

Boron and chlorine isotopic signatures of seawater in the Central Indian Ridge

P. V. Shirodkar, Y. K. Xiao* and Lu Hai*

National Institute of Oceanography, Dona Paula, Goa 403 004, India

*Institute of Salt Lakes, Academia Sinica, Xining, Qinghai 810008, China

Isotopic ratios of boron and chlorine were measured in the upper 2000 m water column of the Central Indian Ridge from two tectonically active areas, one at 5°S and other at 10°S which coincided with the spreading regime of the Central Indian Ridge (CIR). Boron and chlorine isotopic measurements were made using positive thermal ionization mass spectrometry (TIMS) of Cs_2BO_4^+ and Cs_2Cl^+ ions respectively, mainly to understand their isotopic behaviours to elucidate the consistency of boron and chlorine isotopic compositions of seawater in the oceanic regime.

The boron isotopic compositions ($d^{11}\text{B}$ values) varied from 37.77‰ to 39.54‰ at 5°S and from 37.75‰ to 39.82‰ at 10°S with considerably heavier values below 300 m depth. The relatively lighter $d^{11}\text{B}$ values of seawater within the thermocline in the upper 300 m layer gave an average $d^{11}\text{B}$ value of 38.14‰ whereas below the thermocline the average $d^{11}\text{B}$ value was 39.3‰. The release of boron from remineralized organic matter and other unknown factor appears to influence the $d^{11}\text{B}$ values in causing variations in the upper 300 m layer. The chlorine isotopic composition ($d^{37}\text{Cl}$) of seawater lies within $\pm 1\%$ and indicated difference in their vertical variations at 5°S and 10°S. The $d^{37}\text{Cl}$ values ranged from -0.53 to 0.94% at 5°S and from 0.10 to 0.59% at 10°S with most of the lighter values (av. 0.06%) below 300 m depth, showing a trend opposite to that of the boron isotopic variation. The observed heavier $d^{37}\text{Cl}$ values (av. 0.64%) in the upper layer have been attributed to an increase in evaporation to precipitation ratio of seawater that alters the isotopic behaviour of chlorine in the ocean.

BORON and chlorine are two naturally occurring isotopes each. They are ^{10}B and ^{11}B for boron and ^{35}Cl and ^{37}Cl for chlorine. Both the elements show differing isotope characteristics. In nature, the boron isotopic compositions vary widely from -30% to $+60\%$ (ref. 1), on the contrary, the variations in the isotopic compositions of chlorine are minor². Of the two conservative elements in the sea, boron is bio-geochemically active whereas chlorine shows geochemical reactivity. The isotopic compositions of both these elements are considered to be constant in seawater. Some reports gathered by Bassette³ on the isotopic analyses of surface seawater from the oceans like

the Atlantic, the Pacific and the Arctic as well as some other seas and bays over the world showed that the boron isotopic compositions of seawater are constant at around 40 per mil due to enrichment of the heavier isotope of boron, ^{11}B in seawater. There is no report yet practically to ascertain the consistency of boron isotopic compositions of Indian Ocean water. Similarly, in the case of chlorine, its isotopic compositions in seawater are considered to be constant at 0 per mil with no variations⁴. Seawater was therefore used as an isotopic standard reference material for chlorine instead of chlorine isotopic standard reference material, NIST SRM 975.

The developments made in the recent past for precise isotopic measurements of chlorine^{5,6} indicated variations in the isotopic compositions of chlorine in nature. The improved techniques of chlorine isotopic measurements by Cs_2Cl^+ ion showed significant variations in the chlorine isotopic compositions of surface seawater in the Pacific and in the Indian Ocean waters⁷. However, their vertical variations in the sea/ocean are not known.

Understanding the isotopic behaviours of boron and chlorine in the sea particularly in a specialized environment is very important as they act as excellent tracers of various geochemical and hydrothermal processes⁸⁻¹². In the Central Indian Ocean, the mid-oceanic ridge (MOR) area is different from other oceanic areas as the raised topographic features here are caused by magmatic activities during the seafloor spreading. The magmatic activity gives rise to the presence of hydrothermal input. This feature together with the ongoing basalt-seawater interaction at the ridge sites renders MOR an excellent environment for isotopic studies.

The InRidge Program (*Indian Ridge Research Initiative*), initiated in 1997, provided an opportunity to carry out isotopic studies on boron and chlorine in seawater at 5°S and 10°S in the Vityaz and Vema Transform Fault regions of the CIR mainly to understand their distribution, behaviour and consistency in the mid-oceanic regime.

Materials and methods

Sample collection

Seawater samples were collected from the Vema (stn VM3 at 10°43.23'S and 66°36.5'E) and Vityaz regions

*For correspondence. (e-mail: shirod@darya.nio.org)

(stn VT4 at 5°39.55'S and 68°03.77'E and stn VT6 at 5°38.83'S and 67°27.39'E) in ridge area of the CIR (Figure 1) during ORV *Sagar Kanya* cruise No. 125 from July to August 1997. The geological settings of these stations are such that station VM3 lies on the inner flank of the ridge up slope, station VT4 is located at the base of the axial valley whereas stn VT6 lies on the Vityaz fracture zone, slightly away from the ridge axis. Seawater samples were collected at standard depths from surface to 2000 m depth. The technical snag with the winch on board the ship restricted further sampling at deeper depths. The water samples were collected using CTD rosette sampler provided with clean Niskin samplers and the soundings recorded at these stations were 2200 m at stn VM3, 3100 m at stn VT4 and 4020 m at stn VT6.

Temperature and salinity were obtained from the CTD provided with pre-calibrated sensors, whereas pH and dissolved oxygen (DO) were measured on board the ship as per standard methods¹³. Boron (SD $\pm 1.13\%$), calcium (RSD $\pm 0.12\%$) and magnesium (RSD $\pm 0.14\%$) were

analysed by the method of Hulthe *et al.*¹⁴ and by Culkin and Cox¹⁵ at the NIO laboratory. Chloride content in the samples was computed from salinity values. A portion of each of the samples was preserved in clean autoclaveable polyethylene bottles for isotopic measurements of boron and chlorine by mass spectrometry.

Extraction of boron and chlorine

Boron in seawater was extracted using a double ion-exchange technique for efficient recovery as indicated below.

The boron-specific resin Amberlite IRA 743 ground to 80–100 mesh and soaked in distilled water for a few days was loaded onto a polyethylene column of 0.4 cm diameter up to a height of 5.5 cm. It was conditioned with successive additions of 10 ml of 2 M HCl, high purity water, 10 ml of 3 M HCl and finally high purity water to bring it to pH 7.0. In another column, about 5 ml mixture of weakly basic anion exchange resin in HCO_3^- form (Ion Exchanger-II) and a strongly acidic cation exchanger resin in the H^+ form (Shanghai No. 1) were taken in equal proportions. Both the resins were first conditioned separately by treating with 10% NaHCO_3 solution and 4 M HCl respectively and then mixed together at neutral pH.

A 25 ml aliquot of seawater containing approximately 100 μg of boron was first passed through the Amberlite resin at a rate of 0.5 ml/min. This retains all the boron and discards the other ions. The column was rinsed using 10 ml boron-free water, 10 ml 3 M NH_4OH followed by 10 ml high purity water to remove chloride and sulphate ions off the resins. The boron held up by the resin was then eluted using approximately 10 ml 0.1 M HCl at 75°C. After cooling to room temperature, the eluate containing boron was passed again through the other column of mixed resins to remove most of the HCl and make boron free from impurities. Boron was eluted by 60 ml high purity water. Equimolar mannitol and Cs_2CO_3 solutions were added to the eluate and evaporated in the oven at 60°C under air drawn through impregnated filters of KOH to about 0.5 to 1.0 ml volume for isotopic measurements of boron by mass spectrometer.

Chlorine from seawater was separated by ion-exchange technique using two types of resins according to the procedure of Liu *et al.*¹⁶. About 0.5 g each of the Ba-resin (Shanghai No. 732) and H-resin (Dowex 50 \times 8) were conditioned with $\text{Ba}(\text{NO}_3)_2$ solution and HNO_3 respectively and then added to two polyethylene columns. The seawater sample was first passed through the Ba resin bed to remove all SO_4^{2-} ions and then through the Dowex resin to remove all cations and convert Cl^- ions to HCl and finally through the Cs-resin bed to convert HCl to CsCl. Nearly 0.5 to 1.0 ml of CsCl sample was collected for the isotopic measurements of chlorine by mass spectrometer.

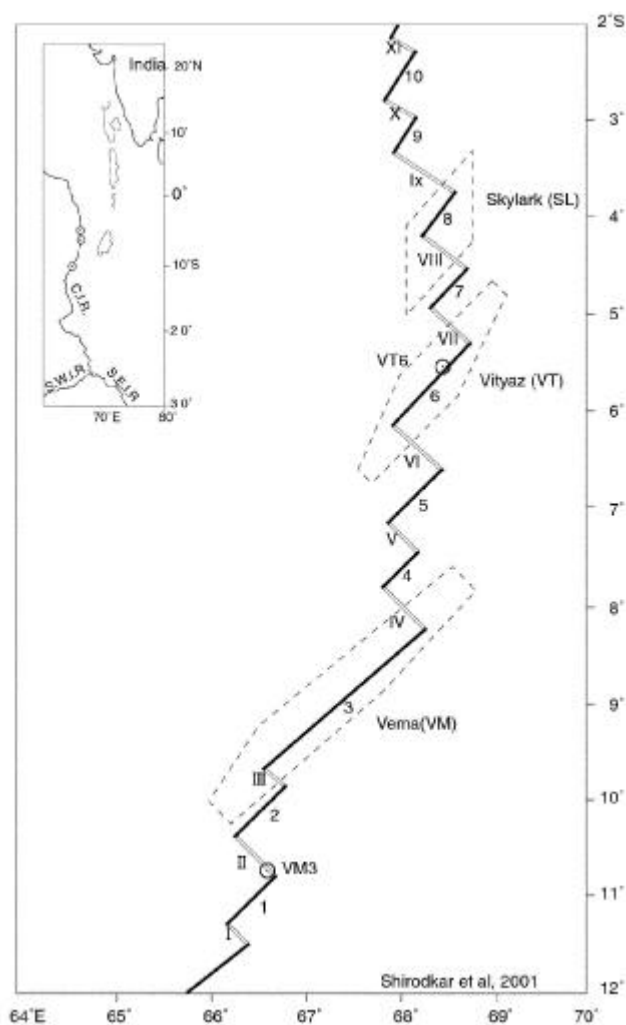


Figure 1. Location map of the study area.

Mass spectrometry procedure

The isotopic ratios of boron and chlorine in seawater were measured by positive thermal ionization mass spectrometry of Cs_2BO_4^+ and Cs_2Cl^+ ions^{17,18} using VG 354 model mass spectrometer. Sample solutions (3–6 μl) containing 1 μg of boron per μl and 5 μg of chlorine per μl solution was loaded onto the Ta filament precoated with a graphite slurry and then dried by heating the filament with a current of 1.0–1.1 A for 3–5 min. The isotopic analyses were started when the base pressure in the source section reached 3×10^{-5} Pa. The intensity of the CsCl^+ ion was adjusted to $(6 \times 8) \times 10^{-12}$ A by controlling the filament current. The data were collected on a Faraday cup by switching magnetically between the masses of 309 ($\text{Cs}_2^{11}\text{B}^{16}\text{O}^{16}\text{O}^+$ plus $\text{Cs}_2^{10}\text{B}^{16}\text{O}^{17}\text{O}^+$) and 308 ($\text{Cs}_2^{10}\text{B}^{16}\text{O}^{16}\text{O}^+$) for boron and 301 ($^{133}\text{Cs}_2^{35}\text{Cl}^+$) and 303 ($^{133}\text{Cs}_2^{37}\text{Cl}^+$) for chlorine. The isotopic ratios are expressed as *del* values relative to their standard reference materials and the $d^{11}\text{B}$ and $d^{37}\text{Cl}$ values of the samples were calculated as follows:

$$d^{11}\text{B} (\text{‰}) = \left\{ \frac{(^{11}\text{B}/^{10}\text{B})_{\text{sample}}}{(^{11}\text{B}/^{10}\text{B})_{\text{std}}} - 1 \right\} \times 1000$$

and

$$d^{37}\text{Cl} (\text{‰}) = \left\{ \frac{(^{37}\text{Cl}/^{35}\text{Cl})_{\text{sample}}}{(^{37}\text{Cl}/^{35}\text{Cl})_{\text{std}}} - 1 \right\} \times 1000.$$

The isotopic standard used was the chlorine isotopic standard material, ISL 354 NaCl, provided by the Institute of Salt Lakes, Xining, China¹⁹. The isotopic compositions of boron standard material NIST SRM 951 ($^{11}\text{B}/^{10}\text{B}$) and of chlorine isotopic standard material ($^{37}\text{Cl}/^{35}\text{Cl}$) were determined to be av. 4.05318 ± 0.00099 and av. 0.3189296 ± 0.000083 respectively.

Results

Boron isotopic ratios in seawater were measured from two stations VM3 and VT6 while chlorine isotopic ratios were measured from three stations VM3, VT4 and VT6. The boron isotopic analyses could not be done in samples from station VT4 due to the lack of availability of sufficient quantity of samples which got exhausted in transportation. The boron isotopic measurements were made with an analytical precision of $\pm 0.03\%$ and chlorine isotopic measurements were made with an analytical precision of less than $\pm 0.09\%$. The calculated isotopic compositions of boron and chlorine and the associated parameters in seawater are given in Tables 1–3. The data showed that boron varies from 4.22 to 4.45 ppm at stn VM3, from 4.20 to 4.45 ppm at stn VT4 and from 4.20 to 4.40 ppm at stn VT6 with an apparent decrease in their concentrations with depth, being more pronounced at VT4. The calculated boron isotopic composition ($d^{11}\text{B}$) values varied from 37.75 to 39.85‰ at stn VM3 and from 37.77 to 39.54‰ at stn VT6.

Table 1. Boron and chlorine isotopic compositions and the hydro-chemical characteristics of seawater at stn VM3

Depth	Temp. (°C)	Sal. (psu)	pH	DO (ml/l)	Ca (gm/kg)	Mg (gm/kg)	B (ppm)	$d^{11}\text{B}$ (‰)	$d^{37}\text{Cl}$ (‰)
0	25.96	35.24	8.18	4.45	–	–	–	–	–
25	25.96	35.25	8.18	4.40	0.4345	1.3132	4.45	38.69	0.59
50	25.97	35.26	8.19	4.40	0.4333	1.2976	4.40	37.92	0.49
100	21.36	35.28	8.12	3.33	0.4406	1.3053	4.33	38.17	0.53
200	13.88	34.86	7.97	1.96	0.4401	1.3041	4.39	37.99	0.42
300	11.72	35.02	8.09	3.39	0.4358	1.2934	4.25	37.75	0.57
500	8.41	34.72	7.94	2.50	0.4340	1.2879	4.42	38.65	0.10
750	6.63	34.71	7.89	1.84	0.4345	1.2778	4.22	39.82	0.30
1000	5.14	34.68	7.90	2.07	0.4367	1.2723	4.43	39.58	0.29
1250	4.31	34.69	7.99	2.32	0.4362	1.2710	4.44	39.85	0.10
1500	3.39	34.72	7.96	2.45	0.4358	1.2934	4.40	39.63	0.41
1750	2.81	34.73	7.98	3.00	0.4350	1.2990	4.26	39.04	0.27

Table 2. Chlorine isotopic compositions and the hydro-chemical characteristics of seawater at stn VT4

Depth	Temp. (°C)	Sal. (psu)	pH	DO (ml/l)	Ca (gm/kg)	Mg (gm/kg)	B (ppm)	$d^{37}\text{Cl}$ (‰)
0	27.48	35.29	8.19	4.47	0.4344	1.3029	4.45	0.82
25	27.46	35.29	8.20	4.46	0.4363	1.3065	4.45	0.84
50	27.45	35.29	8.20	4.45	0.4350	1.3026	4.25	0.87
100	18.60	35.30	8.09	3.03	0.4345	1.2896	4.23	0.75
200	13.21	35.06	8.00	2.45	0.4354	1.2921	4.31	0.12
300	11.05	34.94	7.98	2.32	0.4356	1.2888	4.20	0.11
500	9.08	34.82	7.96	2.22	0.4358	1.2934	4.20	0.33
750	7.10	34.80	7.93	1.92	0.4350	1.2872	4.35	0.39
1000	5.94	34.79	7.94	2.67	0.4350	1.2932	4.26	– 0.03
1250	4.95	34.77	7.95	2.30	0.4362	1.3206	4.20	0.59
1500	4.06	34.75	7.96	2.46	0.4350	1.2909	4.40	– 0.02
2000	2.80	34.74	7.99	3.00	0.4364	1.2975	4.27	0.49

SPECIAL SECTION: MID-OCEANIC RIDGES

The chlorine isotopic compositions ($d^{37}\text{Cl}$) varied in the range of 0.1 to 0.59‰ at stn VM3, from -0.03 to +0.87‰ at stn VT4 and from -0.53 to +0.94‰ at stn VT6 with significantly lighter $d^{37}\text{Cl}$ values below 300 m depth layer.

Salinity varied from 34.68 to 35.28 psu at stn VM3, from 34.74 to 35.30 psu at stn VT4 and from 34.73 to 35.26 psu at stn VT6 with a decrease downwards with depth. The values were consistent in the upper 100 m

layer indicating a well mixed condition. However, the temperature profiles from the CTD indicated mixed layer depths of 85 m at stn VM3, 65 m at stn VT4 and 75 m at stn VT6. So also, the thermocline layers observed were from 85 to 325 m at stn VM3; 65 to 270 m at stn VT4 and from 72 to 325 m at stn VT6. The measured hydro-chemical parameters of seawater indicated interesting correlations with $d^{11}\text{B}$ and $d^{37}\text{Cl}$ values (Figures 2–6 and Table 4).

Table 3. Boron and chlorine isotopic compositions and the hydro-chemical characteristics of seawater at stn VT6

Depth	Temp. (°C)	Sal. (psu)	pH	DO (ml/l)	Ca (gm/kg)	Mg (gm/kg)	B (ppm)	$d^{11}\text{B}$ (‰)	$d^{37}\text{Cl}$ (‰)
0	27.42	35.26	8.28	4.50	0.4365	1.3308	4.40	38.67	0.94
25	27.42	35.26	8.29	4.49	0.4384	1.3270	4.34	38.39	0.77
50	27.43	35.26	8.29	4.47	0.4352	1.3259	4.33	37.87	0.69
100	18.90	35.26	8.10	2.84	0.4373	1.3248	4.27	37.77	0.94
200	13.48	35.10	8.03	2.41	0.4363	1.3218	4.35	38.01	0.87
300	11.01	34.94	8.00	1.88	0.4375	1.3102	4.31	38.39	0.76
500	9.17	34.83	7.98	2.18	0.4375	1.3102	4.30	38.76	-0.36
750	7.39	34.81	7.93	1.71	0.4401	1.3041	4.35	39.54	-0.19
1000	6.03	34.80	7.95	2.11	0.4350	1.2932	4.27	38.99	-0.53
1250	5.31	34.81	7.95	1.88	0.4388	1.2885	4.20	39.14	-0.53
1500	4.12	34.76	7.98	2.41	0.4346	1.3157	4.39	38.54	-0.19
2000	2.66	34.73	8.05	2.99	0.4372	1.3235	4.23	38.82	-0.43

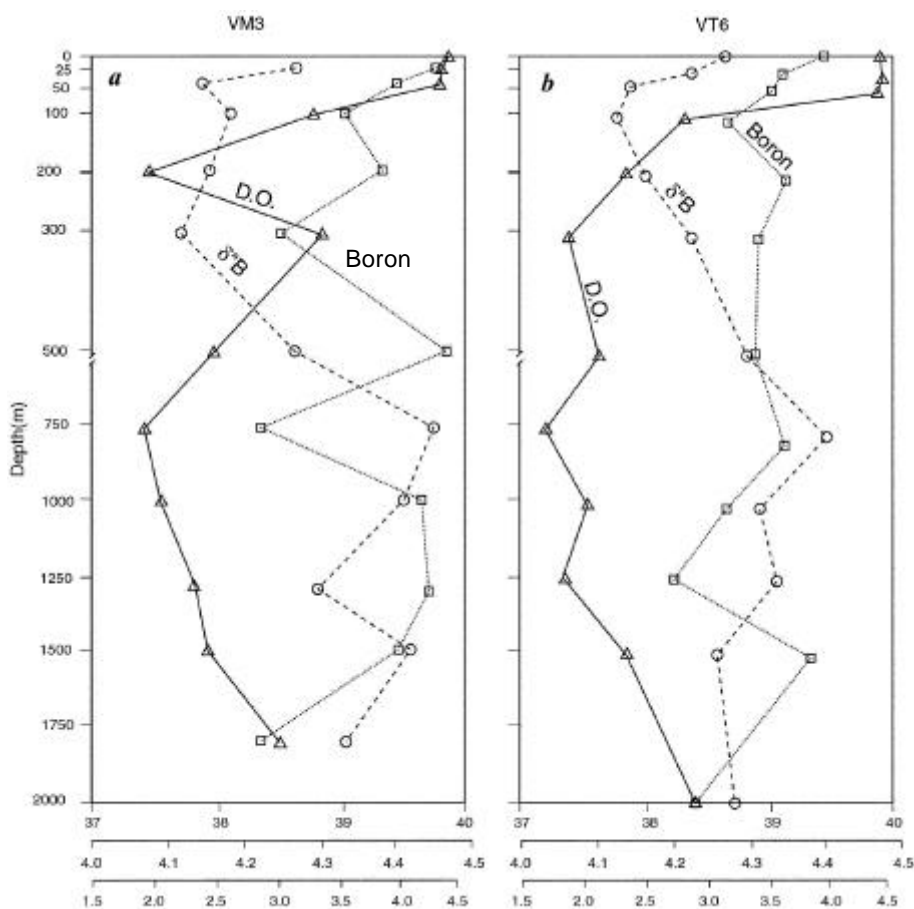


Figure 2. Vertical profiles of $d^{11}\text{B}$, dissolved oxygen and boron at stations VM3 and VT6.

Discussion

The boron and chlorine isotopic compositions of seawater collected from stations VM3 (10°S), VT4 and VT6 (5°S) in ridge area show distinct differences between the upper 300 m layer and the layer down below. In the upper layer, the $d^{11}\text{B}$ values are lighter (av. 38.1‰) while they are heavier (av. 39.3‰) in the lower layer below 300 m.

In contrast, the $d^{37}\text{Cl}$ values are heavier (av. 0.64‰) in the upper layer and lighter (av. 0.06‰) in the lower layer below 300 m depth.

The range of variations of $d^{11}\text{B}$ values of seawater at stn VM3 (37.75–39.82‰) and at stn VT6 (37.77–39.54‰) indicate that all these observed values from the lowest 37.75‰ to the highest 39.82‰ fall in the category of heavier del values which are caused mainly due to the

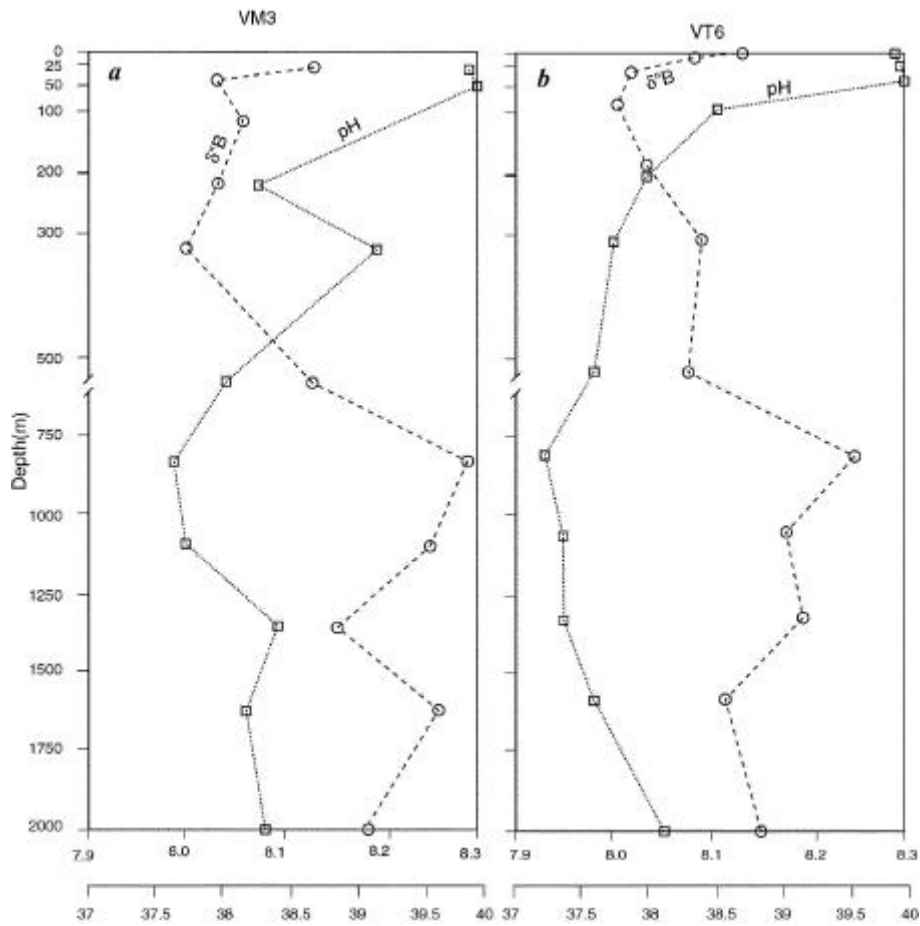


Figure 3. Vertical profiles of $d^{11}\text{B}$ and pH at stations VM3 and VT6.

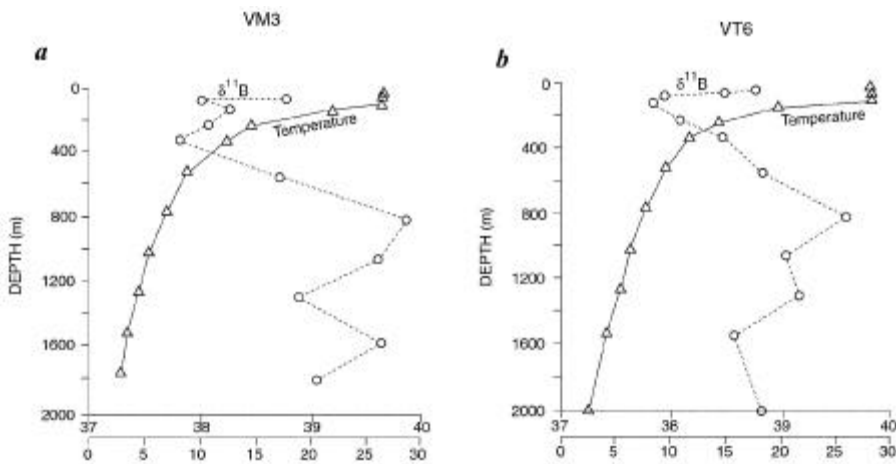


Figure 4. Vertical profiles of $d^{11}\text{B}$ and temperature at stations VM3 and VT6.

enrichment of heavy isotope of boron, ^{11}B , in seawater. The mechanisms underlying the enrichment of the heavier isotope of boron have been explained by earlier investigators²⁰⁻²². However, the difference showed by the lighter $d^{11}\text{B}$ values of the upper layer and those of the heavier ones of the lower layer is to the extent of 1‰ and is very significant in isotopic studies. This difference in $d^{11}\text{B}$ values is more significant in the upper thermocline layer as the average $d^{11}\text{B}$ value (39.3‰) of the lower layer is much closer to the well accepted $d^{11}\text{B}$ value of seawater (39.5‰). Boron is a conservative element in the open sea and has a high residence time, so the $d^{11}\text{B}$ value of seawater is considered to be constant at 39.5‰. The lighter $d^{11}\text{B}$ values observed in the upper thermocline layer therefore indicate an isotopic shift or rather indicate an enrichment of the lighter isotope of boron, ^{10}B , in seawater. The enrichment in ^{10}B isotope can take place only if boron is added to seawater through some sources and the only possible source of boron in the mid-oceanic

regime could be the remineralized organic matter or from the hydrothermal input as the sampling stations are located on the spreading zones of the CIR. The second assumption of addition of boron through hydrothermal input was ruled out because the $d^{11}\text{B}$ values do not show any significant variations in the lower layer below 300 m depth. So the only possibility appears to be the addition of boron through remineralized organic matter. To understand this feature the interrelationships of $d^{11}\text{B}$ values with the measured hydrographic parameters and some chemical elements like calcium, magnesium and boron along with their vertical variations were studied. These interrelationships showed the behavioural patterns of boron synonymous with the well-established features like the relationship of boron isotopic compositions²³⁻²⁵ with temperature, pH, etc.

Of these interrelationships, the one showed by $d^{11}\text{B}$ values with boron concentrations and dissolved oxygen content of seawater (Figure 2) was found to be of impor-

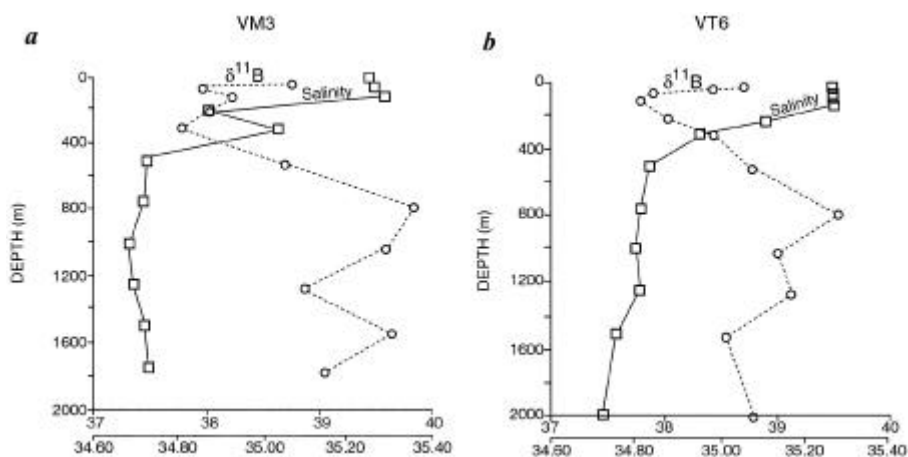


Figure 5. Vertical profiles of $d^{11}\text{B}$ and salinity at stations VM3 and VT6.

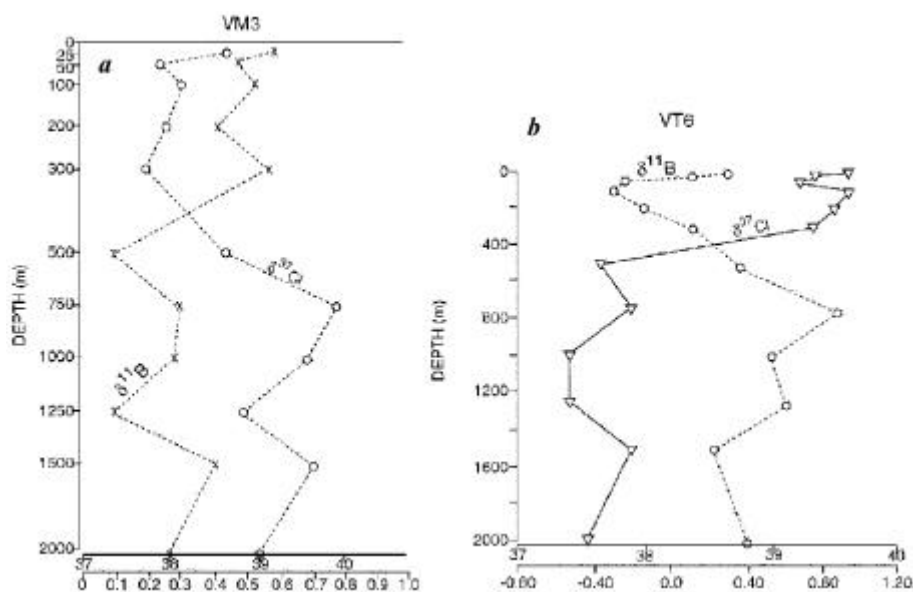


Figure 6. Vertical profiles of $d^{11}\text{B}$, $d^{37}\text{Cl}$ at stations VM3 and VT6.

Table 4. Correlations of $d^{11}\text{B}$ and $d^{37}\text{Cl}$ values with different hydro-chemical characteristics of seawater in the CIR

Stations	Parameters correlated	Correlation coefficient, r
VM3	$d^{11}\text{B}$ v/s Temperature	-0.64
	$d^{11}\text{B}$ v/s Salinity	-0.68
	$d^{11}\text{B}$ v/s pH	-0.69
	$d^{11}\text{B}$ v/s Dissolved oxygen	-0.54
	$d^{11}\text{B}$ v/s $d^{37}\text{Cl}$	-0.46
	$d^{37}\text{Cl}$ v/s Salinity	+0.80
VT4	$d^{37}\text{Cl}$ v/s Salinity	+0.71
VT6	$d^{11}\text{B}$ v/s Temperature	-0.57
	$d^{11}\text{B}$ v/s Salinity	-0.71
	$d^{11}\text{B}$ v/s pH	-0.53
	$d^{11}\text{B}$ v/s Dissolved oxygen	-0.54
	$d^{11}\text{B}$ v/s $d^{37}\text{Cl}$	-0.75
	$d^{37}\text{Cl}$ v/s Salinity	+0.90

tance. Figure 2 indicate that the $d^{11}\text{B}$ values increase and decrease alternately with depth and that the high boron contents are marked by low dissolved oxygen concentrations and lighter $d^{11}\text{B}$ values, suggesting a link between the dissolved oxygen content of seawater, the oxidation of organic matter and the $d^{11}\text{B}$ values. Such a distribution is more pronounced in the upper thermocline layer. Studies have shown that in seawater the decomposition of organic matter takes place as it sinks down from surface to bottom. The oxygen present in seawater is utilized for this decomposition to release nutrients. Boron is one such element found to be released along with nutrients during oxidation²⁶. The released boron lowers boron isotopic ratios and thereby the $d^{11}\text{B}$ values of seawater become lighter. This also suggests that the organically bound boron is mainly the lighter isotope of boron which is, ^{10}B .

However, the organically bound boron alone does not seem to deviate the $d^{11}\text{B}$ values to the extent of 1‰ as the correlation between the $d^{11}\text{B}$ values and dissolved oxygen of seawater though is significant, is not very strong enough to account for 1‰ deviation. This was understood the other way by estimating the amount of boron that could be released by organic matter in seawater based on B : C ratios of organic matter. Calculations made for estimating the B : C ratios for the remineralized organic matter by assuming the $d^{11}\text{B}$ value of organic matter to be fractionated by about 40‰ from seawater indicated that to alter the $d^{11}\text{B}$ value by 1‰ the boron enrichment in seawater should be about 2%. This gives rise to a B : C ratio in organic matter between 1 : 10 and 1 : 20. This means that the organic matter in seawater should be composed of between 5% and 10% of boron which contradicts the earlier findings that organic matter is composed of much less than 5% of boron. So, the organically bound boron alone cannot vary the $d^{11}\text{B}$ values by 1‰. This shows that there must be another factor, apart from organic boron, which is also responsible for the deviation in $d^{11}\text{B}$ values of upper thermocline layer

of seawater in the CIR and this needs to be investigated further in detail.

The chlorine isotopic compositions of seawater measured from three stations in the CIR indicate $d^{37}\text{Cl}$ values to be within $\pm 1\%$. The distribution of $d^{37}\text{Cl}$ values shows variation in the vertical with heavier values in the upper 300 m layer and the lighter ones down below (Figure 6). This correlates well with salinity and establishes a link between $d^{37}\text{Cl}$ values and the evaporation of seawater. Xiao *et al.*²⁷ concluded that the $d^{37}\text{Cl}$ values of seawater are regulated by evaporation to precipitation ratio. During evaporation, the chlorine in seawater is volatilized as HCl causing enrichment in ^{37}Cl isotope in seawater. This increases the evaporation to precipitation ratio and the $d^{37}\text{Cl}$ values become heavier while, the precipitation lowers the ratio. This explains the observed high $d^{37}\text{Cl}$ values in the upper 300 m layer.

Conclusions

- The boron isotopic composition ($d^{11}\text{B}$) values of seawater at stations VM3 and VT6 in the CIR show lower $d^{11}\text{B}$ values in the upper 300 m layer and higher in the lower layer down below.
- A significant difference of 1‰ is observed between the $d^{11}\text{B}$ values of the upper 300 m and the lower layer.
- The difference is more significant in the thermocline layer of the upper 300 m.
- Boron from remineralized organic matter and other unknown factor seems to lower $d^{11}\text{B}$ values in the upper thermocline layer.
- Boron isotopic composition values ($d^{11}\text{B}$) vary inversely with respect to chlorine isotopic compositions ($d^{37}\text{Cl}$) of seawater at all stations in the CIR.
- The increase in evaporation to precipitation ratio of seawater in the CIR gives rise to heavier $d^{37}\text{Cl}$ values in the upper layer relative to those of the lower layer giving rise to variations in the isotopic compositions of chlorine in the ocean.

1. Swihart, G. H., Moore, P. B. and Callis, E. L., Boron isotopic composition of marine and non-marine evaporite borates. *Geochim. Cosmochim. Acta*, 1986, **50**, 1297–1301.
2. Hoering, T. C. and Parker, P. L., The geochemistry of the stable isotopes of chlorine. *Geochim. Cosmochim. Acta*, 1961, **23**, 186–199.
3. Bassette, R. L., A critical evaluation of the available measurements for the stable isotopes of boron. *Appl. Geochem.*, 1990, **5**, 54–65.
4. Shields, W. R., Murphy, T. J., Garner, E. L. and Dibeler, V. H., Absolute isotopic abundance ratio and the atomic weight of chlorine. *J. Am. Chem. Soc.*, 1962, **82**, 1519–1522.
5. Long, A., Eastoe, C. J., Kaufmann, R. S., Martin, J. G., Wirt, L. and Finley, J. B., High precision measurement of chlorine stable isotopic ratios. *Geochim. Cosmochim. Acta*, 1993, **57**, 2907–2912.

6. Xiao, Y. K., Zhou, Y. M. and Liu, W. G., Precise measurement of chlorine isotopes based on Cs_2Cl^+ by thermal ionization mass spectrometry. *Anal. Lett.*, 1995, **28**, 1295–1304.
7. Xiao, Y. K., Zhou, Y. M., Hong, A. S., Liu, W. G., Wang, Y. H. and Shirodkar, P. V., Characteristics of chlorine isotopic compositions in ocean water. *Geol. Rev.*, 2002, **48**, 264–270 (Chinese).
8. You, C. F., Spivack, A. J., Gieskes, J. M., Rosenbever, R. and Bischoff, J. L., Experimental study of boron geochemistry: Implications for pore fluid processes in subduction zones. *Geochim. Cosmochim. Acta*, 1995, **59**, 2435–2442.
9. Ransom, B., Spivack, A. J. and Kastner, M., Stable Cl isotopes in subduction zone pore waters: Implications for fluid rock reactions and the cycling of chlorine. *Geology*, 1995, **23**, 715–718.
10. Eastoe, C. J., Guilbert, J. M. and Kaufmann, R. S., Preliminary evidence for the fractionation of stable chlorine isotopes in ore-forming hydrothermal systems. *Geology*, 1989, **17**, 285–288.
11. Eastoe, C. J. and Guilbert, J. M., Preliminary evidence for the fractionation of stable chlorine isotopes in ore forming hydrothermal systems. *Geochim. Cosmochim. Acta*, 1992, **56**, 4247–4255.
12. Boudreau, A. E., Stewart, M. A. and Spivack, A. J., Stable Cl isotopes and the origin of high-Cl magmas of the stillwater complex, Montana. *Geology*, 1997, **25**, 79–794.
13. Grasshoff, K., Ehrhardt, M. and Kremling, K., *Methods of Seawater Analyses*. Verlag Chemie, 1983, 2nd edn.
14. Hulthe, P., Uppstrom, L. R. and Ostling, G., An automated method for the determination of boron in seawater. *Anal. Chim. Acta*, 1970, **51**, 31.
15. Culkin, F. and Cox, R. A., Sodium, potassium, magnesium, calcium and strontium in seawater. *Deep Sea Res.*, 1966, **13**, 789–804.
16. Liu, W. G., Xiao Y. K., Wang, Q. Z., Qi, H. P., Wang, Y. H., Zhou, Y. M. and Shirodkar, P. V., Chlorine isotopic geochemistry of salt lakes in the Qaidam Basin, China. *Chem. Geol.*, 1997, **136**, 271–279.
17. Xiao, Y. K., Beary, E. S. and Fassette, J. D., An improved method for the high precision isotopic measurements of boron by thermal ionization mass spectrometry. *Int. J. Mass Spectrom. Ion. Proc.*, 1988, **85**, 203–213.
18. Xiao, Y. K. and Zhang, C. G., High precision isotopic measurements of chlorine by thermal ionization mass spectrometry. *Int. J. Mass Spectrom. Ion. Proc.*, 1992, **116**, 183–192.
19. Xiao, Y. K., Zhou, Y. M., Liu, W. G., Wang, Y. H., Wei, H. Z. and Eastoe, C. J., A secondary isotopic reference material of chlorine from selected seawater. *Chem. Geol.*, 2002, **182**, 655–661.
20. Agyei, E. K. and Mc Mullen, C. C., A study of the isotopic abundance of boron from various sources. *Can. J. Earth. Sci.*, 1968, **5**, 921–927.
21. Schwarcz, H. P., Agyei, E. K. and Mc Mullen., Boron isotopic fractionation during clay adsorption from seawater. *Earth Planet. Sci. Lett.*, 1969, **6**, 1–5.
22. Barth, S., Boron isotope variations in nature. *Geol. Rundsch*, 1993, **82**, 649–651.
23. Palmer, M. R., Spivack, A. J. and Edmond, J. M., Temperature and pH controls over isotopic fractionation during adsorption of boron on marine clays. *Geochim. Cosmochim. Acta*, 1987, **51**, 2319–2323.
24. Spivack, A. J., Boron isotope geochemistry. Ph.D. thesis, MIT, WoodsHole Oceanographic Institute, 1986.
25. Spivack, A. J. and Edmond, J. M., Boron exchange between seawater and the oceanic crust. *Geochim. Cosmochim. Acta*, 1987, **51**, 1033–1043.
26. Shirodkar, P. V. and Sankaranarayana, V. N., Boron in seawater of Wadge Bank region in the Indian Ocean. *Indian J. Mar. Sci.*, 1984, **13**, 178–180.
27. Xiao, Y. K., Zhou, Y. M., Hong, A. S., Liu, W. G., Wang, Y. H. and Shirodkar, P. V., Variations in isotopic compositions of chlorine in evaporation controlled salt lakes of Qaidam Basin, China. *Chinese J. Limnol. Oceanol.*, 2000, **18**, 169–177.

ACKNOWLEDGEMENTS. This work was done under Indian Ridge Research Initiative (InRidge Programme) as a part of Indo-US collaboration Project No. CLP 0886 funded by the Office of Naval Research, USA. We thank Third World Academy of Sciences, Trieste, Italy and the Chinese Academy of Sciences, Beijing, China for offering a Fellowship to PVS, to carry out the work. The authors also thank Mr Q. Z. Wang and Mrs Y. H. Wang, Institute of Salt Lakes, Xining for their assistance in sample analyses and InRidge members for onboard assistance in sample collection. Dr E. Desa, Director NIO is thanked for his encouragement in the present study. NIO's contribution # 3834.