Tellus (2000), 52B, 1057–1065
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TELLUS
ISSN 0280–6509

Boron isotope variations in the atmosphere

By YOSHIKI MIYATA, TAKAYUKI TOKIEDA**, HIROSHI AMAKAWA, MITSUO UEMATSU and YOSHIYUKI NOZAKI*, *Marine Inorganic Chemistry Division, The Ocean Research Institute, University of Tokyo, Nakano-ku, Tokyo 164-8639, Japan*

(Manuscript received 29 April 1999; in final form 13 December 1999)

ABSTRACT

We report here the first measurements of boron isotope ratios in the maritime atmosphere together with those of precipitation. The $\delta^{11}B$ values of atmospheric condensates in the western North Pacific and Japanese coast and snow in Tokyo range from -12.8 to $+5.1$‰ and from -0.4 to $+0.4$‰, respectively, which are significantly lower than those of rainwater ($+18.9$ to $+34.7$‰) collected mostly over the North Pacific. Since the $^{11}B/^{10}B$ ratios of the atmosphere are lower than those of volcanic emissions ($\delta^{11}B = +2.3$ to $+21.4$‰), we must seek sources for atmospheric boron other than volcanism. We postulate that the sea may be an important supplier for atmospheric boron under some dynamic conditions and that boron isotope fractionation during evaporation from seawater and removal from the atmosphere may account for the large variations of $^{11}B/^{10}B$ ratios observed in the atmosphere and precipitation.

1. Introduction

Boron is a minor constituent of the atmosphere, existing as both gaseous and particulate forms although the former is predominant (Fogg and Duce, 1985). It can be derived from various sources on the earth's surface. According to Fogg and Duce (1985), potential major sources for gaseous boron are degassing from sea salt and volcanic emissions but the present estimates of those fluxes have large uncertainties. Since ocean water and volcanic gas have different $^{11}B/^{10}B$ isotopic compositions ($\delta^{11}B = +40$‰ for seawater (Spivack and Edmond, 1985) and $\delta^{11}B = +2.3$ to $+21.4$ for fumarolic condensates (Kanzaki et al., 1979; Nomura et al., 1982), measurement of boron isotopes in the atmosphere should help us understand the relative contribution of their sources.

Gast and Thompson (1959) were the first who made purposeful laboratory experiments and suggested that boron in the atmosphere is supplied mainly from the sea through evaporation of boric acid. In contrast, Nishimura and Tanaka (1972) and Nishimura et al. (1973) also conducted laboratory experiments using boron enriched seawater and estimated an equilibrium boron concentration relative to normal seawater by extrapolation to be $\sim 19\ ng\ m^{-3}$ which is even lower than the concentrations commonly observed in the atmosphere. Based on the results, they concluded that the sea may not be a source as suggested by Gast and Thompson (1959) but a sink for gaseous boron in the atmosphere. Although this view has generally been accommodated under synoptic conditions, Fogg and Duce (1985) pointed out an interesting mechanism that sea salt particle production under bubble bursting condition and subsequent degassing of boron from the particles can contribute significantly to the boron content in the atmosphere. Thus, investigation on boron isotopic composition of the atmosphere may pro-

* Corresponding author.
e-mail: nozaki@ori.u-tokyo.ac.jp
** Present affiliation: Geochemical Research Department, Meteorological Research Institute, 1-1 Nagamine, Tukuba 305-0052, Japan.

vide new insights into the atmospheric geochemistry of boron.

Recent technological developments using negative thermal ionization mass spectrometry (NTIMS) have greatly simplified the method of boron isotopic measurements with much better ionization efficiencies up to two orders of magnitude (Swihart, 1996). This has enabled us to determine the variation of isotopic ratios in trace amounts of boron in the atmosphere. Here, we describe the first measurements on maritime air, which resulted in relatively low and variable $^{11}B/^{10}B$ ratios, together with their geochemical implications.

2. Methods

Marine air samples were collected on board R. V. Hakuho-Maru during the KH-98-3 cruise (the Canis Minor Expedition; July–August, 1998) in the western North Pacific, and R. V. Tansei-Maru during the KT-98-3 cruise (March, 1998) from Tokyo and Sagami Bays. Some additional air samples were also obtained at shore-based laboratories. Boron in air samples was collected using dry-ice/ethanol cold traps according to the method of Nakaya and Nishimura (1971) and Nishimura and Tanaka (1972). Air samples were passed through two successive traps consisting of a 60 ml Savillex Teflon cylindrical vessel with inlet and outlet tubes which were bathed with ethanol saturated with dry ice ($\sim -74^{\circ}$C) at a flow rate of <1.8 l/min for 1–3 h. To avoid contamination from ships, samplings were done only when wind blew within $\pm 60^{\circ}$ angles from the bow while steaming. Boron was quantitatively trapped together with water vapor in the tubes (Nakaya and Nishimura, 1971). After sampling, the condensate was melted at room temperature, transferred into a pre-cleaned 15 ml Teflon bottle, and stored in a refrigerator at $\sim 5^{\circ}$C until analysis.

Oceanic rain samples were collected on board the commercial ship "SKAUGRAN" (approximately 46 000 tons) during several traverses between western Canada and Japan in 1995 and 1996. Rainwater was collected on a 20 cm diameter funnel-shaped collector installed on the upper deck of "SKAUGURAN" of ~ 20 m above sea level. Immediately after sampling, the rainwater was filtered through 0.2 μm Versapore filter and stored in a refrigerator until analysis. Due to the larger size of the ship, contribution of sea-salt spray to the rain samples was smaller than that of typical research vessels. In addition, some snow samples were collected in the urban area of Musashimurayama and Kodaira cities in Tokyo district for comparison.

The $^{11}B/^{10}B$ isotopic ratio in the atmospheric condensates and precipitation was measured by NTIMS using a Finnigan MAT THQ quadruple mass spectrometer at the Ocean Research Institute (ORI), University of Tokyo. The water sample (10–20 μl each) was directly loaded onto a platinum filament without any pretreatment and gently evaporated to dryness at a low temperature. Then, 1 μg of La in nitrate form (provided by Spex Industry) was also loaded on top of the boron sample on the filament (Zeininger and Heumann, 1983). The isotopic measurements were done at a filament current of 2.1–2.2 A by monitoring mass numbers, 42 ($^{10}BO_2^-$) and 43 ($^{11}BO_2^-$) relative to the baseline of 40.5 with a peak jumping mode. The isobaric interference of cyanogen (CNO^-) was monitored through count rates at mass number 26 (due to CN^-) and eliminated, if necessary, by heating at a lower filament current of ~ 1.95 A. The $^{11}B/^{10}B$ isotopic ratio can be measured with an uncertainty of less than ± 1.0‰ (2σ) at ~ 10 ng level of boron.

Five replicate measurements of the NIST SRM-951 standard gave an average of 4.0009 ± 0.0066 (2σ standard deviation) for the $^{11}B/^{10}B$ isotopic ratio. This value is used to calculate the isotopic compositions of the atmosphere and precipitation samples reported in this paper as $\delta^{11}B$ values according to the equation given by,

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

The errors in the $\delta^{11}B$ values throughout this paper are those propagated from 2σ of individual $^{11}B/^{10}B$ ratio measurements of the samples and the uncertainty of the $^{11}B/^{10}B$ ratio of the NIST SRM-951 standard given above.

Boron concentrations in the atmospheric condensates and precipitation were also determined by NTIMS isotope dilution using the NIST SRM-952 standard (^{10}B-enriched boric acid) as a spike. When compared with the colorimetric

method (Nakaya and Nishimura, 1971), the isotope dilution method has an order of magnitude greater sensitivity with a comparable precision of measurements (ca. $\pm 5\%$).

The chloride concentration in precipitation was measured by anion liquid chromatography.

3. Results

Since boron has only two isotopes, it is impossible to correct for instrumental mass fractionation. Therefore, to cross-check the method relative to the NIST SRM-951 standard, we first measured a seawater sample from the North Pacific (the Kuroshio Current region near Japan). Three determinations gave $\delta^{11}B$ values of $+40.2 \pm 1.8$‰, $+40.6 \pm 1.7$‰, and $+42.1 \pm 1.7$‰. Barth (1993) summarized the literature values and concluded that the $\delta^{11}B$ value for present-day seawater boron to be constant at $+40$‰. Our results are in good agreement with those in literature (Nomura et al., 1982; Spivack and Edmond, 1987, Hemming and Hanson, 1992), and hence practical application of our NTIMS method is significant.

The boron isotopic compositions of rainwater over the North Pacific and Japan Sea are given in Table 1, together with chloride concentrations. The $\delta^{11}B$ values range from $+18.9$ to $+34.7$‰ which are somewhat lower than the seawater value. There seems no correlation between the boron isotope ratio and chloride concentration in our data, although more data are needed for confirmation. Previous data on rainwater are sparse but show a wide range of variability from $+0.8$ to $+35$‰ over the Pacific Ocean (Spivack, 1986), and of $+16.7$‰ in Qinghai, China (Xiao et al., 1992) and $+13.1$‰ in southeast Germany (Eisenhut and Heumann, 1997) (Barth, 1998).

The results on snow samples are given in Table 2. The $\delta^{11}B$ values (-0.4 to $+0.4$‰) are significantly lower than those of above rain samples. No previous data are available on boron isotopes in snow.

The results for the atmospheric condensates obtained over the ocean are given in Table 3. Our fundamental premise is that the data obtained here largely represent vapor- phase boron, since the particulate phase consists of at most only 10% of total boron (Fogg and Duce, 1985; Anderson et al., 1994). The boron concentrations in the marine atmosphere ranged from 18 to 323 ng m^{-3} which are comparable with those reported by Nishimura and Tanaka (1972) and Fogg and Duce (1985). The boron isotopic composition of the atmosphere over the ocean widely varies from -12.8 to $+5.1$‰. Table 4 also gives the boron isotope data of the atmospheric condensates obtained on shore, which ranged in $\delta^{11}B$ from -5.1 to $+7.8$‰. These values of atmospheric boron are significantly lighter than those of seawater and maritime rain.

Table 1. *Boron isotope ratios in oceanic rains*

Sample code	Location	Date	Latitude	Longitude	$^{11}B/^{10}B$ ratio	$\delta^{11}B$ (‰)	Cl (mg/l)
SK05E	N. Pacific	1995.9.18	46°24′N	170°51′W	4.1396 ± 0.0010	$+34.7 \pm 1.7$	200
SK07W	Bering Sea	1995.12.26	53°54′N	174°46′W	4.1318 ± 0.0012	$+32.7 \pm 1.7$	987
SK10E	N. Pacific	1996.4.5	40°13′N	175°00′W	4.0767 ± 0.0023	$+18.9 \pm 1.8$	165
SK10W	N. Pacific	1996.4.24	50°15′N	129°39′W	4.1183 ± 0.0020	$+29.4 \pm 1.8$	26
SK10W′	N. Pacific	1996.4.25	51°51′N	137°08′W	4.0829 ± 0.0024	$+20.5 \pm 1.8$	186
SK12E	Sea of Japan	1996.7.12	40°42′N	139°21′E	4.1194 ± 0.0014	$+29.6 \pm 1.7$	56

Table 2. *Boron isotope ratios in snow collected in Tokyo district*

Sample no.	Date	Location	$^{11}B/^{10}B$ ratio	$\delta^{11}B$ (‰)	Cl (mg/l)
Snow-1	1998.1.15	Musashimurayama City	3.9992 ± 0.0024	-0.4 ± 1.8	2.0
Snow-2	1998.1.15	Musashimurayama City	4.0024 ± 0.0019	$+0.4 \pm 1.7$	0.5
Snow-3	1998.1.14	Kodaira City	4.0027 ± 0.0034	$+0.4 \pm 1.9$	2.5

Table 3. *Boron concentration and isotopic ratio in marine atmosphere*

Sample code	Date	Latitude	Longitude	$^{11}B/^{10}B$ ratio	$\delta^{11}B$ (‰)	B content (ng m^{-3})
KH-98-3 Hakuho-Maru Cruise						
CMB-2	1998.7.15	34°52.1′N	139°47.3′E	3.9530 ± 0.0075	−12.0 ± 2.5	168
CMB-4	1998.7.15	34°41.3′N	139°50.5′E	ND	—	150
CMB-6	1998.7.16	36°25.6′N	142°02.4′E	ND	—	112
CMB-8	1998.7.16	37°25.4′N	142°39.2′E	ND	—	66
CMB-10	1998.7.16	38°47.9′N	143°31.3′E	3.9879 ± 0.0024	−3.2 ± 1.8	44
CMB-12	1998.7.17	40°53.3′N	144°51.3′E	3.9747 ± 0.0019	−6.5 ± 1.7	44
CMB-18	1998.7.18	43°08.1′N	150°11.4′E	3.9735 ± 0.0016	−6.8 ± 1.7	ND
CMB-20	1998.7.18	43°46.3′N	153°42.1′E	3.9813 ± 0.0023	−4.9 ± 1.7	35
CMB-22	1998.7.21	45°23.1′N	153°10.2′E	ND	—	27
CMB-24	1998.7.21	46°38.6′N	151°30.9′E	3.9968 ± 0.0019	−1.0 ± 1.7	18
CMB-26	1998.7.22	45°24.9′N	145°04.9′E	4.0213 ± 0.0024	+5.1 ± 1.8	ND
CMB-28	1998.7.24	45°06.6′N	143°22.1′E	4.0091 ± 0.0022	+2.1 ± 1.7	19
CMB-30	1998.7.31	43°11.9′N	141°00.1′E	3.9781 ± 0.0017	−5.7 ± 1.7	25
CMB-34	1998.8.5	40°01.3′N	135°15.7′E	3.9497 ± 0.0021	−12.8 ± 1.7	72
CMB-36	1998.8.7	41°20.2′N	140°28.7′E	ND	—	130
CMB-40	1998.8.12	35°26.7′N	139°39.5′E	3.9631 ± 0.0029	−9.5 ± 1.8	323
KT-98-3 Tansei-Maru Cruise						
KT98-3-05	1998.3.12	Sagami Bay		3.9465 ± 0.0015	−13.6 ± 1.7	ND
KT98-3-06	1998.3.13	Tokyo Bay		3.9766 ± 0.0006	−6.1 ± 1.6	ND
KT98-3-07	1998.3.14	Tokyo Bay		3.9740 ± 0.0010	−6.7 ± 1.7	ND

* ND: not determined.

Table 4. *Boron content and isotopic ratio in the air samples collected on shore*

Sample code	Date	Location	$^{11}B/^{10}B$ ratio	$\delta^{11}B$ (‰)	B content (ng m^{-3})
TBH-1	1997.10.8	Harumi pier, Tokyo Bay	4.0089 ± 0.0084	+2.0 ± 2.7	ND
TBH-3	1997.10.8	Harumi pier, Tokyo Bay	4.0321 ± 0.0038	+7.8 ± 1.9	ND
TBH-4	1997.10.8	Harumi pier, Tokyo Bay	4.0134 ± 0.0041	+3.1 ± 1.9	ND
TBH-6	1997.10.9	Harumi pier, Tokyo Bay	4.0181 ± 0.0048	+4.3 ± 2.0	ND
TBH-7	1997.10.9	Harumi pier, Tokyo Bay	4.0202 ± 0.0053	+4.8 ± 2.1	ND
TBH-9	1997.10.9	Harumi pier, Tokyo Bay	4.0305 ± 0.0036	+7.4 ± 1.9	ND
TBH-12	1997.10.9	Harumi pier, Tokyo Bay	4.004 ± 0.0062	−0.1 ± 2.3	ND
TBA-1	1998.5.16	Ariake pier, Tokyo Bay	3.9986 ± 0.0016	−0.6 ± 1.7	ND
TBA-2	1998.5.16	Ariake pier, Tokyo Bay	4.0065 ± 0.0013	+1.4 ± 1.7	ND
ORI-1	1998.5.14	rooftop of ORI building	3.9936 ± 0.0025	−1.8 ± 1.8	52
ORI-2	1998.5.14	rooftop of ORI building	4.0208 ± 0.0018	+5.0 ± 1.7	33
ORI-3	1998.5.14	rooftop of ORI building	3.9804 ± 0.0014	−5.1 ± 1.7	ND

* ND: not determined.

4. Discussion

The boron concentrations in the marine atmosphere (Table 3) are shown in Fig. 1, together with those of Nishimura et al. (1973) which were obtained in July, 1969 and 1970. There is a clear tendency that the atmospheric boron decreases from >100 ng m^{-3} in the mid-latitudes to generally <100 ng m^{-3} in the higher latitudes (above 35°N). Such a latitudinal dependence may have resulted from the different origin of air masses in the two regions; "oceanic" in the former versus "continental" from Asia in the latter. Fogg and Duce (1985) also suggested that such a latitudinal trend might be expected from the colder temperatures at higher latitudes affecting the Henry's

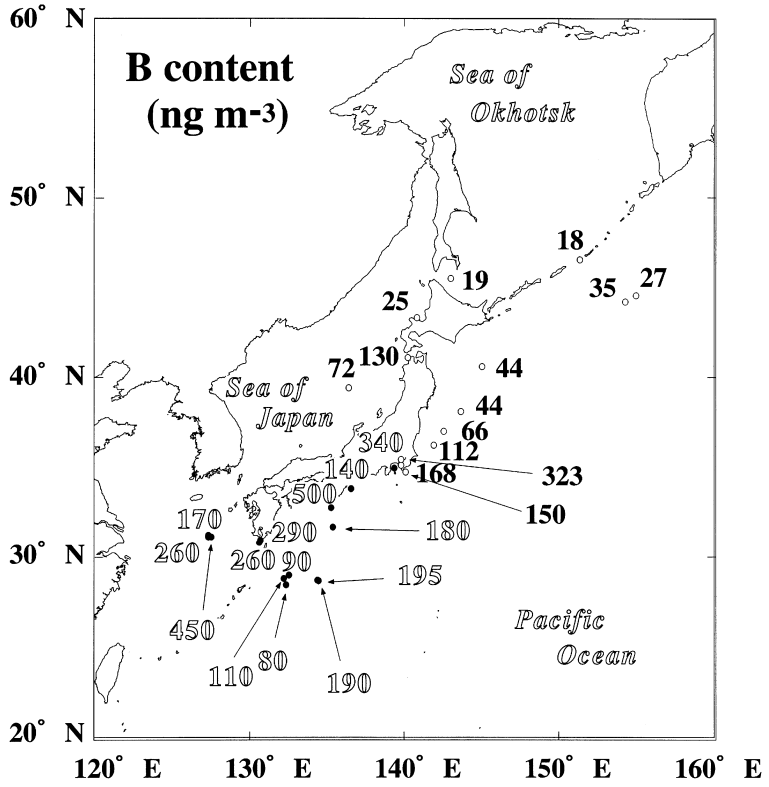

Fig. 1. Boron concentrations in the marine atmosphere. The solid figures are based on this work and the open figures are from Nishimura et al. (1973).

Law constant and thus the release of vapor-phase boron from atmospheric sea-salt particles.

The boron isotopic compositions are also shown in Fig. 2. Although the data are sparse, there seems a regional difference in that higher δ^{11}B values (+5.1 to −1.0‰) in the Sea of Okhotsk and somewhat lower δ^{11}B values (−9.5 to −12.8‰) in the Japan Sea and near Tokyo Bay. It is interesting to note here that the δ^{11}B values are correlated with inverse of boron concentrations (Fig. 3). This suggests that atmospheric boron concentration may be governed by mixing of, at least, two components, and one of the end members must have a δ^{11}B value as low as −12‰ (y-intercept).

The boron isotopic composition varies over a wide range from −30 to +60‰ in various natural reservoirs, and materials with low δ^{11}B values are not uncommon on the earth. For example, some non-marine evaporites and tourmalines have δ^{11}B values lower than −10‰. However, since boron is a widely dispersed trace constituent of the atmosphere, it is hard to believe that those local mineral deposits can significantly and globally contribute to the atmospheric boron. According to Fogg and Duce (1985), most boron (>95%) in the atmosphere exists in gaseous form, and volcanic emission is likely a major source ($\sim 2.1 \times 10^{12}$ g yr^{-1}). Although investigations on boron isotopes of volcanic gases are few, Kanzaki et al. (1979) and Nomura et al. (1982) have reported δ^{11}B values from +2.3 to +21.4‰ for fumarolic condensates collected in northeastern Japan, Ryukyu, Izu-Bonin, and northern Mariana island arcs. These values are undoubtedly too high as for the end member of marine atmosphere (Fig. 3). Another possibility is that the low δ^{11}B values in the atmosphere are derived from anthropogenic sources such as coal and oil combustion. In particular, fly ash leachates show δ^{11}B values of −19.2 to +15.8‰ (Davidson and Bassett,

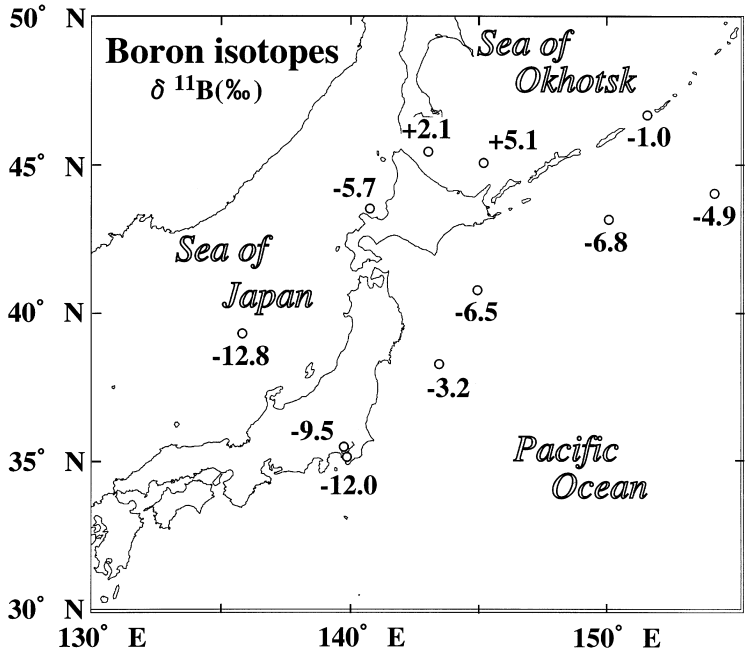

Fig. 2. The δ^{11}B values of atmospheric boron collected over the sea.

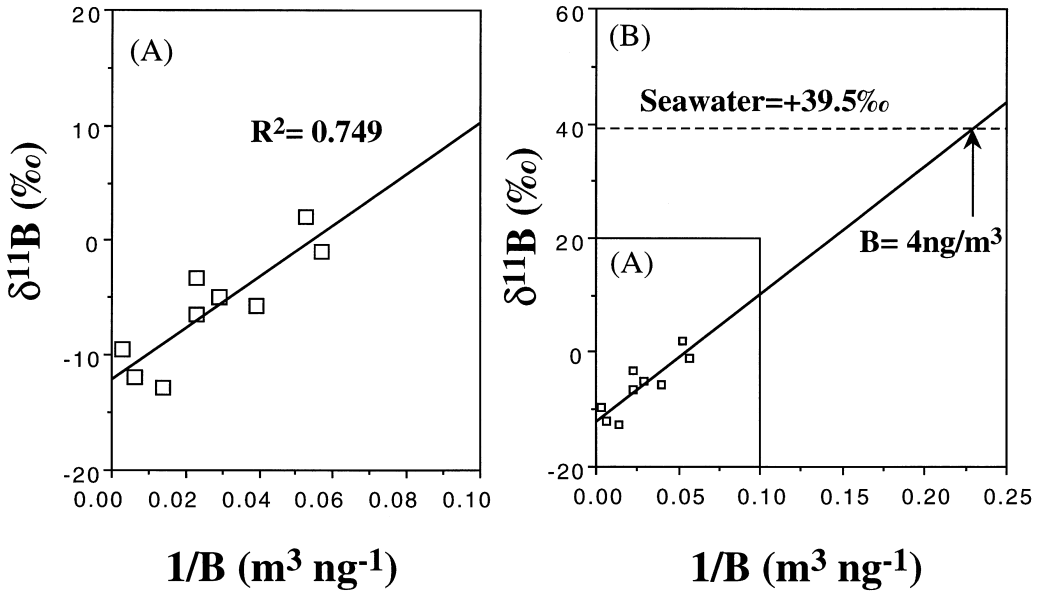

Fig. 3. Diagrams showing the relationship between the δ^{11}B value and an inverse of boron concentration of the marine atmosphere. The area (A) is enlarged on the left.

1993). However, contribution of coal combustion was estimated to be only less than 5% of total boron flux (Fogg and Duce, 1985) and therefore, it can hardly influence the boron isotopic composition in the remote atmosphere. (Local atmospheric pollution by coal combustion would result in anomalously high boron concentrations which we did not observe.)

Fogg and Duce (1985) suggested that bubble bursting and subsequent degassing of $B(OH)_3$ from sea salt aerosols may be a significant source for gaseous boron. Although their estimates of boron flux by this mechanism have large uncertainties of $(3.8–240) \times 10^{10}$ g yr^{-1}, this source is expected to have a $\delta^{11}B$ value of $+39.5‰$ for seawater. (It is assumed here that the boron isotopic fractionation during sea-salt particle formation and subsequent vaporization of boron from them is negligible, see below.) If we extrapolate the regression of Fig. 4 to $+39.5‰$ for $\delta^{11}B$, we obtain the boron concentration of ~ 4 ng m^{-3} which is 1/5 of equilibrium value (~ 20 ng m^{-3}) estimated from laboratory experiments (Nishimura and Tanaka, 1972) and thermodynamic calculation (Savenko, 1977). Atmospheric boron concentrations over the ocean are generally higher than the equilibrium concentration (Fig. 1) and therefore, the ocean should act as a sink for atmospheric boron through gas exchange under synoptic conditions (Nishimura and Tanaka, 1972; Nishimura et al., 1973; Fogg and Duce, 1985). Dynamic aspects of air–sea interaction, such as production of sea salt particles by bubble bursting, photochemical reactions at the particle surfaces, and sublimation need to be considered if boron is supplied from the ocean to the atmosphere.

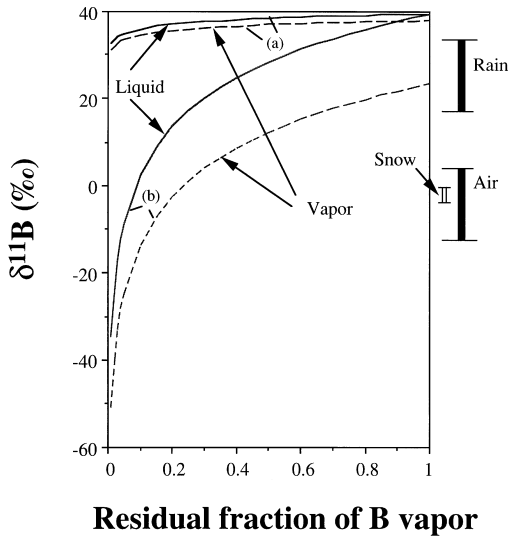

Fig. 4. The variations of $\delta^{11}B$ in liquid (solid) and vapor (dashed) boron under Rayleigh fractionation process. The curves of (a) and (b) are based on the vapor–liquid ^{11}B enrichment factor of $\Delta = -1.5‰$ and $-16.1‰$, respectively (see text). The observed ranges in $\delta^{11}B$ for oceanic rain and air are shown at the right, together with that of snow on land.

The above arguments do not take the possible effect of isotope fractionation of boron into account. It has been demonstrated that large fractionation of boron isotopes occurs in aqueous solutions between undissociated boric acid, $B(OH)_3$ and the borate anion, $B(OH)_4^-$ of which proportion is dependent on pH (Kakihana et al., 1977; Spivack and Edmond, 1987). Some data on liquid–vapor isotopic fractionation processes are available in the literature (Leeman et al., 1992; Palmer and Swihart, 1996). However, those data refer to higher temperature, for example, in natural geothermal systems. The only available data in low temperature are those of Xiao and his coworkers cited in Barth (1998). The results based on evaporation experiments in the following air system were the $\delta^{11}B$ values of $+22.7$ to $+37.7‰$ for coexisting vapor relative to seawater of $\delta^{11}B = +38.8‰$ in their determination. Thus, fractionation during vaporization and condensation can be significant for boron isotopes and may be analogous to the case of hydrogen and oxygen isotopes, both of which show wide ranges of variation from seawater to atmospheric vapor and precipitation.

Fig. 4 shows the variations of $\delta^{11}B$ in liquid and vapor phases under Rayleigh fractionation conditions, assuming the fractionation factors expressed as the relative ^{11}B enrichment in the vapor, $\Delta = -1.5‰$ (minimum) and $-16.1‰$ (maximum) during vaporization/condensation based on the Xiao et al.'s experiments, and an initial liquid $\delta^{11}B = +39.5‰$ for seawater. Since a Rayleigh process leads to much higher fractionation than processes in which the two phases are allowed to equilibrate by exchange, it is clear that negative $\delta^{11}B$ values can hardly be encountered if the isotope fractionation factor is as small as a

few per mil difference during evaporation. Nevertheless, if the fractionation factor is large enough (e.g., $>10‰$ difference), it is possible that the atmospheric boron can have variable isotopic compositions as we observe. Thus, precise knowledge of isotope fractionation during evaporation is urgently needed to understand the boron isotopic composition in the atmosphere. It should be noted that non-equilibrium kinetic processes may control the boron isotopic fractionation during evaporation of seawater as is the case for hydrogen and oxygen isotopes of water (Dansgaard, 1964). Furthermore, Waseda and Nakai (1983) observed that the $\delta^{18}O$ value of water systematically decreases from $-7.5‰$ near sea level to $\sim -14.0‰$ at 2500 m of elevation in Japan, and interpreted the results as a consequence of mixing of 2 air masses which experienced different kinetic processes of seawater evaporation. Such a strong altitude dependency may also be seen for the boron isotopic system. Finally, it is apparent that the determination of boron isotope fractionation during vaporization from sea-salt particles is critical in developing an understanding of sources of atmospheric vapor boron. Further detailed investigations on the boron isotopic behavior during phase transformation as well as temporal and spatial variability of boron concentration and its isotope ratio in the atmosphere remain to be done in the future.

5. Acknowledgements

We thank two anonymous reviewers for providing useful and constructive comments on the manuscript. Mr. Makoto Tsutumi helped in constructing a negative thermal ionization mass spectrometer at the Ocean Research Institute, University of Tokyo. This work was partially supported by the Ministry of Education, Science, Sports and Culture, Japan under Grant-in-Aid No 07404051 to the University of Tokyo (Y. Nozaki, Principal Investigator).

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