Boron isotope variations and its geochemical application in nature

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Boron isotope variations and its geochemical application in nature

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The high geochemical reactivity of boron and the large relative mass difference between ^{10}B and ^{11}B lead to significant boron isotope fractionation in nature. So far the measured range of boron isotope composition (δ^{11}B) varies between –70 and +75‰. The negative δ^{11}B values are found in non-marine evaporite borate minerals and tourmalines, whereas positive δ^{11}B values are common in salt lake brines and evaporated seawater. Since the 1980s, with improved measurement methods, applications of boron isotope analysis have increased rapidly. At present, boron isotopes are successfully applied to reconstruct ancient marine environments, to determine depositional environments and ore genesis, to trace groundwater pollution and seawater intrusion, and to study continental erosion. This paper summarises the methods for boron isotope analysis, the mechanisms of boron isotope fractionation and the distribution of boron isotopes in nature, reviews the achievements and the problems of boron isotopes in geochemical applications, and proposes research directions of boron isotopes in geochemical fields.

KEY WORDS: boron isotope, isotope fractionation, geochemical application, analysis, research directions

INTRODUCTION

Boron is a relatively lighter element in nature with the atomic number of 5. Boron has two stable isotopes, ^{10}B and ^{11}B, which make up approximately 19.82% and 80.18% of total boron, respectively. Boron isotope ratios are given in the delta notation with δ^{11}B (‰) defined as deviation from standard NIST-SRM 951 (Catanzaro *et al.* 1970):

$$\delta^{11}B(‰) = [(^{11}B/^{10}B)_{sample}/(^{11}B/^{10}B)_{NIST\text{-}SRM\text{-}951} - 1] \times 1000$$

The large relative mass difference between ^{10}B and ^{11}B leads to significant boron isotopic fractionation in nature. In addition, boron is highly soluble in aqueous environments and has high geochemical reactivity. Thus, δ^{11}B values in different environments are diverse. In nature, the measured δ^{11}B values vary between –70‰ (Williams & Hervig 2004) and +75‰ (Hogan & Blum 2003). The negative δ^{11}B values are usually found in non-marine borate minerals and tourmalines, while positive δ^{11}B values are found in brines of salt lakes and evaporated seawater. Quantitative extraction of boron and the

precise measurements of its isotopic compositions have considerably hampered the application of δ^{11}B values in nature. Early in the 1940s, Thode (1948) studied the δ^{11}B values using gas mass spectrometry of BF$_3$, but memory effects of BF$_3$ seriously reduced the accuracy of measurement. In the 1960s, McMullen *et al.* (1961) established the Na$_2$BO^{2+} thermoelectric mass spectrometry technology, but owing to its limited precision, the fractionation of boron in nature was poorly understood. Since the 1980s, improved analytical techniques (Ramakumar *et al.* 1985; Spivack & Edmond 1986; Xiao *et al.* 1988; Hemming & Hanson 1992), especially the Cs$_2$BO^{2+}–graphite technique (Xiao *et al.* 1988), and greater precision of boron isotope analyses, led to a rapid increase in the number of applications of boron isotopes. At present, boron isotopes are used in determining depositional environments, tracing groundwater pollution and seawater intrusion, researching ore genesis, reconstructing ancient marine environment, and studying continental chemical weathering, etc. In this paper, the available data are compiled, and some of the most relevant aspects, including possible tracer applications, of boron isotope geochemistry are summarised. Further developments of boron isotope applications are discussed.

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METHODS FOR BORON ISOTOPE DETERMINATION

Boron isotope determination started in the late 1940s using gas mass spectrometry of BF_3 to separate ^{10}B from natural boron for use in nuclear facilities, owing to its high capacity to capture neutrons (Inghram 1946). The serious memory effects in the ion source made this technique rather impractical for precise measurements of natural materials. Today, there are two main methods to determine boron isotopic compositions. One is the solution method. After the sample is dissolved, boron is purified, and the boron isotope ratios are determined by positive thermal ionisation mass spectrometry (P-TIMS), negative thermal ionisation mass spectrometry (N-TIMS) or multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). The second is the *in situ* analysis method, in which the *in situ* boron isotopic ratios in minerals are analysed directly using the secondary ion mass spectrometry (SIMS), also called ion microprobe, or laser ablation multicollector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS).

Solution methods

THERMAL IONISATION MASS SPECTROMETRY (TIMS)

TIMS methods can be divided into those using positive ions (P-TIMS) and those using negative ions (N-TIMS). P-TIMS is a mass-spectrometry detection technique working in positive ion mode to analyse boron ions generated by a thermal ionisation source. This technique involves measurement of the isotopic composition of an alkali-borate complex, which is considered to be the most precise instrumental analysis technique for measuring boron isotopic ratios (Deyhle 2001). In P-TIMS, the boron in the sample is converted into positively charged metaborate ions (BO^{2+}) and exists in the form of alkali or metal metaborate cations (M_2BO^{2+}) (Spivack & Edmond 1986). The types of alkali metaborate ions analysed depend on the alkali salt used in preparing them. Such alkali or metallic metaborate ions include Na_2BO^{2+} (Catanzaro et al. 1970; Quast et al. 2006; Rao et al. 2010), K_2BO^{2+} (Aggarwal & Palmer 1995), Li_2BO^{2+} (Sahoo & Masuda 1995), Rb_2BO^{2+} (Rao et al. 2011) and Cs_2BO^{2+} (Spivack & Edmond 1986; Xiao et al. 1988, 1992, 2001b, 2006, 2008a, 2013; Lemarchand et al. 2007). Palmer (1958) first used the $Na_2B_4O_7$ salt and analysed the Na_2BO^{2+} species at masses of 88 and 89 to establish the P-TIMS. This technique was cited by Catanzaro et al. (1970) and Swihart et al. (1986) but had some disadvantages. First, the loading content was large (10–50 μg B); second, significant isotope fractionation was frequently observed during the course of an individual analysis, with the $^{11}B/^{10}B$ ratio becoming progressively enriched in ^{11}B during the course of the run; and third, the measuring accuracy was 2–3%, which was influenced by loading content, ionisation temperature, sample purity and B/Na ratio. In-run isotope fractionation can be reduced by increasing the molecular mass of the alkali-borate species analysed. Later, the Cs_2BO^{2+} method was widely used because it is more precise and sensitive compared with other Na_2BO^{2+}, K_2BO^{2+} and Rb_2BO^{2+}, all of which suffer from spectral interferences. The Cs_2BO^{2+} method was modified by the use of a graphite slurry and mannitol during the loading procedure, the sample size was reduced to 1 μg of boron with an analytical precision of $<\pm0.4$‰ on most mass spectrometers, and the ionisation efficiency of the filaments was significantly improved (Xiao et al. 1988). P-TIMS offers significant signal stability; however, it requires large sample sizes that must be chemically pure. He et al. (2009) introduced a static double collector method to analyse boron isotopes using a Finnigan-MAT Triton TI TIMS, which could decrease the sample amount to 0.1 μg, and the data-acquisition time to 20 minutes. The main disadvantage of P-TIMS is that Cs has a very low ionisation energy, so deposition of Cs on the lens stack results in charging of the lenses and drift in the focus position during the course of the run, which influences the isotope analyses requiring a high filament current (e.g. Nd or Hf; Aggarwal & Palmer 1995) and the acquisition of high-precision data. In addition, there is also isobaric interference in P-TIMS (Xiao & Wang 1998; Lemarchand et al. 2002a). For example, the presence of NO_3^- can affect the isotopic measurements of boron based on the Cs_2BO^{2+} ion with graphite loading. Under these conditions, the measured 309/308 ratio is considerably reduced by the presence of the NO_3^- ion, especially in the presence of mannitol, owing to the formation of the Cs_2CNO^+ ion, producing ion peaks at masses of 308 and 309. Xiao & Wang (1998) indicated that the procedure of ion exchange using Amberlite IAR 743 resin, a boron-specific resin, and OH-Dowex 1 resin for extracting boron from sample solutions can resolve this problem. Wei et al. (2004) suggested that addition of 1% H_3PO_4 as an ionisation depressor is an effective method to reduce the formation of isobaric ions of CNO^- and Cs_2CNO^+ in the ion source of the mass spectrometer.

N-TIMS operates in a similar way to P-TIMS but uses metaborate anions (BO^{2-}) in a negative ion mode of operation. Unlike P-TIMS, N-TIMS requires no alkali salts or metals to be added, as no alkali or metal metaborate anions are required for mass measurement. Thus, simpler mass measurements are conducted for $^{10}BO^{2-}$ and $^{11}BO^{2-}$, at an m/z of 42 and 43, respectively (Hemming & Hanson 1992; Sanyal et al. 1995, 1997; Hönisch et al. 2008, 2009). The advantage of N-TIMS is that the ionisation efficiency is much higher than that of P-TIMS and allows samples containing <1 ng of boron to be analysed (Hemming & Hanson 1992). In addition, the degree of purification of boron required to perform the analyses is less than that for the alkali-borates so that the boron isotope composition of some water samples can be analysed by loading the solution directly onto the filament without any purification (Hemming & Hanson 1994; Aggarwal & Palmer 1995). The major disadvantage of the N-TIMS is that the low mass numbers of the species analysed can lead to severe isotope fractionation during the course of the run, and the precision is about ±0.7‰ (Foster et al. 2006). Another disadvantage of N-TIMS is the interference of isobaric ions CNO^- (Hemming & Hanson 1994). For example, CNO^- of mass 43 ($^{12}C^{15}N^{16}O^-$ and $^{13}C^{14}N^{16}O$) and mass 42 ($^{12}C^{14}N^{16}O$) can interfere with the $^{11}B^{16}O^{16}O^-$ and $^{10}B^{16}O^{16}O^-$ and yield lower $^{11}B/^{10}B$ ratios, owing to the much higher isotopic abundance of

[14]N than [15]N (Aggarwal & Palmer 1995). Thus, the N-TIMS technique is not suitable for silicate analyses owing to a large isobaric ion interference of CNO-derived from organic substances, such as ion-exchange resins and mannitol used for boron separation (Hemming & Hanson 1994). Monitoring of the CN^- peak at mass 26 can indicate the severity of isobaric interference on the borate peak (Penman *et al.* 2012). Today, N-TIMS is used for analysing boron isotopes in carbonate samples for seawater paleo-pH reconstruction (Hemming & Hanson 1992; Sanyal *et al.* 1995, 1997; Hönisch *et al.* 2008, 2009) and has also been used to analyse dissolved boron (Eisenhut *et al.* 1996; Vengosh & Hendry 2001). Recently, accurate isotopic determinations were obtained on sub-nanogram samples (especially for foraminifer a samples) using total evaporation negative thermal mass spectrometry (TE-N-TIMS) (Foster *et al.* 2006; Ni *et al.* 2010), a technique that reduces the required sample size without reducing analytical precision.

INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP-MS) AND MULTI-COLLECTOR ICP-MS (MC-ICP-MS)

In the ICP-MS method, an aqueous solution of boron is aspirated into the plasma via a Meinhard nebuliser, and the isotope ratio is determined from the ratio of the peak intensities at masses 11 and 10 (Gregoire 1987). Advantages of this technique include: no careful purification of the boron, no interference with atomic masses 10 and 11, little or no suppression of boron ionisation unless the solution contains high levels of dissolved salts, and a high throughput of samples (up to 100 samples per day) (Gäbler & Bahr 1999). The disadvantages of ICP-MS method are that the precision of the technique is much lower than TIMS, the isotope ratios are strongly dependent on the matrix of the solution, and there are strong memory problems (Aggarwal & Palmer 1995; Gäbler & Bahr 1999). The advent of multiple-collector ICP-MS (MC-ICP-MS) offers new possibilities in the precision and range of materials that can be analysed (Lécuyer *et al.* 2002; Aggarwal *et al.* 2003; Louvat *et al.* 2011), but the method still requires mass bias correction, especially for isotope measurements for the light isotopes (e.g., B and Li) (Aggarwal *et al.* 2003). Aggarwal *et al.* (2003) introduced sample using a direct-injection nebuliser to eliminate memory problems, and the 4–9% mass bias can be corrected by bracketing sample measurements with standards. Louvat *et al.* (2011) reported an optimisation of the demountable direct injection high-efficiency nebuliser (d-DIHEN) for isotopic measurements with MC-ICP-MS and described a method for boron isotopic ratio determination. Compared with the classical stable introduction systems, the sensitivity for boron is 2–5 times higher with d-DIHEN and wash times up to 10 times shorter. A comparison between δ^{11}B determined by d-DIHEN MC-ICP-MS and P-TIMS for four modern corals showed an excellent agreement with a bias of less than 0.4‰. Recently, MC-ICP-MS has had a greatly improved sensitivity and sample analysis rate for boron isotopes and many other isotope composition measurements and despite its larger instrumental mass fractionation, it has progressively become an attractive alternative to TIMS techniques despite its larger instrumental mass

fractionation (Pearson *et al.* 2009; Guerrot *et al.* 2011; Louvat *et al.* 2011).

In-situ analysis methods

SECONDARY ION MASS SPECTROMETRY (SIMS)

A polished thin-section of sample (rock and mineral) is placed in an ion microprobe and sputtered with a primary beam of Ga^-, Cs^+ or, more usually, O^-, and the secondary positive boron beams are measured at masses 10 and 11 (Chaussidon & Albaréde 1992). Standardisation is carried out by analysis of a sample of known boron isotope composition and similar chemical composition to reduce matrix effects. SIMS has the advantages of no chemical sample processing, minimal sample preparation, no isobaric ions and very high spatial resolution (spot diameter of a few tens of micrometres). The main disadvantages of SIMS are the poor precision of the analyses ($+4$‰, 2σ) (Aggarwal & Palmer 1995), the removal of boron trace contamination from sample polishing, the low count rate of ^{10}B and ^{11}B for B concentrations of less than 1 μg/g (Chaussidon *et al.* 1997), and its dependence on the availability of solid reference materials with homogeneous isotopic composition and a matrix matching that of the sample (Tonarini *et al.* 2009). Recently, significant improvements in precision and overall data quality have been obtained by SIMS, and this method is used for boron isotope measurements of carbonates and clay mineral transformations (Kobayashi *et al.* 2004; Kasemann *et al.* 2009; Rollion-Bard & Erez 2010; Muttik *et al.* 2011; Rollion-Bard *et al.* 2011).

LASER-ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (LA-MC-ICP-MS)

This technique is based on a laser-ablation system used to extract boron from solid samples, coupled with an ICP-MS equipped with multiple electron multipliers to amplify the ion currents (le Roux *et al.* 2004). This technique requires no sample chemical preparation, and boron amounts in the order of several nanograms can be analysed with a precision of 1–2‰ (Tonarini *et al.* 2009). Le Roux *et al.* (2004) first analysed *in situ* boron isotopic compositions of natural and synthetic glasses with LA-MC-ICP-MS and showed that by rastering relatively large areas of the sample surface (approximately 1 mm^2) using a laser beam of about 200 μm, accuracies and precisions of 1‰ (2σ) or lower can be obtained in samples with boron contents at the ng/g level. LA-MC-ICP-MS *in situ* single spot (60–80 μm) δ^{11}B determination of geological materials with boron content ranging from 12 to 31,400 mg/kg yielded a precision better than 1.6‰ (Tiepolo *et al.* 2006). Using the standard–sample-bracketing (SSB) method, Hou *et al.* (2010) calibrated the mass bias of the instrument and the fractionation of isotopes, and demonstrated the *in situ* determination method of LA-MC-ICP-MS for boron isotopes. *In situ* measurements for boron isotopes performed on different geological samples showed that, within the error range, the results were consistent with those determined by P-TIMS. The accuracy level reached on samples with widely different

compositions suggests that the matrix effects are minimal to negligible.

MECHANISM OF BORON ISOTOPE FRACTIONATION

Boron is constrained by oxygen and forms B–O bonds in nature. The polynuclear boron species are negligible at concentrations smaller than 25 mmol/kg (Su & Suarez 1995), and dissolved boron exists mainly in the form of $B(OH)_3$ (boric acid, trigonal species) and $B(OH)_4^-$ (borate anion, tetrahedral species). Boron has no valence changes and is independent of oxidation–reduction reactions. The fractionation of boron is controlled by the relative content of $B(OH)_3$ and $B(OH)_4^-$, which are a function of pH and are given by the following reaction:

$$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$$
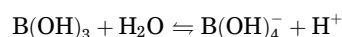
At a low pH (<7), virtually all of the boron is present in the $B(OH)_3$ species; conversely, at a high pH (>10), virtually all of the boron is in the $B(OH)_4^-$ species (Figure 1). The $\delta^{11}B$ of $B(OH)_3$ and $B(OH)_4^-$ are also pH-dependent. At pH 8, $\delta^{11}B$ of $B(OH)_3$ and $B(OH)_4^-$ make up approximately 80% and 20% of the total boron, respectively (Figure 1). The pH value of river water and modern seawater are about 7.0 and 8.2, respectively, thus the existence of boron species in river water and modern seawater are mainly $B(OH)_3$. The differences in geometry and vibrational energy between $B(OH)_3$ and $B(OH)_4^-$ lead to the boron isotope fractionation (Kakihana *et al.* 1977; Oi *et al.* 1988). The isotope exchange reaction between $B(OH)_3$ and $B(OH)_4^-$ is given by:
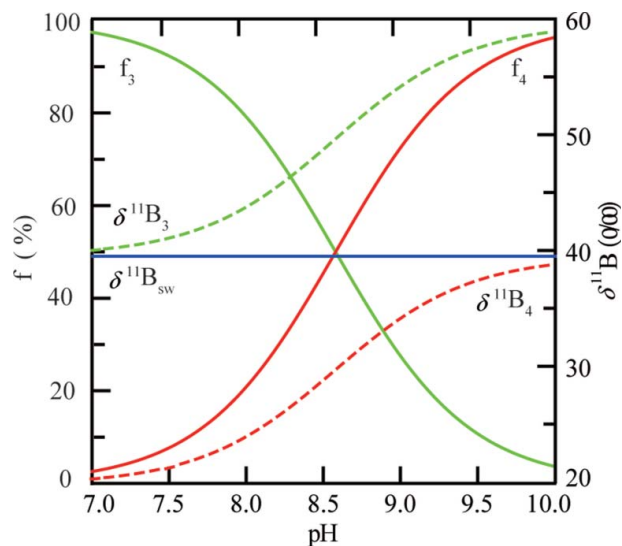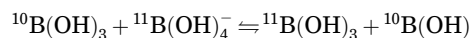
$$^{10}B(OH)_3 + {}^{11}B(OH)_4^- \rightleftharpoons {}^{11}B(OH)_3 + {}^{10}B(OH)$$

Figure 1 Boron species in the seawater ($p\mathrm{K}_b$ value was from Dickson 1990) and the isotopic composition of boron (α_{4-3} value was from Klochko *et al.* 2006). f_3 (green curve) and f_4 (red curve) are the fraction of $B(OH)_3$ and $B(OH)_4^-$, respectively. $\delta^{11}B_3$, $\delta^{11}B_4$ and $\delta^{11}B_{sw}$ are the boron isotopic compositions of $B(OH)_3$, $B(OH)_4^-$ and modern seawater in solution, respectively.

During this process, the stable isotope ^{11}B is enriched in $B(OH)_3$, while ^{10}B is enriched in $B(OH)_4^-$, with an effective isotopic fractionation on the order of 20‰ between the two boron species. Owing to the enrichment in diverse phases, boron isotope fractionates during evaporation, adsorption/coprecipitation, water–rock interaction and biological processes (Palmer *et al.* 1987, 1992; Spivack & Edmond 1987; Vengosh *et al.* 1991a, 1992; Xiao *et al.* 1992, 2001a; Lemarchand *et al.* 2000, 2002b; Cividini *et al.* 2010; Schmitt *et al.* 2012).

Adsorption/coprecipitation processes

The adsorption of boron from seawater onto marine clays results in boron isotope fractionation up to 32‰ with ^{10}B being preferentially incorporated into the adsorbed phase. The isotope fractionation is the result of equilibrium processes, not kinetic effects, and the isotope fractionation is less at higher pH values (Palmer *et al.* 1987). Xiao & Wang (2001) showed that the adsorption and isotopic fractionation of boron between saline brine and sediment were controlled by the pH of saline brine and similar to that between seawater and marine or pure sediments in a certain pH range. The adsorption of boron by clay minerals at high pH caused a decrease in the $\delta^{11}B$ value of the solution.

Williams *et al.* (2001a) investigated the influence of organic matter on boron isotope distribution in oil reservoirs. The results showed that one possibility for the high $\delta^{11}B$ of oil field waters is the preferential incorporation of ^{10}B into the tetrahedral layers of authigenic illite, leaving the water ^{11}B-enriched. The release of boron from organic compounds caused the observed regional ^{10}B enrichment in waters deep in the Gulf Coast basin.

The $\delta^{11}B$ value in modern biocarbonates is about 18‰ lower than in seawater, and the fractionation characteristics between modern biocarbonates and seawater is basically the same with that between $B(OH)_3$ and $B(OH)_4^-$ in seawater (Hemming & Hanson 1992). Hemming & Hanson (1992) showed that only $B(OH)_4^-$ is incorporated into biocarbonates, with a little or no boron isotopic fractionation, so that the $\delta^{11}B$ value in marine biocarbonates records the $\delta^{11}B$ value of $B(OH)_4^-$ in seawater. This allows the use of $\delta^{11}B$ values in foraminifera and coral to reconstruct ancient seawater pH.

Experiments of boron incorporated into deposited brucite ($Mg(OH)_2$) showed that the $\delta^{11}B$ values in brucite were enriched in ^{11}B compared with associated artificial seawater. Fractionation factors ranging between 1.0177 and 1.0569 result from the preferential incorporation of $B(OH)_3$ into brucite (Xiao *et al.* 2011). The existence of brucite in biocarbonates could lead to high $\delta^{11}B$ values in corals and the calculated seawater pH (Xiao *et al.* 2011).

Lemarchand *et al.* (2005) showed that boron sorption on humic acid (HA) could induce a strong pH-dependent isotope fractionation with ^{11}B depleted at the surface of HA, reaching a maximum at $5 < pH < 9$ ($\alpha = 0.975$, $\Delta = -25‰$) and decreasing sharply at $pH > 9$. The extent of isotopic fractionation depends not only on boron aqueous speciation but also on the distribution and structure of the borate surface complexes formed. Boron sorption onto organic matter could have important consequences

for the $\delta^{11}B$ values of surface water reservoirs, and the large isotope fractionation between aqueous boric acid and surface boron–organic complexes makes boron a promising tracer of biological activity (Lemarchand *et al.* 2005).

Lemarchand *et al.* (2007) demonstrated that boron isotopic fractionation was pH-dependent and particularly important during sorption on goethite with ^{10}B enrichment on the solid surface ($\Delta = -40‰$ at pH = 8). Fractionation is less substantial in birnessite ($\Delta = -15‰$ at pH < 8.5) but is reversed at pH > 9 and leads to a strong enrichment of ^{11}B in the birnessite surface ($\Delta = +23‰$ at pH 10.8). In addition to solution pH effects, the type of boron surface complex formed has a strong impact on isotopic fractionation. Lemarchand *et al.* (2005, 2007) demonstrated that $\delta^{11}B$ values can be changed during weathering processes occurring both on continental surfaces and in the oceans.

Water–rock interaction

In geological process ^{10}B is more reactive than ^{11}B, so boron isotopic fractionation occurs during the water–rock reaction. During silicification, ^{11}B is released from rock into water, and the rocks are depleted in ^{11}B. During desilicification, ^{11}B is absorbed from water into the rock and the $\delta^{11}B$ values of rocks increased. During dehydration reactions, ^{11}B is released from rock into the fluid. Peacock & Hervig (1999) showed that the $\delta^{11}B$ values of minerals in subduction-zone metamorphic rocks (–11 to –3‰) were generally lower than the range of $\delta^{11}B$ values reported for both subduction-input pelagic sediments, trench turbidites (–7 to +11‰) and altered oceanic crust (–5 to +25‰), and subduction-output island arc lavas (–6 to +7‰), suggesting that subduction-zone metamorphism significantly lowers the $\delta^{11}B$ values of subducted materials through continuous dehydration reactions. The $\delta^{11}B$ values of metamorphic rocks decreased with increasing metamorphic grade. In closed systems (water/rock ratio < 1), little boron is released from rocks, and water is enriched in boron, i.e. ^{11}B preferentially. In open reaction systems (water/rock ratio > 1), boron is released from rock into water, and the $\delta^{11}B$ values of the rock decrease (Musashi *et al.* 1991). Owing to water–rock interaction, $\delta^{11}B$ values increase from –3.0 to +39.5‰ from fresh seafloor basalt to seawater. During diagenesis, clay minerals recrystallise and incorporate ^{10}B into the mineral structure, which causes a depletion of boron in the pore water with an increase in the $\delta^{11}B$ values in the fluid (Spivack *et al.* 1987). Ishikawa & Nakamura (1993) showed that the $\delta^{11}B$ values of ancient marine sediments (–17.0 to –5.6‰) were systematically lower than in modern sediments (–6.6 to +4.8‰). The lower $\delta^{11}B$ values can be caused by diagenesis, which induced preferential removal of ^{11}B-enriched boron in calcium carbonate and silica during recrystallisation, and boron isotopic exchange in the course of the smectite/illite transition. Williams *et al.* (2001b) also showed that under digenetic conditions, boron is predominantly in trigonal coordination in fluids but substituted into tetrahedral sites of silicates, and the preference of ^{10}B for tetrahedral bonds was the major factor for boron isotope fractionation in silicates.

Several studies have shown that low-temperature chemical reactions can significantly impact boron isotope distribution, with ^{11}B being enriched in the fluid phase (Spivack *et al.* 1987; Rose *et al.* 2000; Lemarchand *et al.* 2002b). For example, the mean $\delta^{11}B$ value of the world's largest rivers is 15–20‰ higher than the $\delta^{11}B$ values of continental rocks (Lemarchand *et al.* 2002b), suggesting that ^{10}B is preferentially retained in secondary solid phases. In peri-Himalayan rivers, the $\delta^{11}B$ values of the dissolved load were explained by the formation of clay minerals, which preferentially captured ^{10}B and left behind complementary solutions enriched in ^{11}B. The gradual increase in $\delta^{11}B$ values from headwaters to the mouth of continental-scale river watersheds is consistent with the formation of clay minerals in plains (Lemarchand *et al.* 2000, 2002b). Overall, at the scale of monolithological watersheds, boron isotope fractionations were mainly controlled by a coupling of mineral dissolution and clay mineral formation, while in larger-scale mixed lithology basins, boron isotopes are controlled by the degree of silicate weathering (Schmitt *et al.* 2012).

Biological processes

In contrast to geochemical systems, there have been few measurements of the $\delta^{11}B$ of plants. Vanderpool & Johnson (1992) reported a range in $\delta^{11}B$ values from –7.5 to +29.3‰ for varieties of commercial produce grown in different regions of North and Central America. The plant tissues did not have $\delta^{11}B$ values identical to those of the nutrient solutions, suggesting that boron isotopes were fractionated during incorporation into the plants. Wieser *et al.* (2001) reported $\delta^{11}B$ values of coffee beans ranging from –12 to +19‰, with most of the values below 0‰. Since boron was not readily translocated once bound in the plant tissue, the $\delta^{11}B$ values of coffee beans represents the cumulative input of the various sources. Wieser *et al.* (2001) proposed that boron-isotope abundance data could be used to study the biogeochemical cycle of boron. The contradictory conclusions from Vanderpool & Johnson (1992) and Wieser *et al.* (2001) may relate to boron bio-availability in soil solutions that affect the way it is absorbed by roots: either passively (channel mediated) or actively (complexation with polyols). Nevertheless, all these studies imply that the primary factor controlling the boron isotope abundance in plants is the influence of local sources (minerals, soils, soil solutions) rather than intrinsic biological effects (Schmitt *et al.* 2012). Cividini *et al.* (2010) showed that the $\delta^{11}B$ values of beech leaves and spruce needles were similar and very close to those measured in the soil solutions. Moreover, B concentrations decreased by 80% with very little isotopic shift between soil solutions sampled at 5 and 30 cm depth of a forest soil during the period of plant growth. The absence of a large isotopic shift in these solutions and the strong concentration decrease indicated that the boron absorption by plant roots did not cause important isotopic fractionations, at least in the Strengbach watershed. Rosner *et al.* (2011) established a comprehensive chemical and mass spectrometric method to determine the $\delta^{11}B$ value of plant tissue with B concentrations of 1 mg/kg and an expanded uncertainty of ≤1.7‰. The measured $\delta^{11}B$ values of the plant samples varied

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between 0 and +34‰, which generally reflected region-ally varying contributions of the natural background as well as anthropogenic activity. Therefore, the δ^{11}B value of plants can be used for food provenance studies.

Evaporation processes

Boron isotopic fractionation during the evaporation of near-neutral and acidic boron-bearing solutions showed that the ratio of the δ^{11}B value of the initial solution (pH 6.33) to that of the solid residue after evaporation was 1.0064 (Xiao *et al.* 1997). This may have resulted from the fractionation of ^{10}B from the solution into the solid resi-due, or by fractionation of ^{11}B from the solution into vapour. The preliminary experimental study of the B con-centration and the δ^{11}B value in vapour derived from air-flow reaction with seawater showed that the δ^{11}B values measured from vapour were distinctly depleted in ^{11}B compared with seawater (Xiao *et al.* 2001a). A quite differ-ent view of boron isotope fractionation during seawater evaporation was proposed by Chetelat *et al.* (2005) from closed system experiments, in which condensates were produced from seawater evaporation at 60°C. The conden-sates collected from seawater with pH 8.1 were found to have δ^{11}B values (+41.9 to +46.5‰) higher than that of sea-water (+39.5‰). The δ^{11}B values in rainwater collected in French Guiana ranged from +30.5 to +45‰, suggesting

that most of its boron originated from a marine compo-nent. Rose-Koga *et al.* (2006) also reported δ^{11}B values of atmospheric precipitations. The δ^{11}B values of instanta-neous and cumulative rains and snows from coastal and continental sites showed a large range of variations, from −1.5 ± 0.4 to +26.0 ± 0.5‰ and from −10.2 ± 0.5 to +34.4 ± 0.2‰, respectively. An empirical vapour–rain isotopic frac-tionation of −31‰ and vapour–seawater fractionation of −25.5‰ was proposed, which has strong implications regarding the origin and evolution of atmospheric boron. A natural seawater–vapour process in quiet air condi-tions and excluding the sea-spray component indicated an enrichment of ^{11}B in the condensate (Xiao *et al.* 2007). This implied that in the natural environment, rainfall with δ^{11}B values lower than that of seawater has been affected either by continental boron sources or by the boron extracted from seawater under airflow conditions.

GEOCHEMICAL CYCLE AND VARIATION OF BORON ISOTOPE COMPOSITIONS IN NATURE

Boron is a soluble and incompatible element, and mainly exists in the hydrosphere and sedimentary rocks of upper crust. Marine sediments, ocean hydrothermal alteration basalts, brines and seawater are the main car-riers of boron. The boron geochemical cycle in nature is shown in Figure 2. Immigration and emigration are the
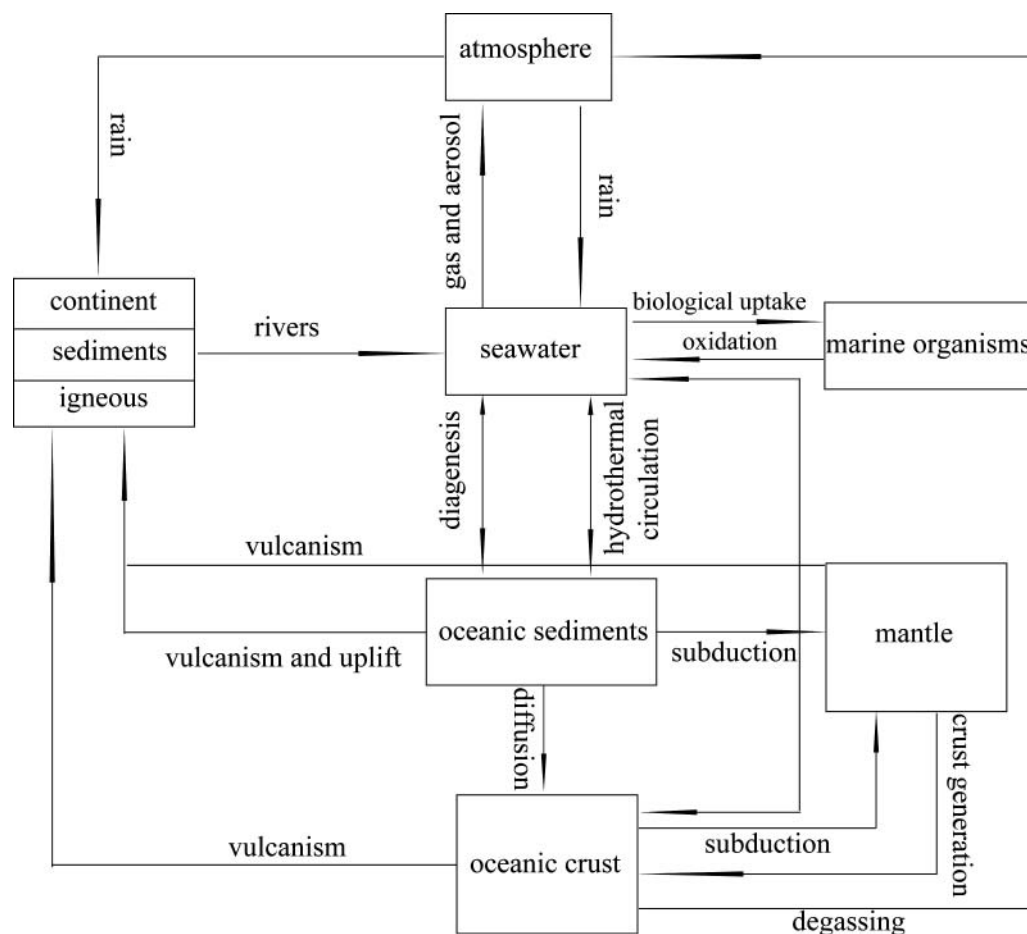

Figure 2 Schematic boron geochemical cycle in nature.

two processes of boron in seawater. The immigration processes include river input, dry and wet deposition, organisms, oxidation and rock weathering. The emigration processes include evaporation, biological uptake, diagenesis, adsorption of clay minerals and suspended matter. Published $\delta^{11}B$ values span a wide range of $\sim$145‰. The lowest $\delta^{11}B$ values of –70‰ are reported in coals (Williams & Hervig 2004) while the highest $\delta^{11}B$ values of +75‰ are found in groundwater infiltrated by seawater (Hogan & Blum 2003). The $\delta^{11}B$ values in different reservoirs are shown in Figure 3.

Owing to the long residence time of boron in seawater (*ca* 10 Ma) (Chaussidon & Albaréde 1992), modern seawater from open marine environments has a fairly constant worldwide $\delta^{11}B$ value of +39.6‰ (Foster *et al.* 2010) and a B concentration of $\sim$4.5 ppm (Spivack & Edmond 1987). The B concentration in river water (about 0.01 mg/L) is 1–2 orders of magnitude lower than the seawater, with more than 85% lower than 25 μg/L. The $\delta^{11}B$ values of river waters vary from –0.7 to +34.9‰, mostly between +3.9 and +17.5‰ (Spivack 1986; Mossadik 1997; Rose *et al.* 2000; Zhao 2002; Chetelat *et al.* 2009b). The B concentration and the $\delta^{11}B$ values for 22 rivers worldwide vary from 1.0 to 201 μg/L and from –6 to +42.8‰, respectively (Lemarchand *et al.* 2000). The B concentration of Yellow River waters is the highest, whereas the Fraser River is the lowest (Lemarchand *et al.* 2000). Seasonal variation in B concentration is significant. The B concentration and $\delta^{11}B$ values in rivers mainly reflect differences in weathering conditions of the river basin.

The B concentration and $\delta^{11}B$ values of fresh groundwater vary from 55 to 2300 μg/L and –15.9 to +32.4‰, respectively, whereas saline groundwaters vary from 5.3 to 13210 μg/L and from –7.4 to +59.7‰, respectively (Vengosh *et al.* 1994; Barth 1998, 2000; Pennisi *et al.* 2000).

Most atmospheric boron is present in the gas phase with B concentrations of 62 $\pm$ 31 ng/m^3. Gaseous B concentrations are higher over the ocean than over the

Figure 3 Boron isotopic compositions in nature (data from McMullen *et al.* 1961; Spivack 1986; Swihart *et al.* 1986; Spivack & Edmond 1987; Musashi *et al.* 1988; Xiao *et al.* 1988, 1992; Slack *et al.* 1989; Oi *et al.* 1989; Palmer & Slack 1989; Swihart & Moore 1989; Bassett 1990; Palmer & Sturchio 1990; Palmer 1991; Vengosh *et al.* 1991a–c; Aggarwal *et al.* 1992, 2000; Chaussidon & Albaréde 1992; Hemming & Hanson 1992; Palmer *et al.* 1992, 1998; Barth 1993, 1998, 2000; Chaussidon & Jambon 1993; Ishikawa & Nakamura 1993; Qi *et al.* 1993; Spivack *et al.* 1993; Vengosh *et al.* 1994; Gaillardet & Allègre 1995; Sanyal *et al.* 1995, 1997; Leeman & Sisson 1996; Oi *et al.* 1996; Palmer & Swihart 1996; Eisenhut & Heumann 1997; Jiang *et al.* 1997; Mossadik 1997; Gäbler & Bahr 1999; Liu *et al.* 1999; Lemarchand *et al.* 2000; Pennisi *et al.* 2000; Rose *et al.* 2000; Mather & Porteous 2001; Nakano & Nakamura 2001; Lécuyer *et al.* 2002; Hogan & Blum 2003; Lemarchand & Gaillardet 2006; Jiang *et al.* 2008; Hönisch *et al.* 2008, 2009; Chetelat *et al.* 2009a, b; Garda *et al.* 2009; Klochko *et al.* 2009; Pearson *et al.* 2009; Foster *et al.* 2010; Zhao & Liu 2010; Rae *et al.* 2011; Rollion-Bard *et al.* 2011).
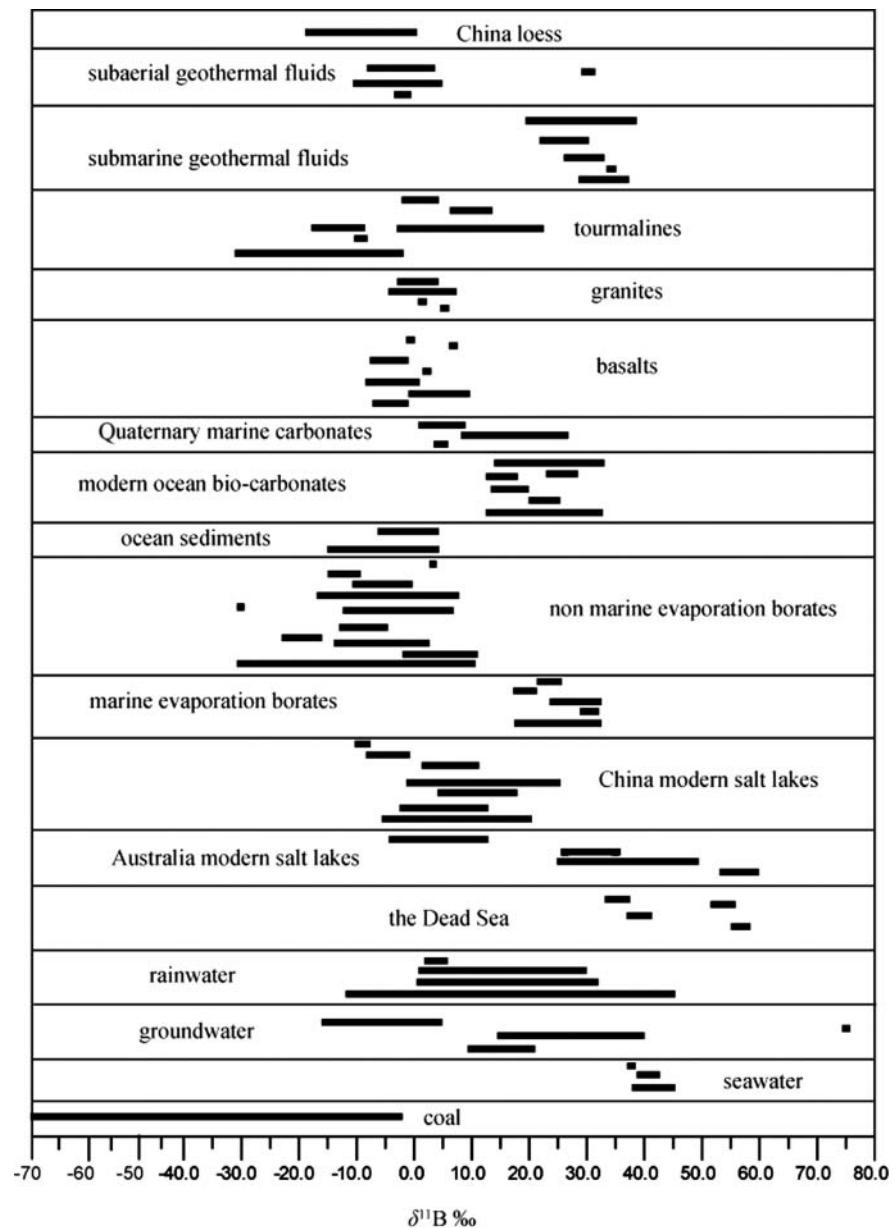
continents, while particulate boron has the opposite distribution. The major global sources of atmospheric boron appear to be volcanic emissions and sea salt aerosol production (Fogg & Duce 1985). The B concentrations in precipitation range widely in different areas, from 0.3 to 15 μg/kg. The δ^{11}B values of precipitation near the ocean are more enriched in ^{11}B compared with precipitation inland (δ^{11}B = +25.1 to +38.9‰) and in areas of volcanic eruptions (δ^{11}B = –5 to +17‰). The B concentration and δ^{11}B values of the precipitation in the Himalayan rivers are 0.09 $\pm$ 0.09 μmol/L and 5.4 $\pm$ 1.7‰, respectively (Rose *et al*. 2000), while those in the UK range from 1 to 18 μg/L and –13 to +48‰, respectively (Mather & Porteous 2001). Boron concentrations in precipitation in the centre of Paris range from 19 to 500 nmol/L, and δ^{11}B values range from 0 to +38‰ (Chetelat *et al*. 2009a), whereas in Guiyang they vary from 2.1 to 4.8 ng/ml, and from +2.0 to +30.0‰, respectively (Zhao & Liu 2010).

The B concentration of lake waters varies significantly, and increases from freshwater lakes to salt lakes. Boron concentration and δ^{11}B values in surface brines in the Dead Sea range from 37.8 to 44.3 μg/g and from +55.7 to +57.4‰, respectively (Vengosh *et al*. 1991c), whereas in Australia they range from 270 to 17310 μg/L, and from +25.5 to +59.2‰, respectively (Vengosh *et al*. 1991a). The δ^{11}B values of salt lakes in China range from –4.4 to +24.6‰ (Xiao *et al*. 1992; Qi *et al*. 1993).

The B concentration of some continental hot springs is very high, and δ^{11}B values vary significantly in different areas (Musashi *et al*. 1988; Palmer & Sturchio 1990; Vengosh *et al*. 1991c; Aggarwal *et al*. 1992, 2000; Leeman & Sisson 1996). For example, the B concentration of hot spring waters ranges from 336 to 208 000 μg/L in central Japan (Musashi *et al*. 1988), and from 0.38 to 9.1 μg/g in Iceland (Aggarwal *et al*. 2000). The δ^{11}B values of hot spring waters in Yellowstone National Park range from –9.3 to +4.4‰ (Palmer & Sturchio 1990) and from +51.7 to +54.9‰ in the Dead Sea (Vengosh *et al*. 1991c).

The δ^{11}B values in carbonates vary from +1.5 to +32.2‰ (Vengosh *et al*. 1991b). The δ^{11}B values of biocarbonates were slightly higher than bottom carbonate sediments (Xiao *et al*. 1988; Vengosh *et al*. 1991b). There is no relationship between B concentration, δ^{11}B values and mineralogy of carbonates (Vengosh *et al*. 1991b; Hemming & Hanson 1992). The biological (vital) effects may affect the boron content of the biogenic skeletons but do not affect their boron isotope composition (Vengosh *et al*. 1991b). The B concentration varies from 1 ppm in gastropod shells to 80 ppm in corals, and the δ^{11}B values range from +14.2 to +32.2‰, which overlaps with the δ^{11}B values of modern deep-sea carbonate sediments (+8.9 to +26.2‰) (Vengosh *et al*. 1991b). The δ^{11}B values of modern marine sediments range from –6.6 to +4.8‰, while that of ancient (Permian to Miocene) marine sediments varies from –17.0 to +5.6‰ (Ishikawa & Nakamura 1993). The δ^{11}B values of foraminifera in Holocene and glacial sediments varied from +20.5 to +23.3‰ and from +22.7 to +25.3‰, respectively (Sanyal *et al*. 1995). Compilation of all available boron-isotope data strongly supports a clear discrimination between marine borate minerals ranging from +18 to +32‰ and non-marine borate minerals ranging from –32 to +10.2‰ (Swihart *et al*. 1986; Oi *et al*. 1989; Bassett 1990; Barth 1993).

Tourmaline is the most abundant boron-bearing mineral in the crust and occurs in a variety of lithologies. The reported δ^{11}B values of tourmaline vary from –30 (Chaussidon & Albaréde 1992) to +24‰ (Palmer & Swihart 1996). Swihart & Moore (1989) suggested that the boron isotope signature of tourmaline was not controlled by its major element composition, mineral paragenesis, metamorphic grade of host rocks or age, and that the δ^{11}B values less than or equal to –5‰ indicate an igneous-related origin, whereas the δ^{11}B values greater than or equal to –1‰ indicate a sedimentary origin. Palmer & Slack (1989) suggested that the δ^{11}B values of tourmaline greater than 0‰ indicate a marine origin, whereas values less than 0‰ indicate a non-marine origin of metaevaporite sequences. Chaussidon & Albaréde (1992) suggested that the δ^{11}B values are correlated with the chemical composition of the tourmalines, the Li-rich tourmalines being enriched in ^{11}B compared with Fe and/or Mg-rich tourmalines, and the δ^{11}B values of the Li-rich tourmalines showed a tendency to decrease with increasing age.

The δ^{11}B values of oceanic basalt glasses vary over a narrow range (Chaussidon & Jambon 1993), but the boron content and the δ^{11}B values of basalts after alteration by submarine hydrothermal fluids were different. For example, the δ^{11}B values of altered oceanic basalts (–2 to +14‰) were enriched in ^{11}B compared with their unaltered counterparts (–8 to –2‰).

The boron concentrations and δ^{11}B values of acid-soluble phases in loess and paleosol were first determined by Zhao *et al*. (2003). The boron contents of acid-soluble phases in the Luochuan loess section (S_0–S_2) vary within the range of 0.8–2.7 ppm, and their δ^{11}B values vary from –1.8 to +18.6‰, mostly within the range of 0 to +10‰. The boron contents and δ^{11}B values of paleosol layers are higher than those from loess layers, particularly in the loess layer S_1.

The δ^{11}B values of 25 coals and three kerogens were measured by Williams & Hervig (2004) to improve knowledge of boron in organic matter. Coals are ^{10}B-enriched compared with most terrestrial waters. The δ^{11}B values measured showed a large variability within a single 'homogenised' coal sample, indicating that boron is heterogeneously bound in various organic macerals. In coals, all the δ^{11}B values were negative. The lowest δ^{11}B value measured was –70‰, representing the most ^{11}B depleted boron isotope ratio ever reported for terrestrial materials. Bulk analyses of coals will not generally have such low δ^{11}B values because of the averaging of values from different organic macerals.

GEOCHEMICAL APPLICATIONS OF BORON ISOTOPES

Reconstructing ancient seawater pH

Marine biocarbonates (foraminifera, coral, brachiopoda, gastropoda and bivalves) were one of the main reservoirs of boron in the marine environment. Since the 1990s, reconstructions of ancient seawater pH have used the δ^{11}B values in bicarbonates, calculations of the past pCO$_2$, and the influences of these two factors on

changes in the ancient climate, have become important issues for the international isotope geochemistry community, and is known as the δ^{11}B–pH proxy (Hemming & Hanson 1992). Corals and foraminifera are the main materials for this proxy. The theoretical basis of this proxy is based on several assumptions:

(a) Boron exists in seawater as boric acid $B(OH)_3$ and as the borate ion $B(OH)_4^-$. The relative proportion of the two species and the δ^{11}B values of $B(OH)_3$ and $B(OH)_4^-$ are dependent on pH (Figure 1). Owing to isotope fractionation, ^{10}B is enriched in $B(OH)_4^-$.

(b) Only $B(OH)_4^-$ is incorporated into biocarbonates with no or very small isotope fractionation, so the δ^{11}B value of biocarbonate is equal to the δ^{11}B value of $B(OH)_4^-$ in seawater, that is $\delta^{11}B_{carb} = \delta^{11}B_4$ (Hemming & Hanson 1992).

(c) The dissolved boron has a long residence time in the ocean of approximately 20 Ma. Thus, the δ^{11}B values of seawater were stable at +39.5‰ for the last 20 Ma.

Based on the above hypotheses, Gaillardet & Allègre (1995) deduced the following formula:

$$pH = pK_a - \lg\{(\delta^{11}B_{sw} - \delta^{11}B_4)/$$
$$[\alpha - 1\delta^{11}B_4 - \delta^{11}B_{sw} + 10^3(\alpha - 1 - 1)]\}$$

where pK_a is the ionisation constant of $B(OH)_3$, $\delta^{11}B_{sw}$ is the boron isotope composition of seawater, $\delta^{11}B_4$ is the boron isotope composition of $B(OH)_4^-$ in seawater, and α was the isotope fractionation factor between $B(OH)_4^-$ and $B(OH)_3$ in seawater. Based on the calculated pH of seawater and the total dissolved inorganic carbon $\sum CO_2$ of the ocean, using the formula:

$$pCO_2 = K_H(1 + K_1/[H^+] + K_1K_2/[H^+]^2)$$

$\sum CO_2$, the partial pressure of atmospheric carbon dioxide [pCO_2] can be calculated. K_1 and K_2 are the first and secondary ionisation constant of H_2CO_3.

This proxy has been used in many important studies of past ocean and atmospheric chemistry (Spivack et al. 1993; Sanyal et al. 1995, 1997; Palmer et al. 1998; Pearson & Palmer 2000; Foster, 2008; Hönisch et al. 2008, 2009; Pearson et al. 2009; Seki et al. 2010). Spivack et al. (1993) found that at 21 Ma, the surface ocean pH was only 7.4 ± 0.2 but then increased to 8.2 ± 0.2 at ca 7.5 Ma. This indicated that atmospheric CO_2 concentrations may have been much higher at 21 Ma than today. Sanyal et al. (1997) indicated that during the penultimate glacial period, the deep ocean pH was about 0.3 ± 0.1 pH units higher compared with the modern deep ocean, and that there was no significant pH difference in the eastern equatorial Pacific surface ocean during the glacial–interglacial transition. Hönisch et al. (2008) suggested that the pH of glacial deep water in the Atlantic was similar to the pH of interglacial Atlantic waters, which resolves the inconsistency between the previously reported high bottom water pH and the lack of significant carbonate preservation in the glacial deep ocean. Hönisch et al. (2009) further found that the pCO_2 was relatively stable

before the mid-Pleistocene climate transition and that the glacial pCO_2 was ∼31 microatmospheres higher before the transition (>1 Ma), but interglacial pCO_2 was similar to that of late Pleistocene interglacial cycles (<450 000 years ago). Seki et al. (2010) found that, during the warm Pliocene, pCO_2 (330–400 ppm) was similar to that today and decreased to values similar to pre-industrial times (275–285 ppm) between 3.2 and 2.8 Ma.

Beerling & Royer (2011) discussed the discrepancies in the pCO_2 reconstruction between different proxies and nominated the marine-based proxy based on the δ^{11}B values of fossil foraminifera, an important proxy. In recent years, the boron–CO_2 proxy has significantly improved, and newer CO_2 reconstructions have addressed earlier limitations associated with an incorrect isotopic fractionation factor, diagenetic alteration and gaps in our understanding of the evolution of seawater boron isotopes and alkalinity. Beerling & Royer (2011) suggested that proxy reconstructions of past atmospheric CO_2 concentrations should be targeted to the past 800 000 years and two relatively recent globally warm climate intervals: the middle of the Pliocene epoch (3.6–2.6 Ma) and the mid-Miocene climatic optimum (18–15 Ma). Although the B/Ca method has not yet been calibrated with laboratory culture experiments, it is used to reconstruct the ancient seawater pH because it is more stable, and less affected by dissolution and post-deposition alternation compared with the conventional method of boron isotopes (Yu et al. 2007, 2010; Rae et al. 2011).

Despite the achievements from the use of the δ^{11}B–pH proxy, the controlling factors (pK_a, $\delta^{11}B_{sw}$, $\delta^{11}B_4$ and α_{4-3}) are still controversial. Spivack & Edmond (1987) showed that the $\delta^{11}B_{sw}$ value is stable at +39.5‰ and cited by many researchers, but Foster et al. (2010) have shown that the $\delta^{11}B_{sw}$ value is stable at +39.6‰. Because it is very difficult to isolate $B(OH)_3$ and $B(OH)_4^-$ from seawater, most pK_a values are estimated theoretically. The $pK\alpha = 8.597$ is currently considered the most accurate estimate (Dickson 1990). The range of α_{4-3} from theoretical calculation is 0.972–0.981 (Kakihana et al. 1977; Byrne et al. 2006), while that from experiments is 0.952–0.976 (Lécuyer et al. 2002; Xiao et al. 2006) with $\alpha_{4-3} = 0.974$ (Klochko et al. 2006) considered the most accurate at present. The assumption that only $B(OH)_4^-$ incorporated into biocarbonates is debatable, with some recent studies suggesting $B(OH)_3$ may also be incorporated into biocarbonates (Pangani et al. 2005; Xiao et al. 2008a; Klochko et al. 2009; Rollion-Bard et al. 2011). Among these controlling factors ($pK\alpha$, $\delta^{11}B_{sw}$, $\delta^{11}B_4$ and α_{4-3}) in the δ^{11}B–pH proxy, uncertainties in pKa and $\delta^{11}B_{sw}$ are less than α_{4-3} and the boron species incorporated into biocarbonates. In addition, precise measurement of boron isotope values in foraminifera is also important for application of this proxy. In the future, it will be necessary and important to establish a 'best-fit empirically equation' between the $\delta^{11}B_{carb}$ values and pH of seawater based on the precipitation experiments of inorganic carbonates or culture experiments of corals or foraminifera. When this empirical model is used, the error in measured pH values is lowest and is independent of solution pH (Xiao et al. 2008a).

Tracing water pollution

Boron isotopes are effective tracers for identifying distinct solute sources in natural waters. Boron is highly soluble in aqueous environments, and δ^{11}B values are controlled by several known parameters, with the solute source compositions, isotope fractionation processes related to adsorption/desorption, mineral precipitation and dissolution, and volatilisation, the most significant. Sodium perborate in industrial and domestic detergent is the major anthropogenic boron pollution source in groundwater. The synthesis process of sodium perborate is:

$$Na_2B_4O_7 + 2NaOH + 4H_2O_2 + 11H_2O \rightarrow 4(NaBO_3 \cdot 4H_2O)$$
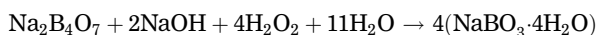
There is no isotopic fractionation during this process (Eisenhut *et al.* 1996; Barth 1998), so the δ^{11}B values of products and raw materials are the same. Non-marine Na-borate minerals (–5.4 to +10.2‰) and Ca-borates (–15‰) are characterised by a rather narrow range of δ^{11}B values (Barth 1998). The anthropogenic water-soluble boron compounds, derived from perborate-enriched detergents and cleaning products, are discharged with domestic aqueous effluents into sewage treatment plants, with little or no boron removed during conventional treatment processing of wastewaters. Hence, the anthropogenic boron load is almost entirely released into aqueous environments by entering receiving surface and underground water systems, where further dilution occurs. Compared with the large range in δ^{11}B values of natural waters (76‰), polluted waters have a small range of δ^{11}B values (Figures 3, 4).

When the δ^{11}B values of pollutant and groundwater are different, the δ^{11}B values of the polluted groundwater fall between them. With the increase in levels of pollution, the B concentration and the δ^{11}B values of polluted groundwater show a non-linear (hyperbolic) relationship (Figure 4). On Figure 4, the intersection of the curve between AA′ and EE′ is the δ^{11}B value of coastal groundwater. Curves BB′, CC′ and EE′ are the change in δ^{11}B values in groundwater after contamination with Ca-borates, seawater, municipal wastewater and Na-borates,
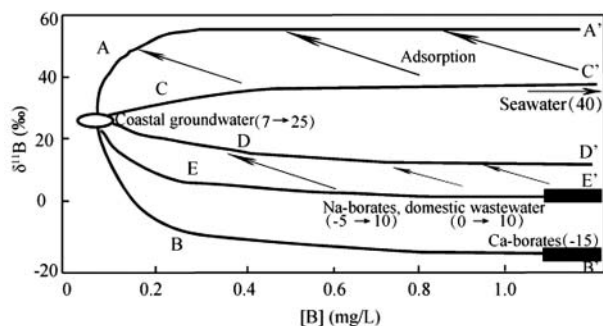

Figure 4 δ^{11}B–B mixing lines between uncontaminated boron in groundwater and possible contaminants: seawater, Na-borates and domestic wastewater, and Ca-borates. Note that: (1) the difference between marine and anthropogenic contamination remains detectable in spite of adsorption modifications; and (2) differences between various anthropogenic sources may be detectable (Vengosh 1998).

respectively. The arrows between AA′ and CC′, and between DD′ and EE′ are the boron isotope fractionation during adsorption by clay minerals, and the variation in the δ^{11}B values. It could be seen that the effect of seawater intrusion and anthropogenic pollution is different (Figure 4). If the δ^{11}B values of the pollutant and groundwater are significantly different (e.g. 5% or more) low levels of the pollutant can be detected. In addition, δ^{11}B values can identify the scale of water dilution.

Vengosh *et al.* (1994) showed that the δ^{11}B values of raw and treated sewage effluents varied from +5.3 to +12.9‰, which overlapped with those of natural non-marine Na-borate minerals (–0.9 to +10.2‰), but differed significantly from those of regional uncontaminated groundwater (+27.7 to +32.4‰) and seawater (+39‰). Bassett *et al.* (1995) showed that the δ^{11}B values of background groundwater (+14‰) and water from anthropogenic sources such as treated municipal wastewater (+6 to +10‰) and irrigation-affected water (>+40‰) in EI Paso, Texas were different. The δ^{11}B values were also used successfully to distinguish fertiliser pollution in different agriculture regions in Minnesota (Komor 1997) and in Arizona (Leenhouts *et al.* 1998); to trace anthropogenic input into surface and groundwater in the Harz Mountains in Germany (Gäbler & Bahr 1999) and in Seine River, France (Chetelat & Gaillardet 2005); to identified the origin of salinity in groundwater from the Mediterranean Coast of Israel (Vengosh *et al.* 1999); and to identify leachate contamination in groundwater (Eisenhut & Heumann 1997; Barth 2000). Although the isotopic fractionation during the evaporation–condensation process influences the δ^{11}B values of precipitations, the δ^{11}B values were successfully used to trace anthropogenic emissions in the atmosphere of Paris, France and Guiyang, China by Chetelat *et al.* (2009a) and Zhao & Liu (2010), respectively.

Seawater intrusion is also a major source of water pollution. In general, seawater intrusion is inferred when the Cl⁻ concentration in groundwater exceeds 200–300 mg/L (Xiao *et al.* 2001b). However, an increase in Cl⁻ concentration may result from contamination with other saline waters and industrial wastes. Thus, Cl⁻ concentration alone can indicate if groundwater is contaminated, but cannot be used to identify the contaminant source(s) and intrusion type(s). Oxygen (δ^{18}O) and sulfur (δ^{34}S) isotope values are also used to trace seawater intrusion, but the difference in δ^{18}O values between fresh groundwater and seawater is often small, and δ^{34}S values are affected by redox reactions, which limit their application. The δ^{11}B values of seawater (+39.5‰), terrestrial water (<+10‰) and brines affected by seawater (+57.5‰) are distinctly different. Groundwater polluted by seawater has increased B concentrations and δ^{11}B values.

Compositions of major dissolved components and δ^{11}B values were investigated (Oi *et al.* 1996) in hot spring waters at Ibusuki and adjacent areas, Kyushu, Japan. The δ^{11}B values of hot spring waters range from +2.1 to +39.4‰. A close inspection of the δ^{11}B values identified two B sources: seawater with a δ^{11}B value of +39‰ and volcanic gases with a δ^{11}B value of +6‰. Aggarwal *et al.* (2000) measured the δ^{11}B values, and B and Cl concentrations of Icelandic geothermal fluids from both high- and low-temperature systems. The δ^{11}B values range from –6.7‰

in the Krafla system to +25.0‰ in a warm spring from the Southern Lowlands. The $\delta^{11}B$ values and Cl/B ratio of the high-temperature systems are dominated by the composition of the local basalts, whereas the lower-temperature systems show evidence of mixing with B and Cl of marine origin, together with some uptake of B into secondary mineral phases. Hogan & Blum (2003) measured the B and Li isotopes of Fresh Kills landfill to investigate the mixing and flow in the groundwater environment. The $\delta^{11}B$ values of end-member waters are distinct, and reflect the solute sources: fresh water (~+30‰), transition zone groundwaters (~+20‰), seawater (+40 to +75‰) and leachate (~+10‰). The wells influenced by seawater exhibit a clear chemical mixing trend, with seawater contributions ranging from 3% to 85%. Well waters with a high percentage of seawater (>30%) have $\delta^{11}B$ values that were within 1‰ of the seawater value (+40‰), whereas a trend of increasing $\delta^{11}B$ values (+55 to +75‰) was observed for wells with a lower percentage of seawater (<30%) (Figure 5a). This deviation from $\delta^{11}B$ values of seawater represents non-conservative behaviour and is likely the result of isotopic fractionation during ion-exchange reactions. Xiao *et al.* (2001b) investigated the modern seawater intrusion into ground brines in Laizhou Bay, China using $\delta^{11}B$, B and Cl concentrations. Results showed that seawater intrusion increased the $\delta^{11}B$ values of ground brines, and B and Cl concentrations were positively related. In contrast to the linear law of chemical compositions, the $\delta^{11}B$ values of water mixed with different B and $\delta^{11}B$ values is non-linear with the extent of intrusion. At the initial intrusion stage, the $\delta^{11}B$ values of the mix increase sharply and allow quantification of small fractions of high-salinity water in groundwater. The $\delta^{11}B$ values have an advantage over other methods, especially along the saline–freshwater interface with a smooth Cl concentration gradient, where the range of $\delta^{11}B$ values is large enough to be detected precisely.

When $\delta^{11}B$ values are used to trace water pollution, fractionation may occur during flow, deposition/dissolution, oxidation/reduction, volatilisation or adsorption processes. For example, after adsorbtion by clay minerals, [11]B can be enriched in solutions (Vengosh 1998) with the $\delta^{11}B$ values of contaminated groundwater different from the original (Figure 3). The precision of measurement of $\delta^{11}B$ values in fresh water with low boron contents restricts its application in tracing water pollution.

Discriminating depositional environments

Boron isotopes are useful geochemical tracers to discriminate depositional environment using marine and non-marine evaporite minerals (Figure 3) (Swihart *et al.* 1986; Bassett 1990). Vengosh *et al.* (1991a) showed that the Victorian volcanic-crater lakes of southeastern Australia had $\delta^{11}B$ values of +54 to +59‰. In contrast, salt lakes from South Australia and Western Australia have $\delta^{11}B$ values between +25 and +48‰, which are different from those of groundwater from the Great Artesian Basin, country rocks and modern detrital sediments present in these salt lakes (Figure 5b). The $\delta^{11}B$ values of these salt lakes overlap with those of surface and brackish waters (+28 to +35‰) and seawater. Both low molar Na/Cl ratios and high $\delta^{11}B$ values suggest that the source of the bulk of the dissolved solids in the Australian brines is dominated by cyclic salts, derived from seawater, rather than from local rock weathering. While the low B/Cl ratios and high $\delta^{11}B$ values (>39‰) of some brines indicate interaction of brines with detrital sediments within the salt lake systems, $\delta^{11}B$ values <+39‰ suggest mixing of brines of marine origin from which boron was partly removed by adsorption, with waters of terrestrial origin with low $\delta^{11}B$ values. The $\delta^{11}B$ values from salt lakes in China (Xiao *et al.* 1992; Vengosh *et al.* 1995; Li & Sun 1996) vary from –4.4 to +24.6‰ and are similar to those measured on country rocks and source waters but are different to seawater (+39.5‰) and indicate their continental origin.

Foraminifera have long been thought to be halobios. Since the 1970s, fossil foraminifera have been discovered in many terrestrial strata in China (Xiao *et al.* 2008b) and have prompted discussion about the depositional environment of the fossil foraminifera strata. Xiao *et al.* (2008b) studied the Quaternary foraminifera in Yanghuzhuang section (YHZS), China where $\delta^{11}B$ values of foraminifera and bivalve fossils (+8.3 to +9.3‰) differed from those of modern marine foraminifera (+24.9‰) and seawater (+39.5‰) but were similar to those of nearby modern terrestrial gastropods (+7.9‰) (Figure 5c). These data suggest that these foraminifera inhabited a non-marine

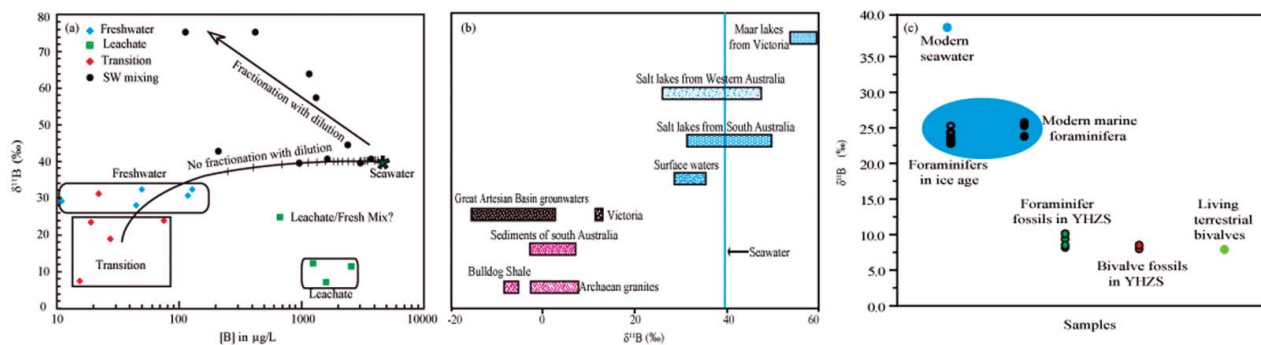**Figure 5** (a) Boron isotope mixing plot of well-water samples from the Fresh Kills landfill (Hogan & Blum 2003); (b) distribution of $\delta^{11}B$ values in some Australian brines, surface waters, groundwaters, sediments and country rocks (Vengosh *et al.* 1991a); and (c) comparison of $\delta^{11}B$ values in samples from Yanghuzhuang Section (YHZS) with those reported in the literature (Xiao *et al.* 2008b).

environment and that they were not restricted to the marine environment and could survive in terrestrial conditions that resembled those of the ocean.

Continental erosion

The δ^{11}B values measured on sedimentary and magmatic rocks, and continental crust are –40‰, +30‰ and –10 ± 2‰ (Chaussidon & Albaréde 1992; Palmer & Swihart 1996), respectively. In contrast, the δ^{11}B value of modern seawater is constant worldwide at +39.6‰ (Foster *et al.* 2010). The significant boron isotope fractionation during water–rock interactions makes δ^{11}B a good tracer for hydrographic circulation, especially using the δ^{11}B values of large rivers to study continental weathering.

The B geochemistry of representative rivers in the world has been studied by many researchers (Spivack 1986; Mossadik 1997; Rose *et al.* 2000; Lemarchand & Gaillardet 2006; Chetelat *et al.* 2009b). Rose *et al.* (2000) showed that no systematic correlation between the δ^{11}B values and the major ion chemistry of the Himalayan Rivers waters was present, except for the most B- and Cl-rich rivers, which have systematically the highest δ^{11}B values, likely controlled by evaporite dissolution. After correction for the evaporite contribution, the riverine B concentrations (0.10 to 5.83 μmol/L) and δ^{11}B values (–5.8 to +24.1‰) reflect different conditions of silicate weathering, with a negligible contribution to the river boron budget from the dissolution of carbonates. At variance with congruent silicate dissolution, incongruent dissolution occurs with a large boron isotope fractionation that depends on pH. The net boron concentrations and δ^{11}B values of Himalayan erosion for the global boron cycle to seawater varied from 0.67 to 0.29 μmol/L, and from +5.0 to +21.0‰ for the Ganga and the Brahmaputra during the monsoon period, respectively. Zhao (2002) studied the sources and spacial variation of dissolved boron in Xijiang, China and showed that the δ^{11}B values of river waters varied little with 80% in the range –2.0 to +l0‰, with an average of 4.4‰. The adsorption by clay particles and precipitation of $CaCO_3$ had no influence on the δ^{11}B values of river waters, which mainly reflect their sources with about 83% of B from carbonate rocks and rainwaters, and ≤13% of B from clastic rocks. Lemarchand & Gaillardet (2006) analysed the boron concentrations and δ^{11}B values of 24 rivers contributing to the Mackenzie basin, Canada. The results showed that most of the dissolved boron was derived from weathering of silicates. Contributions from rainwaters and dissolution of carbonate and evaporite rocks can locally control the boron budget but they remain of secondary importance at the regional to continental scale. The boron geochemical cycle in the Mackenzie basin is not in a steady state, and dissolved boron in rivers is regulated by the input of groundwater. The present boron fluxes are responding to past water–rock interactions with the weathering history a key parameter in interpreting modern geochemical fluxes, and has led to underestimation of the importance of groundwater to the chemical features of large rivers. Chetelat *et al.* (2009b) reported the boron geochemistry during continental erosion in the Changjiang and its main tributaries, and showed that the contribution of silicate weathering to the dissolved boron

load ranged from 40% to 50% for the main channel and from 45% to 88% for the main tributaries. Boron was highly mobile, and isotope fractionation occurred during silicate weathering. The dissolved load was systematically enriched in ^{11}B compared with the suspended particulate matter. The isotope compositions of both the dissolved load and suspended particulate matter are controlled by the competition between boron leaching and boron uptake into secondary phases. Boron leaching is characterised by a loss of boron relative to the bedrock without any apparent isotope fractionation, whereas boron uptake is associated with a large isotope fractionation that enriches the dissolved component in ^{11}B.

Compared with the erosion process of B in rivers, the mechanisms of boron fractionation and intensity in rocks and minerals are less well known. Spivack *et al.* (1987) studied a soil profile in the Orinoco basin in Venezuela and showed that the δ^{11}B values vary little (–1.4 to +1.6‰) over the whole profile. The δ^{11}B values in the weathered region are –1.0‰, which is lower than that in the unweathered region (+1.6‰), and the boron isotope fractionation during silicate weathering is less than 3‰. Zhao *et al.* (2003) first reported the boron contents and δ^{11}B values of acid-soluble phases in loess and paleosol in the Luochuan loess section. The B contents of acid-soluble phases in the Luochuan loess section (S_0–S_2) vary within the range of (0.8–2.7) × 10^{-6}, and their δ^{11}B values vary from –1.8 to +18.6‰, mostly within the range of 0 to +10‰. The B contents of acid-soluble phases were derived from the adsorption phase with a lesser contribution from carbonates. The B contents and δ^{11}B values of paleosol layers were higher than those of the loess layers, especially in the loess layer S_1. The variations of boron contents and δ^{11}B values of acid-soluble phases in the loess section were controlled by the intensity of chemical weathering and loess adsorption capability. Warm humid climates lead to high B contents and δ^{11}B values.

Mineralisation and ore genesis

Tourmalines are the most abundant B-bearing mineral in the crust and occur in a variety of lithologies. The δ^{11}B values of tourmalines are controlled by their sources; hence, the δ^{11}B values of tourmalines in ore bodies are applied to study mineralisation and ore genesis (Jiang 2001; Garda *et al.* 2009; Pal *et al.* 2010), especially in massive sulfide deposits.

Slack *et al.* (1989) reported the δ^{11}B values for tourmalines from the early Proterozoic Broken Hill block, Australia, which hosts giant lead–zinc–silver sulfide deposits. The δ^{11}B values for ores vary from –23.1 to –17.2‰, lower than those for all other tourmalines from massive sulfide deposits and tourmalinites in France and Sweden (–12.3 to –2.0‰), North America (+1.6 to +6.7‰) and South Africa (–13.8‰) but are similar to tourmalines in ore veins and host-rock from Broken Hill. Slack *et al.* (1989) proposed that these low values reflect leaching of B from non-marine evaporitic borates by convecting hydrothermal fluids associated with early Proterozoic continental rifting. A possible modern analogue is the Salton Sea geothermal field in California.

There are many huge, world-class borate deposits in eastern Liaoning, China, but their ore genesis remains

controversial. Jiang *et al.* (1997) studied $\delta^{11}B$ values of borate deposit in the Houxianyu borate deposit, eastern Liaoning, China and showed that the $\delta^{11}B$ values of tourmaline from footwall granite were +0.8‰. The borate ores have the highest $\delta^{11}B$ values (+9.6 to +11.1‰). Tourmaline-bearing rocks (leptite and leptynite) in the footwall have $\delta^{11}B$ values (+3.9 to +4.5‰) that are intermediate between the measured values of the granite and borates, whereas tourmalines from within the orebody and from the hangingwall have $\delta^{11}B$ values (+6.7 to +9.7‰) similar to the borates. The $\delta^{11}B$ values of the borate minerals and associated tourmalines precludes their derivation from granite-related fluids. Rather, the data are compatible with the borate deposit being a metamorphosed evaporite with the depositional environment of the B-bearing sequence possibly overlap the transition from non-marine to marine conditions. The premetamorphic origin of the Houxianyu borate deposit is similar to that of the Cenozoic non-marine evaporite borate deposits of western Turkey. Jiang *et al.* (2008) studied the chemical and boron isotope variations of tourmaline in the Hnilec granite-related hydrothermal system in Slovakia and showed that the $\delta^{11}B$ values of the main stage tourmalines vary from –15.4 to –10.3‰, higher than that of late-stage tourmalines (–17.1 to –16.0‰). These trends reflect a changing fluid source from a dominant magmatic–hydrothermal fluid derived from granites to a late-stage metamorphic fluid derived from the regional metamorphism (chlorite and biotite zone) of metapelites. In addition, $\delta^{11}B$ values of tourmaline are also used as tracers for the P–T conditions, water–rock interactions, and fluid origin and evolution (Palmer & Swihart 1996; Nakano & Nakamura 2001; Pal *et al.* 2010).

FUTURE DIRECTIONS OF BORON ISOTOPE IN GEOCHEMICAL RESEARCH

The high geochemical reactivity of boron and the significant boron isotope fractionation in nature make boron isotopes a good tracer for determining distinct sources and modelling geochemical cycles, but the boron isotope fractionation during flow, deposition/dissolution, volatilisation or adsorption processes may limit its geochemical application. In addition, the quantitative extraction of boron and the precise measurement of its isotopic composition in samples with very low boron content are also important for its geochemical application.

Although many studies using the $\delta^{11}B$–pH proxy have been published over the last decade, the use of boron isotopes, as sources or process proxies, requires that the physicochemical processes that control boron incorporation into carbonates be rigorously characterised and that the related chemical and isotopic fractionation be quantified. The carriers of the $\delta^{11}B$–pH proxy are foraminifera and coral, but foraminifera-bearing deep-sea sediments are limited to the past *ca* 180 Ma, so extended application of this proxy to older parts of the Phanerozoic must rely on different carriers. Articulate brachiopod shells with a low Mg-calcite mineralogy occur in marine sedimentary deposits from the late Cambrian to the present and can tolerate a wide range of depth,

temperature and pH conditions, making brachiopods a promising candidate for extending the boron isotope record as far back as the Cambrian. The controls and possible vital effects on boron isotopes are poorly understood and after resolving these problems, the $\delta^{11}B$ values in brachiopods may be used to reconstruct pH of ancient seawater or sea-level changes. In addition, in contrast to ancient marine environment studies, there have been very few studies of ancient terrestrial environments by using boron isotopes so that the studies of boron isotopes in continental carbonate sediments and biocarbonates (e.g. ostracodes and bivalves) and their environmental significance are worthy of study. The B/Ca ratio method is suitable for high-resolution paleoceanographic studies but is comparably new, and the process of boron absorption by foraminifera is still unclear. Moreover, the mechanisms using the B/Ca ratio to reconstruct pH and CO_3^{2-} concentrations are not well accepted because the method is constructed on the basis of empirical function, and establishment of its theoretical basis is important for use of this method.

Unlike some well-established stable and radiogenic isotope systems (H, C, N, O, S, Sr, Pb), boron chemical and isotopic analyses in plants and living organisms and the knowledge of how boron is cycled, accumulated and isotopically fractionated by plants are extremely scarce. In the future, more data are needed to approximate their impact on the boron aquatic composition and, more generally, on the boron geochemical cycle. In addition, laboratory-controlled experiments are needed to isolate and better quantify the boron fractionation mechanisms.

CONCLUSION

In this paper, the determination methods of boron isotope, the mechanism of boron isotopic fractionation and the distribution of boron isotopes in nature have been summarised systematically. The achievements and the problems in interpretation of boron isotope in geochemical application have been reviewed, and the research directions of boron isotope in geochemical fields have been proposed to highlight future developments of boron isotope research.

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