

## Review Article

# Marine sediments: A sink for geogenic and anthropogenic metals, a case study of Ridge flank and near vent sediments in Carlsberg Ridge, Indian Ocean

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**Abstract:** Marine sediments found in the Mid-Ocean Ridges serve as repositories for both naturally occurring (geogenic) and human-generated (anthropogenic) metals. Understanding the geochemistry and processes of these sediments is crucial for assessing their source, compositional end-members, and environmental impact. This study applied geochemical ratios and proxies to representative samples from the Carlsberg Ridge, Indian Ocean, to determine the influence of hydrothermal circulations on the near-vent hydrothermal sediments (NVS) and ridge flank sediments (RFS) and the potential effect of toxic trace metals on the benthic ecosystems. The bulk chemical compositions of seven representative hydrothermal indicator metals (Ca, Al, Ti, Fe, Mn, Cu, and Zn) and seven representative toxic trace metals (Pb, Ni, Co, Cr, As, Cd, and Co) were analyzed at the A laboratory services in Guangzhou, China, by Agilent 7700 Inductively Couple Plasma Mass Spectrometer (ICPMS). The geochemical signatures  $Fe/(Al + Fe + Mn) > 0.5$ ;  $Al/(Al + Fe + Mn) < 0.3$ ;  $(Fe + Mn)/Al > 2.5$ ; and  $(Fe + Mn)/Ti > 25$  affirm the proximity of the NVS and the distal position of RFS to the Wocan vent site in the Carlsberg Ridge, Indian Ocean. The pollution indices, ecological risk index, and sediment quality guidelines showed low to moderate contamination, low to moderate severity, and low to moderate ecological risk of As, Cd, Sb, Pb, Ni, Co, and Cr to the benthic ecosystems at RFS. This is an indication of low to moderate anthropogenic influence from hydrothermal venting to the ridge flank sediment (RFS). This study has shown that an understanding of background and threshold concentrations can guide the development of strategies to reduce the impact of human activities on marine ecosystems.

**Keywords:** hydrothermal sediments; Mid Ocean Ridges; geochemical ratios; toxic trace metals; benthic ecosystems

## 1. Introduction

Marine sediments are composed of residue settling of any deposit of insoluble materials such as rock, soil particles, marine organisms, e.g., calcareous or siliceous shells of phytoplankton or zooplankton, submarine volcanism, chemical precipitate products from seawater, or products transported from land by climate action such as wind, ice, and rivers<sup>[1]</sup>. It can be referred to as lithogenous, biogenous, hydrogenous, cosmogenous, and hydrothermal sediments<sup>[1]</sup>. They are constituents of pre-existing rock fragments and are predominant in the ocean as a repository. The entire representative range of the classes of particle size (e.g., boulder-8 to -12phi, cobble-6 to -8phi, pebble-2 to -6phi, granule-2 to -1phi, sand-1 to 4phi, silt 4 to 8phi, and clay 9 to 14phi) can be found in lithogeneous sediment<sup>[1]</sup>. Biogenous sediments encompass living organisms' residues and ranges of organic microscopic phytoplankton, zooplankton, aquatic plants, vertebrates, and invertebrates. The deep-sea siliceous deposits can be diatom ooze, siliceous ooze, and radiolarian ooze, whereas their deep-sea carbonate counterparts can be foraminifera ooze, calcareous ooze, and nannofossil ooze<sup>[2]</sup>. Hydrogenous sediments are products of hydrochemical reactions and seawater precipitation in the ocean. The majority of hydrogenous sediment components, such as halite, chemical limestone, Fe, and Mn nodules, possess economic

value<sup>[1]</sup>. Cosmogenous sediments are extra-terrestrial source-derived and are composed of meteorites and microscopic spherules. The latter are primarily Ni, Si, and Mn components.

Hydrothermal sediments are precipitated near hydrothermal circulations, which involve high-temperature fluids (>400 °C) circulating along the mid-Ocean ridge, island arc volcanoes, and back arc basin<sup>[1]</sup>.

Metal-enriched sediments from hydrothermal circulations are one of the products of the hydrothermal process. They were formed by a mixture of metal-bearing matter from hydrothermal sources and pelagic sediment. The driving heat, the recharge, the discharge, and the circulation systems are the essential components of vent fluid circulations<sup>[3]</sup>.

Hydrothermal circulations in different hydrothermal systems have led to the production of unique mineral assemblages that have economic importance. The common products of hydrothermal vent circulations are massive sulfide edifices, hydrothermal mounds, chimneys, breccia, ochreous and gossan deposits, Fe-Mn oxyhydroxides and silica deposits, and metalliferous sediments<sup>[4-6]</sup>. Metal-enriched sediments can act as a repository of the above-mentioned hydrothermal vent circulation products (e.g., massive sulfides, hydrothermal mounds, chimneys, breccias, ochreous and gossan deposits, Fe-oxyhydroxides, and silica deposits). They are unconsolidated deposits formed by a mixture of hydrothermal particles with pelagic background materials. Hydrothermal particles in sediments showed the intensity of hydrothermal activity. The near-vent-field sediments indicate the components of vent fluid discharges<sup>[4]</sup>.

Hydrothermal sediments and minerals are currently receiving increasing attention based on their unique geochemical signatures and their ability to give essential insight into the accompanied hydrothermal systems, which include the vent-fluid temperature, compositions, sea-water-fluid interactions, and heat source. It can further give reliable information on the hydrothermal (e.g., primary and post-depositional) processes in the active and inactive hydrothermal systems. Several notable researchers<sup>[7-19]</sup> have applied the geochemical and mineralogical compositions of S, Pb, and Sr isotopic compositions to hydrothermal sediment to understand hydrothermal processes, as well as geological records on the reconstruction of hydrothermal processes. These authors have used hydrothermal sediment signatures to understand past information on the intensity of hydrothermal circulations and the relative proximity of sampling stations to hydrothermal flow zones.

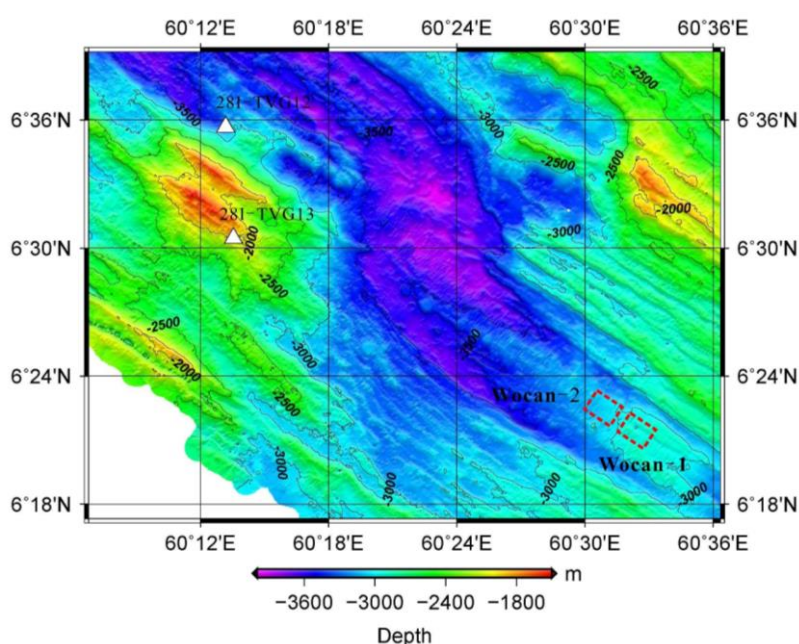
The hydrothermal sediments in the mid-ocean ridges, island arc volcanoes, and back-arc basins are primarily hydrogenous sediments, they are products of precipitations of hydrothermal fluids and seawater-sediment interactions<sup>[1]</sup>. Marine sediment in the ocean is a repository for hydrogenous or geogenic sediments, and the hydrogenous or hydrothermally precipitated sediments' dispersal to the near vent can influence the distal sediments at several hundreds of km within the ridge flanks. It can also cause anthropogenic contamination of the surrounding marine ecosystems.

There are limited studies on the applications of geochemical ratios and proxies in distinguishing between the end members of hydrothermal sediments and pelagic sediments. Moreover, studies on the toxicity index and background concentrations of sediments within the ridge flank are scarce. Suspended sediments and dissolved metals from the support vessels in the form of discharge plumes during mining operations tend to spread over larger distances than the zones of mining activities into several km in the water column<sup>[20]</sup>. These discharged sediment plumes often contain enhanced concentrations of metals, including some toxic elements such as Hg, As, Pb, Cd, Se, Sb, and essential metals (Cu, Zn, and Ag) at hydrothermal venting zones. Heavy metals released into the atmosphere from hydrothermal vents and anthropogenic emissions (from supporting mining vessels) contaminate the waters and sediments. The concentrations of metals in the sediments then tend to exceed the background concentrations and guideline limits of the deep sea waters.

Understanding the geochemical baseline compositions of the toxic trace metals along the Mid-Ocean Ridges and the hydrothermal-pelagic sediment end members will enhance our understanding of the impact and spread extent of suspended sediments. This study applied geochemical ratios and proxies to representative samples from the Carlsberg Ridge, Indian Ocean, to determine the influence of hydrothermal circulations on the ridge flank sediments and the potential effect on the benthic ecosystems.

## 2. Sampling stations and materials and methods

The Carlsberg Ridge (CR) is part of the Indian, Ocean Ridge Systems (IORS) which is a long chain of active submarine volcanoes<sup>[21–23]</sup>. Wocan vent Field (**Figure 1**), is a basalt-hosted vent site, and covers an area of approximately 420 m by 320 m and 420 m by 120 m, in the water depth ranges of 2970 m to 2990 m, and approximately 2700 km respectively<sup>[1]</sup>.



**Figure 1.** Map of study area. Proximal sediment samples were collected close to Wocan-1 (W-1) and Wocan-2 (W-2), while Ridge flank sediment (RFS) samples were collected at TVG-12 and TVG-13. Note: TVG indicate TV-grab.

Sediment samples were collected at a proximal and distal points to the Wocan vent field (**Figure 1**), Carlsberg Ridge, using TV-grab samplers during the Chinese DY 28th cruise in 2013. Samples were collected randomly at two stations near the Wocan-1 and Wocan-2 vent sites, termed ‘representative near vent sediments’, whereas, sediment samples were also collected randomly at two stations within the ridge flanks and referred to as “representative ridge flank sediments”.

The bulk chemical compositions of seven representative hydrothermal indicator metals (Ca, Al, Ti, Fe, Mn, Cu, and Zn) and seven representative toxic trace metals (Pb, Ni, Co, Cr, As, Cd, and Co) were analyzed at the A laboratory services, Guangzhou, China by Agilent 7700 Inductively Couple Plasma Mass Spectrometer (ICPMS), with analytical precision of <10%.

## 3. Results

The results of the representative hydrothermal indicator metals and toxic trace metals are shown in **Table 1**. The Cu and Zn also showed a very high concentration ranges of 33,100 ppm to 51,900 ppm and 6750 ppm to 8330 ppm respectively at near vent sediment (Wocan-1 and Wocan-2) when compared to the ridge flank

sediments (RFS, TVG12 and TVG-13) that ranged from 60 ppm to 171 ppm and 24 ppm to 47 ppm respectively. Aluminium (Al) does not show any significant variations, likewise Mn, although the Wocan-2 stations showed highest Mn concentrations of 646 ppm. Ca and Ti showed higher concentration ranges of 29.5 wt.% to 31.7 wt.% and 0.01 wt.% to 0.04 wt.% respectively compared to the near vent sediment that ranged from 0.2 wt.%–0.3 wt.% and 0.02 wt.% to 0.04 wt.%, respectively.

**Table 1.** Results of geochemical analysis at near vent field and ridge flank sediment.

	Ca (wt.%)	Al (wt.%)	Ti (wt.%)	Fe (wt.%)	Mn (ppm)	Cu (ppm)	Zn (ppm)
W-1	0.3	0.69	0.017	41.2	303	33100	8330
W-2	0.2	0.47	0.025	31.4	646	51900	6750
TVG12	31.7	0.63	0.042	0.63	365	60	24
TVG13	29.5	1.52	0.126	1.46	314	171	47
	Pb (ppm)	Ni (ppm)	Co (ppm)	Cr (ppm)	As (ppm)	Cd (ppm)	Sb (ppm)
W-1	430	9.8	31.1	22	298	23.3	7.52
W-2	404	4	7.7	17	500	21.1	36.5
TVG12	5.3	12.7	4.6	10	4.3	0.33	0.3
TVG13	5.4	35.5	16.7	25	2.9	0.69	0.4

## 4. Discussions

### 4.1. Distinguishing pelagic sediment and hydrothermal sediment

The higher Ca concentrations in the RFS is an indication of abundance of deep sea carbonate such as foraminiferal ooze, compared to the NVS, which indicate less carbonate concentration. Whereas, the enriched Cu and Zn in the NVS is an indication of proximity to the hydrothermal vent.

There are several geochemical signatures that can be used to differentiate hydrothermal enriched sediments from the non-enriched pelagic sediments. Among the geochemical signatures are: (i)  $Fe/(Al + Fe + Mn) > 0.5$ ; (ii)  $Al/(Al + Fe + Mn) < 0.3$ ; (iii)  $(Fe + Mn)/Al > 2.5$ ; (iv)  $(Fe + Mn)/Ti > 25$ ; (v) Fe concentration  $> 10$  wt.% (Table 2<sup>[4,15,16]</sup>).

The NVS all satisfy the above criteria (Figures 2–5), and further affirm the proximity of the NVS and the distal position of RFS to the Wocan vent site. This further makes it very crucial to look at the possible effect of anthropogenic influence, and background conditions toxic trace metals in the representative RFS sediments for future mining operations in the area.

**Table 2.** Geochemical ratio used to discriminate hydrothermal sediment from pelagic sediment.

	$Al/(Al + Fe + Mn)$	$Fe/(Al + Fe + Mn)$	$(Fe + Mn)/Al$	$(Fe + Mn)/Ti$
W-1	0.016	0.983	59.754	2425.312
W-2	0.015	0.983	66.946	1258.584
TVG12	0.486	0.486	1.060	15.869
TVG13	0.505	0.485	0.981	11.837

Note: W-1 and W-2 are near vent sediment (NVS). While TVG-12 and TVG-13 are Ridge Flank Sediment (RFS).

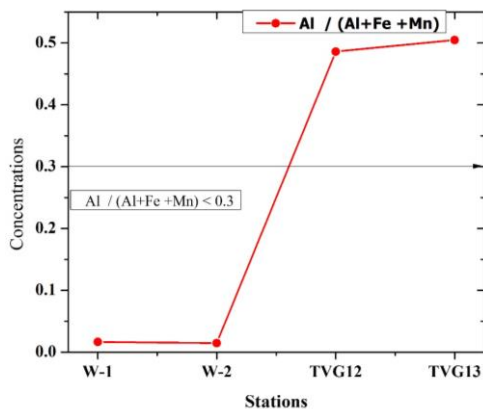


Figure 2. Plot of Al/(Al + Fe + Mn) ratio of near vent sediment (W-1 and W-2) and ridge flank sediment (TVG-12 and TVG-13).

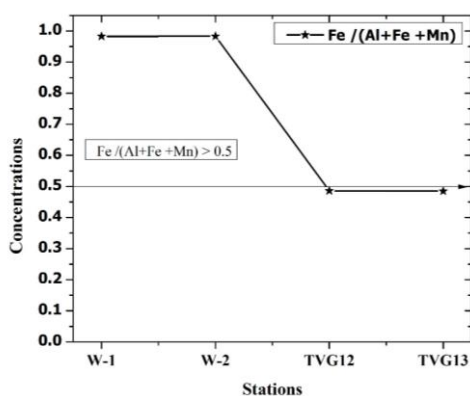


Figure 3. Plot of Fe/(Al + Fe + Mn) ratio of near vent sediment and ridge flank sediment.

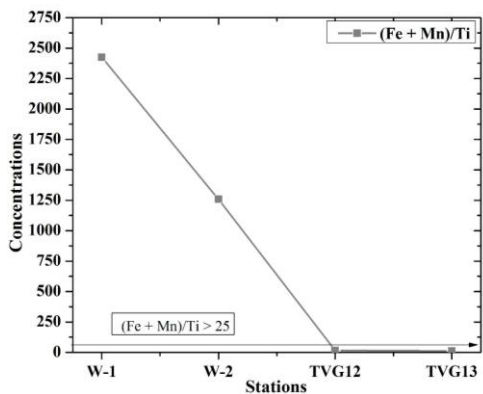


Figure 4. Plot of (Fe + Mn)/Ti ratio of near vent sediment and ridge flank sediment.

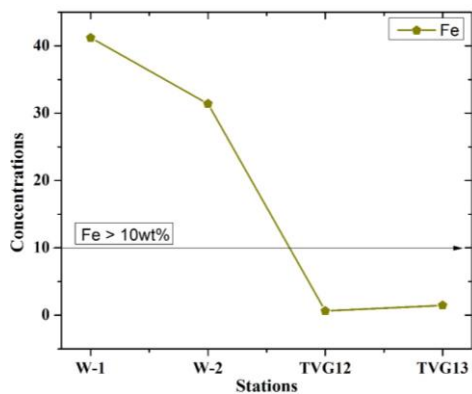


Figure 5. Plot of Fe concentrations of near vent sediment and ridge flank sediment.

#### 4.2. The application of geochemical signature to understand the toxicity of trace metals

Various proxies such as: metal ratio (MR), contamination factor (CF), ecological risk index (RI), pollution risk index (PLI), Modified Hazard Quotient (mHQ) and Toxic Risk Index (TRI) are crucial to understand the effect of anthropogenic influence and background conditions and environmental baseline data on toxic trace metals in the ocean<sup>[24-26]</sup>.

The metal ratio determines the ratio of the concentration of metals in a sample to the standard (background) concentration of metals (e.g., the continental upper crust (CUC) values<sup>[27]</sup>).

$$MR = \frac{\text{Conc of samples}}{\text{Conc of Background}} \tag{1}$$

The contamination factor indicates contamination status of an element in sediment

$$CF = \frac{CF \text{ samples}}{CF \text{ Background}} \tag{2}$$

where CF = Contamination Factor; CF samples = mean concentration of each metal in the sediments; CF Background = CUC values: It differs from the MR based on the mean concentration of CF. The CF modified showed the following classes:  $CF < 1$ , low contamination,  $1 < CF < 3$ , moderate contamination and  $3 < CF < 6$ , considerable contamination,  $CF > 6$ , high contamination.

The pollution load index indicates overall trace metal toxicity in a particular sediment, and is calculated the nth root of the n number of multiplied CF value,

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n} \tag{3}$$

PLI is classified into two categories: The first category ( $PLI < 1$ ) indicates unpolluted, and the second categories ( $PLI > 1$ ) indicates polluted.

The potential ecological risk (Er) use toxicity factors to indicate the potential ecological risk of trace elements in sediments together with their contamination factors (CF) and toxic response factor (Trf) The Trf for each metal and other detail calculation are shown in the are shown in the supplementary data.

$$Er = Trf \times CF. \tag{4}$$

The ecological risk index (RI) is the sum of all the ecological risk factors (Er).

$$RI = \sum Er \tag{5}$$

$Er < 40$  or  $RI < 150$  indicates low ecological risk for water bodies.

$40 \leq Er < 80$  or  $150 \leq RI < 300$ , moderate ecological risk for water body.

$80 \leq Er < 160$  or  $300 \leq RI < 600$ , considerable ecological risk for water body.

$160 \leq Er < 320$  or  $600 \leq RI$ , very high ecological risk for water body.

The modified Hazard Quotient showed the extent of risk posed by trace metals in coastal environments to the benthic organisms by using

$$mHQ = Ci \left[ \left( \frac{1}{TEL} + \frac{1}{PEL} + \frac{1}{SEL} \right) \right]^{1/2} \tag{6}$$

$C_i$  is the concentration of metal ( $i$ ). The threshold effect level (TEL), probable effect level (PEL) and severe effect level (SEL) of marine and estuarine ecosystems were reported by Thompson et al. and Nubi et al.<sup>[28,29]</sup>.

The classification of *mHQ* scale is:

$mHQ < 0.5$  Nil to very low, severity of contamination,  $0.5 < mHQ < 1.0$ , very low severity of contamination;  $1.0 < mHQ < 1.5$ , low severity of contamination;  $1.5 < mHQ < 2.0$ , moderate severity of contamination;  
 $2.0 < mHQ < 2.5$ , considerable severity of contamination;  
 $2.5 < mHQ < 3.0$ , high severity of contamination;  
 $3.0 < mHQ < 3.5$ , very high severity of contamination;  
 $mHQ > 3.5$ , extreme severity of contamination.

The toxic Risk Index utilizes the *TEL* and *PEL* concentrations to evaluate the toxic risk of trace metals in sediments. Since sediments are also a major ecological habitat for various communities of benthic organisms<sup>[26,30]</sup>.

$$TRI_i = \sqrt{\frac{\left(\frac{C_i}{TEL}\right)^2 + \left(\frac{C_i}{PEL}\right)^2}{2}} \tag{8}$$

$$TRI = \sum_{i=1}^n TRI \tag{9}$$

*TRI<sub>i</sub>* represents the toxic risk index of a single metal, *C<sub>i</sub>* trace metal concentration in the sediment sample, *n* is the number of metals, and TRI (integrated toxic risk index).

The classification of TRI is:  $TRI \leq 5$ , no toxic risk,  $5 < TRI \leq 10$ , low toxic risk,  $10 < TRI \leq 15$ , moderate toxic risk,  $15 < TRI \leq 20$ , considerable toxic risk, and  $TRI > 20$ , very high toxic risk.

The calculated high concentrations of metal ration (MR) for Pb, Co, As, Cd and Sb suggest the influence of hydrothermal circulation on the NVS (**Table 3**).

**Table 3.** Calculated metal ratio of the near vent and Ridge flank sediment.

	<b>MRPb</b>	<b>MRNi</b>	<b>MRCo</b>	<b>MRCr</b>	<b>MRAs</b>	<b>MRCd</b>	<b>MRSb</b>
<b>NVS</b>	25.29	0.22	1.83	0.27	198.67	77.67	37.60
<b>NVS</b>	23.76	0.09	0.45	0.20	333.33	70.33	182.50
<b>RFS</b>	0.31	0.29	0.27	0.12	2.87	1.10	1.50
<b>RFS</b>	0.32	0.81	0.98	0.30	0.27	2.30	2.00

Whereas the contamination factor (CF) indicates considerable contamination ( $CF > 6$ ) for Pb, As, Cd, and Sb at NVS, which is an indicator of the influence of hydrothermal circulation or hydrothermal enriched element's (e.g., Cu, Zn, and S) association with Pb, As, Cd and Sb. The CF values for Ni, Co and Cr falls within the low contamination ( $CF < 1$ ) classes.

The RFS sediment which are crucial for long distance transportation or dispersal of sediment plumes indicates moderate contamination ( $1 < CF < 3$ ) for As, Cd and Sb (**Table 4**). However, Pb, Ni, Co, and Cr all falls below the low contamination ( $CF < 1$ ). The low contamination factors of Pb, Ni, Co, and Cr at RFS and Ni, Co, and Cr at NVS showed the background status and condition of the metals at the stations. While the moderate contamination of As, Cd, and Sb, required continuous future monitoring at the stations. The toxic effect of As, Cd, and Sb can create serious ecological problem based on their speciation form in aquatic ecosystem as contaminants, they can cause acute or chronic toxicity to benthic organisms and fish.

**Table 4.** Calculated Contamination Factor (CF), Ecological risk factor (Er), Ecological Risk index (RI) and Pollution load index (PLI) of the near vent sediment and Ridge flank sediment.

	CF NVS	CF RFS	Tir	Er NVS	Er RFS	RI NVS	RI RFS	PLI NVS	PLI RFS
<b>CFPb</b>	24.529	0.31	5.00	122.647	1.574	7093.9	116.12	1.80	0.77
<b>CFNi</b>	0.012	0.55	5.00	0.062	2.739	-	-	-	-
<b>CFCo</b>	0.037	0.63	5.00	0.184	3.132	-	-	-	-
<b>CFCr</b>	0.003	0.21	2.00	0.005	0.422	-	-	-	-
<b>CFAs</b>	266.0	2.40	10.00	2660	24.00	-	-	-	-
<b>CFCd</b>	74.00	1.70	30.00	2220	51.00	-	-	-	-
<b>CFsb</b>	110.05	1.75	19.00	2090.95	33.25	-	-	-	-

The pollution index (PLI) values at the NVS are >1, (**Table 4**), which indicate pollution, high PLI concentration may not be unconnected to the close proximity of the sampling points to the venting sites. Whereas, the PLI values at the RFS are <1, which indicate background status of the sediment metal compositions. The ecological risk factor (Er) of As, Cd, and Sb at NVS are greater than 320 ( $Er > 320$ ) (**Table 4**) which is an indication of very high ecological risk for water body. Pb values falls within considerable ecological risk for water body ( $300 \leq RI < 600$ ). Enriched Pb concentration may be related to galena mineralisation (PbS) or the aforementioned element association with Cu, Zn, and S. However at RFS As, Cd and Sb all falls within the moderate ecological risk for water body ( $40 \leq Er < 80$ ). The RI values of 7093.8 and 116.12 indicate very high ecological risk for water body ( $RI > 600$ ), and moderate ecological risk for water body ( $150 \leq RI < 300$ ) at NVS and RFS respectively.

The modified Hazard Quotient showed extreme severity of contamination ( $mHQ > 3.5$ ) for As and Pb at NVS and very low severity of contamination ( $0.5 < mHQ < 1.0$ ) for As, Cr, Ni and Pb at RFS. Whereas, the toxic risk index (TRI) showed moderate toxic risk ( $10 < TRI \leq 15$ ) for As at NVS and no toxic risk (TRI) for other metals. At the RFS, the TRI values all falls within no toxicity for all metals (**Table 5**).

**Table 5.** Calculated Modified Hazard Quotient (MHQ) and Toxicity Risk Index (TRI) of the near vent sediment and Ridge flank sediment.

	NVS	RFS	NVS	RFS
	MHQ	MHQ	TRI	TRI
<b>As</b>	13.136	0.609	13.136	0.093
<b>Cr</b>	0.649	0.634	0.649	0.0309
<b>Ni</b>	0.627	0.942	0.627	0.654
<b>Pb</b>	3.1923	0.535	3.192	0.008

Generally the targeted hydrothermal influenced from the NVS to the distal RFS sediment showed low to moderate contamination of majority of the metal studies, while the high values recorded at the NFS suggest the nature of the metal enrichment due to hydrothermal vent discharges in the environments.

## 5. Conclusions

Marine sediments have different classifications, sources, and end-members and can act as a repository for naturally occurring (geogenic, hydrogenous, and hydrothermal) and human-generated (anthropogenic) metals.



This study applied geochemical ratios and proxies to representative samples from the Carlsberg Ridge, Indian Ocean, to determine the sediment end member's characteristics (e.g., pelagic or hydrothermal), the effect of hydrothermal circulations on the ridge flank sediments, and its potential effect on the benthic ecosystems.

Our study showed the low to moderate anthropogenic influence of hydrothermal venting from the near vent sediment (NVS) on the ridge flank sediment (RFS). This study further showed that the high pollution indices and sediment quality proxies (MR, CF, PLI, Er, RI, MHQ, and TRI) of Pb, As, Cd and Sb at the NVS may be related to hydrothermal sulfide mineralization or the aforementioned element association of Pb, As, Cd, and Sb with hydrothermal enriched metals such as Cu, Zn, and S. However the pollution indices and sediment quality proxies indicate low to moderate contamination, severity and ecological risk of As, Cd, Sb, Pb, Ni, Co and Cr to the benthic ecosystems at RFS.

Our study has shown that continuous studies on the background concentrations and status of metals in marine sediments are of utmost importance for the protection of our marine ecosystems.

## Supplementary materials

Supplementary material associated with this article can be found in the online version.

## Conflict of interest

The author declares no conflict of interest.

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