning of B into aragonite than into calcite from the parent solution.

INTRODUCTION

Interest in the application of B and its isotopes as tracers for geological processes has increased as a result of recent work on the geochemical cycle of B (Spivack et al., 1987). The variations in B content and isotopic composition in clays and carbonates have important implications in the study of sediment recycling in subduction zones (Morris et al., 1990) and may have application to paleoenvironmental interpretations (Vengosh et al., 1992). A recent study by Hemming and Hanson (1992) suggested that the B concentration and isotopic composition of modern marine carbonates are controlled by the pH of sea water, an important observation considering the possibility of determining paleo-pH from the B isotopic composition of carbonates. However, an important but unknown aspect of B as a trace element is its coordination environment in carbonates, which may have implications as to the mechanism of B incorporation in these geological materials. There has been some speculation as to the coordination of B in carbonates (see Hemming and Hanson, 1992), but no systematic study of the mechanism of B incorporation or the mode of occurrence of B ions in the crystal structures of CaCO_3 polymorphs has been done.

For transition metals or rare-earth elements present in

trace amounts in a material, techniques such as optical, luminescence, and electron paramagnetic resonance spectroscopies can be applied to obtain information regarding their coordination environment and redox state (Rossman, 1988; Waychunus, 1988; Calas, 1988). However, for trace elements such as B or Al, these techniques are generally not useful. NMR spectroscopy can be particularly useful in obtaining short-range structural information for this latter group of elements. For example, trace amounts of Al impurities in rutile (TiO_2) have been successfully detected and characterized by ^{27}Al NMR spectroscopy (Stebbins et al., 1989).

Presented here is a high-resolution ^{11}B magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopic study of the local coordination environment of B in calcite and aragonite. NMR spectroscopy is particularly suitable for this study, as it is element-specific and primarily sensitive to the short-range order around a nucleus; ^{11}B has high natural abundance ($\approx 80\%$) and receptivity, and the coordination state and corresponding NMR spectral characteristics for B atoms in various borate minerals is already well established (Bray et al., 1961; Turner et al., 1986). In this study, both naturally occurring and synthetic calcite and aragonite with a range in B concentration (60–600 ppm) have been analyzed.

TABLE 1. B concentration, isotopic composition, and ¹¹B NMR parameters for carbonate samples and simple borates

Sample	NMR parameters						NMR sample size (mg)	B (ppm)‡	δ ¹¹ B (‰)§
	BO ₃			BO ₄					
	δ _{iso} *	Cq**	η†	δ _{iso}	Cq**	η†			
Calcite									
Synthetic	17.1	3.0	0.67	0.5	0.0	—	170	600	-16.5
Mg-rich algae (<i>Goniolithon</i>)	18.9	2.8	0.50	1.1	0.0	—	144	70	+22.4
Phase transformed from aragonite	22.0	2.7	0.20	—	—	—	148	61	+24.6
Aragonite									
Synthetic	—	—	—	1.6	0.0	—	36	369	-16.5
Coral (<i>Montastrea</i>)	—	—	—	1.2	0.0	—	174	59	+24.7
Simple borates	16.0–18.0	2.3–2.8	0.00–0.10	1.0–2.0	0.0–0.5	0.5–0.8	—	—	—

* Isotropic chemical shift expressed in parts per million from BF₃·Et₂O; the estimated error for calcite samples is ±1 ppm and for aragonite, ±0.5 ppm.

** Nuclear quadrupolar coupling constant in MHz; the estimated error is ±0.3 MHz.

† EFG asymmetry parameter, with an estimated error of ±0.05.

‡ B concentration by isotope dilution mass spectrometry.

§ B isotopic composition in per-mil deviation from SRM951 boric acid standard.

|| Data from Bray et al. (1961) and Turner et al. (1986).

EXPERIMENTAL TECHNIQUES

Synthesis of calcite and aragonite

A free-drift technique developed by Gruzensky (1967) and modified by Paquette and Reeder (1990) was used to synthesize the carbonates. Calcite crystals were grown in a sealed beaker containing a CaCl₂-NH₄Cl solution exposed to solid (NH₄)₂CO₃ for about 17 d (for details of this procedure, see Hemming et al., in preparation). This resulted in equant, 100-μm rhombs. Aragonite was synthesized with the same technique, with the addition of Mg to the experimental solutions, which inhibits the growth of calcite and favors the growth of aragonite. The synthesized aragonite occurs as half-spheres composed of aggregates of radially aligned needles.

Phase transformation of aragonite to calcite

To transform aragonite into calcite, an aragonite coral sample was finely crushed and heated in a Pt crucible at 450 °C and 1 atm in air (Davis and Adams, 1965) for 2 h and finally at 500 °C for 20 min. The experiment product was changed in color from pale yellow to gray, probably because of the oxidation of organic material. The X-ray powder diffraction pattern of the experiment product has all characteristic calcite peaks between 0 and 70° 2θ. The lack of characteristic peaks for aragonite and other phases indicates at least 90% of the powder consists of calcite.

Mass spectrometry

The B content and isotopic composition of the carbonate samples were determined by negative thermal ionization mass spectrometry. Powdered samples were dissolved in 1 N HCl. An aliquot of this solution was loaded directly on a Re filament without separation or concentration of the B (typically 1–20 ng of B), as a salt is necessary to enhance the ionization of B. Isotopic compositions were measured on a solid source mass spectrometer of NBS design and 30-cm radius of curvature by peak jumping between masses 43 and 42 (BO₂⁻). All isotopic compositions reported here are in the δ notation, which is the per-mil deviation from the National Institute of

Standards and Technology Standard Reference Material 951 boric acid. Detailed sample preparation procedures and mass spectrometry analytical techniques for both B abundance and isotopic composition are described in Hemming and Hanson (1992, 1994).

NMR spectroscopy

The ¹¹B MAS NMR spectra were collected with a Varian VXR-400S spectrometer operating at a ¹¹B Larmor frequency of 128.317 MHz. Powdered samples were packed in sapphire rotors and spun at the magic angle with a spinning speed of 9.4–9.7 kHz. An rf pulse length of 0.5 μs was used with a 0.1-s delay between pulses, except for a 1-s delay for the synthetic calcite sample. The solution 90° pulse length for boric acid was 9.75 μs. From 46500 to 100000 free induction decays were averaged to produce each spectrum. Aqueous boric acid (H₃BO₃) solution was used as a standard, which has a known chemical shift of -19.6 ppm (Dewar and Jones, 1967) from boron trifluoride etherate (BF₃·Et₂O), the usual standard for B NMR. To check the accuracy of our standard, the ¹¹B chemical shift for danburite (CaB₂Si₂O₈) was measured from the same boric acid solution. This yielded a value of ≈0.8 ppm from BF₃·Et₂O after necessary corrections and is in extremely good agreement with the value of 0.7 ± 0.2 ppm obtained by Turner et al. (1986) using BF₃·Et₂O as a standard. For the synthetic calcite sample, a set of experiments with varying pulse lengths (0.5–10 μs) and delay time between pulses (0.1–10 s) was carried out. Because of the extremely low B concentration in the samples, a spectrum was collected under identical conditions with an empty sapphire rotor to negate the possible presence of any B background. For the amounts of samples used in obtaining each spectrum, see Table 1.

SPECTROSCOPIC RESULTS

The ¹¹B nuclide is quadrupolar, with nuclear spin quantum number *I* = 3/2. As a result, nuclear Zeeman levels are perturbed by interaction between the nuclear quad-

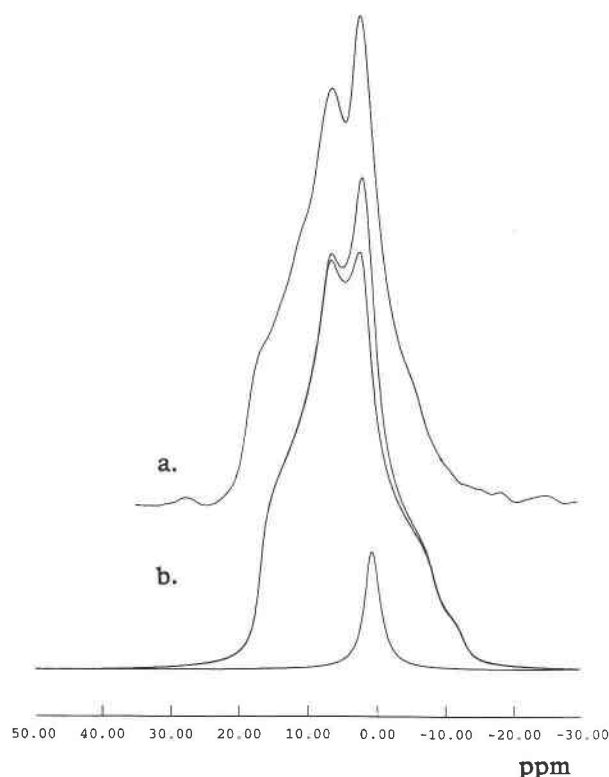


Fig. 1. Experimental (a) and simulated (b) ¹¹B MAS NMR spectra of a synthetic calcite sample. The simulated spectrum shows the presence of two components corresponding to BO₃ ($Cq \neq 0$) and BO₄ ($Cq = 0$) groups. Simulation parameters of these two components are listed in Table 1.

rupole moment and the electric field gradient (EFG) at the B site. This causes line broadening and gives rise to characteristic NMR line shapes from which the quadrupolar coupling constant, Cq ($= e^2qQ/h$), and asymmetry parameter, η , for the EFG can be calculated from a well-resolved spectrum (see Engelhardt and Michel, 1987). In particular, the two common coordination environments of B, trigonal planar BO₃ and tetrahedral BO₄, can be differentiated on the basis of differences in Cq . Previous studies of borates (Turner et al., 1986; Bray et al., 1961) have shown that Cq for the BO₃ group ranges from 2.3 to 2.8 MHz, whereas for the BO₄ group it varies from 0 to 0.8 MHz. Isotropic chemical shifts (δ_{iso} , from BF₃·Et₂O) for B in simple borates have been found to be about 17 ± 1 ppm for the BO₃ group and 1.5 ± 0.5 ppm for the BO₄ group (Turner et al., 1986). The ¹¹B isotropic chemical shift, Cq , and η values for different samples used in the present study are listed in Table 1.

Synthetic calcite

The ¹¹B MAS NMR spectrum of the synthetic calcite specimen is shown in Figure 1a. The spectrum shows a typical quadrupolar powder pattern, with a nonzero Cq and an isotropic chemical shift of about 19.4 ppm. However, experiments with varying pulse lengths (Fig. 2) and with varying delay time between pulses resolved the pres-

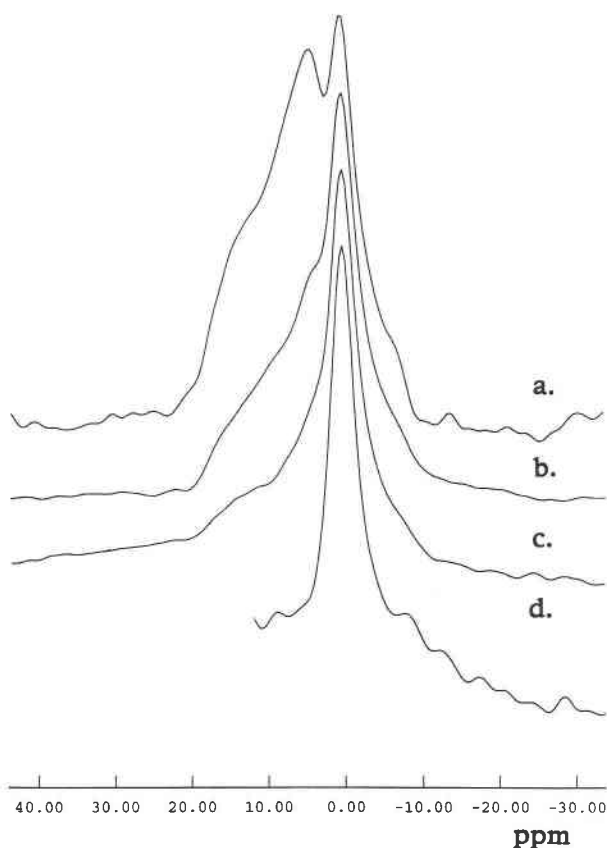


Fig. 2. The effect of changing pulse length on the ¹¹B MAS NMR spectrum of synthetic calcite. The different pulse lengths used are (a) 0.5, (b) 2.5, (c) 5.0, and (d) 7.5 μ s. The delay time between pulses is always 1 s. Note the increasing signal from the Gaussian component centered at 0.5 ppm (corresponding to BO₄ groups) with increasing pulse width. This indicates a slower nutation frequency of the BO₄ component (90° pulse length ≥ 7.5 μ s) with respect to that of the BO₃ component (90° pulse length ≤ 7.5 μ s).

ence of two components with different relaxation times and nutation frequencies. The slower relaxing component with higher nutation frequency has an isotropic chemical shift at about 17.1 ppm and thus corresponds to BO₃ groups. The faster relaxing component with a lower nutation frequency has a Gaussian peak shape (EFG ≈ 0 and $Cq \approx 0$) centered at 0.5 ppm and thus corresponds to BO₄ groups. Simulation of the spectrum with these two components (Fig. 1b) indicates that about 90% of the B impurities in calcite are in threefold coordination and the remainder are in fourfold coordination. The Cq for the BO₃ component is about 3 MHz, in good agreement with the corresponding values obtained for borate minerals (Turner et al., 1986). However, the EFG asymmetry parameter for BO₃ in calcite, $\eta = 0.67$, lies outside the range of $\eta = 0.06$ – 0.12 for BO₃ in synthetic borate compounds and minerals, as determined by Bray et al. (1961) using wide-line methods. This difference in η values can arise because of any of the following reasons: (1) different B-O bond lengths or distortion in the groups when they reside

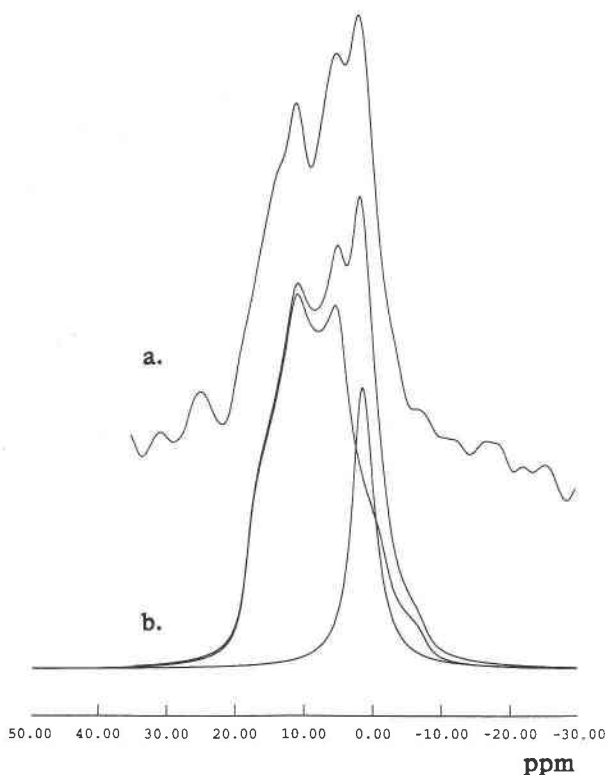


Fig. 3. Experimental (a) and simulated (b) ¹¹B MAS NMR spectra of a magnesian calcite sample. The simulated spectrum shows the presence of two components corresponding to BO₃ ($Cq \neq 0$) and BO₄ ($Cq = 0$) groups. The simulation parameters of these two components are listed in Table 1.

in a carbonate crystal structure rather than in a borate; (2) difference in the host crystal structure (which is a carbonate in the present case instead of a borate); (3) the presence of monovalent or trivalent charge balancing cations arising from coupled substitution associated with the introduction of borate groups in the carbonate structure may also have some effect.

Natural magnesian calcite

The ¹¹B MAS NMR spectrum for magnesian calcite (Fig. 3a) is very similar to that of the synthetic calcite, except for a reduced signal to noise ratio due to the lower B concentration in the natural sample (Table 1). This indicates the presence of both BO₃ and BO₄ groups. Simulation of the spectrum (Fig. 3b) yields an isotropic chemical shift of 18.9 ppm for BO₃ groups and 1.1 ppm for BO₄ groups. Cq values of about 2.8 MHz and η values of about 0.5 for BO₃ groups are consistent with those obtained for the spectrum of synthetic calcite. Minor differences may exist because the crystal structure of magnesian calcite is not exactly the same as that of pure calcite (Reeder, 1983). Relative peak areas show that about 80% of the B is in trigonal planar coordination and the remainder is in tetrahedral coordination.

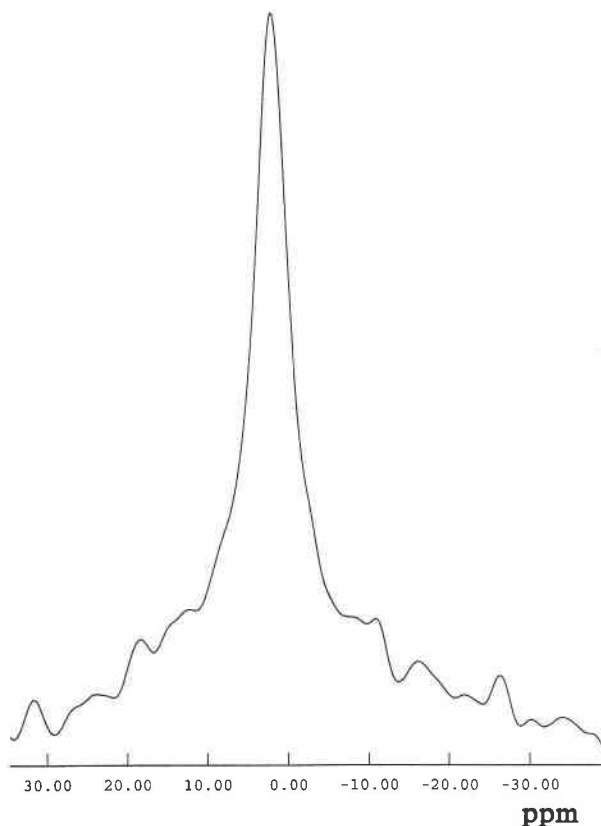


Fig. 4. A ¹¹B MAS NMR spectrum of a synthetic aragonite sample showing the presence of a single Gaussian peak ($Cq = 0$) centered at 1.6 ppm, corresponding to the BO₄ groups.

Synthetic aragonite and aragonitic coral (*Montastrea*)

The synthetic aragonite sample has a ¹¹B MAS NMR spectrum that is clearly different from that of the calcite samples and consists of a single Gaussian peak centered at 1.6 ppm, characteristic of BO₄ groups (Fig. 4). Variation of delay times and pulse widths does not show any observable quadrupolar peak with nonzero Cq corresponding to BO₃ groups. Hence all B impurities in aragonite, within experimental uncertainties, are in tetrahedral coordination. The ¹¹B MAS NMR spectrum of the natural aragonite is very similar to that of the synthetic aragonite, with a single Gaussian peak centered at 1.2 ppm corresponding to BO₄ units (Fig. 5).

Calcite phase transformed from aragonitic coral

Upon transformation of the aragonitic coral sample into calcite, the ¹¹B MAS NMR spectrum changes dramatically (Fig. 6). The Gaussian peak corresponding to the BO₄ units in the aragonite changes in the calcite to a quadrupolar powder pattern with a Cq of about 2.7 MHz and an isotropic chemical shift of about 22 ppm, indicating a transformation to the BO₃ structure. The asymmetry parameter in this case is significantly lower ($\eta = 0.2$) than for synthetic and natural calcite samples (Table 1). This difference in η is somewhat surprising but may

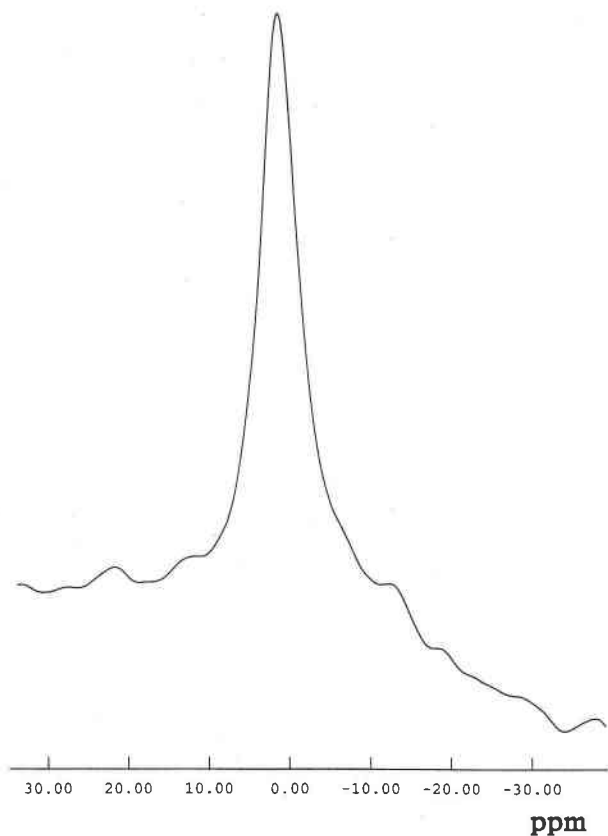


Fig. 5. A ¹¹B MAS NMR spectrum of an aragonite coral sample showing the presence of a single Gaussian peak ($Cq = 0$) centered at 1.2 ppm, corresponding to the BO_4 groups.

result from slight distortion in bond lengths and bond angles in BO_3 groups in the high-temperature phase-transformed calcite sample. The spectrum does not show any evidence of the presence of BO_4 groups. Hence most or all B changes to trigonal planar coordination from a tetrahedral coordination upon phase transformation from aragonite to calcite. The B isotropic chemical shifts for the BO_3 groups in natural magnesian calcite and phase-transformed calcite samples lie slightly outside (1–4 ppm less shielded) the corresponding range obtained for simple borates (see Table 1). However, the NMR spectra of these two samples are the noisiest ones because of the low B content of these samples, and thus very accurate determination of the chemical shifts is not possible. Hence, no physicochemical significance is attached to this shift difference.

DISCUSSION

The ¹¹B MAS NMR spectroscopic data presented here have important implications for understanding the mechanism and mode of occurrence of B in the carbonate structure. Interpretations based on these data are discussed considering constraints on B incorporation provided by other studies.

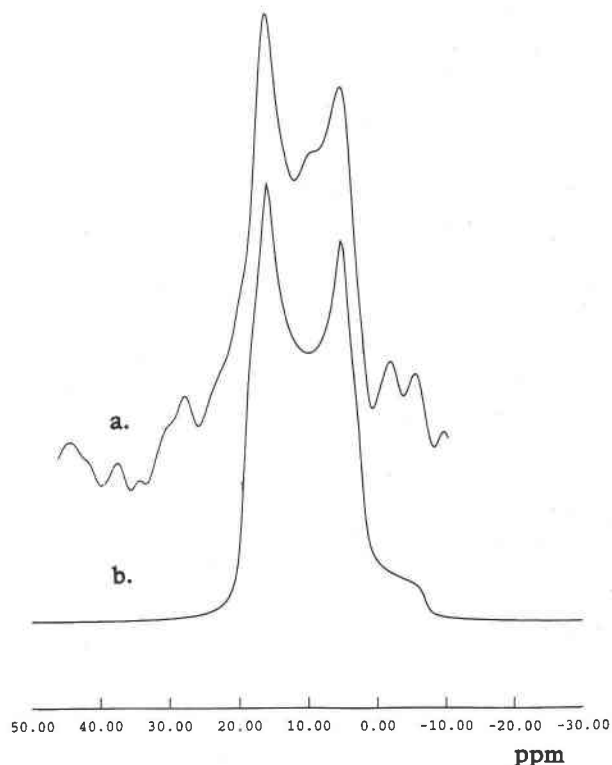


Fig. 6. Experimental (a) and simulated (b) ¹¹B MAS NMR spectra of a calcite sample phase transformed from the aragonitic coral at 450 °C. The simulated spectrum shows the presence of one component corresponding to BO_3 groups. Simulation parameters are listed in Table 1.

Structural implications

The ¹¹B MAS NMR spectroscopy provides convincing evidence that B resides in structural sites in aragonite and calcite. The dependence of the B coordination environment on the crystal structure of both natural and synthetic carbonates, with calcite favoring a trigonal B coordination and aragonite favoring a tetrahedral B coordination, is consistent with the structural incorporation of the B rather than its presence in fluid inclusions or trace mineral phases. This is in agreement with recent experimental results (Hemming et al., in preparation), which provide evidence for structural incorporation, including (1) an influence of B in the parent fluid on the crystal habit; (2) a systematic increase in B concentration in synthetic carbonates with increasing B in the parent fluid; and (3) higher B concentrations in the synthetic crystals than in the parent fluid, precluding the possibility of fluid inclusions. Isotopic data also argue against the presence of significant B in fluid inclusions. Hemming and Hanson (1992) found a narrow range in the B isotopic composition of modern marine carbonates, with an average isotopic offset from sea water of about -17% . Likewise, the $\delta^{11}B$ of the synthetic carbonates is -12% lower than the experimental fluids (Hemming et al., in preparation).

These findings alone, however, cannot rule out inclusions of some other B-bearing mineral. The present study, however, does exclude the possibility of solid inclusions. NMR spectra of synthetic aragonite and calcite were collected from the same samples as those used in Hemming et al. (in preparation), which had no impurities in the experimental solutions except B and NH₄. The presence of an impurity phase other than borates is thus unlikely. The B concentrations of these fluids are too low to favor the precipitation of borates, and, further, it would be unlikely that phase transformation from aragonite to calcite would fortuitously alter the B coordination in a solid mineral inclusion from tetrahedral to trigonal coordination.

Although there has been little study of B incorporation in carbonates, it is generally believed that B species reside in the CO₃ site (Hemming and Hanson, 1992; Vengosh et al., 1992). Hemming and Hanson (1992) speculated that B may occur in trigonal coordination in aragonite and calcite, possibly as a species such as HBO₃²⁻. This species was postulated on the basis of size and charge considerations. B-O bond lengths are about 0.137 nm (Moore and Araki, 1974; Gupta and Tossell, 1981), whereas the C-O bond length is about 0.128 nm in carbonates. For calcite, the NMR data presented here indicating trigonal coordination are consistent with the HBO₃²⁻ species postulated by Hemming and Hanson (1992), although other trigonal ions are also possible. On the other hand, the NMR data are clearly inconsistent with trigonal borate groups in aragonite. Cross-polarization NMR experiments were carried out on ¹¹B to identify any H nuclei in close proximity to B. Unfortunately, the results of these experiments are inconclusive, and further work is needed to resolve the nature of the charge-balancing cation (other than Ca²⁺) associated with the BO₃²⁻ and BO₄⁻ groups in the CaCO₃ structure.

Isotopic implications

The partitioning of B into aragonite from aqueous solution is greater than for calcite (Kitano et al., 1978; Hemming et al., in preparation), even though the anion site in the former is smaller than in the latter. This observation is difficult to explain by normal size and charge arguments. NMR spectroscopic data clearly indicate that a larger ion (boron in tetrahedral coordination) is substituting into a smaller site (aragonite), whereas the smaller ion (boron in trigonal coordination) is substituting into a larger site (calcite). The difference in coordination between the CaCO₃ polymorphs may thus be an important hint as to the difference in the magnitude of B uptake between aragonite and calcite, particularly in light of what is known about the mechanism of B uptake from isotopic studies.

B occurs in natural waters predominantly in two species, B(OH)₃ and B(OH)₄⁻. There is an isotopic offset between these two aqueous B species due to differences in vibrational energies associated with the difference in coordination (Kakahana et al., 1977), with the result that

the tetrahedral species is isotopically lighter than the trigonal species. It has been observed that B adsorbed onto marine clays has an isotopic composition significantly lighter than sea water, which was interpreted to result from the uptake of the charged and isotopically lighter B(OH)₄⁻ species (Schwarcz et al., 1969; Palmer et al., 1987; Spivack and Edmond, 1987). A similar fractionation is seen in marine carbonates (Hemming and Hanson, 1992; Vengosh et al., 1992). Hemming and Hanson (1992) interpreted the narrow range in isotopic composition of a variety of modern marine carbonates to be the result of preferential uptake of the tetrahedral species, as the average composition of the marine carbonates is identical to the composition of the B(OH)₄⁻ species in sea water, calculated at pH = 8.2. These authors suggested that the mechanism of B incorporation into marine carbonates requires an adsorption step onto the crystal surface. Further evidence that this is the case is provided by experimental results, where, under more controlled conditions, the isotopic composition of synthetic aragonite and calcite is identical to the isotopic composition of the B(OH)₄⁻ species of the parent fluid (Hemming et al., in preparation). If this is correct, then our spectroscopic results indicate that the surface-adsorbed B(OH)₄⁻ species keeps its coordination unchanged from the surface into the aragonite crystal structure, whereas for calcite a change in coordination is required. Because of the change in coordination in calcite, it might be expected that the trigonal structural B would be isotopically heavier than the tetrahedral surface-adsorbed B, but this is not seen in the isotopic compositions. One explanation for this is that all the B that is surface-adsorbed is structurally incorporated, so no fractionation takes place.

However, if a change in coordination is necessary for B to be incorporated in the calcite structure but not in the aragonite structure, there may be an energy barrier to B uptake in calcite, which is consistent with the depletion of B in that polymorph relative to aragonite. If this is the case, this energy barrier has a greater influence on B uptake than site size and charge considerations. Consistent with this interpretation, NMR spectra indicate that magnesian calcite may have more ¹⁰B than calcite, and the magnitude of B uptake in magnesian calcite is intermediate between calcite and aragonite. The ratios of the two coordinations are, however, not very precise, and this question requires further study.

The observation that B occurs in different coordination environments in calcite and aragonite, as indicated by NMR spectroscopy, suggests that the very similar isotopic compositions observed in calcite and aragonite can be consistently explained by a single-stage isotopic fractionation between the aqueous and surface-adsorbed B species (Hemming and Hanson, 1992; Hemming et al., in preparation). This scenario clearly implies disequilibrium between B included in these mineral structures and that in the parent solution, as all surface-adsorbed B enters into the CaCO₃ structure without further isotopic fractionation.

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MANUSCRIPT RECEIVED DECEMBER 17, 1993

MANUSCRIPT ACCEPTED MAY 6, 1994