

## A Revisit to Vityaz Transform Fault Area, Central Indian Ridge: Isotopic Evidence of Probable Hydrothermal Activity

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### Abstract

Boron and chlorine isotopes have been used as a proxy for tracing the presence of hydrothermal activity in the CIR area. Isotopic compositions of boron ( $\delta^{11}\text{B}$ ) and chlorine ( $\delta^{37}\text{Cl}$ ) measured from seawater in a 2000 m water column at Vema (VM3: 10° 43.23'S and 66° 36.5'E) and Vityaz, (VT4: 5° 39.55'S and 68° 03.77'E and VT6: 5° 38.83'S and 67° 27.39'E) transform fault areas in the Central Indian Ridge showed significant variations below 300 m water depth at VT6 relative to VT4 and VM3. An appreciable decrease in  $\delta^{11}\text{B}$  (av. 38.9‰) with a concomitant increase in  $\delta^{37}\text{Cl}$  (av. 1.15‰) by ~1‰ below 300 m water depth at VT6, relative to normal seawater value and those at VM3 and VT4, indicated the presence of hydrothermal activity at VT6.

This study coupled with earlier studies on serpentinite peridotites from the Vityaz transform fault area showed signatures of low temperature alteration, signifying the presence of hydrothermal activity at around this slow spreading ridge area. The observed features support the possible presence of hydrothermal activity at Vityaz transforms fault area in the Central Indian Ridge.

**Keywords:**  $\delta^{11}\text{B}$  and  $\delta^{37}\text{Cl}$  variations; Seawater; Vema and Vityaz transform faults; CIR; Hydrothermal activity

### Introduction

Boron and chlorine are excess volatiles and are readily mobilized during hydration and melting. They partition strongly into the liquid phase during water-rock interactions at high temperatures [1,2]. Boron is one of the major elements of seawater and is significantly involved in the marine biogeochemical cycles. The two stable isotopes of boron,  $^{10}\text{B}$  and  $^{11}\text{B}$ , with a relative abundance of 18.38% and 81.17%, respectively, fractionate to the extent of 90‰, with a low of -30‰ in non-marine evaporite minerals (tourmalines) to a high of +60‰ in marine salt lake brines [3,4]. Chlorine is a major anion in crustal and magmatic fluids and its two stable isotopes,  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  with a relative abundance of 75.53% and 24.47% respectively, fractionate to the extent of 15‰, with a lowest value of -8.0‰ in pore waters to the highest value of +7‰ in minerals [5].

Estimates showed that approximately 60% of the earth's chlorine resides within the mantle and 40% within the crustal reservoir. Several studies indicated the mantle to be isotopically heavy whereas the oceans, asthenosphere and the crust to be isotopically lighter. Studies of depleted mantle beneath the oceanic ridges showed that chlorine gets isotopically fractionated between these two reservoirs. Each of these reservoirs has a distinctly different chlorine isotopic signature of +4.7‰ for mantle, 0‰ for the crustal rocks and within  $\pm 1\%$  for seawater. Similarly, the boron isotopic signature of these reservoirs also shows a value of +39.7‰ for seawater,  $\pm 5\%$  for sediments and -4‰ for fresh basalts or unaltered oceanic crust [1,5,6].

Tectonic activity in the mid-oceanic ridge (MOR) area leads to rifting and crustal generation and creates severe deformities in the oceanic crust, giving rise to hydrothermalism. The basalt-seawater interaction at the ridge sites brings about further changes in the chemistry of seawater and also precipitates sulfidic and silicate minerals at the hydrothermal sites. Till date, many hydrothermal sites have been identified in the Central Indian Ridge (CIR), along the South East and South West Indian Ridges and within 19°S to 25°S at Rodriguez Triple Junction [7,8]. No information however is yet available on hydrothermalism at the CIR area between 5°S and 8°S. The CIR is a slow

to intermediate spreading ridge with a spreading rate of 40-60 mm/yr (full rate) [9], which can be considered similar to MAR. The aim of this study was to detect the presence of hydrothermal activity at Vema and Vityaz transform fault areas in this slow spreading ridge system of the CIR between 5° and 10° S. To achieve this objective, boron and chlorine isotopes have been used as tracers.

### Material and Methods

Seawater samples were collected from VM3 (10° 43.23'S and 66° 36.5'E), VT4 (5° 39.55'S and 68° 03.77'E) and VT6 (5° 38.83'S and 67° 27.39'E) transform fault areas in the Central Indian Ridge (Figure 1, Table 1), during ORV Sagar Kanya cruise 125 (July-August 1997). The study was constrained by the collection of seawater samples from these areas (VM3, VT4 and VT6, Table 4) only up to 2000 m water depth as against the actual sea floor depths of 2200 m at VM3, 3100 m at VT4 and 4020 m at VT6. All the seawater samples were collected from standard water depths using a CTD and the collected samples were stored in deep freeze on board the ship prior to their analyses for boron and chloride content at the onshore laboratory. The boron was analysed by the non-aqueous solvent method of Hulthe et al., [10] while the chloride content was calculated from the measured salinity values obtained from the CTD. The calcium and magnesium were analysed by titrimetric method at the onshore laboratory following the methodology as described by Culkin and Cox [11]. The magnesium values were corrected for strontium (0.6%) and for the end point overestimate (1%), as suggested by Carpenter and Manella [12].

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Stn. No.	Latitude	Longitude
VM	10° 43.23'S	66° 36.5'E
VT4	5° 39.55'S	68° 03.77'E
VT6	5° 38.83'S	67° 27.39'E

Table 1: Position of stations in the CIR area.

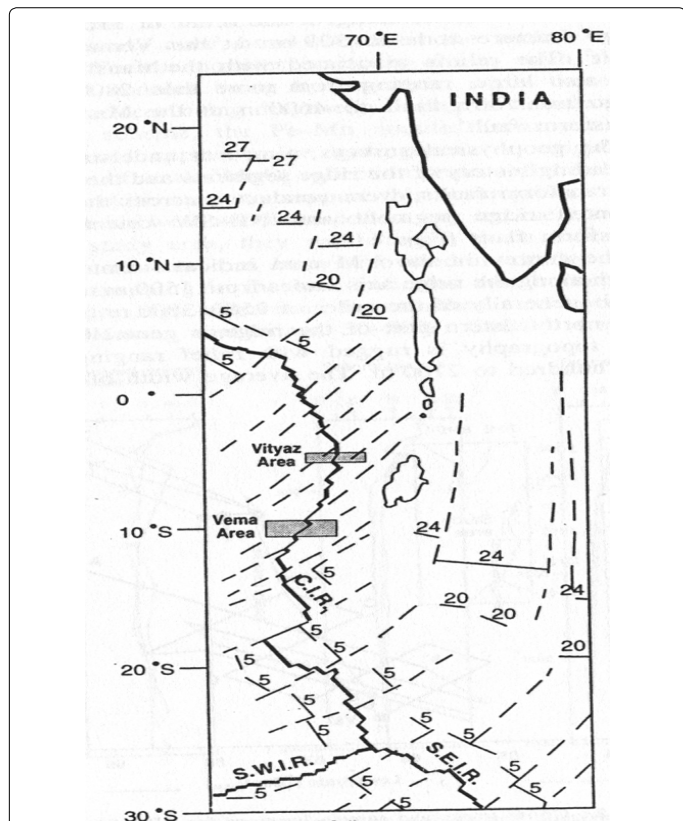


Figure 1: Map showing study area at Vema and Vityaz fracture zone areas in CIR.

For isotopic measurements, the boron and chlorine were extracted from each of these water samples using ion exchange technique. Amberlite IRA 743 and a mixture of Ion exchanger II and Shanghai No.1 ion exchange resins were used for the separation of boron while chlorine was separated using Shanghai No.732 and Dowex (50 x 8), conditioned with Ba(NO<sub>3</sub>) solution [13]. The isotopic measurements of boron and chlorine in the extracted samples were carried out at the Institute of Salt Lakes, China by +ve thermal ionisation mass spectrometry of Cs<sub>2</sub>BO<sub>4</sub><sup>+</sup> and Cs<sub>2</sub>Cl<sup>+</sup> ions respectively, using a VG 354 model TIMS [14]. The measured isotopic ratios were expressed as del values relative to their standard reference materials and were calculated as follows:

$$\delta^{11}B = \left[ \frac{(^{11}B / ^{10}B)_{sam}}{(^{11}B / ^{10}B)_{ref}} - 1 \right] \times 1000 - 0.19$$

where, 0.19 is the correction for <sup>17</sup>O. and

$$\delta^{37}Cl = \left[ \frac{(^{37}Cl / ^{35}Cl)_{sam}}{(^{37}Cl / ^{35}Cl)_{ref}} - 1 \right] \times 1000$$

The standard used for boron isotopic measurements was NIST SRM 951 and for chlorine, the isotopic standard used was the ISL

354 NaCl, provided by the Institute of Salt Lakes, Xining, China. The average ratios observed for boron and chlorine standards were 4.05318 ± 0.00099 and 0.3189296 ± 0.000083, respectively.

## Results

### Station VM3

The δ<sup>11</sup>B values of seawater vary from 37.75 to 38.69‰ (av. 38.10‰) in the upper 300 m depth layer and from 38.65 to 39.85‰ (av. 39.43‰) below 300 m water depth. The δ<sup>37</sup>Cl values vary from 0.42 to 0.57‰ (av. 0.52‰) in the upper 300 m layer and from 0.1 to 0.41‰ (av. 0.25‰) down depth. Other major elements measured in the water column at this station showed calcium to vary from 0.4333 to 0.4406 gm/kg (av. 0.4360 gm/kg) and magnesium from 1.2710 to 1.3132 gm/kg (av. 1.2920 gm/kg) (Table 2).

The temperature measurements showed a highest value of 25.97°C in the upper layer to a low of 2.81°C at 1750 m depth, while, the variation in pH was from 8.18 in the surface layer to 7.98 at 1750 m depth layer. This station showed higher salinity of 35.28 psu in the upper surface layer to a low of 34.73 psu at 1750 m depth layer (Figure 2 and Table 2).

### Station VT4

No data are available for δ<sup>11</sup>B values of seawater at VT4 as no measurements could be made due to the loss of extracted seawater samples. However, the δ<sup>37</sup>Cl values measured at VT4 vary from 0.11 to 0.87‰ (av. 0.58‰) in the upper 300 m layer and from -0.03 to 0.59‰ (av. 0.29‰) down below. The calcium content was found to vary from 0.4344 to 0.4364 gm/kg (av. 0.4354 gm/kg) and magnesium from 1.2872 to 1.3206 gm/kg (av. 1.2971 gm/kg) (Table 3).

The temperature values showed a variation from 27.48°C in the surface layer to 2.8°C at 2000 m depth, while the pH variation was from 8.20 at surface to 7.99 at 2000 m depth layer. Salinity showed a variation from 35.30 psu in the upper layer to 34.74 psu at 2000 m water depth layer (Figure 3 and Table 3).

### Station VT6

At this station, the δ<sup>11</sup>B values vary from 37.77 to 38.67‰ (av. 38.18‰) in the upper 300 m layer and from 38.76 to 39.54‰ (av. 38.9‰) down below. Similarly, the δ<sup>37</sup>Cl values show variation from 0.69 to 1.23‰ (av. 1‰) in the upper 300 m layer and from -0.87 to 1.57‰ (av. 1.15‰) down below. The variation in calcium was from 0.4350 to 0.4401 gm/kg (av. 0.4370 gm/kg) and magnesium from 1.2885 to 1.3308 gm/kg (av. 1.3150 gm/kg) (Table 4).

The temperature varies from 27.43°C in the upper layer to 2.66°C at

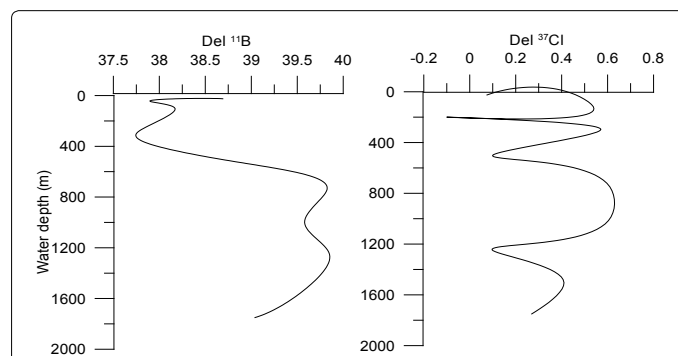


Figure 2: Vertical profiles of δ<sup>11</sup>B and δ<sup>37</sup>Cl in water column at Stn. VM3 in the CIR.

Depth (m)	Temp (°C)	Sal. (psu)	pH	DO (ml/l)	Ca (gm/kg)	Mg (gm/kg)	B (ppm)	$\delta^{11}\text{B}$ (‰)	$\delta^{37}\text{Cl}$ (‰)
0	25.96	35.24	8.18	4.45	-	-	-	-	-
25	25.96	35.25	8.18	4.40	0.4345	1.312	4.45	38.69	0.075
50	25.97	35.26	8.19	4.40	0.4333	1.296	4.40	37.92	0.49
100	21.36	35.28	8.12	3.33	0.4406	1.303	4.33	38.17	0.53
200	13.88	34.86	7.97	1.96	0.4401	1.301	4.39	37.99	-0.10
300	11.72	35.02	8.09	3.39	0.4358	1.294	4.25	37.75	0.57
500	8.41	34.72	7.94	2.50	0.4340	1.289	4.42	38.65	0.10
750	6.63	34.71	7.89	1.84	0.4345	1.278	4.22	39.82	0.61
1000	5.14	34.68	7.90	2.07	0.4367	1.273	4.43	39.58	0.61
1250	4.31	34.69	7.99	2.32	0.4362	1.270	4.44	39.85	0.10
1500	3.39	34.72	7.96	2.45	0.4358	1.294	4.40	39.63	0.41
1750	2.81	34.73	7.98	3.00	0.4350	1.290	4.26	39.04	0.27

Table 2: Hydro-chemical characteristics,  $\delta^{11}\text{B}$  and  $\delta^{37}\text{Cl}$  values of seawater at stn.VM3.

Depth (m)	Temp (°C)	Sal. (psu)	pH	DO (ml/l)	Ca (gm/kg)	Mg (gm/kg)	B (ppm)	$\delta^{37}\text{Cl}$ (‰)
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	0.65
750	7.10	34.80	7.93	1.92	0.4350	1.2872	4.35	0.70
1000	5.94	34.79	7.94	2.67	0.4350	1.2932	4.26	-0.025
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	-0.016
1950	2.80	34.74	7.99	3.00	0.4364	1.2975	4.27	0.49

Table 3: Hydro-chemical characteristics and  $\delta^{37}\text{Cl}$  values of seawater at stn.VT4.

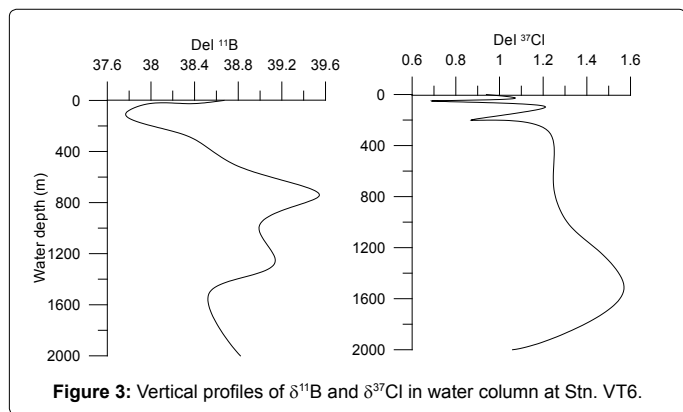


Figure 3: Vertical profiles of  $\delta^{11}\text{B}$  and  $\delta^{37}\text{Cl}$  in water column at Stn. VT6.

2000 m depth layer. The pH also shows a minor difference in values at VT6 compared to those at VM3 and VT4. At VT6, the pH varies from 8.29 at surface to 8.05 at 2000 m depth layer. The salinity variation was from 35.26 psu at surface to 34.73 psu at 2000 m depth layer (Figure 4 and Table 4).

### Discussion

The decrease in  $\delta^{11}\text{B}$  values and an increase in  $\delta^{37}\text{Cl}$  below 300 m water depth at VT6 (Figure 4 and Table 4) as compared to VM3 and VT4 stations and the normal seawater values ( $\delta^{11}\text{B}=39.8‰$  and  $\delta^{37}\text{Cl}=0.3‰$ ), suggested the removal and addition of boron (as  $^{10}\text{B}$ ) and chlorine (as  $^{37}\text{Cl}$ ), respectively, to the seawater at VT6. In MOR areas, this is due to the tectonic and magmatic activities at the seafloor. Since

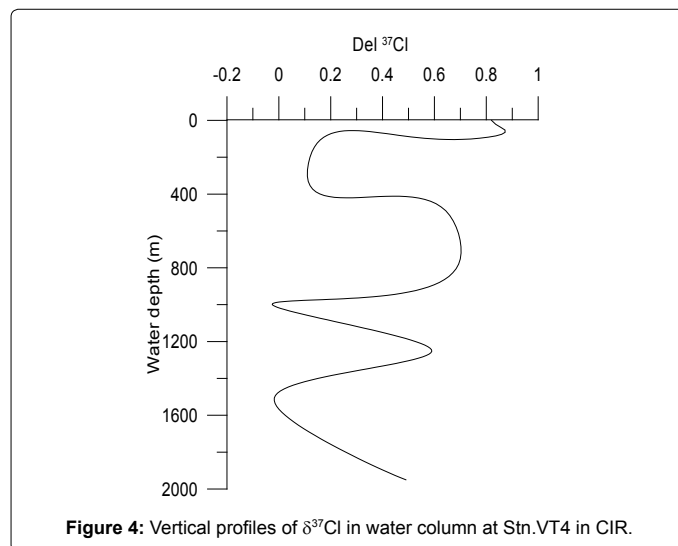


Figure 4: Vertical profiles of  $\delta^{37}\text{Cl}$  in water column at Stn. VT4 in CIR.

the sampling site has a basaltic basement, the first assumption that the observed isotopic difference at VT6 is due to the seawater interaction with basalts does not hold good as it cannot lead to low values only at VT6. Because, if this is the case, then similar low values should have been observed at VM3 and VT4 stations too, as all the 3 sampled sites have the same basaltic basement. In the absence of such a situation, the other possibility could be the hydrothermal circulation of seawater through the permeable basement rocks.

At MOR sites, where new crust is generated, the seawater circulates

Depth (m)	Temp. (°C)	Salinity (psu)	pH	DO (ml/l)	Ca (gm/kg)	Mg (gm/kg)	B (ppm)	$\delta^{11}\text{B}$ (‰)	$\delta^{37}\text{Cl}$ (‰)
0	27.42	35.26	8.28	4.5	0.4365	1.3308	4.4	38.67	0.94
25	27.42	35.26	8.29	4.49	0.4384	1.327	4.34	38.39	1.07
50	27.43	35.26	8.29	4.47	0.4352	1.3259	4.33	37.87	0.69
100	18.9	35.26	8.1	2.84	4.4373	1.3248	4.27	37.77	1.21
200	13.48	35.1	8.03	2.49	0.4363	1.3218	4.35	38.01	0.87
300	11.01	34.94	8	1.88	0.4375	1.3102	4.31	38.39	1.23
500	9.17	34.83	7.98	2.18	0.4375	1.3102	4.3	38.76	1.25
750	7.39	34.81	7.93	1.71	0.4401	1.3041	4.35	39.54	1.25
1000	6.03	34.8	7.95	2.11	0.435	1.2932	4.27	38.99	1.31
1250	5.31	34.81	7.95	1.88	0.4388	1.2885	4.2	39.14	1.47
1500	4.12	34.76	7.98	2.41	0.4346	1.3157	4.39	38.54	1.57
2000	2.66	34.73	8.05	2.99	0.4372	1.3235	4.23	38.82	1.06

**Table 4:** Hydro-chemical characteristics,  $\delta^{11}\text{B}$  and  $\delta^{37}\text{Cl}$  values of sea water at stn. VT6.

through the porous rocks, first at lower temperature (<150°C) in the down flowing limb called the “recharge zone”. Thereafter, the circulation reaches higher temperature (>150°C) in the deepest portion of the oceanic crust called the “reaction zone” and lastly, the hot, buoyant fluid rises rapidly through the “up flow zone” to exit at the seafloor as hydrothermal fluid [15]. This circulation is driven by the heat source from the magma chamber located down below the circulating system.

During this hydrothermal circulation, large exchange of elements occurs between the circulating seawater and the oceanic crust and these are reflected in the isotopic compositions of most of the elements. Among the elemental isotopes, the isotopes of boron and chlorine act as excellent tracers of hydrothermal activity [16,17]. The findings of Palmer [18] showed that the boron isotopic composition of hydrothermal fluids depends upon the amount of seawater passing through the convection cell, uptake of boron from seawater by oceanic crust at low temperature (<150°C) on the down welling limb and leaching of boron from the oceanic crust by hot fluids (>150°C) on the upwelling limb. His studies indicated that the removal of boron from the circulating seawater as  $^{10}\text{B}$  takes place by its incorporation into the low temperature weathering products. This causes variation in the initial boron isotopic composition of the circulating seawater. As the seawater circulates further down, its temperature increases and at higher temperature (>150°C), the boron is leached out from the wall rock without any isotopic fractionation, because at higher temperatures, the fractionation of boron is nil ( $\alpha=1$ ; [19]). Thus, at higher temperatures, boron is extracted from the oceanic crustal rock with no resolvable isotopic fractionation. The boron isotopic composition of hydrothermal fluid is therefore determined by the  $\delta^{11}\text{B}$  value of the wall rocks [19]. Hence, the change in  $^{11}\text{B}$  value of hydrothermal fluid depends upon the  $\delta^{11}\text{B}$  value of the oceanic crust. Chaussidon and Jambon [20] have shown that the fresh basalts contain boron up to 0.5 ppm with a  $\delta^{11}\text{B}$  value of -4‰. This suggested initial enrichment of the lighter isotope of boron,  $^{10}\text{B}$ , in the fresh oceanic crust, which on subsequent leaching, lowers the  $\delta^{11}\text{B}$  value of the hydrothermal fluid than that of the surrounding seawater value ( $\delta^{11}\text{B}=+39.8\%$ ).

However, the amount of boron removed from the circulating seawater depends upon the type of ridge environment as boron removal differs in areas of slow and fast spreading ridges. Nearly 50% of boron is removed from seawater at hydrothermal sites from the slow spreading areas like the MAR at a low temperature due to greater circulating depths. Conversely, little boron is removed at fast spreading areas like the East Pacific Rise (EPR) [18]. This is attributed to the magma

chambers that are shallow seated and steady at fast spreading ridges in contrast to deeper, more episodic chambers at slow spreading ridges [21]. Thus, the boron isotopic compositions of hydrothermal fluids from the slow spreading ridges do not show a simple mixing between the oceanic crust and seawater as is the case for fast spreading ridges. The uptake of boron from the circulating seawater is accompanied by hydration of the oceanic crust including serpentinisation of the upper mantle. Serpentinites therefore contain higher concentrations of boron than the other low temperature alteration products of the upper oceanic crust [22-24].

Earlier geological findings indicate signatures of low temperature alteration on serpentinised peridotites from 6° 38'S [25], an off axis region around the Vityaz transform fault area, which is nearly 1° away from VT6 location. The serpentinisation of peridotites is a good indication of the presence of hydrothermal activity. Normally, at slow spreading ridges, the deep penetration of hydrothermally driven seawater along the faults allows reaction of circulating seawater with peridotites and thus the formation of serpentinites, vis-à-vis, on the fast spreading ridges, where the circulation of hydrothermally driven seawater occurs above the peridotites with the absence of serpentinisation [21].

During serpentinisation, boron and water are removed from the circulating seawater by the upper mantle [22,24] over a temperature range of 0-500°C. However, the boron uptake decreases with an increase in temperature up to 250°C and above this temperature, uptake of boron stops. Analyses of the serpentinites obtained from the Vityaz transform fault have shown high Mg-rich lizardite and chrysotile pseudomorphs with varying morphologies [25]. Similarly, their elemental analyses have shown a very low Sr content (<2 ppm), positive Eu anomaly (Eu/Eu up to + 3.38) and high boron content (118-713 ppm), indicating a substantial hydrothermal influence during serpentinisation [25]. Moreover, the presence of high ratios of La/Sm (up to 4.40) and Nb/La (1.06 to 6.34) further support this idea of hydrothermal influence [9]. Another study of fine scale chemical composition of the ferromanganese crusts obtained from the Vityaz transform fault area indicated high Si/Al ratio (av. 7.32), higher shale normalised La/Ce values (av. 0.91) and a positive europium anomaly [7]. Those authors suggested a mixed hydrogenous-hydrothermal metal input during the formation of the crusts [8].

The reported  $\delta^{11}\text{B}$  values from seawater dominated hydrothermal systems from MOR areas showed a range of values from + 30‰ to + 36.8‰ (Table 5a) [16,19]. Comparatively, our measurements showed average  $\delta^{11}\text{B}$  values of +39.43‰ and +38.90‰ below 300 m water depth at VM3 and VT6 respectively, indicating the value at VT6 to be distinctly lower by ~1‰ as compared to that at VM3 as well as the established seawater  $^{11}\text{B}$  value of 39.8‰. Such a decrease in  $\delta^{11}\text{B}$  value possibly indicates the role of hydrothermal circulation of seawater at VT6. However, the observed low  $^{11}\text{B}$  value at VT6 is beyond the range of values observed for hydrothermal fluids from other MOR environments mentioned above. This is due to the fact that, the  $\delta^{11}\text{B}$  values cited above have been measured from in situ hydrothermal fluids collected from active hydrothermal sites. While, in our investigation, the isotopic measurements are of seawater collected from a depth much above a plausible, the suspected hydrothermal site at stn. VT6. It can therefore be inferred that the mixing of suspected vent fluid (with low  $\delta^{11}\text{B}$  value), with the overlying seawater, restored the  $\delta^{11}\text{B}$  value of seawater at VT6 to the observed value of 38.90‰.

Chloride is the main anion of oceanic hydrothermal systems and as  $\text{CaCl}_2$ , it is a major input to seawater at hydrothermal discharge sites



Location	Sample	Range $\delta^{11}\text{B}$ (‰)	Average $\delta^{11}\text{B}$ (‰)	Source
Pacific and Atlantic oceans	Surface Seawater	39.5 to 39.8	39.7	Spivack and Edmond [20]
13°N to 21°N South West Vent areas	Hydrothermal fluids	30.0 to 36.8	33.36	Spivack and Edmond [20]
Mid-Atlantic Ridge (Broken Spur, TAG, MARK and East Pacific Rise)	Hydrothermal fluids	24.3 to 35	32.6	Palmer [19]
Icelandic Hydrothermal systems	Hydrothermal fluids	-6.7 to + 3.1	- 1.82	Palmer [33]
VT6 in the CIR	Seawater at 2000 m above the seafloor	37.77 to 38.67	38.90	Present study

**Table 5a:** Measured  $\delta^{11}\text{B}$  values of sea water and hydrothermal fluids by earlier workers from various oceanic locations.

Location	Sample	Range $\delta^{37}\text{Cl}$ (‰)	Average $\delta^{37}\text{Cl}$ (‰)	Source
Atlantic, Pacific, Indian and Southern oceans	Surface Seawater	- 0.76 to + 0.74	+ 0.039 ± 0.04	Shirodkar et al.,
Atlantic, Indian, Pacific oceans and Mediterranean and Red Sea	Surface seawater	- 0.07 to + 0.08		Godon et al., [29]
Indian and Antarctic ocean	22 m to 4560 m depth	- 0.04 to + 0.09		Godon et al., [29]
Atlantic, Pacific, Indian and Southern ocean	Surface Seawater	- 0.56 to + 0.66	+ 0.03	Xiao et al., [30]
Ore forming systems	Hydrothermal fluids	- 1.0 to 0.5		Eastoe and Guilbert [18]
Slow spreading, high temperature field (MAR)	Hydrothermal fluids	- 0.09 to + 0.00	- 0.03 ± 0.06	Bonifacie et al., [28]
Fast spreading, high temperature field (EPR)	Hydrothermal fluids	- 0.08 to 0.00	- 0.03 ± 0.06	Bonifacie et al., [28]
VT6 in the CIR	Seawater at 2000 m above the seafloor	- 0.87 to 1.57	1.07	Present study

**Table 5b:** Measured  $\delta^{37}\text{Cl}$  values of sea water and hydrothermal fluids by earlier workers from various oceanic locations.

[26]. It is important in hydrothermal systems because the distribution of other elements or compounds between the rock forming minerals and circulating seawater depends upon chloride. The chlorine isotopic fractionation in hydrothermal systems is associated with mineralisation and phase separation processes during seawater circulation at low and high temperatures. These processes decide the final  $\delta^{37}\text{Cl}$  value of the hydrothermal fluid.

Our measurements on  $\delta^{37}\text{Cl}$  values of seawater from Vema and Vityaz areas indicate a variation vis-à-vis that of boron with significantly higher  $\delta^{37}\text{Cl}$  value (av. +1.15‰) at VT6 relative to those at VM3 (av. +0.25%) and VT4 (av. +0.29%) from 300 m depth downward. This variation gives an indication of some other processes of chlorine isotopic fractionation to be operating at MOR areas [27]. It has been shown that in hydrothermal systems of MOR environments, the phase separation processes associated with interaction of seawater with wall rock during sub-critical (low T and P) and supercritical conditions (high T and P) play a significant role. They partition volatile chlorides into the vapour phase and non-volatile elements into the condensed phase. At sub-critical condition, the circulating seawater is associated with small amount of vapour phase with lower chlorinity separated from large amount of seawater enriched in salts and depleted in volatile species. While, during a super-critical condition, the vapour phase is associated with seawater-like liquid accompanied by brine of high salinity, high metal content and low volatiles. The chlorine isotopic fractionation involved in this case, either chemically transfers chlorine from aqueous chloride ion to gaseous molecule (NaCl, HCl and Chlorine) or chlorine is incorporated into the solid phases [27].

It has been observed experimentally that the isotopic fractionation factors,  $\alpha$ , between the aqueous chlorine and HCl ( $\alpha_{\text{aq. Chlorine-HCl}}$ ) and that between vapour and liquid or between seawater and brine (vapour-liquid) are from 0 to 1‰ at very high temperatures (300-450°C). This suggested low salinity vapour phase to have  $\delta^{37}\text{Cl}$  values from 0 to +1‰ and a conjugate high salinity phase to have  $\delta^{37}\text{Cl}$  values from -1 to 0‰. In an extreme case of HCl and  $\text{Cl}_2$  co-existence, the  $\alpha_{\text{HCl-Cl}_2}$  is less than 0.30% at temperature >200°C and the  $\delta^{37}\text{Cl}$  values are -ve to +1%. Phase separation processes also precipitate chloride salts and produce a small fractionation, which decreases at higher temperature [27].

The observed low temperature serpentinisation of peridotites

around the Vityaz transform fault area at 6° 38'[25], clearly indicates the presence of a subcritical condition at the suspected hydrothermal site at Vityaz transform fault at VT6 (5° 38.83'S), envisaging small amount of vapour with lower chlorinity to be separated from seawater. Hence, this should give a  $\delta^{37}\text{Cl}$  value of +1‰ for the vent fluid and this expected value matches very well with our measured  $\delta^{37}\text{Cl}$  value (av. +1.07%) for the 2000 m water column at VT6 as compared to the other two stations VM3 and VT4 whose average  $\delta^{37}\text{Cl}$  values are much lower for the 2000 m water column (+0.38% and 0.43%, respectively).

A comparison of  $\delta^{37}\text{Cl}$  values of hydrothermal fluids from different spreading areas (Table 5b) shows that from fast spreading MOR, the  $\delta^{37}\text{Cl}$  are having values of around -0.3‰ type, while, Eastoe and Guilbert (1992) observed a variation in  $\delta^{37}\text{Cl}$  from -1 to 0.5‰ in hydrothermal fluids from ore forming systems. All these  $\delta^{37}\text{Cl}$  values have been measured from active hydrothermal fluids collected from known sites, whereas, our values are measured from seawater collected much above the seafloor. These measurements show the observed average  $\delta^{37}\text{Cl}$  values of +0.25% at VM3, +0.29% at VT4 and a significantly higher value of +1.07‰ at VT6, below 300 m water depth. The location of VT4 and VT6 are very close to each other, while station VM3 is 5° apart from both VT4 and VT6 stations (Table 4). Despite large distance between them, the stations VT4 and VM3 show similar, low  $\delta^{37}\text{Cl}$  values, while the value at VT6 is different and significantly higher. This suggests a probable event of hydrothermal activity at VT6 area in the CIR.

During the investigations on chlorine isotopic measurements of seawater from various locations in the world oceans, including CIR and SWIR, Godon et al., [28] remarked that the high  $\delta^{37}\text{Cl}$  values of up to +0.94‰ from surface seawater within the Vityaz transform fault area [29] in the CIR are unique and may have been influenced by the presence of hydrothermal plume.

Normally, during hydrothermal circulation, calcium is released from the wall rocks and magnesium is removed from the circulating seawater for authigenic mineral formation. The calcium and magnesium values of seawater measured from VM3, VT4 and VT6 stations are found to be nearly similar and their concentrations are also similar to normal seawater values (Tables 2-4). This is because, calcium and magnesium are conservative elements and their addition and removal respectively, from seawater circulating the suspected

convection cell will not indicate any change in their values in seawater lying much above the suspected hydrothermal site as the fluid diffuses upwards. This is due to the constancy in composition of seawater [30-34] with respect to major elements, which maintains the ratio of the element to chlorinity at a constant level as the suspected fluid devoid of magnesium rises upwards in the water column [34-37].

## Conclusions

The isotopic studies of boron and chlorine in 2000 m seawater column at Vema (VM3) and Vityaz (VT4 and VT6) transform fault areas in the CIR indicate:

- Significant variations in boron and chlorine isotopic compositions below 300 m depth at VT6 as compared to VT4 and VM3 and the normal seawater values.
- A considerable decrease in  $\delta^{11}\text{B}$  (av. 38.9‰) with a concomitant increase in  $\delta^{37}\text{Cl}$  (av. 1.15‰) by ~1‰ below 300 m water depth at VT6 relative to normal seawater and the seawaters at stns. VT4 and VM3 indicate a feature characteristic of the presence of hydrothermal activity.
- The presence of the signatures of low temperature alteration of serpentinised peridotites from the off axis region of the Vityaz transform fault area at station VT6 also supports the presence of hydrothermal activity at VT6.
- The observed features thus strongly support the possible presence of hydrothermal activity at Vityaz transform fault (VT6) area in the Central Indian Ridge.

These findings should be confirmed further by undertaking studies in the CIR by additional sampling at deeper water levels.

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## References

1. Palmer MR (1991) Boron-isotope systematic of Halmahera arc (Indonesia) lavas: Evidence for involvement of the subducted slab. *Geology* 19: 215-217.
2. Smith HJ, Spivack AJ, Staudigel H, Hart SR (1995) The boron isotopic composition of altered oceanic crust. *Chem Geol* 126: 119-135.
3. Swihart GH, Moore PR, Callis EI (1986) Boron isotopic compositions of marine and non-marine evaporate borates. *Geochim Cosmochim Acta* 50: 1297-1301.
4. Vengosh A, Chivas AR, Mc Culloch M, Starinsky TA, Kolodny Y (1991) Boron isotope geochemistry of Australian salt lakes. *Geochim Cosmochim Acta* 55: 2591-2606.
5. Magenheimer AJ, Spivack AJ, Michael PJ, Gieskes JM (1995) Chlorine stable isotope compositions of the oceanic crust: Implications for Earth's distribution of chlorine. *Earth Planet Sci Lett* 131: 427-432.
6. Spivack AJ (1986) Boron isotope geochemistry (Unpublished, Ph. D. thesis): Cambridge, Massachusetts, Woods Hole Oceanographic Institution -Massachusetts Institute of Technology Joint program.
7. Banerjee R, Miura H (2003) Variations in the fine scale composition of a Vityaz Fracture Zone, Central Indian Ridge ferromanganese crust: Paleooceanographic implications.
8. Banerjee R, Ray D (2003) Metallogenesis along the Indian Ocean Ridge System. *Current Science* 85: 321-327.
9. Ray D, Banerjee R, Iyer SD, Rao TG (2005) Serpentinites from the Northern Central Indian Ridge: Implications on low temperature hydrothermal alteration.
10. Hulthe P, Uppstrom LR, Ostling G (1970) An automated method for the determination of boron in seawater. *Anal Chim Acta* 51: 31-37.
11. Culkin F, Cox RA (1966) Sodium, potassium, magnesium, calcium and strontium in seawater. *Deep Sea Res* 13: 789-804.
12. Carpenter JH, Manella ME (1973) Magnesium to chlorinity ratios in seawater. *J Geophys Res* 78: 3621-3626.
13. Liu WG, Xiao QZ, Wang HP, Wang YH, Zhou YM, et al., (1997) Chlorine isotopic geochemistry of salt lakes in Qaidam Basin, China. *Chem Geol* 136: 271-279.
14. Xiao YK, Beary ES, Fassette JD (1988) An improved method for high precision isotopic measurement of boron by thermal ionization mass spectrometry. *Int J Mass Spectrom Ion Proc* 85: 203-213.
15. Alt J (1995) Sub-seafloor processes in mid ocean ridge hydrothermal systems. In: Humphris SE, Zierenberg RA, Mullineaux LS, Thomson RE: *Seafloor Hydrothermal Systems: Physical, Chemical, Biological and Geological Interactions*.
16. Xiao YK, Zhang CG (1992) Precise measurements of chlorine by thermal ionization mass spectrometry of Cs<sup>2</sup>Cl<sup>-</sup> ion. *Int J Mass Spectrom Ion Processes* 116: 183-192.
17. Aggarwal JK, Palmer MR, Ragnarsdottir KV (1992) Boron isotopic composition of Icelandic hydrothermal systems. *Balkema Rotterdam*: 893-895.
18. Eastoe CJ, Guilbert JM (1992) Stable chlorine isotopes in hydrothermal processes. *Geochim Cosmochim Acta* 56: 4247-4255.
19. Palmer MR (1996) Hydration and uplift of the oceanic crust on the Mid-Atlantic Ridge associated with hydrothermal activity: Evidence from boron isotopes. *Geophys Res Lett* 23: 3479-3482.
20. Palmer MR, Spivack AJ, Edmond JM (1987) Temperature and pH controls over isotopic fractionation during adsorption of boron onto marine clays. *Geochim Cosmochim Acta* 51: 2319-2323.
21. Chaussidon M, Jambon A (1984) Boron content and isotopic composition of oceanic basalts: Geochemical and cosmochemical implications. *Earth Planet Sci Lett* 121: 277-291.
22. Purdy GM, Kong LSL, Christenson GL, Solomon SC (1992) Relationship between spreading rate and the seismic structure of mid ocean ridges. *Nature* 355: 815-817.
23. Bonatti E (1976) Serpentinization protrusions in the oceanic crust. *Earth Planet Sci Lett* 32: 107-113.
24. Donnelly TW, Thompson G, Salisbury MH (1979) The chemistry of altered basalts at site 417, DSDP, Leg 51. *Initial Reports on Deep Sea Drilling Project* 51: 1319-1330.
25. Bonatti E, Lawrence JR, Morandi N (1984) Serpentinization of oceanic peridotites: temperature dependence of mineralogy and boron content. *Earth Planet Sci Lett* 70: 88-94.
26. Ray D, Banerjee R, Iyer SD, Mukhopadhyay S (2007) Serpentinized harzburgites from Central Indian Ridge – an implication for hydrothermal activity.
27. Spencer RJ, Hardie LA (1990) Control of seawater composition by mixing of river water and mid ocean ridge hydrothermal brines. *Geochem Soc Spl Publ* 2: 409-420.
28. Bonifacie M, Charlou JL, Jendrzewski N, Agrinier P, Donval JP (2005) Chlorine isotopic compositions of high temperature hydrothermal vent fluids over ridge axes. *Chemical Geology* 221: 279-288.
29. Godon A, Jendrzewski N, Eggenkamp HGM, Banks DA, Ader M, et al., (2004) A cross calibration of chlorine isotopic measurements and suitability of seawater as the international reference material. *Chemical Geology* 207: 1-12.
30. Xiao YK, Zhou YM, Liu WG, Wang YH, Wei HZ, et al., (2002) A secondary isotopic reference material of chlorine from selected seawater. *Chem Geol* 182: 655-661.
31. Wilson TRS (1975) *Salinity and the major elements of seawater*. 2nd Edn. Academic Press, London, UK.

32. Dickens GR, Owen RM (1994) Late Miocene-early Pliocene manganese redirection in the Central Indian Ocean: Expansion of the intermediate water oxygen minimum zone. *Paleoceanography* 9: 169-181.
33. Farrell JW, Raffi I, Janecek TR, Murray DW, Levitan M, et al., (1995) Late Neogene sedimentation patterns in the eastern equatorial Pacific Ocean. In: Piasis NG, Mayer LA, Janecek TR, Palmer-Julson A, van Andel TH (ed.), *Proceedings of the Ocean Drilling Program, Scientific Results* 138: 717-756.
34. Guptha MVS, Banerjee R, Mergulhao L (2002) On the nature of the calcareous substrate of a ferromanganese crust from the Vityaz Fracture Zone, Central Indian Ridge: inferences on paleoceanography. *Geo-Marine Lett* 22: 12-18.
35. Kolla V, Kidd RB (1982) Sedimentation and sedimentary processes in the Indian Ocean. *The Ocean Basins and Margins*: 1-50.
36. Palmer MR (1992) Boron isotope systematic of hydrothermal fluids and tourmalines: a synthesis. *Chemical Geology: Isotope Geoscience Section* 94: 111-121.
37. Spivack AJ, Edmond JM (1987) Boron isotope exchange between seawater and the oceanic crust. *Geochim Cosmochim Acta* 51: 1033-1043.

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