ELSEVIER

Boron isotopic fractionation during seawater evaporation

Y.K. Xiao [a,b,c,*], S.Z. Li [a], H.Z. Wei [a], A.D. Sun [a], W.G. Liu [b],
W.J. Zhou [b], Z.Q. Zhao [c], C.Q. Liu [c], G.H. Swihart [d]

[a] *Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining, Qinghai 810008, China*
[b] *State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment,*
Chinese Academy of Sciences, Xi'an, Shaanxi 710075, China
[c] *State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry,*
Chinese Academy of Sciences, Guiyang, Guizhou 550002, China
[d] *Department of Earth Sciences, University of Memphis, Memphis TN 38152, USA*

Abstract

Laboratory experiments were undertaken to investigate the behaviour of boron at the seawater–air interface during seawater evaporation. Seawaters adjusted to different pH values were heated to 27, 33 and 40 °C inside a quartz evaporator. The vapor was collected with a quartz condenser using a cold trap. A natural seawater–vapor process in quiet air conditions and excluding the sea-spray component was realized using this arrangement. The results indicate an enrichment of ^{11}B in the condensate. This implies that in the natural environment, rainfall with $\delta^{11}B$ values lower than that of seawater has been affected either by continental boron sources or by the boron extracted from seawater under airflow conditions. While the net flux of boron carried away from the ocean by air masses due to seawater evaporation is significant compared to other fractionation-associated processes removing boron from the ocean, the effect of isotopic fractionation as boron enters the vapor phase on the isotopic composition of boron in the ocean over time is small.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Boron isotope; Isotopic fractionation; Evaporation; Seawater

1. Introduction

Several experimental investigations of boron volatility at the seawater–atmosphere interface have been described in the literature. In a flowing air experiment, Gast and Thompson (1959) found up to 65 µg B/l present in the condensate. They postulated that most of the atmo-sphere's boron content is derived from seawater evaporation. Nishimura and Tanaka (1972) used seawater with 20 to 60 times the normal boron concentration in a similar experiment. By extrapolating their results to the normal seawater boron concentration, they estimated that there should be 0.42 µg B/l in condensate from air passed over seawater and 1.1 µg B/l in condensate from air equilibrated with seawater. Nishimura and Tanaka (1972) compared these results to the boron content of 4.7 ± 1.1 µg/l measured in precipitation over the ocean, and concluded that the sea is a sink rather than a source for atmospheric boron. Fogg et al. (1983) used a filter

* Corresponding author. Qinghai Institute of salt Lakes, Chinese Academy of Sciences, 18 Xinning Road, Xining, Qinghai 810008, China. Tel.: +86 8515895472; fax: +86 8515891609.

E-mail addresses: xiaoyk@isl.ac.cn, qhyhyjs@public.xn.qh.cn (Y.K. Xiao).

sampling system to directly collect boron from the atmosphere and separate it into gaseous and particulate components. Fogg and Duce (1985) determined that gaseous boron concentrations in the atmosphere range from 1 to 223 ng/m^3, and estimated the particulate boron to be 10 to 100 times lower in concentration.

Few isotopic studies of boron in precipitates and the atmosphere have been reported. The available boron isotopic data for precipitates show a wide range of variability, with $\delta^{11}B$ values ranging from 0.8 to 35‰ over the Pacific Ocean (Spivack, 1986), 16.7‰ in Qinghai, China (Xiao et al., 1992), 13.1‰ in southeast Germany (Eisenhut and Heumann, 1997), 3.8 to 9.1‰ (5 samples) with an average value of 6.4‰ in the Himalayan area (Rose et al., 2000), and −13 to 48‰ (20 samples) in the southern coast of England (Mather and Porteous, 2001). Miyata et al. (2000) reported measurements of boron isotopes in the atmosphere and precipitation of the North Pacific. The $\delta^{11}B$ values of atmospheric condensates in the western North Pacific and Japanese coast range from −12.8 to 5.1‰ with an average value of −5.4‰, whereas oceanic rains range from 18.9 to 34.7‰ with an average value of 27.6‰. Miyata et al. (2000) suggest that the wide range of $^{11}B/^{10}B$ ratios observed in the atmosphere and precipitation may result from boron isotopic fractionation during evaporation from seawater and condensation from the atmosphere.

Xiao et al. (1997) reported boron isotopic fractionation during the evaporation of near-neutral and acidic boron-bearing solutions. The ratio of the boron isotopic composition of an initial solution (pH 6.33) to that of the solid residue after evaporation was 1.0064. This result could have come about by fractionation of ^{10}B from the solution into the solid residue while boron volatilized from the solution, or by fractionation of ^{11}B from the solution into vapour. A preliminary experimental study of the boron concentration and isotopic composition in vapor derived from airflow reaction with seawater was reported by Xiao et al. (2001a). The isotopic composition of boron collected from vapor in this study was distinctly lighter than that of seawater. A quite different view of B isotopic 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 condensates collected for seawater with pH 8.1 were found to have $\delta^{11}B$ values (+41.9‰ and +46.5‰) higher than that of seawater (+39.5‰). The isotopic compositions of boron in rainwater collected in French Guiana are also reported and range from +30.5‰ to +45‰, suggesting that most of the boron in French

Guiana precipitation originates from a marine component. Recently, Rose-Koga et al. (2006) also reported boron isotopic composition of atmospheric precipitations. The $^{11}B/^{10}B$ ratios of instantaneous and cumulative rains and snows from coastal and continental sites show 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. The empirical vapor−rain isotopic fractionation of −31‰ and vapor–seawater fractionation of −25.5‰ was proposed, which has strong implications regarding the origin and evolution of atmospheric boron.

It is clear that further experiments allowing back seawater evaporation in quiet condition and additional isotopic measurements of boron in precipitation collected over the ocean are necessary to further characterize the behaviour of boron at the seawater–atmosphere interface.

This paper reports on the boron concentration and isotopic composition of condensate under quiet air and open system conditions during seawater evaporation at various temperatures and pH values. The results should be useful in identifying the origin of boron in the atmosphere and precipitation.

2. Experimental and analytical methods

2.1. Reagents and experimental apparatus for the seawater evaporation experiment

All chemicals used were of analytical or higher grade. The seawater used was collected on October 22, 1994 at 4°18′N, 161°08′E. Low boron, deionized water with a concentration of 0.5 ng B/ml was obtained by passing distilled water through a boron specific resin column, followed by sub-boiling distillation. All solutions were made, stored, and used in plastic containers throughout the process, with the exception of the quartz distillation apparatus.

Fig. 1 shows the experimental apparatus used for seawater evaporation, designed and constructed by Xiao et al. (2001b). It is made of quartz glass and consists of a condenser (A) and evaporator (B). Parts A and B are connected at interface C. This apparatus is designed to minimize loss of vapor and obtain a complete recovery of vapor. Its construction is much simpler than that used in the study reported previously (Xiao et al., 2001a). There are no filters, tubes, or airflow to consider as potential sources of contamination. Vapor condensation on the surface of the condenser takes place in a single step, and no seawater spray is produced. This apparatus closely reproduces an actual open system, quiet air condition at the seawater–air interface.
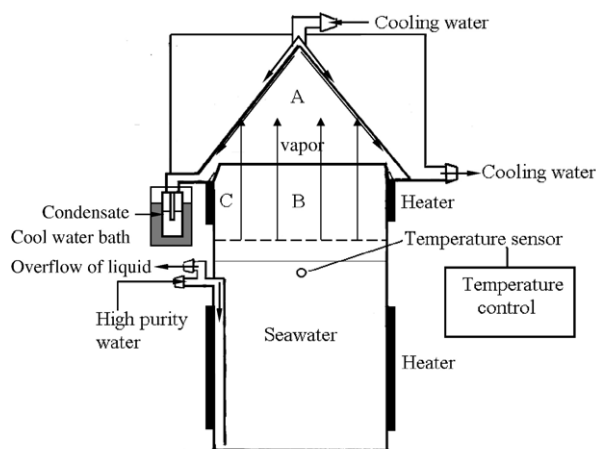
Fig. 1. Sketch of the seawater evaporation apparatus.

2.2. Seawater evaporation experiment

The evaporation apparatus was washed with a high-purity HCl–water solution before each experiment. After being washed, about 2.5 l of high-purity water was evaporated in the apparatus over 2 days to clean the condenser unit. The evaporation unit was then rinsed twice with seawater, after which the seawater evapora-

tion was started. Three types of experiments were carried out.

2.2.1. Experiment 1 (Nos. 1-1 to 1-10)

This experiment was carried out under conditions resembling an open oceanic environment, in order to understand the behavior of boron isotopes during seawater evaporation in nature. About 2.5 l of seawater was injected into the evaporator. The pH of the seawater was adjusted prior to evaporation in tests 1–9 and 1–10 by adding HCl solution. The other pH values were initially as normal for seawater (pH 8.11). However, the pH value of the seawater usually changed a little during evaporation due to the addition of high-purity water (see below) and the natural evolution of temperature at the start of each test. After two hours, the temperature and pH of the evaporating seawater were basically constant. The variation in pH observed during condensate collection was 0.05 pH units in a typical daily measurement. The pH values listed in Table 1 are the average of the initial and final values measured during the stable period of condensate collection. The temperature of the seawater was set to 27 °C, 33 °C or 40 °C using a temperature controller, and measured throughout the test by a temperature sensor. The variation in temperature observed during the experiments ranged from −1 to +2 °C.

Table 1
Seawater-vapor experiments

Experiments	No.	Sample type	T °C	PH SW	Condensate (CD), seawater (SW) and salt						α^3
					CD	B^1 (ppb)	Evap B (%)	Cl (ppb)	Cl/B (mol)	$\delta^{11}B^2$ (‰)	
1	1-1	CD	27	8.11	5.94	1.51	0.032	na	–	39.6±0.5 (2)	1.0006
	1-2	CD	33	8.32	5.83	3.42	0.073	310	27.6	–	
	1-3	CD	33	8.21	6.01	4.62	0.099	na	–	42.7±0.4 (2)	1.0036
	1-4	CD	40	na	5.87	na	–	na	–	41.8±0.1 (1)	1.0027
	1-5	CD	40	8.49	5.23	3.42	0.073	434	38.7	42.6±0.7 (1)	1.0035
	1-6	CD	40	8.23	5.44	4.85	0.104	506	32.8	40.2±0.1 (2)	1.0012
	1-7	CD	40	8.31	5.70	4.17	0.089	na	–	40.9±1.9 (2)	1.0011
	1-8	CD	40	8.31	5.89	3.96	0.085	na	–	39.4±0.4 (1)	1.0004
	1-9	CD	40	7.71	5.92	10.7	0.229	691	19.7	42.4±1.5 (3)	1.0033
	1-10	CD	40	7.76	5.70	9.81	0.210	102	3.2	39.5±0.5 (2)	1.0005
2	2-1	CD	33	8.11	6.19	11.2	0.240	na	–	46.7±0.5 (4)	1.0074±0.0005
	2-2	CD	33	8.03	4.82	265	1.42	na	–	57.9±1.7 (3)	1.0182±0.0016
	2-3	Dried salt	–	–	–	na	–	na	–	36.2±0.6 (7)	–
Initial seawater (experiment 1 and 2)			–	–	–	3.74×10^3	–	18.2×10^6	1485	39.0±0.7 (10)	–
3	3-1-1(a)	SW	–	8.17	–	19.7×10^3	–	–	–	13.1±0.2 (5)	α_{ba}=1.0072±0.0009
	3-1-2(b)	CD	40	–	na	15.1	0.061	–	–	20.4±0.9 (3)	
	3-2-1(c)	SW	–	8.17	–	63.5×10^3	–	–	–	9.3±0.1 (3)	α_{dc}=1.0107±0.0010
	3-2-2(d)	CD	40	–	5.90	42.7	0.054	–	–	20.1±1.0 (3)	

1: The average boron concentration of condensate for samples Nos. 1-1 to 1-8 (with normal pH values of seawater) is 3.71±0.81(2σ) μg/l.
2: The data in parentheses are the number of replicate analyses. The uncertainty given for $\delta^{11}B$ values with only one analysis is the internal precision.
3: The isotopic fractionation factor α is defined as $\alpha=(1000+\delta^{11}B_{cond/salt})/(1000+\delta^{11}B_{sw})$.
na: not analyzed.

High purity water with a concentration of 0.5 ng B/ml was supplied continuously to keep the volume of evaporated seawater solution and hence the boron concentration almost constant. The vapor was condensed by running an isolated current of cold water (temperature less than 10 °C) through the condenser. The first 50 ml of condensate was discarded in each experiment to avoid cross-contamination. Interface C was heated to about 40 °C in all experiments to prevent condensation of vapor on its interior and protect the seawater from contamination through climbing up the interface wall. The condensate was transferred into a large plastic bottle when the collection bottle was full (about 1000 ml). The volume of collected condensate was about 2 l for each test. A test run in which 4245 g of high purity water were supplied to keep the volume of solution in the evaporator constant, and 4258 g of condensate were produced, shows that a complete recovery of vapor as condensate is achieved in this apparatus. The result reported by Nishimura and Tanaka (1972) shows that the boron in the air equilibrated with seawater at 25 °C was 0.019 ng/l, which is insignificant comparing to the boron in the condensate (1.1 µg/l). Therefore the shift of boron isotopic composition of boron during vapour condensation can be ignored in this study. The condensate production rates, at normal atmospheric pressure, were about 80, 120, and 180 ml per day at 27, 33, and 40 °C, respectively.

2.2.2. Experiment 2 (Nos. 2-1, 2-2, 2-3)

In experiment 2 there was no high-purity water supply and the seawater was allowed to completely evaporate in order to compare the isotopic compositions of boron in condensate and solid. About 2.5 l of seawater was introduced into the evaporator. The temperature of the seawater was set to 33 °C. First, 2000 ml of condensate was collected (No. 2-1) and isolated. Next, about 500 ml of the condensate was collected (No. 2-2) until the quartz reservoir contained only solid residue (No. 2-3). The isotopic composition of boron in the two condensates (Nos. 2-1 and 2-2) and the solid residue (No. 2-3) were measured and compared to the results of Experiment 1.

2.2.3. Experiment 3 (Nos. 3-1-1, 3-1-2, 3-2-1, 3-2-2)

Experiments 3 and 1 were carried out under identical conditions, except that boron-amended seawater was used in order to improve precision of the boron isotopic measurement and separate the equilibrium and kinetic isotopic fractionation effects under quiet air conditions.

About 2.5 l of seawater with added $Na_2B_4O_7$ (chemical reagent) and different boron concentrations

were injected into the evaporator. The boron concentrations used were 19.7 and 62.3 µg/ml, or 4.4 and 14 times the normal boron concentration in seawater, which are almost constant during evaporation. The temperature of the seawater was set to 40 °C. After condensation the isotopic compositions of boron in the boron-amended seawater samples (Nos. 3-1-1 and 3-2-1) and condensates (Nos. 3-1-2 and 3-2-2) were measured.

2.3. Boron blank

By evaporating high-purity water (boron concentration = 0.5 ng/ml) instead of seawater, the boron content in 2 l of condensate (the total boron blank) was repeatedly measured by the isotope dilution technique to be 86 ng B. This total blank includes 26 ng of boron from chemical processing, 1 ng (0.1% of the total boron in 2 l of high-purity water) from the evaporation of high purity water, and 1 ng from filament loading. Thus the boron blank contributed by the experimental apparatus and laboratory environment was less than 60 ng. We cannot distinguish the experimental apparatus blank from the laboratory environment blank, but we estimate that the laboratory environment blank is the major portion. Each experimental run required more than 15 days to complete in a clean laboratory environment, so the laboratory environment blank was difficult to reduce further. The 86 ng boron blank is less than 1% of the approximately 10 µg of boron collected in experiment 1, where it perhaps reduces the $\delta^{11}B$ of vapor by less than 0.5‰. The boron content collected in experiments 2 and 3 ranges from 22.4 to 132 µg, and for these results the 86 ng boron blank is small enough in comparison to ignore.

2.4. Separation of boron

In preparation for isotopic measurement, boron was extracted from evaporated seawater and condensate using a two-step ion exchange procedure (Wang et al., 2002). About 0.5 ml of Amberlite IRA 743 boron-specific resin (80–100 mesh) was placed in a 0.2 cm diameter polyethylene column. The length of the resin bed was 1.5 cm. 50 ml of seawater, or about 2 l of condensate solution or rainwater, were passed through a boron-specific resin column at a flow rate of about 0.4 ml/min. The boron held by the resin was eluted using approximately 5 ml of 0.1 M HCl at 75 °C. An amount of mannitol approximately equimolar to the boron content was added to the eluate, which was then concentrated to near dryness by evaporation in a super-clean oven under laminar flow at 60 °C (Xiao et al.,

2001a). The remaining solution was loaded onto a second column filled with a mixed resin consisting of 0.5 ml of cation-exchange resin (H^+ form) and 0.5 ml of anion-exchange resin (ion-exchanger II, HCO_3^- form). The boron was eluted from the mixed resin column using 5 ml of high purity water. Finally, this eluate was evaporated at 60 °C to produce a solution with a boron concentration of about 1 µg/µl for isotopic measurement. The results from Wang et al. (2002) demonstrated that the isotopic fractionation of boron could be negligible, within the precision of the isotopic measurement using procedure mentioned above.

2.5. Analytical methods

For most of the solutions, the boron content was determined using the azomethine–H spectrophotometric method. In a few cases, however, the boron content was determined by isotope dilution mass spectrometry (IDMS). The procedures described by Kiss (1988) were followed for the spectrophotometry, with slight modifications. One ml of boron solution, 2 ml of buffer solution (250 g of NH_4AC, 15 g EDTA, and 125 g glacial HAC, diluted to 400 ml), and 2 ml of azomethine–H solution (0.45 g azomethine–H and 1 g ascorbic acid in 100 ml water) were added in the sequence given. After mixing well, each intermediate solution was allowed to stand for 30 min. The absorption of the boron–azomethine–H complex was measured at 420 nm using a spectrophotometer (Shanghai model 721). The external precision of the azomethine–H method used here was 2% (2σ). The concentration of chlorine in condensates was measured using IDMS and based on the Cs_2Cl^+ ion (Xiao and Zhang, 1992).

The isotopic composition of boron in the condensates was measured using a thermal ionization technique (Xiao et al., 1988). A VG 354 mass spectrometer was used for isotopic analysis of boron. First, the top of an outgassed tantalum filament was evenly spread with 3 µl of graphite slurry. Next the filament was loaded with 1–2 µl of sample solution containing approximately 1–2 µg of boron and an equimolar amount of mannitol. This was followed by 1–2 µl of a Cs_2CO_3 solution containing an amount of cesium approximately equimolar to the amount of boron on the filament. The load was dried by heating the filament at 1.2 A for 5 min. The mass spectrometry procedure was essentially the same as that described by Xiao et al. (1988). The external precision of the isotopic analysis for NIST SRM 951 boric acid was better than 0.2‰ (2σ). The normal external precision for samples, however, was seen to be about 1‰ based on the scatter observed in repeated measurements. The boron

isotopic compositions of the samples are expressed as $\delta^{11}B$ (‰) relative to the NIST SRM 951 standard:

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

The measured average $^{11}B/^{10}B$ ratio of NIST SRM 951 was 4.05062 ± 0.00077 ($2\sigma=0.02\%$, $n=9$).

3. Results and discussion

3.1. Concentrations of boron in experimental condensates and rain samples

Table 1 summarizes the results obtained from the collection of condensates produced during seawater evaporation. More condensate was collected in the present study than in the experiments of Xiao et al. (2001a). These data demonstrate the following results.

1) In experiment 1 the concentrations of boron in the condensates collected at temperatures between 27 °C and 40 °C vary from 1.51 to 10.7 µg/l, resulting proportions of evaporated boron range from 0.032% to 0.229%, which shows that the loss of boron by evaporation is not significant (Chetelat et al., 2005). However, the losses of boron during evaporation at low pH are significant higher than that reported by Chetelat et al. (2005). The relationship between the boron concentration in condensates collected at 40 °C and the pH of evaporated seawater is shown in Fig. 2. The data resemble a negative exponential relation, and imply that the higher vaporization rate of boric
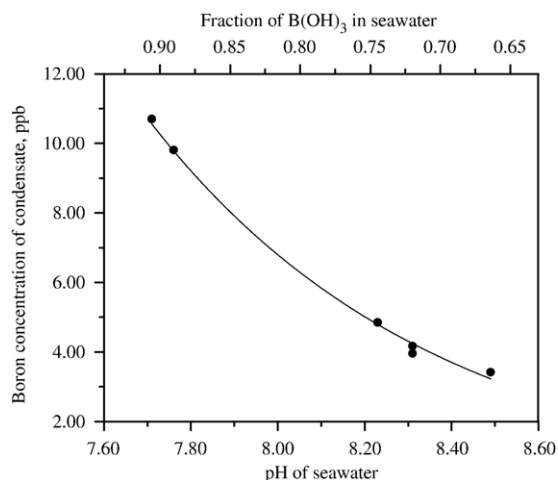

Fig. 2. Boron concentration in condensate vs. pH of seawater and B $(OH)_3$ fraction in seawater at 40 °C (experiment 1).
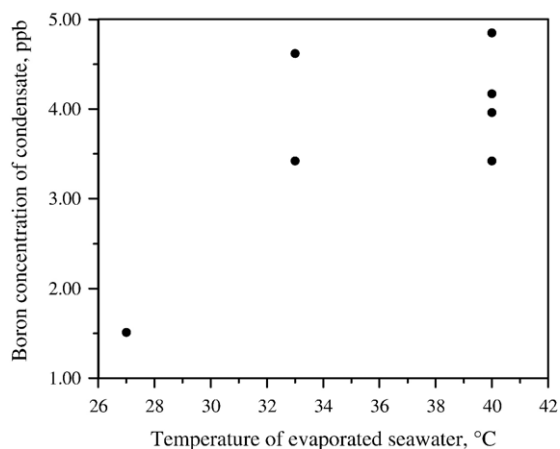
Fig. 3. Boron concentration in condensate vs. temperature of evaporated seawater with normal pH values (experiment 1, Nos. 1-1 to 1-8 excluding 1-4).

acid at lower pH may be due to higher $B(OH)_3$ fraction in seawater. As shown in Fig. 2 (*x*-axis label on the top), the boron concentration in condensates increases along with the $B(OH)_3$ fraction in seawater. The results shown in Fig. 3 indicate that the rate of boric acid vaporization in seawater of normal acidity is unlikely to be affected by temperature over the given range. The median concentration of 5.16 µg B/l found in condensate is higher than the 1.1 µg/l estimated by Nishimura and Tanaka (1972), and much lower than the 60–65 µg/l obtained by Gast and Thompson (1959). According to Bruyevich and Korzh (1971), the average value ranges from a minimum of 4 µg B/l to a maximum of 32 µg B/l in condensates collected in the Black Sea region during offshore and onshore winds. The boron concentrations in rainfall collected in Xining (XN in Table 2) and Nanhai (NH in Table 2) range from 3.50 to 14.7 µg/l, which is comparable with the range of 7.0 to 12.0 µg/l observed in coastal North Florida rainfall (Christopher et al., 1976).

2) The condensate boron concentrations in experiments 2 and 3 are much higher than those found in experiment 1, due to the increasing boron concentration of the evaporating seawater in experiment 2

and the higher concentration of boron in the evaporated solutions in experiment 3. The higher proportions of evaporated boron compared to that reported by Chetelat et al. (2005) should be attributed to high evaporation degree of 80% in experiment 2.

3) The chlorine content in the condensate varied from 102 to 691 g/l with a median value of 409 ± 220 g/l, which can be attributed to both contamination by the environment and emission of aerosols, as well as evaporation of seawater. We cannot distinguish between them. The contribution of aerosol emissions for boron was calculated to be, at the most, 0.17 µg based on the Cl/B ratio of seawater and assuming that all the chlorine in the condensate came from the emission of aerosols. The contribution of aerosol emissions for boron is perhaps lower than one percent of the total boron in the condensate. The chlorine contents yield Cl/B values ranging from 3.2 to 38.7 (mol ratio), much lower than seawater's value of 1485. The 38.7 value for Cl/B is approximately the same as that (42.0) obtained in a non-bubbling run under airflow conditions reported by Xiao et al. (2001a). The lower Cl/B ratios found in the condensate are attributed to the preferential evaporation of boron as boric acid, and imply that B in condensate is mainly from the evaporation of seawater and that the emission of aerosols is ignored in both the present study and the previous study under non-bubbling conditions (Xiao et al., 2001a).

3.2. Isotopic compositions of boron in condensate from seawater evaporation

The isotopic compositions of boron in condensate and seawater are shown in Table 1.

3.2.1. Experiment 1

The $\delta^{11}B_{cond}$ values of condensates for experiment 1 are plotted in Fig. 4 (not including No. 1-4, due to the deficiency of pH measurement), which shows that all the condensates have $\delta^{11}B_{cond}$ values slightly higher than that of seawater. The isotopic fractionation factor between condensate and seawater (α_{c-s}) range from 1.0004 to

Table 2
Rainfall sample data

Sample	Location	Sampling time	Wind direction	Temperature (°C)	pH	B µg/l	Cl µg /l	$\delta^{11}B_{rain}$ [a] (‰)
XN-1	Xining City,	16 August, 2000	Southeast	14	6.63	7.47	666	12.1 (1)
XN-2	Qinghai	29 May, 2004	West	13.2	5.61	3.50	–	9.0 ± 0.2 (3)
NH-1	South China Sea 114°58′31″E;	13 May, 2000	West	–	7.38	8.88	332	8.4 (1)
NH-2	21°16′18″N	20 May, 2004	Southeast	–	6.24	14.7	–	33.2 ± 0.4 (3)

[a] In parentheses is the number of replicate analyses. The uncertainty for $\delta^{11}B$ values with only one analysis is not given.
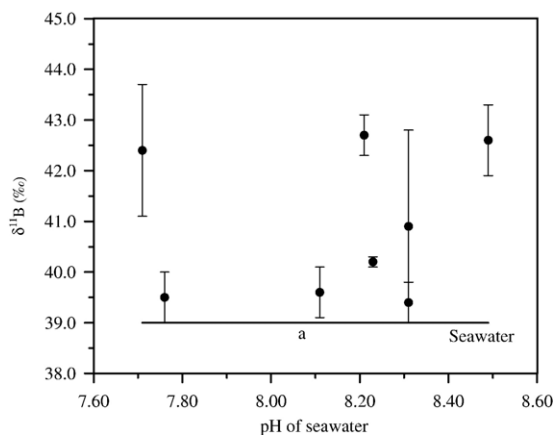
Fig. 4. $\delta^{11}B_{cond}$ values of condensate vs. pH of evaporated seawater, not including No. 1-4 due to the deficiency of the pH data (experiment 1).

1.0036, indicating a ^{11}B enrichment in condensate during the seawater evaporation. This observation is the reverse, however, of that reported in the airflow experiment of Xiao et al. (2001a), in which the isotopic composition of boron collected from condensate was distinctly lighter than that of seawater. It is therefore likely that airflow conditions were a significant factor in the light $\delta^{11}B$ values of condensate found in the latter experiment. Under airflow conditions a kinetic fractionation during the evaporation of seawater may arise from the fact that molecules bearing ^{10}B move faster than those bearing ^{11}B. The kinetic fractionation under this condition should favor the incorporation of ^{10}B into the vapor, whereas in the present study partial thermodynamic equilibrium should have been reached.

A seawater evaporation experiment in a closed Teflon system at 60 °C was carried out by Chetelat et al. (2005). The volume of evaporated seawater decreased continuously during the evaporation process because the system was closed and no high purity water was supplied. The condensates of natural seawater were collected until the degrees of evaporation reached 49.859% and 50.222%, at which points the $\delta^{11}B$ value of the condensates were measured to be 41.9 and 46.5‰ and that of the initial seawater to be 39.5‰. The resulting isotopic fractionation level of 1.0023 and 1.0067 between condensate and seawater are higher than the median value of 1.0020 ± 0.0014 found in experiment 1 of this study, and the latter is comparable to the value of 1.0074 measured for condensate collected with an evaporation degree of 0.80 in experiment 2 (see below).

The abundance of $B(OH)_3$ and $B(OH)_4^-$, the two dominant aqueous species of boron, in solution is a function of pH and highly dependent on the temperature of seawater (Dickson, 1990). The $\delta^{11}B_{3/4}$ values of $B(OH)_3$

and $B(OH)_4^-$ at different pH values and temperatures of 27 °C, 33 °C and 40 °C can be calculated using a fractionation coefficient, α_{43}, of 0.981 (Kakihana et al., 1977) and the measured $\delta^{11}B_{sw}$ value of 39.0‰ for seawater. The $\delta^{11}B$ values of $B(OH)_3$ and $B(OH)_4^-$ calculated for seawater and measured in the condensates are shown in Fig. 5. The figure shows that the $\delta^{11}B_{cond}$ values of condensates in experiment 1 are all slightly lower than the $\delta^{11}B_3$ value and higher than the $\delta^{11}B_4$ value at the same temperature. The boron in seawater is probably evaporated primarily as boric acid, however, which should result in $\delta^{11}B_{cond}$ being equal to the corresponding value for $B(OH)_3$ in seawater.

3.2.2. Experiment 2

Fig. 6 plots the boron isotopic compositions of seawater, solid residue and condensate, as well as the pH of evaporated seawater, against the degree of evaporation. The degree of evaporation, D, is defined as the ratio of evaporated seawater volume (V_e) to initial seawater volume (V_i). The measured value of $\delta^{11}B_{cond}$ for the first 2000 ml of condensate collected (No. 2-1) is 46.7‰ (the line labeled a-a in Fig. 6). The first 2000 ml of condensate were collected for evaporation degrees ranging from 0 (initial seawater) up to 0.80 (concentrated seawater) ($0 \le D < 0.80$), so the stated $\delta^{11}B_{cond}$ value is an accumulative over this period. The resulting α_{c-s} value is 1.0074. The measured value of $\delta^{11}B_{cond}$ for the approximately 500 ml of condensate that remained to be collected (No. 2-2) ($0.80 \le D \le 1$) is 57.9‰ (the line
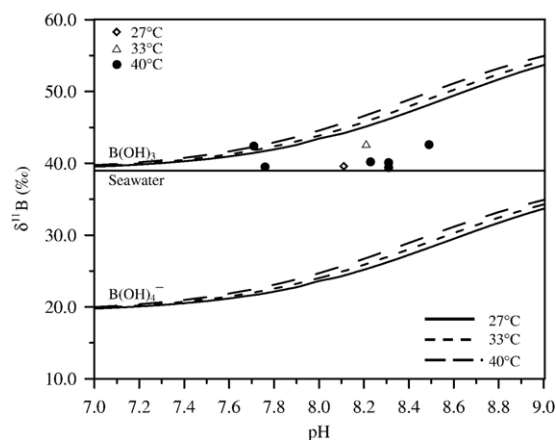

Fig. 5. $\delta^{11}B$ values of $B(OH)_3$ and $B(OH)_4^-$, the two dominant species of boron in seawater, as a function of pH calculated from the isotopic fractionation coefficient of 0.981 reported by Kakihana et al. (1977) and pK (dissociation constant of boric acid) values at 27 °C, 33 °C and 40 °C. (Dickson, 1990). The measured $\delta^{11}B_{cond}$ values of the condensates are shown (experiment 1). $\delta^{11}B_3$ and $\delta^{11}B_4$ were calculated with: $\delta^{11}B_3 = (39.0 + 19 \times f_4)/(0.981 \times f_4 + f_3)$ and $\delta^{11}B_4 = \delta^{11}B_3 \times 0.981 - 19$.
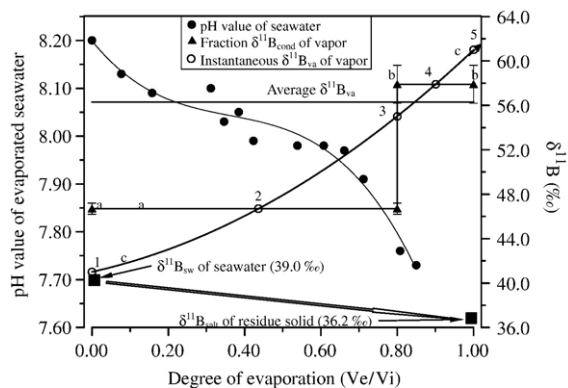
Fig. 6. Variation in the pH of residual seawater and condensate $\delta^{11}B_{cond}$ values with degree of evaporation (experiment 2). Line aa and Line bb display the $\delta^{11}B_{cond}$ values in the first 2000 ml and last 500 ml of condensate, respectively, which were fractionally collected. Line cc plots the instantaneous condensate $\delta^{11}B$ values based on a polynomial fit to points 1, 3, and 5. The $\delta^{11}B$ value of seawater decreases from 39.0‰ (seawater) to 36.2‰ (solid) when seawater was evaporated to dry.

labeled b-b in Fig. 6), resulting in an α_{c-s} of 1.0182. Based on the isotopic composition and boron content of each condensate sample, the calculated $\delta^{11}B_{cond}$ for bulk condensate is 56.3‰, resulting in an apparent fractionation factor, α_{c-s}, of 1.0166 between bulk condensate and initial seawater. The calculated instantaneous $\delta^{11}B_{cond}$ (the line labeled c-c Fig. 6) based the data of point 1, line aa and line bb as showing following equation gradually increases during evaporation,

$$\delta^{11}B(‰) = 41.0 + 7.66D + 12.32D^2. \qquad (2)$$

from an initial value of 41.0‰ (point 1 of Fig. 6, based on the results of experiment 1) through an intermediate value of 55.0‰ (point 3, Fig. 6) measured at an evaporation degree of 0.80, to a final value of 61.0‰ (point 5 of Fig. 6, the dry moment). Eq. (2) shows a polynomial relation between $\delta^{11}B_{cond}$ and evaporation degree. The instantaneous $\delta^{11}B_{cond}$ values for condensates at any evaporation degree can be calculated using this equation. For example, the evaporation degrees corresponding to our measurements of the accumulative condensate $\delta^{11}B_{cond}$ values during the two evaporation phases can be calculated as $D_2 = 0.436$ and $D_4 = 0.901$ for point 2 ($\delta^{11}B_{cond} = 46.7\%$) and point 4 ($\delta^{11}B_{cond} = 57.9\%$) of Fig. 6, respectively.

A bulk solid was formed as the seawater solution reached saturation and dried. The amount of boron in the bulk solid is equal to the difference between the total boron in the initial seawater and the total boron in condensate. The $\delta^{11}B$ of the bulk solid residue is 36.2‰, which indicate a shift of −2.8‰ due to the preferential loss of ^{11}B during evaporation. This result

confirms that the vapor is enriched in ^{11}B. This observation is consistent with the result of boron volatilization during evaporation of a boron solution reported by Xiao et al. (1997). Here, however, a mass budget is not possible to be calculated because the weights of evaporated seawater of 2.5 l and formed salts cannot be weighed precisely. The $\delta^{11}B$ of gaseous boron calculated by mass balance have been reported by Chetelat et al. (2005). Vengosh et al. (1992) reported on boron isotope variations during the fractional evaporation of seawater. They collected the solid fractionally but did not collect the vapor. Their results indicate a gradual increase in the $\delta^{11}B_{sw}$ value of the concentrating seawater, from 39.0 to 54.7‰, with the degree of evaporation. The increasing $\delta^{11}B$ values of the evaporating seawater and uniformly lower $\delta^{11}B$ values found in the coexisting precipitation (from 11.4 to 36.0‰) suggest selective uptake of ^{10}B by the salts (Vengosh et al., 1992). The increase in the $\delta^{11}B_{cond}$ and boron concentration of the condensate may be attributed to the rising $\delta^{11}B_{sw}$ and boron concentration of the seawater, rather than to the variation in pH of the concentrating seawater. The results displayed in Fig. 6 show that the residual seawater pH decreased from 8.20 to 7.73 as the evaporation degree increased from 0 to 0.85. In this evaporation interval the fraction of $B(OH)_3$ in seawater increases from 81 to 93% and the $\delta^{11}B_3$ value of $B(OH)_3$ decreases from 42.7 to 40.4‰, assuming that $\delta^{11}B_{sw}$ remains constant. The $\delta^{11}B_{cond}$ values should decrease with the degree of evaporation if the $\delta^{11}B_{cond}$ values are controlled by the pH of seawater. The results therefore seem to indicate that the fractionation of ^{10}B into the precipitate and increase of boron concentration in seawater have larger effect than the accompanying pH shift on the $\delta^{11}B$ and thus $\delta^{11}B_3$ of evaporating seawater.

3.2.3. Experiment 3

The results derived from experiment 1 may suffer from measurement errors due to the very low boron concentrations of the condensate. The purpose of experiment 3 was to produce high-precision results by increasing the boron concentration in the condensate using boron-amended seawater. The results listed in Table 1 show that the boron concentration in condensate increased from 5.16 to 42.7 µg/l as the boron concentration in seawater increased from 3.74 µg/ml (normal seawater, experiment 1) to 63.5 µg/ml (experiment 3). The condensates from experiment 3 contained high enough concentrations of boron to run many replicate analyses of the boron isotopes. The measurement precisions for these data are 1.0‰ or better.
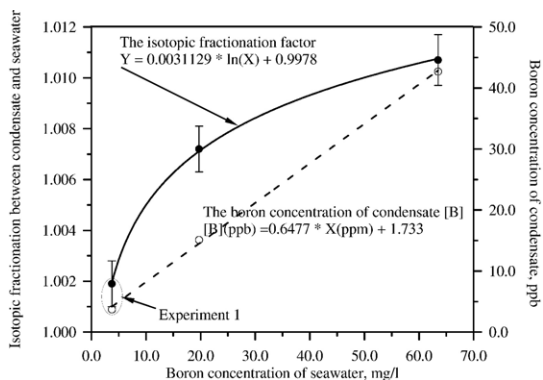
Fig. 7. Isotopic fractionation factors (solid dots) and boron concentrations of condensate (open circles) vs. concentration of boron in boron-amended seawater (experiment 3).

The boron isotopic fractionation factors (α_{c-s}) and boron concentrations of condensate ($C_{B/cond}$) for boron-amended seawater, together with the median isotopic fractionation factor and boron concentration of condensate from experiment 1, are plotted against the boron concentration of boron-amended seawater ($C_{B/sea}$) in Fig. 7. The best-fitting linear relation between $C_{B/cond}$ and $C_{B/sea}$ is as follows:

$$C_{B/cond}(pbb) = 0.6477 \times C_{B/sea}(ppm) + 1.733 \qquad (3)$$

Eq. (3) implies that $C_{B/cond}$ should be 1.733 ppb, corresponding to total boron of 3.466 μg in 2 l of condensate, when $C_{B/sea}$ equates to zero. The 3.466 μg of B is not a contribution from either from sea-salt emission or seawater evaporation due to $C_{B/sea}=0$, or from a boron blank because the measured boron blank is only 86 ng. A possible implication is the presence of an error in the measurement of the boron concentrations. The $\alpha_{c-s}-C_{B/sea}$ data can be fit by the following equation:

$$\alpha_{c-s} = 0.0031129 \times \ln C_{B/sea} + 0.9978 \qquad (4)$$

It is very interesting that the boron isotopic fractionation factor increases with the boron concentration in seawater ($C_{B/sea}$). This increase may be associated with a change in boric acid volatilization, the distribution of boron species in seawater, or the formation of other boron species. The observed relationship between isotopic fractionation and boron concentration could then be interpreted as the result of a competition between opposed equilibrium and kinetic effects affecting B. At higher B concentrations kinetic effects should be less important because there is relatively little need for B transport, so isotopic data

should be closer to the equilibrium value. Equation 4 implies that α_{c-s} is lower than 1 when $C_{B/sea}$ is lower than 2.027 (ppm) and α_{c-s} will approach 0.950 when the boron concentration is very low. Further experimentation is required to both validate this finding and understand the physical processes responsible.

3.3. Isotopic composition of boron in rainwater

In this study, rainfall samples were collected in Xining City and Xijiang (South China Sea), China. Information on the sampling conditions and locations is given in Table 2. Xining City, the capital of Qinghai Province, is very far from the ocean (2000 km distant). The Xijiang sampling location is an oil platform in the South China Sea about 120 km from Hong Kong. The atmospheric environment of the Xijiang oil platform is influenced to varying degrees by the mainland and ocean, depending on the wind direction. The measured $\delta^{11}B_{rian}$ values, together with the concentrations of boron and chlorine, are shown in Table 2. The $\delta^{11}B_{rain}$ values for Xining City rainfall collected on different days with different wind directions are similar (9.0‰ and 12.1‰). This suggests that the atmosphere in Xining is not strongly affected by the ocean. The $\delta^{11}B_{rain}$ values for rainfall from the Xijiang sampling location, however, change significantly (8.4‰ and 33.2‰) with wind direction. The $\delta^{11}B_{rian}$ values for Xijiang rainfall suggest that the mainland has a significant effect on the local atmosphere when the wind direction is from the west, while the ocean is more important when the wind direction is from the southeast.

As noted in the introduction Miyata et al. (2000) suggested that non-equilibrium kinetic processes may control boron isotopic fractionation during evaporation of seawater, as is the case for oxygen isotope enrichment of water by evaporation (Lloyd, 1966). The present study, however, suggests that non-equilibrium kinetic processes in seawater evaporation are insignificant under calm conditions, but isotopic exchange between $B(OH)_3$ and $B(OH)_4^-$ in solution plays an important role. The $\delta^{11}B_{rain}$ value observed in rainfall by Miyata et al. (2000) ranges from 18.9‰ to 34.7‰, and their higher $\delta^{11}B$ values (32.7‰ and 34.7‰) are virtually the same as that of Xijiang rainwater (33.2‰) when the wind is from the southeast (Fig. 8). This may imply that boron with high $\delta^{11}B$ values in rainfalls for Miyata's study and this study have maritime sources. The isotopic ratios of boron in rainwater collected from southern Britain reported by Mather and Porteous (2001) are highly variable and can be unpredictable, ranging from −13‰ to 48‰ (Fig. 8). Mather and Porteous (2001) indicated
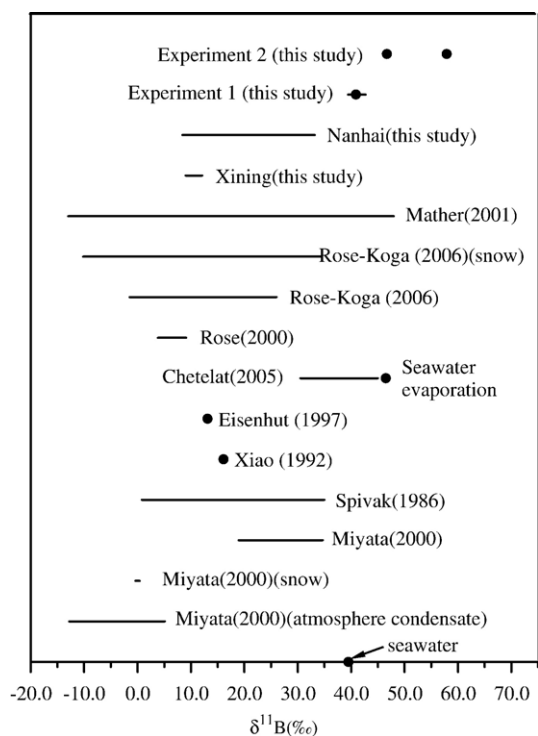
Fig. 8. Published isotopic compositions of boron in rainwater.

that the enriched signatures may be representative of Atlantic air over Britain.

Previously published boron isotopic data for precipitates show a wide range of variability, but most of the $\delta^{11}B$ values reported are lower than that of seawater (Fig. 8). This indicates that boron in the atmosphere of continental interior and coastal regions 1) is influenced by continental sources, which can also impact the oceanic atmosphere by means of offshore winds; 2) has a reduced $\delta^{11}B$ ratio due to condensation events, which may preferentially remove ^{11}B; 3) has been extracted from seawater under airflow conditions, resulting in non-equilibrium kinetic fractionation and the enrichment of ^{10}B in the air; or 4) is affected by some combination of the foregoing factors. Consideration of the sea-spray component would not shift the boron isotopic composition of the atmosphere below that of seawater, if the sea-spray component enters directly into atmosphere as do most fine drops.

3.4. The effect of evaporation on the boron isotopic composition of seawater

Boron is removed from seawater by: (1) uptake during low-temperature alteration of the oceanic crust, (2) adsorption on clastic sediments, and (3) co-precipitation

in biogenic carbonates (Lemarchand et al., 2000, 2002). Each of these boron uptake processes is characterized by a preferential removal of ^{10}B. Boron is also removed from the ocean by the evaporation of seawater (Gast and Thompson, 1959; Savenko, 1977; Fogg and Duce, 1985; this study). Only boron uptake from seawater by evaporation under quiet air conditions is characterized by a preferential removal of ^{11}B. About 3.34×10^5 cubic kilometers of seawater are evaporated from the ocean each year, about 80% of which passes through the atmosphere and returns directly to the ocean as precipitation. [1] The remaining 20% is transferred to continental land, and most of this vapor is then returned to the ocean through rivers. All in all, less than 6.45×10^4 km^3 of seawater per year are removed as vapor from the ocean and perhaps go down into the deep earth. Based on a boron concentration of 3.71 μg/l (or 3.71 mg/m^3) in the condensate of seawater having a normal pH value (see Table 1) and the isotopic data from this study, the total amount of boron removed is less than 2.39×10^{11} g/yr with a mean isotopic composition of 41.0‰ (assuming that most is removed under quiet air conditions). The boron removed by seawater evaporation is significant compared with other uptakes (Lemarchand et al., 2000). The ocean holds 1.37×10^9 km^3 of seawater[1] and 6.16×10^{18} g of boron (assuming that the average boron concentration in seawater is 4.5 ppm), with a mean isotopic composition of 39.5‰ (Spivack and Edmond, 1987). Given an α_{c-s} of 1.0020 between vapor and seawater during evaporation under calm conditions, we can estimate that the $\delta^{11}B$ value of seawater would decrease through evaporation by less than 0.06‰/Myr. We believe therefore that the effect of boron isotopic fractionation on the isotopic composition during seawater evaporation is insignificant on human timescales.

4. Conclusions

The enrichment of ^{11}B in vapor produced during the seawater evaporation air under quiet air conditions is established and quantified. The isotopic fractionation factors between condensate and seawater range from 1.0004 to 1.0036 in the pH range examined. The α_{c-s} value increases with boron concentration in boron-amended seawater.

Mixing of oceanic and continental boron sources and fractionation during evaporation and condensation together probably cause the large $^{11}B/^{10}B$ variations observed in the atmosphere and precipitation. The

---

[1] Oceanic data are from Canadian Waters, at the web site (http://www.dfo-mpo.gc.ca/canwaters-eauxcan/index_ e.asp).

isotopic fractionation of boron during the seawater evaporation should have had only a minor effect on the boron isotopic composition of seawater over time, due to low isotopic fractionation and most of the boron that leaves the ocean by bubble bursting or evaporated is very quickly returned to the ocean.

Acknowledgements

References

Bruyevich, S.V., Korzh, V.D., 1971. Boron exchange between the sea and the atmosphere. Oceanology 11, 345–351.

Chetelat, B., Gaillardet, J., Freydie, rR., Négrel, Ph., 2005. Boron isotopes in precipitation: experimental constraints and field evidence from French Guiana. Earth Planet. Sci. Lett. 235, 16–30.

Christopher, S., Martens, C., Harriss, R., 1976. Boron in coastal North Florida rainfall. J. Geophys. Res. 81, 6371–6375.

Dickson, A.G., 1990. Thermodynamics of the dissociation of boric acid in synthetic seawater from 273.15 to 318.15 K. Deep-Sea Res. 37 (5), 755–766.

Eisenhut, S., Heumann, K.G., 1997. Identification of ground water contaminations by landfills using precise boron isotope ratio measurements with negative thermal ionization mass spectrometry. Fresenius' J. Anal. Chem. 359, 375–377.

Fogg, T.R., Duce, R.A., 1985. Boron in the troposphere: distribution and fluxes. J. Geophys. Res. 90, 3781–3796.

Fogg, T.R., Duce, R.A., Fasching, J.L., 1983. Sampling and determination of boron in the atmosphere. Anal. Chem. 55, 2179–2184.

Gast, J.A., Thompson, T.G., 1959. Evaporation of boric acid from seawater. Tellus 6, 344–347.

Kakihana, H., Kotaka, M., Satoh, S., Nomura, M., Okamoto, M., 1977. Fundamental studies on the ion-exchange separation of boron isotopes. Bull. Chem. Soc. Jpn. 50, 158–163.

Kiss, E., 1988. Ion-exchange separation and spectrophotometric determination of boron in geological materials. Anal. Chim. Acta 211, 243–256.

Lemarchand, D., Gaillardet, J., Lewin, È., Allègre, C.J., 2000. The influence of rivers on marine boron isotopes and implications for reconstructing past ocean pH. Nature 408, 21–28.

Lemarchand, D., Gaillardet, J., Lewin, È., Allègre, C.J., 2002. Boron isotope systematics in large rivers: implications for the marine boron budget and paleo-pH reconstruction over the Cenozoic. Chem. Geol. 190, 123–140.

Lloyd, R.M., 1966. Oxygen isotope enrichment of sea water by evaporation. Geochim. Cosmochim. Acta 30, 801–814.

Mather, J.D., Porteous, N.C., 2001. The geochemistry of boron and its isotopes in groundwaters from marine and non-marine sandstone aquifers. Appl. Geochem. 16, 821–834.

Miyata, Y., Tokieda, T., Amakawa, H., Uematsu, M., Nozaki, Y., 2000. Boron isotope variations in the atmosphere. Tellus 52 B, 1057–1065.

Nishimura, M., Tanaka, K., 1972. Seawater may not be a source of boron in the atmosphere. J. Geophys. Res. 77, 5239–5242.

Rose, E.F., Chaussidon, M., France-Lanord, C., 2000. Fractionation of boron isotopes during erosion processes: the example of Himalayan rivers. Geochim. Cosmochim. Acta 64 (3), 397–408.

Rose-Koga, E.F., Sheppard, S.M.F., Chaussidon, M., Carignan, J., 2006. Boron isotopic composition of atmospheric precipitations and liquid-vapour fractionations. Geochim. Cosmochim. Acta 70, 1603–1615.

Savenko, V.S., 1977. Is boric acid evaporation from sea water the major boron source in the atmosphere? Oceanology 17, 290–292.

Spivack, A.J., 1986. Boron isotope geochemistry. PhD Thesis. MIT-WHOI Joint Program in Oceanography. Cambridge, Massachusetts, USA.

Spivack, A.J., Edmond, J.M., 1987. Boron isotope exchange between seawater and the oceanic crust. Geochim. Cosmochim. Acta 51, 1033–1043.

Wang, Q.Z., Xiao, Y.K., Wang, Y.H., Zhang, C.G., Wei, H.Z., 2002. Boron separation by the two-step ion-exchange for the isotopic measurement of boron. Chin. J. Chem. 20, 45–50.

Vengosh, A., Starinsky, A., Kolodny, Y., Chivas, A.R., McCulloch, M.T., 1992. Boron isotope variations during fractional evaporation of seawater: new constraints on the marine vs. nonmarine debate. Geology 20, 799–802.

Xiao, Y.K., Zhang, C.G., 1992. High precision isotopic measurement of chlorine by thermal ionization mass spectrometry of the Cs_2Cl^+ ion. Int. J. Mass Spectrom. Ion Process. 116, 183–192.

Xiao, Y.K., Beary, E.S., Fassett, J.D., 1988. An improved method for the high-precision isotopic measurement of boron by thermal ionization mass spectrometry. Int. J. Mass Spectrom. Ion Process. 85, 203–213.

Xiao, Y.K., Sun, D.P., Wang, Y.H., Qi, H.P., Jin, L., 1992. Boron isotopic composition of brine, sediments, and source water in Da Qaidam Lake, Qinghai, China. Geochim. Cosmochim. Acta 56, 1561–1568.

Xiao, Y.K., Vocke, R.D., Swihart, G.H., Xiao, Y., 1997. Boron volatilization and its isotope fractionation during evaporation of boron solution. Anal. Chem. 69 (12), 5203–5207.

Xiao, Y.K., Swihart, G.H., Xiao, Y., Vocke, R.D., 2001a. A preliminary experimental study of the boron concentration in vapor and the isotopic fractionation of boron between seawater and vapor during evaporation of seawater. Sci. China, Ser B Chem. Life Sci. Earth Sci. 44 (5), 540–551.

Xiao, Y.K., Sun, A.D., Liao, B.Y., Zhang, C.G., 2001b. Super clean evaporation oven, Chinese patent (No ZL 01 2 73759.3).