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 ($^{11}\text{B}$) and chlorine ($^{37}\text{Cl}$) measured from seawater in a 2000 m water column at Vema (VM3: 100 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 $^{11}\text{B}$ (av. 38.9%) with a concomitant increase in $^{37}\text{Cl}$ (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: $^{8}\text{B}$ and $^{8}\text{Cl}$ 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%o 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 isotope signature of +4.7% for mantle, 0% for the crustal rocks and within ± 1% for seawater. Similarly, the boron isotopic signature of these reservoirs also shows a value of +39.7% for seawater, ± 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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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(NO₃) 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 Cs₂BO₄⁺ and Cs₂Cl⁺ ions respectively, using a VG 354 model TIMS [14]. The measured isotopic ratios were expressed as δ values relative to their standard reference materials and were calculated as follows:

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

where, 0.19 is the correction for 17O. and

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

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 δ¹¹B 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%o (av. 39.43%) below 300 m water depth. The δ³⁷Cl values vary from 0.42 to 0.57% (av. 0.52%) in the upper 300 m layer and from 0.1 to 0.41%o (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 δ¹¹B values of seawater at VT4 as no measurements could be made due to the loss of extracted seawater samples. However, the δ³⁷Cl 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%o (av. 0.29%o) 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 δ¹¹B values vary from 37.77 to 38.67%o (av. 38.18%o) in the upper 300 m layer and from 38.76 to 39.54%o (av.38.9%o) down below. Similarly, the δ³⁷Cl values show variation from 0.69 to 1.23%o (av.1%o) in the upper 300 m layer and from -0.87 to 1.57%o (av. 1.15%o) down below. The variation in calcium was from 0.4350 to 0.4401gm/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...
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 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 δ¹¹B values and an increase in δ³⁷Cl below 300 m water depth at VT6 (Figure 4 and Table 4) as compared to VM3 and VT4 stations and the normal seawater values (δ¹¹B=39.8‰ and δ³⁷Cl=0.3‰), suggested the removal and addition of boron (as ¹⁰B) and chlorine (as ³⁷Cl), respectively, to the seawater at VT6. In MOR areas, this is due to the tectonic and magmatic activities at the seafloor. Since
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 10B takes place by its incorporation 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.

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### Table 4: Hydro-chemical characteristics, δ11B and δ35Cl values of sea water at stn. VT6.

| Depth (m) | Temp. (°C) | Salinity (psu) | pH | DO (m/l) | Ca (g/kg) | Mg (g/kg) | B (ppm) | δ11B (%) | δ35Cl (%) |
|----------|------------|----------------|-----|---------|-----------|-----------|---------|----------|----------|
| 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    | 4.3     | 38.39    | 1.07     |
| 50       | 27.43      | 35.26          | 8.29 | 4.47    | 0.4352    | 1.3257   | 4.3     | 37.87    | 0.69     |
| 100      | 18.9       | 35.26          | 8.1  | 2.84    | 0.4367    | 1.3161   | 4.3     | 38.01    | 0.87     |
| 200      | 13.48      | 35.1           | 8.1  | 2.84    | 0.4367    | 1.3161   | 4.3     | 38.01    | 0.87     |
| 300      | 11.01      | 34.94          | 8.1  | 1.85    | 0.4352    | 1.3102   | 4.3     | 38.39    | 1.23     |
| 500      | 9.17       | 34.83          | 7.98 | 2.18    | 0.4356    | 1.3102   | 4.3     | 38.76    | 1.25     |
| 750      | 7.39       | 34.81          | 7.93 | 1.71    | 0.4401    | 1.3041   | 4.3     | 39.54    | 1.25     |
| 1000     | 6.03       | 34.8           | 7.95 | 2.11    | 0.435     | 1.2932   | 4.3     | 38.99    | 1.31     |
| 1250     | 5.31       | 34.81          | 7.95 | 1.88    | 0.4388    | 1.2885   | 4.3     | 39.14    | 1.47     |
| 1500     | 4.12       | 34.76          | 7.98 | 2.41    | 0.4348    | 1.3157   | 4.3     | 38.54    | 1.57     |
| 2000     | 2.66       | 34.73          | 8.05 | 2.99    | 0.4372    | 1.3235   | 4.3     | 38.82    | 1.06     |

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/Sr (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 Sr/Sr 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 δ10B 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 δ10B 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 δ10B value of 39.8%. Such a decrease in δ10B value possibly indicates the role of hydrothermal circulation of seawater at VT6. However, the observed low δ10B 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 δ10B values cited above have been measured from 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 δ10B value), with the overlying seawater, restored the δ10B value of seawater at VT6 to the observed value of 38.90‰.

Chloride is the main anion of oceanic hydrothermal systems and as CaCl₂, it is a major input to seawater at hydrothermal discharge sites...
This suggested low salinity vapour phase to have δ 37Cl values (αvapour-liquid) are from 0 to 1% at very high temperatures (300-450°C). This is consistent with the observed δ 37Cl values of seawater from Vema and Vityaz areas indicating a variation vis-à-vis that of boron with significantly higher δ 37Cl values (av. +1.15‰) at VT6 relative to those at VM3 (av. +0.25‰) and VT4 (av. +0.00‰) from 300 m depth downward. This variation gives an indication of some other processes of chlorine isotopic fractionation involved in this case, either chemically transfers of high salinity, high metal content and low volatiles. The chlorine isotopic fractionation involved in this case, either chemically transfers into the vapour phase and non-volatile elements into the condensed phase. At sub-critical condition, the circulating seawater 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 may have been influenced by the presence of a subcritical condition at the suspected hydrothermal site at Vityaz transform fault at VT6 (5° 38.01’S), envisaging small amount of vapour with lower chlorinity to be separated from seawater. Hence, this should give a δ 37Cl value of +1% for the vent fluid and this expected value matches very well with our measured δ 37Cl value (av. +0.76‰) at VT6 for the 2000 m water column at VT6 as compared to the other two stations VM3 and VT4 whose average δ 37Cl values are much lower for the 2000 m water column (+0.38‰ to +0.43‰, respectively).

Our measurements on the δ 37Cl values of seawater from Vema and Vityaz areas indicate a variation vis-à-vis that of boron with significantly higher δ 37Cl value (av. +1.15‰) at VT6 relative to those at VM3 (av. +0.25‰) and VT4 (av. +0.00‰) 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, between the aqueous chlorine and HCl (α aq. Chlorine-HCl) and that between vapour and liquid or between seawater and brine (avapour-liquid) are from 0 to 1‰ at very high temperatures (300-450°C). This suggested low salinity vapour phase to have δ 37Cl values from 0 to +1% and a conjugate high salinity phase to have δ 37Cl values from -1 to 0%. In an extreme case of HCl and Cl2 co-existence, the αHCl-Cl2 is less than 0.30% at temperature >200°C and the δ 37Cl 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’S [25], clearly indicates the presence of a subcritical condition at the suspected hydrothermal site at Vityaz transform fault at VT6 (5° 38.01’S), envisaging small amount of vapour with lower chlorinity to be separated from seawater. Hence, this should give a δ 37Cl value of +1% for the vent fluid and this expected value matches very well with our measured δ 37Cl value (av. +0.76‰) at VT6 for the 2000 m water column at VT6 as compared to the other two stations VM3 and VT4 whose average δ 37Cl values are much lower for the 2000 m water column (+0.38‰ to +0.43‰, respectively).

A comparison of δ 37Cl values of hydrothermal fluids from different spreading areas (Table 5b) shows that from fast spreading MOR, the δ 37Cl values being varying from -0.3‰ to +1.1‰, type, while, Eastoe and Guilbert (1992) observed a variation in δ 37Cl from -1 to 0.5‰ in hydrothermal fluids from ore forming systems. All these δ 37Cl 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 δ 37Cl 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 δ 37Cl 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 chloride isotopic measurements of seawater from various locations in the world oceans, including CIR and SWIR, Godon et al., [28] remarked that the high δ 37Cl 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...
convention 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 $\delta^{18}B$ (av. 38.9‰) with a concomitant increase in $\delta^{37}Cl$ (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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