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Boron Stable Isotopes

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Properties

Boron, a group 13 metalloid, has two natural occurring stable isotopes, ¹¹B (11.00930536[45]) and ¹⁰B (10.01293695[41]), with relative abundances of 0.199(7) and 0.801(7), respectively, and hence occurs approximately in a 4:1 ratio (source of data: National Institute of Standards and Technology, <http://www.nist.gov/pml/data/comp.cfm>). Numerous radioisotopes of boron also occur with masses from ⁷B to ¹⁷B, but their half-lives are all <1 s. As with other stable isotopic systems, natural isotope variation is described using delta notation, i.e., the per mil variation from the ¹¹B/¹⁰B ratio of the synthetic boric acid international reference material NIST SRM-951 (atom%: ¹¹B = 80.173 ± 0.013; ¹⁰B = 19.827 ± 0.013; Catanzaro et al., 1970). This can be described by the following equation:

$$\delta^{11}\text{B} = \left(\frac{{}^{11}\text{B}/{}^{10}\text{B}_{\text{sample}}}{{}^{11}\text{B}/{}^{10}\text{B}_{\text{reference}}} - 1 \right) \times 10^3 \quad (1)$$

In natural systems, boron is almost exclusively found bound to oxygen in either tetrahedral (e.g., borate ion, B(OH)₄⁻) or

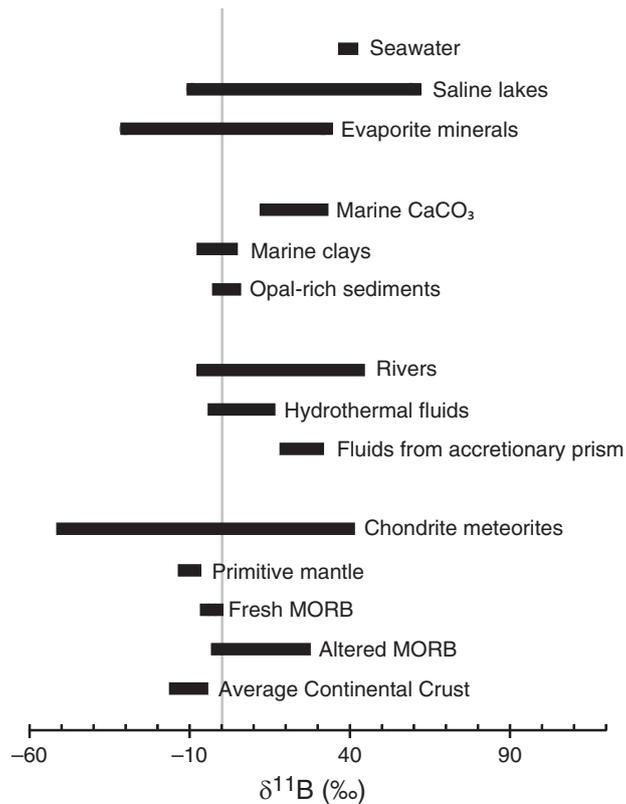
trigonal complexes (e.g., boric acid, B(OH)₃). Natural fractionation of the two isotopes is governed principally by their distribution between such complexes, with a tendency for ¹¹B to be incorporated preferentially in the stronger bonded trigonal molecules (e.g., boric acid in seawater). Boron is very soluble and hence fluid mobile and exhibits a dynamic speciation at low temperature. These features, coupled with its relatively light mass (10.806–10.821) and the large mass difference between its isotopes (~10 %), combine to cause a very wide range in natural isotopic compositions (from -50 ‰ to +60 ‰; Barth, 1993; Figure 1).

History and Use

F.W. Aston made the first determinations of the isotopic composition of naturally occurring boron in 1920 using what was then known as a “positive ray spectrograph” and what is now known as mass spectrometry (Aston, 1920). Due to its utility in tracing low-temperature geochemical processes, relative to other nongaseous stable isotope systems (e.g., Li, Ca, Cu, Co, etc.), boron isotope research in the Earth sciences has a relatively long history with the first measurement of natural materials in the early 1960s (e.g., McMullen et al., 1961). Like many isotopic systems, technological developments have led the expansion in the use of boron isotopes as a geochemical tracer with significant growth in the 1980s with the improvement and development of thermal ionization techniques (e.g., Zeininger and Heumann, 1983), and a more recent expansion with plasma-based analytical methods in the 2000s for both bulk and in situ measurements (e.g., Lécuyer et al., 2002; Foster, 2008; Fietzke et al., 2010).

Geochemical and Isotopic Behavior

Figure 1 shows the large range (>100 ‰) of δ¹¹B observed in terrestrial and extraterrestrial materials. The building blocks



Boron Stable Isotopes, Figure 1 Boron isotopic composition of some terrestrial and extraterrestrial materials (Sources are either as in text or from Barth 1993).

of the terrestrial planets, the carbonaceous chondrites, have a relatively low boron concentration (~ 0.8 $\mu\text{g/g}$; Lodders, 2010), and chondrules exhibit an isotopic variation that spans nearly the entire range of observed values in terrestrial materials (from -50 ± 10 ‰ to $+40 \pm 10$ ‰; Figure 1; Chaussidon, 1995), while more restricted variations ($\delta^{11}\text{B} = +25 \pm 15$ ‰) have been observed in the Allende CV3 meteorite. This is thought to be the result of the synthesis of B via spallation processes involving nebular hydrogen and cosmic rays (Chaussidon and Robert, 1995). This process also offers an explanation of why ^{11}B is more abundant than ^{10}B , in a similar fashion to lithium.

In contrast to the chondrites, the boron content of the Earth's mantle is relatively low (~ 0.3 $\mu\text{g/g}$; Menard et al., 2013), and its isotopic composition is ≈ -10 ‰ (Chaussidon and Marty, 1995). Unaltered (i.e., fresh) mid-ocean ridge basalts (MORB) have ~ 1 $\mu\text{g/g}$ B with a $\delta^{11}\text{B}$ in the range -10 to -2 ‰ (e.g., Spivak and Edmond, 1987). Alteration through reaction with seawater increases their B content (up to 120 $\mu\text{g/g}$) and drives the $\delta^{11}\text{B}$ up (-2 to $+26$ ‰; Smith et al., 1995). The mean $\delta^{11}\text{B}$ of the continental crust is hard to define but is most likely in the range -15 to -5 ‰ (Ishikawa and Nakamura, 1993). Tourmaline is the most common boron-bearing mineral (borosilicate) in the

continental crust and has $\delta^{11}\text{B}$ values ranging from -30 ‰ to $+37$ ‰ reflecting the nature of the fluids and rock types it is associated with (Marschall and Jiang, 2011). The isotopic composition of the common ores of boron (hydrated sodium and calcium borates such as borax, kernite or rasorite, ulexite, and colemanite) depends on the nature of their parent fluid. Borates from marine evaporite deposits have $\delta^{11}\text{B}$ values that range from $+18$ ‰ to $+32$ ‰, in average much higher than those measured in nonmarine evaporation borates (-30 ‰ $< \delta^{11}\text{B} < +12$ ‰), thus reflecting their highly isotopically contrasted source reservoirs, which are seawater (today $\delta^{11}\text{B} = +39.6$ ‰; Foster et al., 2010) and the continental crust ($\delta^{11}\text{B} \approx -15$ to -5 ‰), respectively.

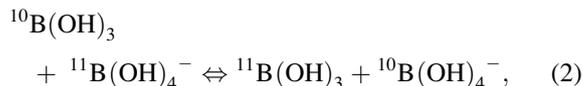
The isotopic composition of boron is also fractionated in the terrestrial weathering environment with ^{10}B preferentially retained in secondary clays (Schmitt et al., 2012). As a consequence, river water has low boron concentrations (1 to <40 ng/g) and has a $\delta^{11}\text{B}$ (-6 to $+43$ ‰) that is typically heavier than average continental crust (Lemarchand et al., 2002). The flux-weighted mean $\delta^{11}\text{B}$ of riverine boron supply to the oceans is $+10$ ‰ (Lemarchand et al., 2002). Freshwater lakes have variable boron contents (0.3 to 44 $\mu\text{g/g}$) and also exhibit a wide range in $\delta^{11}\text{B}$ from -4.4 to $+59$ ‰ (Vengosh et al., 1991). Additional fractionations can occur in the

terrestrial realm through the uptake and fractionation of boron in plants (Xu et al., 2015).

Boron has a long residence time in the oceans (10–20 million years; Simon et al., 2006) and is both uniform in concentration (4.5 $\mu\text{g/g}$; Lee et al., 2010) and isotopic composition ($\delta^{11}\text{B} = 39.61\text{‰}$; Foster et al., 2010). Boron is also supplied to the ocean via hydrothermal fluids with $\delta^{11}\text{B} = -2.5$ to $+14.5\text{‰}$ and fluids expelled from accretionary prisms ($+25 \pm 5\text{‰}$; Smith et al., 1995). Since the boron isotopic composition of the ocean is significantly heavier than these inputs (Figure 1), other processes must operate that preferentially remove ^{10}B to isotopically enrich the remaining boron. Three major sinks have been recognized: (1) the alteration of oceanic crust (see above; Smith et al., 1995), (2) the adsorption of boron onto clays such that marine clays have $\delta^{11}\text{B} = -6$ to $+2.8\text{‰}$ (Ishikawa and Nakamura, 1993), and (3) coprecipitation of boron in calcium carbonate and biogenic silica (Figure 1; Ishikawa and Nakamura, 1993).

The magnitude of fractionation via adsorption to clays and coprecipitation with calcium carbonate is a well-described function of pH (Palmer et al., 1987; Zeebe and Wolf-Gladrow, 2001). This pH sensitivity arises because of the pH dependency of speciation of aqueous boron species: at low pH, trigonal boric acid ($\text{B}(\text{OH})_3$) dominates, and at high pH, boron is predominantly in the tetrahedral borate ion ($\text{B}(\text{OH})_4^-$) complex (Figure 2). Due to the structural differences between the two aqueous forms of boron found

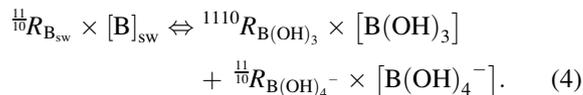
in seawater, there is a large isotopic fractionation between them, with ^{11}B preferentially incorporated into boric acid. The isotopic exchange between these species can be described by the reaction:



with the isotopic fractionation, α_{B} (also written $^{11-10}\text{K}_{\text{B}}$ and $\alpha_{\text{B}4-3}$), given as:

$$\alpha_{\text{B}} = \frac{^{11}\text{R}_{\text{B}(\text{OH})_3}}{^{11}\text{R}_{\text{B}(\text{OH})_4^-}}, \quad (3)$$

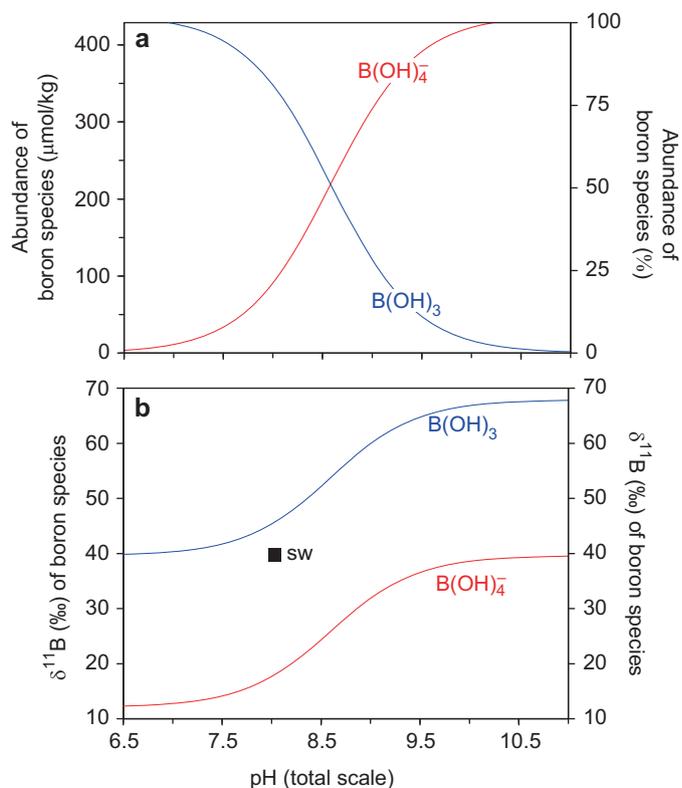
where $^{11/10}\text{R}$ is the $^{11}\text{B}/^{10}\text{B}$ ratio of each dissolved species. At any given pH, the sum of total boron in seawater and its $\delta^{11}\text{B}$ can be described by the following reaction:



It follows therefore that as the abundance of each species changes with pH so does their isotopic composition (Figure 2). There have been numerous attempts to define α_{B} , and recent direct measurements place its value in seawater at

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Figure 2 The variation of concentration (a) and isotopic composition (b) of borate ion ($\text{B}(\text{OH})_4^-$) and boric acid ($\text{B}(\text{OH})_3$) with changing seawater pH (total scale) at typical surface ocean conditions ($T = 25\text{ °C}$, $S = 35$ psu). Also shown in (b) is the $\delta^{11}\text{B}$ of total boron in seawater (39.61 ‰; Foster et al., 2010).

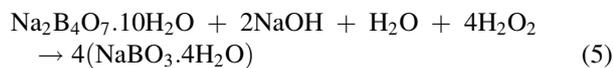


1.0272 ± 0.0006 to 1.0260 ± 0.0010 at $25\text{ }^\circ\text{C}$ (Klochko et al., 2006; Nir et al., 2015). At present, the temperature sensitivity of α_B is uncertain, but it is likely to be small (Rae et al., 2011). It has been experimentally determined and observed through isotopic measurements of natural materials that both boron adsorbed to clays (e.g., Palmer et al., 1987) and boron coprecipitated with CaCO_3 are isotopically lighter than seawater (Sanyal et al., 2000; Figure 1). This arises due to the preferential absorption of the charged and isotopically light borate ion species to clay particles in seawater and to the growing surfaces of CaCO_3 . The latter behavior forms the basis of the boron isotope pH proxy (see below and Foster and Rae, 2016).

Applications to Geochemical Studies

Boron Isotopes as a Tracer of Human Activities

Xiao et al. (2013) reviewed the potential use of boron isotopes to track pollution of surface and groundwaters. Sodium perborate is the main source of boron pollution in water resulting from human activity. The synthesis of sodium perborate operates through the decomposition of sodium tetraborate decahydrate (a kind of borax) as follows:



As this chemical reaction does not involve any boron isotope fractionation (e.g., Barth, 1998), the product of this reaction preserves the isotopic composition of its source, making it possible to track boron pollution in natural waters under the condition that reservoirs involved have distinct $\delta^{11}\text{B}$ values.

Warner et al. (2014) also recently proposed the use of boron isotopes to trace contamination of groundwater and rivers by hydraulic fracturing fluids (HFF) from oil and gas operations. Distinct boron isotopic fingerprints for HFF relate to either the process of hydraulic fracturing liberating the light isotope from clay surfaces, boron associated with the liberated hydrocarbons or trapped brine, and/or from chemical additives to the fluid.

Phase Partitioning

Fractionation of Boron Isotopes Between Mineral and Fluid: The Case of Tourmaline

Boron isotopes are valuable to track processes of mass transfer between Earth's surficial and rock reservoirs. Both the solubility of most boron-bearing minerals and the incompatible behavior of this element during magmatic processes enable its isotopic composition to fingerprint dehydration and water-rock interaction during lithospheric subduction,

metamorphic reactions, and magmatic activity along with associated hydrothermal circulations. Tourmaline is a mineral of predominant interest as it is stable over a wide range of pressure and temperature. The fractionation of boron in tourmaline relative to the aqueous fluids in which it forms was first identified to be temperature dependent by Palmer et al. (1992) and more recently defined as $\Delta^{11}\text{B}(\text{tourmaline-aqueous fluid}) = -4.20(10^3 \cdot \text{T}^{-1}) + 3.52$, by Meyer et al. (2008), with no dependence on pressure (at least between 200 and 500 MPa). These experimentally determined tourmaline-fluid isotope fractionation factors are employed, for example, to quantify the evolution of fluids involved in the genesis of large ore deposits (e.g., Bast et al., 2014).

Fractionation of Boron Isotopes Between CaCO_3 and Seawater: The $\delta^{11}\text{B}$ -pH Proxy

The pH of the ocean, like its CO_2 content, is determined by the ratio of total alkalinity (the charge balance, TA) to the sum of dissolved inorganic carbon species (DIC): as the CO_2 content of the water increases, its pH decreases. Reconstructions of ocean pH in the past therefore offer the ability to trace the CO_2 content of the oceans through time. This is useful because (i) the partitioning of CO_2 between the ocean and the atmosphere is thought to govern atmospheric CO_2 change on glacial-interglacial timescales, and (ii) on a global-scale, the CO_2 content of the oceans determines the CO_2 content of the atmosphere, thereby allowing pH reconstructions to constrain the CO_2 content of the ancient atmosphere (e.g., Martínez-Botí et al., 2015).

The boron isotopic composition of marine CaCO_3 is well-defined proxy of ocean pH because it is predominantly the borate ion that is incorporated into the growing CaCO_3 (Hemming and Hanson, 1992) resulting in the $\delta^{11}\text{B}$ of CaCO_3 ($\delta^{11}\text{B}_c$) varying as a strong function of pH (at pH = 8.2, +0.1 pH units = +1 ‰ $\delta^{11}\text{B}$), as defined by Zeebe and Wolf-Gladrow (2001):

$$\text{pH} = \text{p}K_B^* - \log \left(-\frac{\delta^{11}\text{B}_{\text{sw}} - \delta^{11}\text{B}_c}{\delta^{11}\text{B}_{\text{sw}} - \alpha_B \delta^{11}\text{B}_c - \varepsilon_B} \right). \quad (6)$$

where $\delta^{11}\text{B}_{\text{sw}}$ is the boron isotopic composition of seawater, α_B is defined above and $\varepsilon_B = (\alpha_B - 1) * 1000$. $\text{p}K_B^*$ is the dissociation constant of boron in seawater which is a function of temperature, pressure, and salinity.

Although biogenic marine CaCO_3 largely conforms to this simple inorganic model a number of complications arise. For instance, life processes in some, but not all (e.g., Rae et al., 2011), CaCO_3 secreting organisms modify either the pH around themselves or internally in the calcifying space (e.g., coral; McCulloch et al., 2012), such that $\delta^{11}\text{B}$ of the marine carbonate is offset from the $\delta^{11}\text{B}$ of borate ion ($\delta^{11}\text{B}_{\text{borate}}$).

The existence of such “vital effects” therefore requires species-specific calibrations to account for the $\delta^{11}\text{B}_c \neq \delta^{11}\text{B}_{\text{borate}}$ and allow pH to be reconstructed (e.g., Henehan et al., 2013).

Despite these limitations, $\delta^{11}\text{B}$ in carbonates can reconstruct past pH with a typical accuracy of around ± 0.02 pH units, and under favorable conditions, this translates into reconstructions of ancient atmospheric CO_2 with an uncertainty of ± 20 ppm (Foster, 2008).

Tracing the Recycling of Subducted Oceanic Crust

Island-arc magmas are commonly interpreted as resulting from the partial melting of the mantle wedge metasomatized by liquids (aqueous fluids, silicate melts) or solids (sediments, altered oceanic basalts) derived from the subducted lithospheric plate. Those “contaminants” are also considered to play a significant role in generating the geochemical “signatures” of arc magmas. As emphasized by Rosner et al. (2003), boron is a highly mobile element in the aqueous phase with an incompatible behavior during processes of partial melting. Moreover, boron is highly concentrated in oceanic sediments and hydrothermally altered oceanic crust compared to fresh rocks derived from upper mantle melting. Consequently, boron can be considered as a key tracer of slab contribution to island-arc volcanic rocks. Moreover, the hydrothermally altered oceanic crust and the subducted sediments constitute two geochemical reservoirs of highly contrasted boron isotope compositions. As a result, $\delta^{11}\text{B}$ values of volcanic arc rocks reflect their relative contributions during their petrogenesis, albeit modified by fractionation that occurs during dehydration of the subducted slab (Leeman et al., 2004).

Summary

The stable isotopes of boron exhibit a very wide range in natural and extraterrestrial materials. This is virtue of their light mass, large mass difference between ^{11}B and ^{10}B , and the geochemical behavior of B itself. As a consequence, however, the boron isotope system has great utility in the Earth sciences, and the use of boron to trace low-temperature geochemical and extraterrestrial processes has a long history and is continuing to grow.

Cross-References

- ▶ Acid-Base Reactions
- ▶ Boron
- ▶ Calcium Carbonate and the Carbonic Acid System
- ▶ Carbon Cycle
- ▶ Chondrites
- ▶ Clay Minerals

- ▶ Earth’s Oceanic Crust
- ▶ Hydrothermal Alteration
- ▶ Hydrothermal Solutions
- ▶ Lithophile Elements
- ▶ Marine Geochemistry
- ▶ Ocean pH
- ▶ Solubility
- ▶ Subduction Zone Geochemistry
- ▶ Weathering: Chemical

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