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A preliminary experimental study of the boron concentration in vapor and the isotopic fractionation of boron between seawater and vapor during evaporation of seawater

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Abstract A laboratory experiment was undertaken to investigate the behaviour of boron at the seawater-air interface under air flow conditions. Dried air at 25 and 35℃ was passed over or bubbled through seawater at the same temperature. A combination of ice-chilled condensers and KOH impregnated cellulose fibre filters was used to collect boron from the reacted air. When air stripped of boron was passed over the seawater, boron was found in the reacted air, and its concentration was higher in the higher temperature test. In the tests where air was bubbled through seawater the concentration of boron in the reacted air was directly proportional to the air flow rate. In this situation the boron in the reacted air was mainly introduced as a spray of microdroplets. Isotopic analysis of the collected boron in the non-bubbled tests yields fractionation factors which demonstrate that the lighter isotope, ^{10}B, is enriched in the reacted air. The size of the fractionation changes with temperature, ruling out a purely kinetic effect.

Keywords: boron isotope, isotopic fractionation, evaporation, seawater.

Several experimental investigations of the volatility of boron at the seawater-air interface have been made in the past four decades. Earlier work was reviewed by Gast et al.[1]. Gast et al. passed air over seawater in a polyethylene bottle and recovered vapor with a condenser. They found that as much as 65 μg B/L was present in the condensate. From this result they postulated that most of the boron content of the atmosphere, and thus of rain and snow, is a result of evaporation from seawater. Nishimura et al.[2] conducted a similar experiment to that of Gast et al., but using seawater with 20—60 times normal boron concentration of seawater. By extrapolating their results down to 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. Comparing these results with a measured boron content of (4.7±1.1) μg B/L in precipitation over the sea, Nishimura et al.[2] concluded that the sea is not a source but rather a sink of atmospheric boron. More recently, Fogg et al.[3] used a simple KOH impregnated filter sampling system for collecting boron from the atmosphere. Using this system atmospheric boron was separated into gaseous and particulate components. Fogg et al.[4] determined gaseous boron concentrations in the atmosphere in various locations ranging from 1 to 223 ng/m^3 of air. The latter paper also provides a good review of the literature on boron in precipitation, and gaseous and particulate boron in the atmosphere.

An experimental study of boron isotopic fractionation during supercritical phase separation was conducted by Spivack et al.[5]. The results indicated an equilibrium fractionation of less than 0.05% between vapor and brine phases, which is much smaller than the predicted fractionation of approximately 0.8% between trigonal and tetrahedral boron. This result suggests that the proportion of trigonal to tetrahedral boron species was similar in the two phases. An experimental determination of the equilibrium fractionation of the boron isotopes between tourmaline and aqueous vapor[6] showed that the heavy isotope, ^{11}B, was preferentially partitioned into the vapor phase and the extent of fractionation was inversely dependent on temperature. An experiment with high-silica melt also produced hydrous vapor enriched in heavy boron[7].

No investigation of the isotopic fractionation of boron between seawater and vapor has been reported. Many studies on isotopic composition of oxygen and hydrogen in precipitation have been carried out[8,9], however, very few isotopic data for boron in precipitation have been reported and there are no isotopic data for boron in the atmosphere, probably due to the difficulties in sampling and precise determination of low concentrations of boron. This paper reports on the boron concentration and isotopic composition of air blown over or through seawater at 25 and 35℃. The results should be useful in the study of the sources of boron in the atmosphere and precipitation.

1 Experimental methods

1.1 Standards and reagents

All chemicals used were of analytical or higher grade. The Gulf of Mexico seawater used was purchased commercially. Low boron deionized water with a concentration of 0.6 ng B/mL was obtained by passing distilled/deionized water through a boron specific resin column. All solutions were made, stored, and used in plastic containers.

1.2 Filter preparation

The filter preparation procedure was essentially the same as that described by Fogg et al.[3]. Gelman 37 mm cellulose fiber filters were dipped into a 0.5 mol • L^{-1} KOH solution for 5 s and then placed in an oven to dry for about 1 h at 60℃ under a stream of filtered air. The KOH impregnated filters were used for†vapor phase boron collection. Porotic polycarbonate membranes (37 mm diameter, 0.4 mm pore size) were directly used for particulate filtration. In this study the intent was to isolate and analyze the gaseous boron. The gaseous boron portion may contain particulate boron where the particles are less than the pore size of the membrane filter.

1.3 Evaporation of seawater

When seawater evaporates the vapor may contain small quantities of boron of a different isotopic composition from that in seawater. To investigate this problem an experimental apparatus, shown in fig. 1, was assembled. Air from a building-wide compressed air system was utilized in this experiment. Forcing air through the experimental apparatus, rather than drawing it by vacuum, assured a positive pressure within the apparatus and thus eliminated the possibility of boron-containing laboratory air being drawn into the system through a leak. The building compressed air supply was initially purified at its source by passage through a condensing unit and an oil filter. In the laboratory, the building compressed air was further purified and stripped of boron by bubbling through low boron water (fig. 1), followed by passage through an ice-chilled condenser (condenser 1), three KOH impregnated cellulose filters, and a polycarbonate membrane. Before each experiment runs, the entire apparatus was purged using low boron water in the reaction vessel instead of seawater.

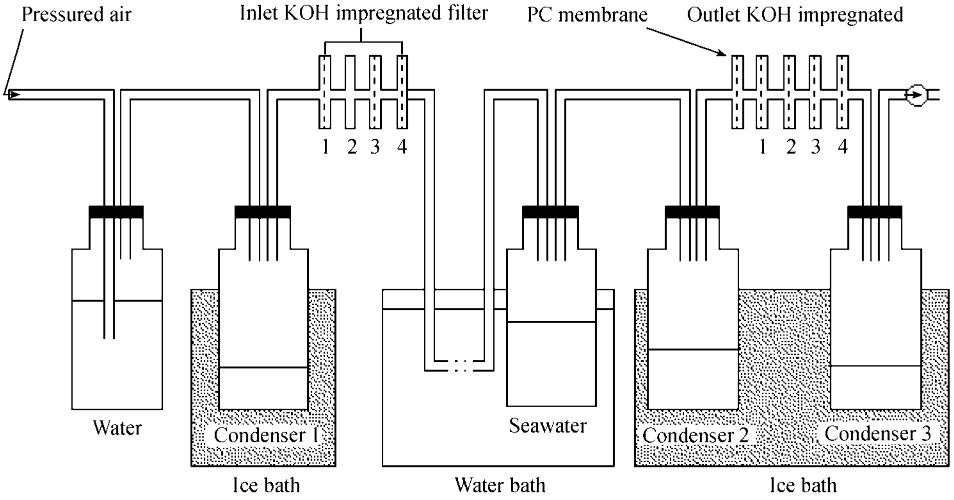

Fig. 1. The seawater-vapor experimental apparatus.

Low boron and dried air was blown across the surface of a seawater sample in non-bubbling tests, and through the seawater in bubbling tests. The seawater-air reaction vessel was filled with 1800 mL of seawater and placed in a water bath with a constant temperature. Experiments were conducted at (25±0.5) and (35±0.5)℃. Feed air was warmed prior to entering the reaction vessel by passing through a large coil of plastic tubing immersed in the water bath (fig. 1). The results of a solar pan seawater evaporation experiment carried out by Vengosh et al.[8] indicated that ^{11}B was enriched in the residual brine due to preferential co-precipitation of ^{10}B with salts. Consequently, in the present experiment low boron water was intermittently added to the seawater reaction vessel to maintain the volume and salinity of the seawater sample throughout an experimental run.

Boron in vapor extracted from the seawater reaction vessel was collected in an ice-chilled condenser (condenser 2), four KOH impregnated cellulose fiber filters, and a final ice-chilled condenser (condenser 3). The combination of the first ice-chilled condenser on the outlet side of the seawater reaction vessel and the KOH impregnated filters ensured nearly complete recovery of boron from the vapor. The final ice-chilled condenser was used to determine the amount of boron in the air not collected by the preceding condenser and filters. The air exited the apparatus through a flow meter (fig. 1) used to monitor air flow rate variations during the course of experimental runs. Individual reaction runs ranged from 8 to 13 d in length and air flow rates of 4.2 and 5.3 L/min were investigated.

1.4 Separation of boron

The boron trapped on the KOH impregnated filters was leached for more than 2 h with low boron water and then added to condensate collected in condenser 2. In preparation for isotopic measurement, boron was extracted from reacted seawater and condensate using an ion exchange technique. About 1 mL of boron-specific Amberlite IRA 743 resin (80—100 mesh) was placed into a 0.4 cm diameter polyethylene column. The length of the resin bed was 5.5 cm. The sample solution was passed through the column at a flow rate of 0.5—0.8 mL/min. The boron held by the resin was eluted using approximately 10 mL of 0.1 mol/L HCl at 75℃. An amount of mannitol approximately equimolar to the boron content was added to the eluate and concentrated by partial evaporation in an oven at 60℃ under laboratory air drawn through four KOH impregnated filters. Further details of the preparation procedures for isotopic analysis are described elsewhere[10,11].

1.5 Boron blanks

Boron blanks were very important in this study because of the very small quantities of boron were collected from the vapor. Two kinds of blanks were measured. One was the chemical processing blank mainly coming from the boron separation procedures described above. The chemical processing blank was collected using the same procedures as for a sample, but using low boron water instead of a sample solution. The chemical processing blank was measured to be 68 ng B per sample by isotope dilution mass spectrometry (IDMS).

The other blank was a total blank originating from both the evaporation apparatus and subsequent boron separation procedures. To determine the total blank, the experimental apparatus was initially cleaned with 2 mol/L HCl solution and then with high purity, low boron water. Sixty stere of purified air was blown at (4.2±0.5) L/min through the reaction vessel which contained 1500 mL of low boron water at 25℃. The boron collected by two KOH impregnated filters (inlets 1 and 2) situated in the line upflow from the reaction vessel was measured. This represents the level of boron in the building compressed air system.

The portion of the total blank contributed by the experimental apparatus was collected by two KOH impregnated filters (outlets 3 and 4 in table 1) situated in the line down-flow from the reaction vessel. The boron collected by each filter or filter pair was dissolved in water, extracted by the above-described separation procedures, and then measured by the IDMS method. The results in table 1 show that the total blank, which includes the chemical processing blank, is almost the same as the chemical processing blank alone. This means that the boron blank from the experimental reaction apparatus alone was very low. The total boron blank in this test was 70 ng B.

Table 1 Boron blank of the evaporation apparatus[a)]

	T / ℃	Time /h	Air flow rate /L • min^{-1}	V_{air}/m^3	Boron blank/ng		
					filter inlet 1	filter inlet 2	filters outlet 3 & outlet 4
NB[b)]	25	240	4.2	60.0	72	55	70

Reaction vessel containing purified water instead of seawater. Analyzed by IDMS. a) Includes blank of chemical preparation steps for boron measurement; b) NB-non-bubbling run.

1.6 Analytical methods

Most of the concentrations of boron in solution were determined by the azomethine-H spectrophotometric method. A few were determined by IDMS, as noted in the text. For the spectrophotometry, the procedures described by Kiss[12] were followed, with slight modification. 1 mL of boron solution, 2 mL of buffer solution (251 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 sequentially added into a 1.0 cm diameter quartz tube. After being mixed well, the solution was allowed to stand for 30 min and then the absorbance of the boron-azomethine-H complex at 420 nm was measured using a Turner 330 spectrophotometer. The external precision (2σ) of the azomethine-H method used here was 2%.

The isotopic composition of boron in the vapors was measured using a thermal ionization technique[13]. VG 354 and NBS design mass spectrometers were used for isotopic analysis of boron. First, 3 μL of graphite slurry was spread across the whole outgased tantalum filament. Next, 1 μL of sample solution containing approximately 1 μg of boron and an equimolar amount of mannitol were loaded. This was followed by 1 μL of Cs_2CO_3 solution containing an equimolar amount of cesium. The load was dried by heating the filament at 1.2 A for 5 min. The mass spectrometric procedure was essentially the same as that described by Xiao et al.[13]. The internal precision of the isotopic analysis for most samples and NIST SRM 951 boric acid was better than 0.02% (2σ). The boron isotopic compositions of the samples are expressed as $\delta^{11}B$(‰) relative to the NIST SRM 951 standard:

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

2 Results and discussion

2.1 Collection and recovery of boron

Fogg et al.[4] estimated that particulate boron is less than 1% of the total atmospheric boron over the ocean. In the present study only gaseous boron was considered and the experimental apparatus was designed to filter out particulate boron (＞0.4 mm) at its inlet. Fogg et al.[3] showed that gaseous boron in the atmosphere is efficiently collected by KOH impregnated Whatman No. 41 filters. Their experiments demonstrated that at flow rates of 2—4 L/min virtually 100% of the boric acid collected from vapor was on the first KOH impregnated filter.

In the present isotopic experiment it was critical that nearly 100% of the gaseous boron was trapped in order to avoid fractionation effects. Thus boron trapping efficiency of KOH impregnated cellulose fibre filters and ice-chilled condensers was revisited. The trapping efficiency of the impregnated filters was evaluated with the results from the final ice-chilled condenser in the flow line (condenser 3, fig. 1). Using three KOH impregnated filters in series to trap boron, at a flow rate of 10.2 L/min (double more than the rate used in the main experiments) significant boron still was found in condenser 3. The results (table 2) show that un-trapped boron decreases as the number of KOH impregnated filters in series increases.

Table 2 Boron collection efficiency of KOH impregnated filters

	T/℃	Time /h	Air flow rate /L • min^{-1}	$V_{\mathrm{air}}/\mathrm{m}^3$	Filter number	Collected boron /μg		Boron loss [B/(A+B)] (%)
						in filter (A)	in condensate (B)	
NB[a)]	25	120	10	72	2	4.5	0.72	13.7
NB[a)]	25	240	10	144	3	13	0.89	6.6

Analyses of boron concentration by colorimetry. a) NB-non-bubbling runs.

In the main experiments of this study a combination of ice-chilled condensers, KOH impregnated filters, and lower air flow rates were finally used to assure complete trapping of gaseous boron released from seawater. The boron in the vapor exiting in the seawater reaction vessel initially encountered an ice-chilled condenser (condenser 2, fig. 1) and then four KOH impregnated filters. The boron in a final condenser (condenser 3, fig. 1) was determined to be 0.0 μg in both non-bubbling runs and 0.1 μg in both bubbling runs. These various tests demonstrate that the collection efficiency of boron from vapor produced without bubbling (at 25 and 35℃), using one ice-chilled condenser and four KOH impregnated filters, and a flow rate of 4.2 L/min, is essentially 100% (table 3). Both bubbling runs, on the other hand, show some leak through of boron into the final condenser. The amount of leak-through boron, 0.1 μg, was insignificant in comparison to the amounts collected by condenser 2 and the impregnated filters (table 3) and did not compromise the isotopic measurements.

Solutions of various pHs were investigated for recovering boron trapped on the impregnated filters. Known amount of boron in water was deposited on KOH impregnated filters. The filters were dried and then each was leached in 20 mL of acid, neutral or basic aqueous solution. Each leachate was tested for recovery of boron over various time intervals ranging from 10 min to 24 h. The results (table 4) indicate that leaching efficiency is greater for the lower pH solutions. But the boron on the KOH impregnated filters was completely recovered with low boron water when the leaching time was 90 min or more. The boron recovery from impregnated filters leached with basic solutions was lower and inconsistent. In the present study 10 mL of low boron water was used for leaching boron from KOH impregnated filters used in the main experiments. The leaching times were normally more than 2 h.

Table 3 Experimental of seawater evaporation

No.[a)]	T/℃	Time/h	Air flow rate /L • min^{-1}	V_{air}/m^3	Collected condensate			[B]		[Cl] /μg • kg^{-1}	[Cl]/[B] mole ratio ×10^3	Boron in cond 3
					weight /kg	pH	Boron /μg [b)]	in cond 2 /μg • kg^{-1}	in air /ng • m^{-3}			
Seawater						7.94					1.41	
NB25	25	287	4.2	71.8	0.843	6.14	5.24	6.2	72			0
NB35	35	217	4.2	54.2	0.944	5.86	4.15	4.4	76	60.2	0.042	0
B25	25	319	5.3	102	1.088	6.32	43.1	40	420	182000	1.40	0.10
B35	35	189	4.2	47.3	0.953	6.09	16.0	17	340	64100	1.16	0.10

Analyses of boron concentration by colorimetry. a) NB-non-bubbling runs; B-bubbling runs; b) total collected boron, including boron in condenser 2 and in KOH impregnated filters.

Table 4 Boron recovery (%) from KOH impregnated filters as a function of pH of the leaching solution

Solution	Final pH	Leaching time/min								
		10	20	40	60	90	120	300	600	1440
HCl	2	88.1	99.1	99.0	99.9	99.0		98.9	97.6	98.4
H_2O	10	83.5	97.3	100.0	96.6	99.1	98.1	100.1	101.2	98.5
KOH	12	83.8	89.3	94.3	93.4	93.8	98.6	98.8		95.1

Analyses of boron concentration by colorimetry.

2.2 Boron in vapor evaporated from seawater

Table 3 summarizes the results obtained from the collection of gaseous boron produced during evaporation of seawater. In the present study condensate collected was more than that in the studies of Gast et al.[1] and Nishimura et al.[2]. The data show that (i) the boron concentrations in the vapor from the non-bubbling tests are much lower than those from the bubbling tests; (ii) the pH values of the condensates are lower than that of the seawater; (iii) the pH values of the condensates in the non-bubbling tests are lower than those in the bubbling tests at the same temperatures, suggesting that a direct fine spray of seawater was carried out with the vapor in the bubbling tests; and (iv) the boron concentration in the vapor increases with the temperature of the seawater in the non-bubbling tests, but in the bubbling tests is mainly controlled by the air flow rate. The higher pH value of the condensate in the higher flow rate bubbling test also suggests that a larger fraction of seawater microdroplets sprayed into the vapor.

In order to pursue the question of seawater microdroplet incorporation in the vapor flow, chlorine concentration in the condensates was measured by IDMS. Chlorine isotopic measurements were made following the methods described by Xiao et al.[14]. As shown in table 3, the Cl/B mole ratio of the condensate from the bubbling experiment run at the higher air flow rate is nearly the same as that of the seawater sample. The ratio from the lower flow rate bubbling run is somewhat less than that of the seawater. But the ratio from the non-bubbling run at 35℃ is completely different from that of the seawater sample. It is apparent that during the bubbling runs seawater microdroplets were drawn out of the reaction vessel with the vapor flow.

The boron concentrations in the condensates (with the KOH filter extracts included) obtained in the non-bubbling tests at 25 and 35℃ are 6.2 and 4.4 μg/kg, respectively, which are higher than the 1.1 μg/L estimated by Nishimura et al.[2] and much lower than the 60—65 μg/L obtained by Gast et al.[1]. Boron concentrations in precipitation have been reported in a number of studies[2, 4, 15, 16]. The measurements in these studies defined a wide range from 0.3 to 38 μg B/L. Bruyevich et al.[15] reported concentrations of boron in condensates collected in the Black Sea region to be a minimum of 4 μg B/L and a maximum of 32 μg B/L during offshore and onshore winds, respectively. These values are well agreement with the 4.4 and 6.2 μg B/kg obtained here for the non-bubbling tests and 17 and 40 μg B/kg for the bubbling tests, suggesting that sea spray is a major source of boron in precipitation over the oceans and coastal areas.

2.3 Boron isotopic composition of vapor evaporated from seawater

The total boron blank determined in this work was 70 ng B which is 0.16%—1.7% of the boron collected from the vapors. Any effect of this blank on the isotopic composition of boron in the vapor should be within the external precision of the isotopic measurement, and can thus be ignored. The δ^{11}B values of boron collected from vapor evaporated from seawater at 25 and 35 °C are shown in table 5. Due to the small amount of boron removed into the vapor during each run compared to the amount in the seawater sample, the boron isotopic composition of the seawater remained unchanged. The data demonstrate an isotopic fractionation of boron between seawater and vapor, with $\alpha_{\text{(vapor-seawater)}} = (\delta^{11}\text{B}_{\text{vapor}}+1000) / (\delta^{11}\text{B}_{\text{seawater}}+1000)$ for the non-bubbling tests equaling 0.9902 at 25℃ and 0.9845 at 35℃, and for the bubbling tests equaling 0.9983 at 25℃ and 0.9986 at 35℃. The extent of fractionation in the non-bubbling tests is much larger than that in the bubbling tests. The light isotope, ^{10}B, was enriched in the vapor in all the tests.

Table 5 Isotopic composition of boron in vapor evaporated from seawater

Samples	Measured δ^{11}B (‰)	Average δ^{11}B（2σ）	α a)
Seawater (before experiment)	38.8, 38.9	38.8	
Seawater (after experiment)	39.1, 38.9, 38.6, 38.8	38.8 (4)	
NB25	28.6, 28.7, 28.7	28.7 (1)	0.9902
NB35	22.9, 22.6	22.7	0.9845
B25	37.4, 36.9	37.1	0.9983
B35	36.8, 37.8	37.3	0.9986

a) The isotopic fractionation factor defined as $\alpha = (\delta^{11}B_{\text{vapor}}+1000) / (\delta^{11}B_{\text{seawater}}+1000)$.

The apparent isotopic fractionations between seawater and vapor for the bubbling tests are smaller than that for the non-bubbling tests. In line with the pH and Cl/B data presented above, this result also indicates that in the bubbling tests some boron without fractionation from seawater was introduced into the vapor stream. The fractions of vapor boron (B_v) and boron carried in fine seawater droplets (B_d) in the bubbling tests can be estimated as follows:

$$(\delta^{11}B_{mixed}+1000) = a\,(\delta^{11}B_v+1000) + b\,(\delta^{11}B_d+1000),$$

where a and b are the fractions of vapor boron and microdroplet boron, and $\delta^{11}B_{mixed}$, $\delta^{11}B_v$ and $\delta^{11}B_d$ are the isotopic compositions of boron measured in the bubbling test, non-bubbling test and seawater, respectively, equal 37.1‰, 28.7‰ and 38.8‰ at 25℃, and 37.3‰, 22.7‰ and 38.8‰ at 35℃, respectively. Accordingly, a and b are calculated to be 0.168 and 0.832 at 25℃, and 0.093 and 0.907 at 35℃. This demonstrates that the boron collected in the bubbling tests predominantly originates from fine seawater droplets incorporated in the vapor flow.

The isotopic resulting from the non-bubbling tests must be considered in the context of chemical and kinetic fractionations. Boron is present as $B(OH)_3$ and $B(OH)_4^-$ in seawater. The boric acid-borate apparent dissociation constant was determined by Byrne et al.[17] to be 8.73 in seawater of 36.47‰ salinity at 25℃. The $B(OH)_3/B(OH)_4^-$ ratio is dependent on the pH value of seawater. Based on the dissociation constant of Byrne et al.[17], approximately 86% of the dissolved boron was three-coordinated in the seawater of the present study (at 25℃), which has a pH value of 7.94.

Kakihana et al.[18] determined an isotopic fractionation factor of 1.0194 for trigonal and tetrahedral boron at 25℃. If it is assumed that boron escapes from seawater solely as $B(OH)_3$, without fractionation between the liquid and vapor $B(OH)_3$, the $\delta^{11}B$ of boron in vapor derived from seawater with a $\delta^{11}B$ of 38.8‰ was calculated to be 41.6‰. This would give isotopic fractionation $\alpha_{(vapor\text{-}seawater)}$ of 1.0028, meaning that ^{11}B would be enriched in the vapor relative to the seawater. The non-bubbling tests, however, resulted in $\alpha_{(vapor\text{-}seawater)}$ factors of less than 1, indicating that ^{10}B was enriched in the vapor (fig. 2). Consequently, fractionation may be caused by a kinetic factor during evaporation of seawater. This result is different from that of boron isotopic fractionation between vapor and brine during supercritical phase separation reported by Spivack[5]. The data obtained by Spivack indicate that boron isotopic fractionation between vapor and brine separated under supercritical condition is less than 0.5‰. A conclusion was educed based on the data that the trigonal /tetrahedral speciation of boron is similar in the two phases. Apparently, the kinetic effect of isotopic fractionation is not present in this experiment due to equilibrium of phase separation to be achieved. The result in this study is reverse comparing with that of isotopic fractionation of boron between tourmaline and aqueous vapor reported by Palmer et al.[6]. The Palmer’s experiment indicated that boron isotopic fractionations between tourmaline and aqueous vapor over the P-T range 50—200 MPa and 350—750℃ range from 1.00225 to 1.00844, indi-

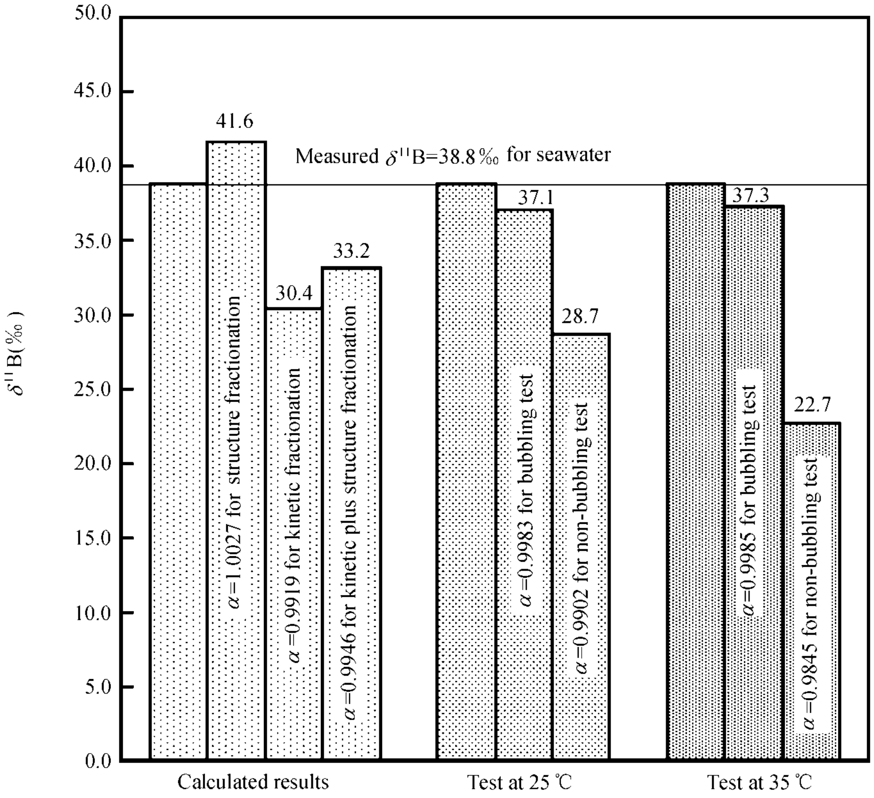

Fig. 2. The measured fractionation factors of the boron isotopes between seawater and vapor. Also shown is a calculated result for a model where only $B(OH)_3$ is volatilized, with no fractionation between the liquid and vapor species.

cating an enrich of ^{11}B in aqueous vapor. Palmer believed that the synthesis experiments employed were valid as near-equilibrium results and no kinetic effects on isotopic fractionation of boron.

A kinetic effect on boron isotopic fractionation should be considered likely during evaporation of seawater because the equilibrium of isotope exchange between seawater and vapor was not established in this study. The light isotopic species, $^{10}B(OH)_3$, would escape from the seawater surface more quickly than the heavy isotopic species, $^{11}B(OH)_3$, with an isotopic fractionation proportional to the square root of the mass ratio of the two species, which is 0.9919 resulting a $\delta^{11}B$ of 30.4‰ for gaseous boron. This value is comparative with the observed $\delta^{11}B$ value of 28.7‰ at 25℃, but is discrepancy from the observed $\delta^{11}B$ value of 22.7‰ at 35℃. When chemical and kinetic effects are considered simultaneously the calculated $\delta^{11}B$ is to be 33.2‰ (fig. 2), which is much higher than the observed values of 28.7‰ at 25℃, indicating that the kinetic effect on isotopic fractionation of boron during evaporation of seawater in non-equilibrium condition is primary. The differences of the observed $\delta^{11}B$ value of 28.7‰ at 25℃ and 22.7‰ at 35℃ from calculated $\delta^{11}B$ of 30.4‰ may come from small boron blank having low $\delta^{11}B$ value comparing to seawater. The isotopic composition of boron blank cannot be measured accurately because of very little amount. The isotopic composition of boron blank, however, may be took for an average value of continental materials with much lower δ^{11}B value than that of vapor. The δ^{11}B value in vapor should be reduced by boron blank in vapor. The effect of boron blank on the δ^{11}B value in vapor can be estimated. The δ^{11}B values for non-bubbling tests at 25 and 35℃ were calculated to be 30.0‰ and 29.9‰, respectively, when boron blank of 70 ng having δ^{11}B value of 0.0‰ was introduced. An alteration of 0.5‰ in δ^{11}B value of vapor was introduced by boron blank of 70 ng in this study. The calculated δ^{11}B values of 30.0‰ and 29.9‰ both are higher than the observed δ^{11}B values of 28.7‰ and 22.7‰ for the non-bubbling tests at 25 and 35℃, which suggests that more boron blank may be present.

3 Conclusions

The range of measured concentration of boron in the present experiments where air was blown over or bubbled through seawater (72—420 ng/m^3) is similar to the range of measurements of gaseous boron in the atmosphere reported by Fogg et al.[4] (1—223 ng/m^3). The isotopic composition of boron collected from vapor during evaporation of seawater under air flow conditions (at 25 and 35℃) is distinctly lighter than that of seawater. This indicates that a kinetic effect would be considered primarily for isotopic fractionation of boron during evaporation of seawater. It is clear that experiments allowing back reaction (non-flow conditions) and actual isotopic measurements of vapor collected over the ocean will be necessary for further characterization of the behavior of boron at the seawater-atmosphere interface. But these first experimental data for the isotopic behavior of boron at the seawater-vapor boundary under air flow conditions will be useful in the study of sources of boron in the atmosphere.

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