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Boron Isotopes in the Earth and Planetary Sciences—A Short History and Introduction

Horst R. Marschall and Gavin L. Foster

> *Me fifth element – supreme being. Me protect you.*
> Leeloo

Abstract

This volume on boron isotope geochemistry contains chapters reviewing the low- and high-temperature geochemistry, marine chemistry, and cosmochemistry of boron isotopes. It covers theoretical aspects of B isotope fractionation, experiments and atomic modeling, as well as all aspects of boron isotope analyses in geologic materials by the full range of solution and in situ methods. The book provides guidance for researchers on the analytical and theoretical end, and introduces the various scientific applications and research fields in which boron isotopes play a growing role today. This chapter provides a brief history of boron isotope research and analytical development and provides an overview of the other chapters of the volume "Boron Isotopes—The Fifth Element" in the series *Advancements in Isotope Geochemistry*.

Keywords

Boron isotopes · History of boron · Geochemistry

1.1 Introduction

Boron is a moderately volatile, lithophile metalloid with a low atomic mass and two stable isotopes (^{10}B and ^{11}B). The ^{11}B/^{10}B ratio in terrestrial materials is approximately 4, but shows a variation of ~100 ‰ in nature (Palmer and Swihart 1996; Foster et al. 2016).The large B isotopic fractionation at low temperatures has led to the use of the B stable isotope system for studies on processes acting on the Earth's surface (e.g. Hemming and Hanson 1992; Barth 1998) and for the detection of fluid-rock interaction

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processes, such as in seafloor hydrothermal systems or enrichment processes in subduction zones (e.g. Spivack and Edmond 1987; Ishikawa and Nakamura 1994; Scambelluri and Tonarini 2012). The pH-dependent speciation of B in water and hydrous fluids leads to pH-dependent boron isotope fractionation between water and solids (Kakihana et al. 1977; Wunder et al. 2005; Klochko et al. 2006). Consequently, the boron isotopic composition of biogenic carbonate can be employed as a paleo-pH proxy for seawater during, for example, glacial-interglacial cycles and periods of the more distant geological past (e.g., Hönisch and Hemming 2005; Martínez-Botí et al. 2015).

The strong enrichment of B in the crust and the significant difference in B isotopic composition among continental crust, modern seawater and the depleted mantle make boron a powerful tracer for the secular evolution of the ocean-crust-mantle system (e.g., Leeman and Sisson 1996; Marschall et al. 2017). In cosmochemistry, boron isotope ratios are employed to investigate the timing of condensation and accretion, and in particular irradiation processes in the early solar system that led to the production of short-lived ^{10}Be and the subsequent ingrowth of radiogenic ^{10}B (e.g., McKeegan et al. 2000; Hoppe et al. 2001; MacPherson et al. 2003; Gounelle et al. 2013).

1.2 A Short History of Boron Isotope Analyses

1.2.1 The Discovery of Boron Stable Isotopes

The invention of the mass spectrometer by F.W. Aston and J.J. Thomson at Cambridge University (Thomson 1913; Aston 1919) and by A. J. Dempster at the University of Chicago (Dempster 1918) led to the discovery of stable isotopes in 1920 for which F. W. Aston was awarded the Noble Price in chemistry in 1922. Boron was among the first elements investigated with the new instrument and the discovery of its two stable isotopes was already reported in one of the first papers (Aston 1920). Soon, the masses of ^{10}B and ^{11}B were determined from ionized BF_3 (Aston 1927), and the results were already within 0.02‰ of the currently accepted values.

1.2.2 Natural Abundances and Variations

Other workers used acid titration of BCl_3 and BBr_3 solution to determine the atomic mass of boron and, hence, the natural abundances of the two stable isotopes (Baxter and Scott 1921). Discrepancies among different workers led to the consideration that natural isotopic abundances could vary depending on the source of boron, and attempts to demonstrate this experimentally occurred as early as 1925 (Briscoe and Robinson 1925). However the δ^{11}B values determined for sassolite from Italy, colemanite from California and boracite from Turkey by Briscoe and Robinson (1925) ranged from +54 to +208‰.[1] These values are much higher and show a much larger spread than any values determined for natural boron minerals more recently, suggesting that fractionation occured in the laboratory during sample preparation. The results and other contrasting reports of the 1920s for natural variations of boron isotope abundance ratios were questioned in the 1930s and explained as due to experimental errors. The quest for the determination of *the* atomic mass of boron (and hence its natural isotopic abundance ratio) continued.

Photometric analysis of boron from BF_3 and from boron oxide in the 1930s led to the establishment of the atomic mass of boron closer to the presently accepted value, and it was assumed that natural variations would not be resolvable analytically with the methods available at the time (Elliott 1930a, b; Jenkins and McKellar 1932; Ornstein and Vreeswijk 1933). These early pioneers quickly recognised something that modern analysts know all too well: the isotopic composition of boron was difficult to measure

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[1] δ^{11}B values are calculated from the reported ^{11}B/^{10}B ratios relative to the certified ratio of SRM951.

precisely. In this case, it was suspected that the widely used BF_3 method caused instrumental fractionation and memory effects, leading to the use of other boron compounds instead, such as trimethyl boroxine, $B_3O_3(CH_3)_3$ (Inghram 1946).

The lighter boron isotope, ^{10}B, has a very large cross section for thermal neutrons that is only rivaled by Cd and some of the rare earths (Sears 1992). The cross section of ^{11}B is approximately six orders of magnitude smaller than that of ^{10}B; the efficacy of boron as a neutron absorber in nuclear reactors, therefore, depends strongly on its isotopic composition. Following the discovery of nuclear fission in the 1930s and 1940s there was a growing interest in the natural isotopic abundance of boron. Indeed, such investigations played an important role in the discovery of the neutron itself (Chadwick 1933). The high neutron absorption of boron was also investigated early on in the context of neutron irradiation treatment of cancer (Zahl and Cooper 1941; Conger 1953). However, the natural isotope abundances became less important for technical applications once efficient isotope enrichment methods were developed (e.g., Beams and Haynes 1936; Yates 1938).

Nevertheless, the debate on the natural isotope abundances of boron continued, and some authors still suspected that natural variations of boron isotope ratios could exist (e.g. Aston 1931). This hypothesis was encouraged especially after Urey and Greiff (1935) had predicted variations in the atomic masses of light elements in nature; they argued for natural stable isotope fractionation based on a theoretical discussion of mass-dependent fractionation among molecules. This renewed the interest in the natural variation of the abundances of boron isotopes (Thode et al. 1948). However, most of these early studies did not include controlled sample preparation strategies from sampling of natural material to the stage of sample introduction into the mass spectrometer. Instead, commercially available, industrially processed boric acid was used for which the mine sources and original mineralogy were known (Thode et al. 1948). The possibility (and likelihood) of isotope fractionation during chemical processing was not discussed, and indeed all published boron isotope ratios from this early period are suspiciously enriched in the heavy isotope with $\delta^{11}B$ ranging from +56 to +94‰ (see Footnote 1) (Inghram 1946; Thode et al. 1948).

The debate continued with improvements in mass spectrometric methods, but subsequent papers reporting full preparation procedures for analyzed minerals found no resolvable variation for a large selection of borates and borosilicates (Osberghaus 1950; Parwel et al. 1956). This also includes the first analyses of borosilicates (axinite and tourmaline) and of seawater, but unfortunately, no actual values were reported by Parwel et al. (1956). Analytical methods initially included the use of single-focussing mass spectrometers, but then moved to double-focussing instruments, and employed a range of boron compounds, such as boron hydride, trimethyl borane $(CH_3)_3B$, and trimethyl boroxine (Inghram 1946; Lehmann and Shapiro 1959; Abernathey 1960), as well as BF_3 and BCl_3 (Inghram 1946; Thode et al. 1948; Osberghaus 1950; Bentley 1960), all of which resulted in very high $^{11}B/^{10}B$ ratios and hence high estimates for the atomic mass of boron.

1.2.3 TIMS and the Establishment of Standards

The debate was resolved in the 1960s with the introduction of isotope reference materials that could be used to correct for instrumental mass fractionation, and the use of thermal-ionization mass spectrometry (TIMS), in which boron compounds with higher masses (and so with reduced machine induced mass fractionation) were analyzed (McMullen et al. 1961). Ions of boron compounds were analyzed in P-TIMS, most importantly $Na_2BO_2^+$, but also $K_2BO_2^+$, which show less instrumental fractionation than BF_3 due to the much smaller relative mass difference between the ^{10}B- and ^{11}B-bearing compounds, respectively (McMullen et al. 1961; Finley et al. 1962; Shima 1962, 1963; Agyei and McMullen 1968). Other alkali-borate compounds were also used later on, including $Rb_2BO_2{}^+$ and $Li_2BO_2{}^+$ (Gensho and Honda 1971), and $Cs_2BO_2{}^+$ (Ramakumar et al. 1985; Spivack and Edmond 1986). In particular the cesium borate method produced very precise data, owing to the low instrumental fractionation of masses 309/308. In the early 1980s, TIMS employing the analysis of negative ions ($BO_2{}^-$) was developed, which enabled the analyses of much smaller samples compared to P-TIMS (Zeininger and Heumann 1983; Duchateau and De Bièvre 1983).

The first modern studies on minerals, rocks and waters included the investigation of borates and borosilicates, which contain boron as a major component, but also meteorites, igneous and sedimentary rocks and seawater, all of which contain B as a trace element (Finley et al. 1962; Shima 1962, 1963; Agyei and McMullen 1968). The possibility of interlaboratory comparison was given with the establishment of an internationally distributed boron isotope standard, a boric acid distributed by NIST (then the NBS) in 1970, named standard reference material 951 (Catanzaro et al. 1970). This material was established as the primary standard for boron isotopes, and boron isotope ratios of terrestrial materials are since reported in delta notation relative to NIST-SRM951:

$$\delta^{11}\mathrm{B} = \left(\frac{{}^{11}\mathrm{B}/{}^{10}\mathrm{B}_{\mathrm{sample}}}{{}^{11}\mathrm{B}/{}^{10}\mathrm{B}_{\mathrm{SRM951}}} - 1\right) \cdot 1000 \qquad (1.1)$$

A number of secondary reference materials have since been established, as listed in this book (see Foster et al. 2017). These materials include a range of silicate glasses, silicate minerals, boro-silicates, borates, waters, rocks, and carbonates and cover a large compositional and structural range (e.g., Kasemann et al. 2001, 2009; Tonarini et al. 2003; Rosner and Meixner 2004; Brand et al. 2014).

1.2.4 Plasma Mass Spectrometry and Interlaboratory Comparison

Inductively-coupled plasma mass spectrometry (ICP-MS) was first utilized for the determination of boron isotopes in the late 1980s using quadropole mass spectrometers for the analysis of waters, borates and borosilicates (Gregoire 1987; Porteous et al. 1995; Al-Ammar et al. 2000). This was followed by the use of magnetic sector-field instruments (Gäbler and Bahr 1999) and eventually the employment of multi-collector ICP-MS, which led to improvements in precision and accuracy to the sub-permil level (Lécuyer et al. 2002; Aggarwal et al. 2003; Foster 2008).

The growing number of laboratories and analytical techniques necessitated the execution of interlaboratory comparison studies. The first two such intercomparison studies involved the majority of labs worldwide that had been working on boron isotopes at the time (Gonfiantini et al. 2003; Aggarwal et al. 2009, with 27 and 28 different labs, respectively). The outcomes of these studies were sobering: in both studies half of the laboratories did not release their analyses; and the results from the labs that did showed interlaboratory discrepancies that were much larger than the uncertainties reported by individual labs. For example, most laboratories reported sub-permil uncertainties, whereas reported values would vary by up to 15‰ between labs for the same reference material with non-systematic off-sets among different labs (Gonfiantini et al. 2003; Aggarwal et al. 2009). This demonstrated that analyses of boron isotope ratios in geologic materials and even in simple boric acid solutions is still challenging, and that reported uncertainties did not reflect accuracies of the measurements—at least for a number of laboratories.

A more encouraging outcome was presented by a more recent intercomparison study on boron isotopes in seawater and carbonates, which included only four different labs (Foster et al.

2013). This study showed agreement of reported δ^{11}B values for seawater that agreed within the reported uncertainties (2SD ≈ 0.4‰), and only a slightly larger discrepancy for the analysed carbonates (1.5‰).

1.2.5 The Development of in Situ Techniques

It was realised early on that geological samples can show small-scale heterogeneity in boron isotopes that bear a wealth of information on the physical or geochemical evolution of their formation environments. These heterogeneities are inaccessible through bulk methods and require in situ analytical methods instead.

The development of in situ analytical methods followed the development of the bulk methods, which provided boron isotope reference values for solid materials (glasses and minerals) that could be used to correct for instrumental mass fractionation. The first published B isotope analyses by secondary-ion mass spectrometry ("ionprobe") were completed in the late 1970s and early 1980s (Phinney et al. 1979; Christie et al. 1981; Shimizu and Hart 1982), but it took ten years before quantitative B isotope data became available for a larger number of samples, mostly produced by the group of Chaussidon et al. (Chaussidon and Albarède 1992; Chakraborty et al. 1993; Chaussidon and Jambon 1994; Chaussidon and Robert 1995; Chaussidon et al. 1997) and studies by Smith and Yardley (1996) and Peacock and Hervig (1999). And it was not until the early 2000s that SIMS was applied to boron isotope geochemistry and cosmochemistry in a more widespread manner, as the number of installed facilities grew larger (e.g., Kasemann et al. 2001; Williams et al. 2001; Hoppe et al. 2001; Nakano and Nakamura 2001; Sugiura et al. 2001; Rose et al. 2001; Gurenko and Schmincke 2002; Kobayashi et al. 2004; Altherr et al. 2004). In situ analyses of boron isotopes by laser-ablation ICP-MS has also been completed more recently with a growing number of laboratories applying this method (e.g., le Roux et al. 2004; Tiepolo et al. 2006; Fietzke et al. 2010; Hou et al. 2010). Advantages and limitations of modern, state-of-the-art boron isotope analyses by various mass-spectrometric methods are discussed in this book (Foster et al. 2017) and in earlier reviews (You 2004; Aggarwal and You 2016).

1.2.6 Theoretical and Experimental Boron Isotope Fractionation

Boron isotope fractionation was demonstrated experimentally and calculated theoretically by Kakihana et al. (1977) and applied to pH-dependent B isotope fractionation between carbonates and seawater by Hemming and Hanson (1992). Equilibrium stable isotope fractionation is dominated by differences in the bond strength of the element of interest to its bonding partners. Boron does not form B^{3+} ions, but is almost exclusively bonded to O in nature with a strongly covalent character of the B–O bonds (Hawthorne et al. 1996). It forms $B(OH)_3$, $B(OH)_4{}^-$ or other complex ions in fluids. Fractionation effects are notably large where the coordination polyhedra of B between two phases differ. Boron in minerals, melts and fluids is either trigonally (3-fold) or tetrahedrally (4-fold) coordinated to oxygen, and therefore, displays large isotopic fractionation between different phases (Kakihana et al. 1977). The higher bond strength of the trigonal coordination leads to a fractionation of ^{11}B into the trigonal sites, and a relative enrichment of the light isotope ^{10}B in the phase with tetrahedrally coordinated B.

In the early 2000s various laboratories started to conduct experiments on boron isotope fractionation at a range of pressures and temperatures that were compared to the theoretical predictions. These experimentally derived fractionation factors were used to calibrate temperature- and pH-dependent fractionation laws for specific mineral–fluid (± melt) systems (Williams et al. 2001; Hervig et al. 2002; Williams and Hervig 2005; Wunder et al. 2005). Experiments on boron sorption onto organic and inorganic surfaces demonstrated the importance of boron speciation in surface complexes (Lemarchand et al. 2007), and carbonate–water B isotope fractionation experiments improved the accuracy of B isotopes as a tool of paleo-pH indicator for seawater from fossil biogenic carbonate (Hemming et al. 1995; Sanyal et al. 2000; Klochko et al. 2006). Theoretical predictions also became more sophisticated with the application of *ab initio* calculations (Rustad and Bylaska 2007; Kowalski et al. 2013). These theoretical studies have accompanied and informed the gradual improvement in the analysis of boron in natural materials.

1.3 The Fifth Element

The last compendium that summarized the geochemistry of boron, with some coverage of its isotope geochemistry, was published more than 20 years ago (Grew and Anovitz 1996), and we have since seen significant progress in analytical techniques, applications and scientific insight in the isotope geochemistry of boron. The present volume, therefore, provides a unique resource for students and professionals alike, including those who will use it as an introduction into a new field and those who use it as a reference in their ongoing research.

This introductory chapter is followed by a review and outlook by Foster et al. (2017, Chap. 2) of the laboratory methods employed to analyze the boron isotopic compositions of geologic materials, which may include waters, glasses, minerals or biogenic carbonates. Major obstacles in the accurate and precise analysis of boron isotopes are evaluated that arise from sample preparation, chemical purification and mass spectrometric methods. The treatment of reference materials and matrix bias are discussed, as well as recent improvements in precision and accuracy. Contamination and unintended isotope fractionation in the laboratory are highlighted as major sources of inaccuracy.

In Chap. 3, Kowalski and Wunder (2017) discuss boron isotope fractionation in vapor–fluid–melt–mineral systems from a theoretical standpoint together with a review of fractionation experiments that have been reported. The current state of atomistic modeling of boron isotope fractionation among fluid and solid phases is discussed and the experimental work conducted at a range of pressure-temperature conditions is summarized and critically evaluated. The authors then explore the feedback between the two approaches and identify areas in the geosciences where further experimental data is sorely needed.

These three general chapters of the volume are followed by a block of four Chaps. (4–7) on the low-temperature geochemistry of boron isotopes in the surface environments of the Earth, such as during weathering and in riverine and marine environments, and by a block of four Chaps. (8–11) on the high-temperature geochemistry and cosmochemistry of boron isotopes.

Chapter 4 provides a detailed discussion of boron incorporation into calcium carbonate on the molecular and crystallographic level. Branson (2017) discusses the adsorption and structural incorporation of boron into inorganic carbonate (calcite and aragonite) and their dependence on seawater chemical composition, temperature, pH and abundances of boron, as well as on growth rates and structure of the carbonate. The relevant experimental work is reviewed and discussed in the context of isotope fractionation among aqueous dissolved boron species and boron adsorbed to $CaCO_3$ growth surfaces and incorporated in the mineral structure. The chapter then proceeds to discuss boron isotope fractionation between seawater and biogenic carbonate and the vital effects that offset various species from the inorganic fractionation line. The chapter lays out the framework on which the following two chapter discuss the specific application of boron isotope signatures in foraminifera and corals, respectively.

Chapter 5 discusses the systematics of boron isotopes in foraminifera and their use as a pH proxy for paleo-seawater. Rae (2017) reviews calibration studies for benthic and planktic species using culturing experiments and the results from natural specimen sampled in the seawater column and in sediment cores. His chapter provides an overview of the applications of boron isotopes in foraminifera in studies of past seawater pH and atmospheric CO_2 levels and discusses current obstacles and future opportunities in these fields.

Chapter 6 reviews the use of boron isotopes in scleractinian corals for the reconstruction of seawater pH. Emphasis is placed on the pH offset between seawater and the calcification fluid generated by the organism itself to stabilize the aragonite skeleton. McCulloch et al. (2017) describe how the investigation of boron isotopes in corals has led to the detailed study of, and new insight into, the process of calcification and pH regulation by different species. The chapter highlights the complexities of pH variations in the calcifying fluid in scleractinian corals and, therefore, of their boron isotopic compositions. Both parameters may depend on more than just temperature, seawater pH and availability of light, but are also influenced by seawater chemistry including the level of dissolved inorganic carbon, as well as vital processes that produce different responses for example between symbiont and asymbiont species.

The use of boron isotopes as a tracer for rock weathering and erosion is reviewed in Chap. 7. Gaillardet and Lemarchand (2017) discuss boron isotope fractionation in subaerial weathering processes including isotopic signatures recorded in soil, vegetation, groundwater and by rivers. Fractionation mechanisms during chemical weathering and the formation of secondary minerals are examined, as well as the influence of precipitation and of the vegetation cycle. The riverine transport is estimated with its effects on the global budget of the ocean, including fluctuations caused by changes in climate and vegetation. The anthropogenic influence, such as land use, on the boron cycle is also explored.

The boron isotopic composition of oceanic basalts and the Earth's mantle are discussed in Chap. 8. Marschall (2017) also reviews the available data on altered oceanic crust, serpentinized abyssal peridotites, and oceanic sediments, as well as hydrothermal vent fluids. The fractionation of boron isotopes during low- and high-temperature alteration of the oceanic crust is discussed based on these data. The chapter also reviews the Earth boron budget and isotopic composition of the crust–mantle system and its major reservoirs, and provides an overview of our current knowledge of the secular evolution of seawater over geological time.

The boron isotope systematics of subduction zones is evaluated in Chap. 9. De Hoog and Savov (2017) review the boron isotope variations observed in fore-arc materials and magmas erupted along active convergent margins and show that boron and its isotope ratio varies systematically with the physical geometry of subduction zones and with a range of regularly employed geochemical tracers. The boron budget of the slab entering subduction zones is summarized, followed by a discussion of boron isotope fractionation processes related to slab dehydration and the role of the serpentinized mantle wedge as an important boron reservoir.

In Chap. 10 Trumbull and Slack (2017) elucidate the geochemistry of boron isotopes in the continental crust with a discussion of prograde metamorphism, of various types of granite and pegmatites, and of hydrothermal systems including ore deposits. They show via a compilation of global granite data that S-type granites are on average isotopically lighter then the mantle, which is in agreement with their interpretation as derived from melting of sedimentary rocks. In contrast, I-type granites, which may be to a large degree derived from fractionated or remelted mantle-derived magmas or magmatic rocks, are on average isotopically heavier than the mantle. This agrees with the isotopically heavy composition of basaltic magmas erupted along modern subduction zones. The authors show that this S-type/I-type dichotomy also holds for the hydrothermal ore deposits that are associated with the respective granitic magmatism.

Finally, Chap. 11 reviews the cosmochemistry of boron isotopes. Liu and Chaussidon (2017) summarize our knowledge of the boron isotopic composition of the solar system and its components, as well as that of other stars of the galaxy and of the interstellar medium as derived from spectroscopy. The possible sources of the two isotopes of boron and their nucleosynthesis are discussed along with the meteoritic record of boron in the early solar system. The isotopic record of live ^{10}Be in the early solar system as recorded in early condensates is reviewed, which points not only to spallation processes during this phase, but also to boron isotopic heterogeneity in the planetary disc. Liu and Chaussidon (2017) close their chapter with a number of major unresolved questions of boron isotope cosmochemistry that concern for example the origin of the boron isotopic composition of the solar system near a ^{11}B/^{10}B ratio of 4, which is shared by other stars of the galaxy, and the origin of the small-scale isotopic heterogeneity observed among primitive meteorites and individual components of meteorites.

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