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Boron isotopic compositions of some boron minerals

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Abstract—Boron minerals that have different structural formulae but are supposed to have the same geologic origin have been collected and analyzed for the $^{11}B/^{10}B$ isotopic ratio. It has been reconfirmed that minerals of marine origin have higher $^{11}B/^{10}B$ ratios than those of nonmarine origin. It has been found that the sequence of decreasing $^{11}B/^{10}B$ values among the minerals with the same geologic origin is; borax, tincal, kernite (Na borates) > ulexite (Na/Ca borate) > colemanite, iyoite, meyerhofferite (Ca borates). This sequence is explainable on the basis of the difference in crystal structure among the minerals. That is, minerals with higher BO_3/BO_4 ratios, (the ratio of the number of the BO_3 triangle units to the number of the BO_4 tetrahedron units in the structural formula of a mineral) have higher $^{11}B/^{10}B$ ratios.

INTRODUCTION

BORON HAS THE largest relative uncertainty in atomic weight among all the chemical elements that have stable isotopes. This is not because of experimental errors (the use of mass-spectrometric measurements, especially those with the surface ionization technique, has yielded results of very high precision) but because the abundance ratio of the two stable isotopes ^{10}B and ^{11}B varies relatively widely in nature. For instance, the $^{11}B/^{10}B$ data of sea water (SCHWARCZ et al., 1969; NOMURA et al., 1984) give 10.818 as the value of the atomic weight of boron. This value should be compared to the IUPAC-quoted value of 10.81. Confining the subject to boron minerals, the natural variation in the boron atomic weight is at least 0.006 about the quoted value (calculated using the $^{11}B/^{10}B$ data tabulated by SWIHART et al., 1986).

The natural variation of the boron isotopic ratio is of great geochemical interest and importance because it could be used for understanding geochemical cycles and interactions. The sedimentary cycle of the boron isotopes and related subjects were studied by Spivack and his coworkers (SPIVACK and EDMOND, 1987; SPIVACK et al., 1987; PALMER et al., 1987). Others indicated that the boron isotopic composition in fumarolic condensates could be an index for the degree of the geological interaction of magmas with sea water (KANZAKI et al., 1979; NOMURA et al., 1982). It was also shown that the boron isotopic composition of hot spring waters may be an alternative to that of fumarolic condensates for the purpose of investigating regional variations of the boron isotopic composition (KAKIHANA et al., 1987).

The boron isotopic ratios, $^{11}B/^{10}B$, of boron minerals determined by the surface ionization mass spectrometric method are summarized by SWIHART et al. (1986), including their own measurements. It is seen in the tabulation (Tables 1 and 2 in their paper) that not only do different minerals show different $^{11}B/^{10}B$ values, but minerals with the same structural formula have different $^{11}B/^{10}B$ values if their origins differ. SWIHART et al. (1986) extracted from the tabulation the fact that the $^{11}B/^{10}B$ value for marine evaporite deposits is larger than that for nonmarine evaporite deposits. This is consistent with the fact that sea water is enriched in ^{11}B relative to boron minerals and boron-containing rocks (SCHWARCZ et al., 1969). In parallel with the study on the boron isotopic composition of fumarolic condensates and hot spring waters, we also have made precise measurements of the $^{11}B/^{10}B$ ratios of some boron minerals. A close examination of our own data and the data in the tabulation by SWIHART et al. (1986) revealed a very stimulating point in addition to the findings of SWIHART et al. That is, there is a strong indication that the $^{11}B/^{10}B$ ratios of minerals depend on their crystal structures if they were derived from the same geologic origin. In this paper, we present the results of our measurements and discuss the variation of the $^{11}B/^{10}B$ ratio from mineral to mineral in connection with the crystal structures of the minerals.

EXPERIMENTAL

Sampling

For the purpose of our study, it is important to collect and analyze boron minerals that have different structural formulae but are expected to have the same boron origin. It is also important that the origins of analyzed samples are well known. We chose for the present study mineral samples from four well-known areas; Boron, Searles Lake, and Death Valley, all in California, U.S.A. and Bigadic, Turkey.

Borax, kernite, and colemanite samples from Boron, borax samples from Searles Lake, and a colemanite sample from Death Valley were obtained from the U.S. Geological Survey. A ulexite sample from Boron was donated by Dr. T. Kumagai of the National Research Center for Disaster Prevention, Japan. Ulexite and colemanite samples from Bigadic were obtained through Mr. T. Horiguchi of Kyoritsu Yogyo Genryo Co. X-ray diffraction and conventional chemical analyses were employed to verify the chemical composition and purity of each of the mineral samples; the purity ranged from 94.0% for ulexite from Boron to 97.9% for borax from Searles Lake.

Borax from the deposit at Boron was deposited during Miocene time from an inland lake that was enriched in boron by thermal springs, presumably related to contemporaneous volcanic activity. Kernite is a diagenetic product of post-depositional increases in pressure and temperature, whereas colemanite and ulexite formed by reaction of calcium-bearing groundwater with borax at some time after initial deposition of the borax (G. I. SMITH, U.S. Geological Survey, written commun., 1988).

Borax from Searles Lake was formed in late Quaternary time from a large saline lake. Some borax horizons are products of crystallization caused by cooling of the lake waters, and other horizons are concentrations that resulted from high concentrations of the several types of ions that were in solution (G. I. SMITH, U.S. Geological Survey, written commun., 1988).

Colemanite from Death Valley was formed in late Tertiary time by reaction of one or more primary minerals (ulexite or inyoite (?)) to the lower-hydrate species, undergoing recrystallization in the process; deposition of the primary borate minerals may have been on a playa lake surface or along undergound conduits that carried high-borate waters to the surface where they formed thermal springs (G. I. SMITH, U.S. Geological Survey, written commun., 1988).

Explanation of the geologic setting of the above three American borate localities is also found in publications of Dr. Smith (SMITH et al., 1973; SMITH, 1985).

Ulexite and colemanite at Bigadic exist in strata. Colemanite is not a primary mineral but it is probably not derived from ulexite. Ulexite and the primary mineral of colemanite were deposited one after another, depending on the chemical composition in solution, during the Neogene period from a lake rich in boron that was probably supplied by contemporaneous volcanic activity (ONO, 1985; T. HORIGUCHI, Kyoritsu Yogyo Genryo Co., pers. commun., 1988).

Analytical

The procedure for the $^{11}B/^{10}B$ ratio measurements was as follows. About 1 g of each sample was treated. The sample was first powdered (100–200 mesh) and was dissolved in about 50 cm^3 of triply distilled water. Borax samples were completely dissolved. For the other samples, 1–2 cm^3 of about 6 mol/dm^3 HCl solution was added. In most cases, the water insoluble matter disappeared visually by the HCl addition; when it still exists, it was removed by filtration. The volume of the final boron compound solutions was adjusted to 100 cm^3 by adding pure water. Boron was extracted from each boron compound solution by the methyl borate distillation method (KANZAKI et al., 1978). For some of the samples, cations were removed by passing the boron solution through a column packed with cation exchange resin (Bio-Rad AG 50W-12X, H$^+$ form, 100–200 mesh) prior to the distillation. Samples used in mass spectrometry were prepared from the extracted boron. A blank test showed that boron contamination during the process of the sample preparation was negligible.

The $^{11}B/^{10}B$ isotopic ratio of each sample was measured as the peak-height ratio of $Na_2{}^{11}BO_2^+$ and $Na_2{}^{10}BO_2^+$ ionized by the surface ionization technique using a MAT 261 or a Varian MAT CH-5 mass spectrometer (NOMURA et al., 1973). Table 1 lists ten $^{11}B/^{10}B$ values randomly selected from those of occasional measurements on the NBS SRM 951 boric acid isotope standard over a period of recent eight years. As is seen in the table, the typical standard deviation of a measurement was ±0.07% (i.e., the reproducibility expressed as standard deviation was ±0.07%), and the 95% confidence limit of the ten measurements was ±0.05%. (The repeatability in a relatively short period (three months) expressed in terms of standard deviation was less than ±0.04%; NOMURA et al., 1973.) As for the samples in the present work, the 95% confidence limit of a measurement was typically about ±0.2%. The $^{11}B/^{10}B$ ratio of a sample was measured independently three or four times, with the result that the 95% confidence limit of the final $^{11}B/^{10}B$ value (the average of the multiple measurements) was about ±0.15%.

Table 1. $^{11}B/^{10}B$ values of the NBS SRM 951 boric acid sample randomly chosen from the occasional measurements during past eight years.

Run No.	$^{11}B/^{10}B$*	Run No.	$^{11}B/^{10}B$*
1.	4.045 ± 0.003	6.	4.043 ± 0.002
2.	4.040 ± 0.004	7.	4.044 ± 0.004
3.	4.048 ± 0.002	8.	4.041 ± 0.004
4.	4.042 ± 0.003	9.	4.039 ± 0.007
5.	4.046 ± 0.004	10.	4.044 ± 0.007

Average = 4.0432 ± 0.0020**

cf: NBS value = 4.0436 ± 0.0014

* The errors are the standard deviations.

** The error is the 95% confidence limit.

Table 2. Present boron isotopic data of the boron minerals.

Locality	Mineral	$^{11}B/^{10}B$*	$\delta^{11}B$ (permil)
Boron, U.S.A.	borax	4.053 ± 0.006	+2.3
	kernite	4.046 ± 0.006	+0.6
	ulexite	4.031 ± 0.008	-3.1
	colemanite	3.992 ± 0.006	-12.8
Searles Lake, U.S.A.	borax	4.085 ± 0.006	+10.2
		4.078 ± 0.006	+8.5
Death valley, U.S.A.	colemanite	4.024 ± 0.006	-4.9
Bigadic, Turkey	ulexite	4.038 ± 0.008	-1.4
		4.039 ± 0.008	-1.1
	colemanite	4.004 ± 0.006	-9.8
		4.016 ± 0.007	-6.8

Multiple results on a mineral of one locality means that they were obtained for different mineral samples.

* The errors are the 95% confidence limits.

In Table 1, it is also seen that our values are in agreement with the certified value of 4.0436 (CATANZARO et al., 1970) within experimental error. Hence, all the results reported here remained uncorrected. $\delta^{11}B$ values were calculated as $\delta^{11}B = [(^{11}B/^{10}B)_{sample}/(^{11}B/^{10}B)_{std.} - 1] \cdot 1000$ where the NBS SRM 951 boric acid standard was used as the standard.

RESULTS

The results of the present $^{11}B/^{10}B$ measurements are presented in Table 2. The error on each $^{11}B/^{10}B$ value is at the 95% confidence limit. Table 3 summarizes the present and previous results for the areas studied in this work. Data on Lake Inder, U.S.S.R., are also included in the table for later discussion, although there are no data of our own for this area. The third column of the table shows the basic atomic configuration of the polyborate anion in each mineral. $2BO_3 + 3BO_4$ of ulexite, for instance, means that the pentaborate polyanion, $B_5O_6(OH)_6^{3-}$, consists of two BO_3 planar triangles and three BO_4 tetrahedra with boron atoms at the center in both units, understanding that some of the oxygen atoms in BO_3 and BO_4 units are replaced by OH groups.

The following conclusions can be extracted from Table 3:

(1) The $\delta^{11}B$ value is larger for Lake Inder, U.S.S.R., than for the other areas examined.

(2) In each area, minerals may be classified into three groups based on the $\delta^{11}B$ value, i.e., borax, tincal, kernite (Na borates); ulexite (Na/Ca borate); and colemanite, inyoite, meyerhofferite (Ca borates). The members of each group have similar $\delta^{11}B$ values in each area. This classification agrees with the one based on the basic atomic configuration (cf., column 3 of Table 3).

(3) The $\delta^{11}B$ value decreases in the sequence; Na borates > Na/Ca borate > Ca borates in Boron; Na/Ca borate > Ca borates in Bigadic and in Lake Inder.

The first conclusion has already been pointed out by SWIHART et al. (1986) and explained as being due to the difference between marine and nonmarine boron origins. The minerals

Table 3. Summary of literature $\delta^{11}B$ values and new values from this study.

Boron mineral	Structural formula	Basic atomic configuration	$\delta^{11}B$ value (permil)					Ref.
			Boron	Searles Lake	Death Valley	Bigadic	Lake Inder	
borax	$Na_2B_4O_5(OH)_4 \cdot 8H_2O$	$2BO_3+2BO_4$	+2.3	+10.2, +8.5				1)
			+0.4					2)
				-0.9, -0.9				3)
tincal (borax)				+7.0, +6.0				3)
kernite	$Na_2B_4O_5(OH)_4 \cdot 2H_2O$		+0.6					1)
ulexite	$NaCaB_5O_6(OH)_6 \cdot 5H_2O$	$2BO_3+3BO_4$	-3.1			-1.4, -1.1		1)
							+31.7	2)
colemanite	$Ca_2[B_3O_4(OH)_3]_2 \cdot 2H_2O$	BO_3+2BO_4	-12.8		-4.9	-9.8, -6.8		1)
					-12.0			4)
inyoite	$CaB_3O_3(OH)_5 \cdot 4H_2O$		-11.8				+24.2	2)
							+24.1	4)
meyerhofferite	$CaB_3O_3(OH)_5 \cdot H_2O$				-8.1			2)

1) this work; 2) Swihart et al., 1986; 3) McMullen et al., 1961; 4) Finley et al., 1962.

of Boron, Searles Lake, Death Valley, and Bigadic are nonmarine evaporite deposits and those of Lake Inder are marine evaporite deposits. We shall now discuss the latter two observations.

DISCUSSION

Items (2) and (3) in Results suggest that for the boron minerals with the same geologic origin, there is some correlation between the crystal structure of the mineral and its $\delta^{11}B$ value. Based on a general theory on isotope effects, the distribution pattern of two isotopes between two chemical species (and/or between two phases) depends on the isotopic reduced partition function ratios (RPFRs), $(s/s')f$ of the species, and the heavier isotope is preferentially fractionated into the species with the larger RPFR value. The general theory could also be applied to the $^{11}B/^{10}B$ ratio of boron minerals; if two boron minerals are in equilibrium or are formed from a common solution, the one with the larger ^{11}B-to-^{10}B RPFR value would be more enriched in ^{11}B than the other. In any case, it is important to estimate the RPFR values of the boron minerals investigated in this paper in order to understand the present results.

In principle, the RPFR of a chemical species can be calculated by knowing all its vibrational frequencies. Unfortunately, not all the vibrational frequencies are known for each of the boron minerals studied. Nevertheless, it is possible to calculate its RPFR value under appropriate assumptions.

The RPFR of a boron mineral is to a good approximation equal to the RPFR of the polyborate anion in it, since metal cations (counterions to the borate anion) and crystal water molecules in the mineral have little effect on the kinetic and the potential energies of the polyanion for the purpose of the calculation of the boron isotopic RPFR. As for the approximate calculation of the RPFRs of polynuclear borate anions, KAKIHANA et al. (1977) proposed a simplifying formula and by applying it succeeded in explaining boron isotope effects observed in the systems of ion-exchange chromatographic separation of boron isotopes using strongly and weakly basic anion exchange resins. They regarded a polynuclear species as being composed of monomeric parts, $B(OH)_3$ and $B(OH)_4^-$, and substituted its ln (RPFR) value by a weighted sum of the ln (RPFR) values of the monomeric species. We take advantage of their formula here. The RPFR of a polyanion and consequently that of a boron mineral whose basic atomic configuration is $nBO_3 + mBO_4$ can be approximated as

$$\ln (s/s')f = [n/(n+m)] \ln (s/s')f_{B3} + [m/(n+m)] \ln (s/s')f_{B4}, \quad (1)$$

where $(s/s')f_{B3}$ and $(s/s')f_{B4}$ are the RPFRs of BO_3 and BO_4 units, respectively. Equation (1) can be regarded as an application or an extension of the rule of the geometric mean about the RPFR to polyborate anions.

The RPFRs of BO_3 and BO_4 units (actually those of $B(OH)_3$ and $B(OH)_4^-$) have been calculated theoretically (KAKIHANA and KOTAKA, 1977; KAKIHANA et al., 1977). We reproduce them in Table 4. We also list in Table 4 the RPFRs of the polyanions calculated by Eqn. (1).

It is seen in Table 4 that the RPFR of the BO_3 unit is larger than that of the BO_4 unit, and consequently the polyanion that has the higher BO_3/BO_4 ratio shows the higher $^{11}B/^{10}B$ ratio (larger $\delta^{11}B$) than the polyanion that has the lower $BO_3/$

Table 4. The ^{11}B-to-^{10}B reduced partition function ratios (RPFR's) of $B(OH)_3$, $B(OH)_4^-$ and polyborate anions at several temperatures.

Temperature (K)	200.0	273.1	298.1	323.1	400.0	500.0
$B(OH)_3$	1.3796	1.2315	1.2008	1.1758	1.1225	1.0827
$B(OH)_4^-$	1.3449	1.2066	1.1780	1.1549	1.1061	1.0705
$(BO_3 + BO_4)/2$	1.3622	1.2191	1.1894	1.1654	1.1143	1.0766
$(2BO_3 + 3BO_4)/5$	1.3588	1.2166	1.1871	1.1633	1.1127	1.0754
$(BO_3 + 2BO_4)/3$	1.3565	1.2149	1.1856	1.1619	1.1116	1.0746

BO_4 ratio at any temperature. Then, if a boron mineral is formed from another mineral or two minerals are formed from a common solution, the following decreasing sequence in the $\delta^{11}B$ value should result: borax, tincal, kernite (BO_3: BO_4 = 1:1) > ulexite (2:3) > colemanite, inyoite, meyerhofferite (1:2). Also, there should be little difference in $\delta^{11}B$ among borax, tincal, and kernite and among colemanite, inyoite, and meyerhofferite because each group has the basic atomic configuration in the polyborate anions common to all the members in the group.

The results summarized in Table 3 are consistent with what is theoretically predicted for the boron minerals with the same geologic origin. Thus, the experimentally found correlation between the boron isotopic composition of a mineral and its crystal structure is not something accidental but has a theoretical foundation and is explainable, at least qualitatively, in the light of the RPFRs of polyborate anions, the good approximate RPFRs of the corresponding boron minerals.

Now we consider each area individually.

Boron

Kernite, ulexite, inyoite, and colemanite in Boron were derived from borax. Kernite is a diagenetic product of borax and differs structurally from borax only in the number of molecules of crystal water, which means that there should not be any substantial differences in RPFR and $\delta^{11}B$ values between kernite and borax (cf., Table 3).

Colemanite and inyoite have the same basic atomic configuration, $BO_3 + 2BO_4$, and consequently, they should have similar $\delta^{11}B$ values, which was in fact observed experimentally (cf., Table 3). Judging from a phase diagram of $Na_2O \cdot 2B_2O_3 \cdot 4H_2O\text{-}2CaO \cdot 3B_2O_3 \cdot 5H_2O\text{-}H_2O$ (CHRIST et al., 1967), colemanite can be considered to be a diagenetic product of inyoite.

In the formation of inyoite, borax might be first dissolved in water. The boron isotope effect accompanying this dissolution is expected to be very small, and thus the $\delta^{11}B$ in the solution was expected to be very close to +1.1 permil (average of +2.3, +0.4, and +0.6 for borax and kernite in Table 3). In the solution, boron would exist in the forms of $B(OH)_3$, $B(OH)_4^-$, and polyborate anions, their relative abundances being dependent on the boron concentration, pH of the solution, temperature, etc., as the solution chemistry of boron (INGRI et al., 1957) teaches. As stated above, however, polyborate anions can be regarded as being composed of $B(OH)_3$ and $B(OH)_4^-$ for the purpose of the boron isotopic ratio consideration. Hence, we can assume for the purpose of understanding the $\delta^{11}B$ values of the minerals that the boron species existing in the solution phase were $B(OH)_3$ and $B(OH)_4^-$ alone and the $\delta^{11}B$ value of the solution was +1.1 permil before the formation of inyoite. If the amount of $B(OH)_4^-$ was small compared to that of $B(OH)_3$ in the solution, that is, if almost all the boron in the solution existed in the form of $B(OH)_3$, then the $^{11}B/^{10}B$ ratio of $B(OH)_4^- = 4.048 \times 1.1780/1.2008 = 3.971$ (−18.0 permil) while that of $B(OH)_3$ remained 4.048 (+1.1), at 25°C. If the amount of inyoite deposited from the solution was small compared to the amount of the total boron in the solution phase, which means that the boron isotopic composition of the solution remained unchanged during the deposition of inyoite and seems reasonable and very likely, then the $^{11}B/^{10}B$ value of inyoite whose basic atomic configuration is $BO_3 + 2BO_4$ would be $(4.048)^{1/3} \cdot (3.971)^{2/3} = 3.997$ ($\delta^{11}B = -11.7$) at 25°C. This value is very close to $\delta^{11}B = -12.3$, the one found in nature (average of −12.8 and −11.8 for colemanite and inyoite in Table 3).

The satisfactory agreement between the two values might be accidental. The following are conceivable factors affecting the boron isotopic composition of inyoite. (Of course, they are significant factors not only in Boron but also in the other areas.)

(1) Temperature. Lower temperature at the time of mineral deposition would make the theoretical $\delta^{11}B$ value of the mineral lower. However, the temperature dependence of the $\delta^{11}B$ is not so large. For example, a calculation similar to the one given above gives $\delta^{11}B = -12.5$ at 0°C; a 25°C temperature difference yields only a 0.8 difference in $\delta^{11}B$ value. Thus, as long as the deposition of the borate occurs at ambient temperatures, temperature is not a major factor for determining the $\delta^{11}B$ value of the mineral.

(2) Abundance ratio of the $B(OH)_3$ and $B(OH)_4^-$ species in the solution. This factor has a very profound effect on the boron isotopic composition of the mineral formed. Table 5 lists the theoretically expected $^{11}B/^{10}B$ and $\delta^{11}B$ values as a function of the mole fraction of $B(OH)_3$ for a given value of $^{11}B/^{10}B = 4.048$ ($\delta^{11}B = +1.1$) at 25°C. The $\delta^{11}B$ value for inyoite (Ca borate) can vary between −11.5 and +7.5 permil, depending on the value of the mole fraction of the $B(OH)_3$ species in the solution. Several factors determine the abundance ratio of the $B(OH)_3$ and $B(OH)_4^-$ species in the solution and, among them, the most predominant will be the pH of the solution. Using the equilibrium constant data on boric acid systems in aqueous solution by INGRI (1963), we calculated the mole fractions of the $B(OH)_3$ and $B(OH)_4^-$ species as a function of the pH of the solution and plotted the results in Fig. 1. The total boron concentration was 0.80 M (about the concentration of the saturated aqueous boric acid solution at room temperature). Polyborate anions were regarded as consisting of the monomeric species, $B(OH)_3$ and $B(OH)_4^-$, and the mole fractions of the monomeric species were calculated accordingly. For instance, the $B_3O_3(OH)_4^-$ species can be regarded as consisting of two $B(OH)_3$ units and one $B(OH)_4^-$ unit, and thus, if its concentration is 0.1 M, its existence increases the total concentration of the $B(OH)_3$ species by 0.2 M and that of the $B(OH)_4^-$ species by 0.1 M. As is seen in the figure, boron is practically all in the form of $B(OH)_3$ if the pH is lower than 5, and is practically all in the form of $B(OH)_4^-$ if the pH is higher than 12. Between pH = 5 and 12, the $B(OH)_3/B(OH)_4^-$ distribution varies and the mole fraction of $B(OH)_3$ decreases with increasing pH.

(3) Isotope effects accompanying the phase change. There could be an isotope effect when a species is transferred from one phase to another (from the solution phase to the solid phase in this case), because interactions of the species with its environments could be different between the two phases. However, this effect is generally considered to be small. In this paper, we totally neglected it.

(4) Amount of boron in the deposited mineral. When the

Table 5. Isotopic compositions of Na, Na/Ca and Ca borates as functions of the $B(OH)_3/B(OH)_4^-$ distribution in the original solution at 25°C.

Mole fraction of $B(OH)_3$	1.0	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0.0
Mole fraction of $B(OH)_4^-$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
$B(OH)_3$	4.048 (+1.1)	4.056 (+3.8)	4.064 (+5.1)	4.071 (+6.8)	4.079 (+8.8)	4.087 (+10.7)	4.095 (+12.7)	4.103 (+14.7)	4.111 (+16.7)	4.118 (+18.4)	4.126 (+20.4)
$B(OH)_4^-$	3.971 (-18.0)	3.976 (-16.7)	3.986 (-14.2)	3.994 (-12.3)	4.002 (-10.3)	4.009 (-8.6)	4.017 (-6.6)	4.025 (-4.6)	4.033 (-2.6)	4.040 (-0.9)	4.048 (+1.1)
Na borate	4.009 (-8.6)	4.017 (-6.6)	4.025 (-4.6)	4.033 (-2.6)	4.040 (-0.9)	4.048 (+1.1)	4.056 (+3.1)	4.064 (+5.1)	4.071 (+6.8)	4.079 (+8.8)	4.087 (+10.7)
Na/Ca borate	4.002 (-10.3)	4.009 (-8.6)	4.017 (-6.6)	4.025 (-4.6)	4.033 (-2.6)	4.040 (-0.9)	4.048 (+1.1)	4.056 (+3.1)	4.064 (+5.1)	4.071 (+6.8)	4.079 (+8.8)
Ca borate	3.997 (-11.5)	4.004 (-9.8)	4.012 (-7.8)	4.020 (-5.8)	4.027 (-4.1)	4.035 (-2.1)	4.043 (-0.2)	4.051 (+1.8)	4.058 (+3.6)	4.066 (+5.5)	4.074 (+7.5)

The $^{11}B/^{10}B$ value of original solution is assumed to be 4.048 ($\delta^{11}B$ = +1.1).
In each row, the numbers are the $^{11}B/^{10}B$ values and the numbers in the parentheses are $\delta^{11}B$ values.

amount of boron in the mineral deposited is not negligible compared to that of the solution, it could be possible that the solution was being isotopically fractionated during the precipitation of the borate, which caused the continuous change in the isotopic composition of the mineral. (The change in the isotopic composition of the original solution is also possible by later influx of boron with different isotopic composition.) McMullen et al. (1961) measured the $^{11}B/^{10}B$ ratios of borax and tincal from Searles Lake and reported that the isotopic ratio of a mineral is independent of the depth of the deposit (cf. Table 3). Our measurements of the $^{11}B/^{10}B$ values of ulexite and colemanite from Bigadic also suggest that the isotopic composition of a mineral seems nearly independent of its location (see below). Considering these experimental facts, it is very likely that the isotopic composition of the solution was kept almost constant during the deposition of inyoite at Boron, although we have no direct evidence for this.

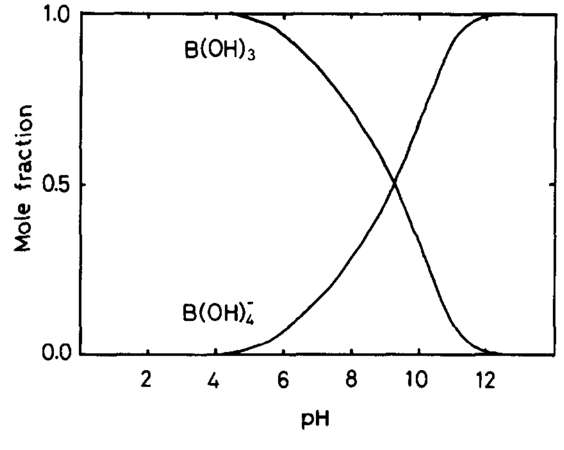

Fig. 1. Distribution of $B(OH)_3$ and $B(OH)_4^-$ in 0.8 M boric acid solution as a function of the pH of the solution.

Among the factors listed above, the abundance ratio of the $B(OH)_3$ and $B(OH)_4^-$ species in the solution from which the mineral was formed seems most influential in determining the boron isotopic composition of the mineral. The above agreement between the theoretical and experimental $\delta^{11}B$ values suggests that when inyoite was deposited, the boron species in the solution was mostly $B(OH)_3$, which means the solution had, most probably, the pH value lower than, say, 6.5 (cf. Fig. 1).

Ulexite is a secondary mineral formed indirectly from borax. A consideration similar to that on inyoite yields −10.3 permil at 25°C as the $\delta^{11}B$ value for ulexite whose basic atomic configuration is $2BO_3 + 3BO_4$. This calculated value should be compared to −3.1 permil, the one observed in nature. The discrepancy between the calculated and observed values is substantial. The most effective and only practical way to make the theoretical value agree with the observed one is to assume a larger portion of the $B(OH)_4^-$ species in the solution; the mole fraction of $B(OH)_3$ in the solution = 0.62 and that of $B(OH)_4^-$ = 0.38 when ulexite was formed resulted in the theoretical $\delta^{11}B = -3.1$ permil at 25°C (cf. Table 5). This corresponds to the situation that the pH of the solution was about 8.6 (cf. Fig. 1).

The above model calculations on the Ca and Na/Ca borates (inyoite and ulexite) suggest that the solution was richer in the $B(OH)_4^-$ species when the Na/Ca borate was deposited than when the Ca borate was. This means that the pH of the solution was higher when ulexite was deposited (the pH is about 8.6; cf. Fig. 1) than when inyoite was formed (the pH is below 6.5). This situation does not seem unreasonable, because the basicity of Na^+ is stronger than that of Ca^{2+}.

Extension of the above consideration to Na borates results in that the pH of the solution should have been higher than 8.6 when the Na borates were deposited. If the mole fraction of $B(OH)_3$ and $B(OH)_4^-$ were the same (each 0.5) in the solution, a situation realized at the pH = about 9.2 according to Fig. 1, then the $\delta^{11}B$ value of the Na borates would have been the same as that of the solution, because the Na borates have the $BO_3 + BO_4$ basic atomic configuration.

Searles Lake and Death Valley

Because we have only one kind of basic atomic configuration for each of Searles Lake and Death Valley, it is impossible to discuss the relationship between the $\delta^{11}B$ value of a mineral and its crystal structure. However, it is interesting to note the following.

We make two assumptions. The first one is that the $\delta^{11}B$ value of the original solution at Searles Lake from which minerals were deposited was the same as that of the minerals, i.e., +5.0 permil (the average of six data for borax and tincal in Table 3). This assumption is based on the fact that the Na borates ($BO_3 + BO_4$ configuration) are almost the only minerals found in Searles Lake and on the speculation in the previous subsection that the $\delta^{11}B$ value of the Na borates would not be very different from that of the original solution from which they were formed. The second assumption is that the $\delta^{11}B$ values of the two boron sources at Searles Lake and Death Valley from which boron in the original solutions at the two areas were supplied had similar $\delta^{11}B$ values. This assumption is also not unreasonable, because the two areas are geographically near to each other, belonging to the same drainage chain (SMITH, 1976), and in both areas boron came from thermal waters related to volcanic activity, although the times of boron arrival may differ.

Colemanite (and meyerhofferite too) of Death Valley is a secondary mineral. If the primary mineral was inyoite, a calculation on the $\delta^{11}B$ value of colemanite (and meyerhofferite) from Death Valley similar to that of inyoite of Boron gives −7.8 permil at 25°C. This should be compared to the observed value of −8.3 permil (the average of three data for colemanite and meyerhofferite from Death Valley in Table 3). Both values agree quite well. The good agreement between the two values in turn indicates that the assumptions made above are very close to what existed in reality.

Unfortunately, it is at present impossible to do a model calculation on the $\delta^{11}B$ value of colemanite when the primary mineral was ulexite, because of lack of sufficient knowledge on how colemanite was formed from ulexite. It is strongly hoped that the $\delta^{11}B$ value(s) of the primary mineral(s) will be measured.

Bigadic

Ulexite and colemanite at Bigadic were deposited in strata. Based on the phase diagram by CHRIST et al. (1967), colemanite must be a diagenetic product of inyoite which has the same $BO_3 + BO_4$ basic atomic configuration as that of colemanite. Two ulexite samples (cf. Table 2) were presumably mined from different horizons, but, unfortunately, their exact locations (depths) could not be specified; their $\delta^{11}B$ values are about the same. Similar things can be said concerning the two colemanite samples. A slight difference in $\delta^{11}B$ value of the two colemanite samples may indicate that the $\delta^{11}B$ value of the original solution from which the boron minerals were formed varied slightly with time.

Without knowledge on the exact locations of the mined mineral samples and because of the fact that $\delta^{11}B$ fluctionations are in fact small, we suggest that the $\delta^{11}B$ value of the original solution was kept constant during the deposition of the minerals. The constancy of the $\delta^{11}B$ value of the solution also indicates that the amount of the deposited boron was negligible compared to the amount of boron left in solution.

The $\delta^{11}B$ value of the boron source at Bigadic, and consequently that of the original solution too, is unknown, but it may have been similar to the $\delta^{11}B$ values of the boron sources in California. Tentatively assuming the $\delta^{11}B$ value of the solution is +3.7 permil (the average of nine data on the Na borates at Boron and Searles Lake; Na borates are considered to have $\delta^{11}B$ values similar to those of their original solutions; see above), and applying consideration similar to that of inyoite at Boron, we obtain −9.1 and −7.6 permil as the $\delta^{11}B$ values of colemanite and ulexite at Bigadic, respectively. These should be compared with the observed values of −8.3 (the average of two data on colemanite in Table 2) and −1.3 (the average of two data on the ulexite samples in Table 2). The theoretical and observed results for colemanite are almost the same, while the discrepancy between the two results for ulexite is substantial. If one would like to fill the discrepancy for ulexite solely by changing the $B(OH)_3/B(OH)_4^-$ distribution in the solution, the mole fractions of $B(OH)_3 = 0.67$ and of $B(OH)_4^- = 0.33$ result in the agreement. The corresponding pH of the solution is about 8.3 (cf. Fig. 1).

SUMMARY AND CONCLUSIONS

As was seen in the model calculations in which we assumed that the boron species in the original solutions is mostly $B(OH)_3$, calculated differences of the $\delta^{11}B$ value between the Na/Ca borates and the Ca borates were much smaller than the observed ones (at Boron, the calculated difference is 1.4 and the observed one is 9.2; at Bigadic, 1.5 vs. 7.0). It seems quite reasonable to have assumed the larger portions of the $B(OH)_4^-$ species in the original solutions for the Na/Ca borates (precipitates) than for the Ca borates in order to make the theoretical $\delta^{11}B$ match the observed ones. Such assumption agrees well with the difference in basicity between Na^+ and Ca^{2+}.

To summarize, the observed $\delta^{11}B$ values of various boron minerals are explainable in a satisfactory manner by: 1) using the RPFR values of the minerals, which can be decomposed into the RPFRs of BO_3 and BO_4 units in the borate anions in the minerals, and 2) assuming appropriate distributions of the $B(OH)_3$ and $B(OH)_4^-$ species in the original solutions, or equivalently, assuming appropriate pH values of the solutions. (The pH of the solution decreases from Na borates through Na/Ca to Ca borates.)

In Table 6, we list the ratios of two $^{11}B/^{10}B$ ratios; Na/Ca borate:Ca borates (Na/Ca:Ca) and Na borates:Ca borates (Na:Ca). Assuming that the $^{11}B/^{10}B$ values of the boron sources of Searles Lake and Death Valley are the same, we put these two areas together. The Na/Ca:Ca ratios of Boron, U.S.A.,

Table 6. Ratios of $^{11}B/^{10}B$ values in boron minerals with different cation ratios (see text).

	Boron	Biqadic	Lake Inder
Na/Ca:Ca1)	1.0092	1.0071	1.0074

	Boron	Searlas Lake-Death Valley
Na:Ca2)	1.014	1.015

1) Na/Ca = ulexite; Ca = colemanite or inyoite.
2) Na = borax, tincal or kernite; Ca = colemanite, inyoite or meyerhofferite.

and of Bigadic, Turkey, are very similar to one another. Even the Na/Ca:Ca value of Lake Inder, U.S.S.R. is very close to those of Boron and Bigadic, despite the fact that the $^{11}B/^{10}B$ ratios themselves are much larger for Lake Inder than for the other two areas. It is also seen in the table that the Na:Ca ratios of Boron and of Searles Lake-Death Valley are nearly equal to each other. These results strongly suggest that the basic boron isotope effect governing the boron isotope fractionation among the minerals at different areas is quite universal and support the above developed consideration that the theoretical approach based on the RPFRs of the boron minerals involved can be applied to understanding the $\delta^{11}B$ variations among minerals with the same geologic origin, even if formation processes of the minerals may differ from area to area.

More boron isotopic data on boron minerals will be required to confirm our consideration further. More detailed analysis on how and when different minerals were formed and more exact estimation of the RPFRs will, among others, certainly be required for a more quantitatively satisfactory agreement between the experimental and theoretical results.

The findings of this study on the boron isotopic composition of boron minerals can be summarized as follows:

(1) Our results on $\delta^{11}B$ values of some boron minerals with the nonmarine origin supported the previously reported results by SWIHART et al. (1986) that minerals of the marine origin have larger $\delta^{11}B$ values than those of the nonmarine origin.

(2) The decreasing sequence of the $\delta^{11}B$ value of the minerals with the same geologic origin is: borax, tincal, kernite (Na borates) > ulexite (Na/Ca borate) > colemanite, inyoite, meyerhofferite (Ca borates). This sequence is correlated with the crystal structures of the minerals.

(3) The sequence is qualitatively explainable on the basis of the RPFR values of the minerals. A rather quantitative explanation is possible with an appropriate assumption on the $B(OH)_3/B(OH)_4^-$ distribution in the original solutions.

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