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Selective leaching studies of sediments from a seamount flank in the Central Indian Basin: Resolving hydrothermal, volcanogenic and terrigenous sources using major, trace and rare-earth elements

M.B.L. Mascarenhas-Pereira *, B. Nagender Nath

Geological Oceanography Division, National Institute of Oceanography, Dona Paula, Goa, 403004, India

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ABSTRACT

We have investigated the sediments from a site where a newly discovered submarine hydrothermal alteration of recent origin is located to identify the source components and estimate their relative contribution. The site is situated on the flank of a seamount in the Central Indian Basin along the 76° 30′ E fracture zone which traces the movement of the Rodriguez triple junction. Detailed analyses of major, trace and rare earth elements (REE) on the bulk, leach, residue and clay fraction, and infra red spectroscopy studies of the clay fraction helped characterize the hydrothermal nature of the sediments. Selective dissolution carried out using HCl has allowed the discrimination between a leach phase (leachable Fe–Mn oxide) and a residue phase (refractory). The sediments are iron-rich, majority of Fe, Mn is in leachable fraction and are compositionally comparable to ridge-crest metalliferous sediments. Elemental ratios and geochemical discrimination plots of major element data reveal that the sediments are a mixture of Fe-rich mineral phases on one hand apparently from hydrothermal sources and aluminosilicates such as illite, zeolites, micaceous clays and smectites contributed from the Bengal fan, weathering of basinal basalts and authigenic processes. Ternary mixing calculations of bulk sediment major element data show that 35–45% metalliferous sediments could reproduce Fe and Mn values of our sediments.

The shale normalized REE patterns of the bulk sediments are remarkably similar to those of the HCl soluble leach fraction, implying that the REEs in the HCl soluble leach fraction dominate the bulk fraction. HCl leacheates exhibit characteristics of vent fluids as well as seawater with pronounced Eu anomaly with HREE enrichment and negative Ce anomaly. The residue on the other hand has a high concentration of Fe, V, Zn, and Pb indicating a sulfidic input to the sediments. Ternary mixing calculations of REEs carried out on the residual fraction indicate that the sulfide-like material dominates (64–72%) over terrigenous (10–20%) and MORB derived (16–18%) components.

This study helped us identify and quantify two types of hydrothermal material in the sediments, dominated by Fe–Mn phases (ferruginous oxides and silicates; Mn-oxides) in leachable fraction and sulfide-like material in residual phases. The clay fraction is mainly composed of dioctahedral smectites and has a composition similar to Alvin nontronite. The geochemical and mineralogical characteristics collectively suggest that these sediment-hosted precipitates formed at relatively low temperatures ranging between 50 and 100 °C from a mixture of seawater and hydrothermal fluids.

The presence of hydrothermal sediments in the vicinity of a fracture zone suggests the occurrence of localized hydrothermal activity associated with intra plate volcanism. This is probably induced by reactivation of tectonic forces along the fracture zones.

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1. Introduction

Submarine hydrothermal activity is a widespread feature occurring in all the oceans along the spreading centers at mid oceanic ridges and at subduction areas. Most of the sites discovered in the Indian

Ocean so far are located along the mid-oceanic ridge system with some at the Andaman back arc basin (Banerjee and Ray, 2003; Gallant and Von Damm, 2006; Bach et al., 2002; Kurian et al., 2008). In addition to the spreading centers, hydrothermal activity can also occur in oceanic seamount areas. Intraplate seamounts are produced from the upwelling of "small plumes" which transport lower mantle material underneath the ridge axis. The leaking of this lower mantle material gives rise to axial and off axial volcanism (Hékinian et al., 1999). Hydrothermal deposits at intraplate seamounts are less

^{*} Corresponding author. Fax: +91 832 2450602. E-mail address: mariab@nio.org (M.B.L. Mascarenhas-Pereira).

common, although the seamount morphology associated fracturing and volcanism could favor hydrothermalism (Alt, 1988). Such seamounts have been reported from the Pacific viz., Macdonald, Loihi (Karl et al., 1988), Vailulu'u (Staudigel et al., 2004). Signatures of the hydrothermal nature of the Central Indian Basin (CIB) sediments were only reported through microscopic spherules (see lyer, 2005 and references therein). Native aluminum-rich particles of hydrothermal origin (lyer et al., 2007), volcanic glass associated with pumice and palagonites (Mascarenhas-Pereira et al., 2006) was recovered from the sediments located on the flank of a seamount along the 76° 30′ E Fracture zone in the CIB and indicated the occurrence of intraplate submarine volcanism and hydrothermal activity. Recent isotopic studies (²¹⁰Pb, ¹⁰Be and ²³⁰Th) on the sediments from the same area have revealed hydrothermal alteration of sediments of recent origin through ascending fluid flow (Nath et al., 2008).

In this study, we have employed major, trace and rare-earth element (REE) geochemistry (along with other elements) to characterize the different source components and to estimate their relative contribution to the sediments from the flank of a seamount along the fracture zone. We have extracted the hydrothermal component in the sediments by selective leaching using 50% HCl. The chemistry of hydrothermal component in these sediments allowed a comparison with previously published geochemical data of hydrothermal material from other major spreading centers (Rainbow, TAG, MAR and EPR). Bulk and leach data was used for mixing calculation to find the proportion of the different source components. Based on these studies, we report the occurrence of sediments of distinctly metalliferous nature with ferruginous smectites and nontronite at this intraplate seamount setting. This is the first report of hydrothermal signatures being imprinted on the bulk chemistry of the sediments in an intraplate region of the CIB.

2. Regional setting and hydrothermalism

The CIB is bounded by the Ninety East ridge, the Central Indian ridge and the Southeast Indian ridge, and is between 50 and 60 Ma in age (Mukhopadhyay and Batiza, 1994). There exists three major fracture zones that trend along 73° E (Vishnu or La Boussole), 76° 30′ E and 79° E (Indrani or L'Astrolabe) and the Triple Junction Trace on the Indian Plate (TJT-In) between 76 and 78° E longitude (Kamesh Raju and Ramprasad, 1989). The sediment core studied here is recovered from the southern end of the 76° 30′ E fracture zone (Fig. 1b) which represents the trace of Indian Ocean Triple Junction movement (Kamesh Raju and Ramprasad, 1989; Kamesh Raju, 1993). This is one of the six N-S fracture zones represented in the CIB (Kamesh Raju, 1993, and references therein). Several seamounts were delineated along the fracture zones in the CIB, with the majority clustering along 76° 30′ E and 79° E fracture zones (Fig. 1b). Clustering of seamounts along the fracture zones as seen here, is similar to non-hotspot volcanoes in the Pacific (Das et al., 2007), which preferentially occur either on or very near to the fracture zone. The fracture zones may provide easy conduits for formation of seamounts (Batiza, 1982). There may also be local perturbations to the plumbing system or other zones of weakness that control the location of seamounts (Epp and Smooth, 1989; Kamesh Raju, 1993). Such local perturbations to the plumbing system possibly from tectonic reactivation of the fracture zones may be responsible for the intraplate volcanism and the hydrothermal activity metalliferous sediments in this area.

Possibility of intraplate volcanism and the associated hydrothermal activity in CIB has been reported in the past. Occurrence of volcanic spherules, glass shards (Gupta, 1988; Iyer et al., 1997; Mascarenhas-Pereira et al., 2006; Nath and Rao, 1998; Sukumaran et al., 1999); volcanogenic-hydrothermal material consisting of Fe-Si oxyhydroxides, volcanic spherules, glass shards, ochrous metalliferous sediments and spherules (Iyer et al., 1997), spillites in the vicinity of 79° E fracture zone (Karisiddaiah and Iyer, 1992), zeolitites (Iyer and Sudhakar, 1993), fossil free smectite-rich pyroclastic layers at different subsurface depths representing episodic volcanic activity (Nath and Rao, 1998) in CIB were reported in the past. In a recent study by Iyer et al. (2007), native aluminium of submarine hydrothermal origin was reported from the core AAS 61/BC 8.

3. Sampling and analytical work

A short sediment core AAS 61/BC 8 was collected using a large box corer $(50 \times 50 \times 50 \text{ cm})$ at 16° S and 75° 30′ E from the flanks of a seamount from the CIB along the southern end of the 76° 30′ E fracture zone from a water depth of 5010 m (Fig. 1) during the 61 st cruise of RVAA Sidorenko during the year 2003. The core was sampled from pelagic red clay sediment domain (see Nath et al., 1989 for sediment types in CIB). The core was sub sectioned into 2 cm intervals. Clays of $<2 \text{ }\mu\text{m}$ size were separated using standard settling velocity technique.

Bulk samples along with clay samples were dissolved following acid dissolution procedure of Balaram and Rao (2003). The resulting solutions were analyzed for REE along with some trace and major elements by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) at the National Geophysical Research Institute, Hyderabad, India. 10 ml of acid mixture containing HF, HNO3 and HClO4 (in the ratio of 6:3:1) was added to ~50 mg of sample and USGS Marine mud standard MAG-1 in teflon beakers. The solutions were then evaporated to dryness in the fume hood. After 30 min, 2 ml of conc. HCl was added to remove any black particles, if present. The acid mixture was kept on sand bath till it was evaporated to dryness. 5 ml of 1 ppm Rh solution and 20 ml of 1:1 HNO3 were added and made up to 250 ml and cooled. The clear solutions were then introduced into ICP-MS for elemental analysis.

Following the bulk analyses, selective chemical leaching was carried out using hot 50% HCl on 4 sample intervals and USGS standard MAG-1 (following the technique described in Cronan, 1976). Accurately weighed representative subsamples of 1 g each were leached with hot 50% HCl and kept hot by continuous shaking in a heated water bath for 4 h prior to filtration. The dissolved material was filtered through previously weighed filter papers and the residues were weighed. The leach solutions were analyzed by ICP-MS for the same elements as the bulk samples, using standards made up in the same solutions as the samples. The same leaching procedure (with hot 50% HCl) was carried out on a different subsample (4 sediment sections) for major element analyses. MAG-1 was included during this batch of leaching. Bulk sediments and the residue left after leaching were analyzed for major elements using X-ray Flourescence Spectroscopy (XRF) at NIO, Goa. Elemental data of Fe, Al and Mn are obtained by both ICP-MS (Table 1) and XRF methods (Table 2) for four subsections, The results of Fe and Al by both the methods agree well (<11% variability), while the variability for Mn is relatively large probably due to inhomogeneity between the two subsamples used. It should also be mentioned here that the Mn values for MAG-1 obtained by both the methods concur well with the certified value (Tables 2

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