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Hydrothermal Components in Marine Sediments: An Insight into Sea Floor Mineralization Process

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Abstract

Hydrothermal process is an essential phenomenon for seafloor metallic enrichments and mineral accumulations. The sea-water-oceanic crust circulations near all the submarine volcanic structures had led to the production of essential base metals, metallic sulfides and natural hydrogen. The non-renewable, slow growth and accumulation rate of the mineral deposits has made the search for more hydrothermal fields to be of utmost importance. Hydrothermal components in sediments are liable to act as geological records on the reconstruction of: history, intensity, location and environmental conditions of hydrothermal activities, with respect to their unique mineralogy and geochemistry. It further provides essential data for locating active and inactive hydrothermal systems. Here we highlight some of the integrated approach on the applications of isotopes, mineralogical and chemical investigations on hydrothermal influenced sediments from Mid Ocean Ridge System. These investigations on near ridge metalliferous sediments have been used to complement fluids and rock geochemistry, with respect to having an insight into the processes of sea-floor mineralization. This review has further suggested some important methodological approach to the understanding of the near vent marine sediments' fingerprints.

Keywords: Hydrothermal process; Seafloor metallic enrichments; Geological records; Mid ocean ridge system; Sea-floor mineralization.

1. Introduction

Marine sediments are generally pelagic and are made up of high constituents of calcareous, or siliceous ooze, with minor contents of red clay [1]. Whereas, others may be precipitated from sea water (e.g., authigenic sediments), or as a product of precipitations of hydrothermal fluids, seawater-sediments interactions (commonly referred to as hydrothermal sediments [2]. Hydrothermal components in marine sediments are often enriched in metal contents termed 'metalliferous', with respects to the background pelagic sediments, and are related to the global Mid Ocean Ridge System (MORS) [3-9]. They are generally adjudged to be derived from two processes: (1) Mass wasting, slumping, erosion and transportation of sulfide debris from sulfide mounds. (2) Hydrothermal plume fallouts from neutrally buoyant plume [6, 10-13] The former had been related to be deposited in close proximity to the hydrothermal vent [14], and constitutes <10% of medium-coarse grained enriched hydrothermal particles. Whereas, the latter constitutes >90% dispersed hydrothermal fluid precipitates deposited distal to the vent [15-18]. The drifting away of hydrothermal plume particles from the Mid Ocean Ridges has led to the scavenging of Fe - Mn oxyhydroxides, trace elements and Rare Earth Elements as a sink into the surrounding sediments [19]. The top core characteristics of the Al/ (AI+Fe+Mn) ratio had been used to reveal Fe and Mn enriched sediments along the MORS, and to effectively delineate the spreading centres [6, 20]. The metalliferous sediments in the Red Sea were adjudged to constitute the largest hydrothermal mineral deposit in the world's oceans, and are liable to provide a substrate on which the macro and micro fauna live [21].

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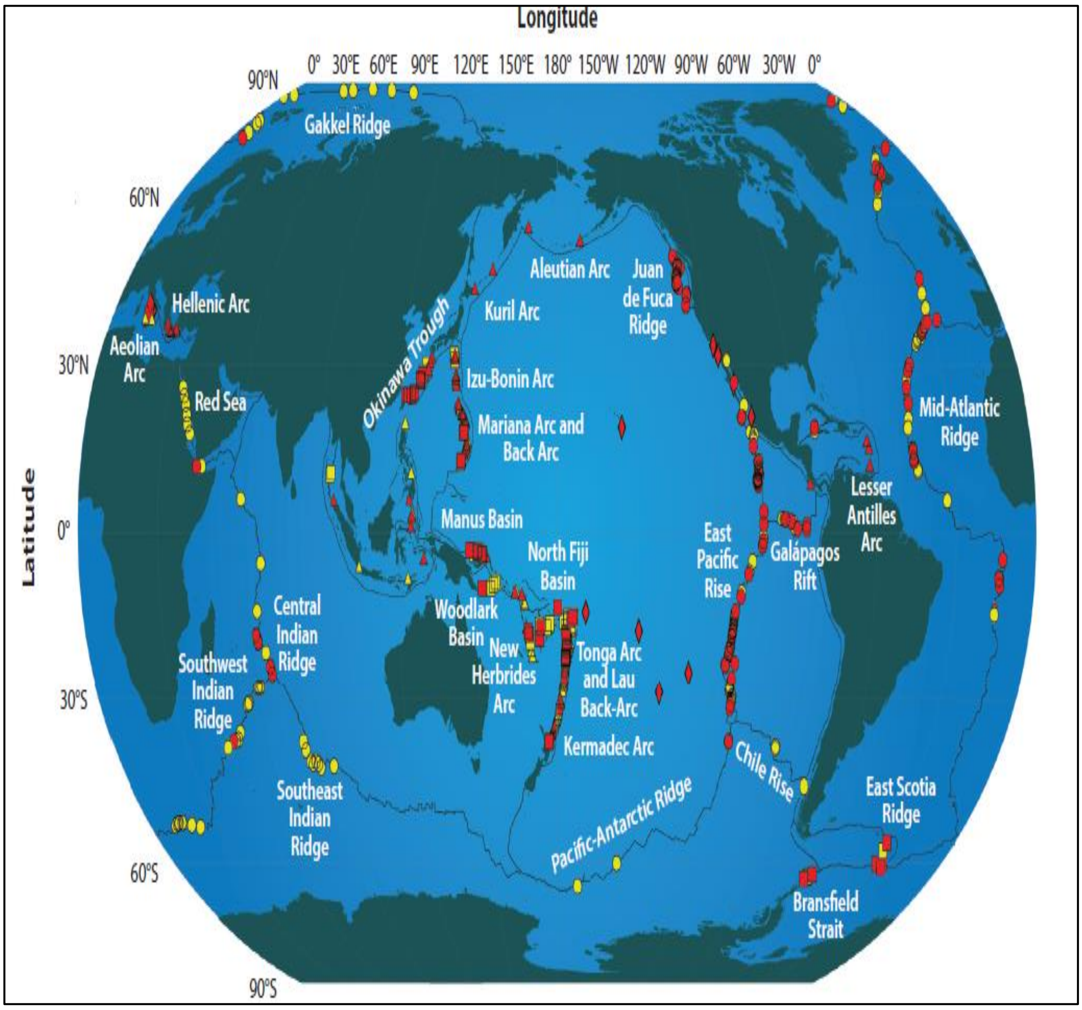
With the advent of high temperature active black smokers in 1979, at East Paific Ridge (EPR), near 21°N [22-25], concerted efforts and concentrations had been directed to the studies on hydrothermal fluids, sulfide mounds and chimney structures. Thereby limiting several interests and research on distal metalliferous sediments [20]. Metalliferous sediments across the ocean possess a genetic affinity to minerals precipitated in close proximity to the hydrothermal upflow zones [20]. They are liable to act as geological records on the reconstruction of: history, intensity, location and environmental conditions of hydrothermal activities, with respect to their unique mineralogy and geochemistry [26, 27]. It further provides essential data for locating active and inactive hydrothermal systems [26, 27].

This paper, aim to review the previous studies on the use of distinct signatures of sediment mineralogy and geochemistry to complement fluids, rocks and seawater; as an insight into sea floor mineralization along the Mid Ocean Ridges. It also focuses on the needed area of research and directions.

Fig-1. Map of confirmed (red symbol) and inferred (yellow symbol) vent sites in the ocean adapted from Humphris and Klein, 2018 and the reference therein.



2. Methodology and Approach of Isolating Hydrothermal Mineral Grains from Bulk Sediments

The process begins with the removal of carbonate in the samples either by dilute HCl or acetic acid. The solution may be centrifuged and repeatedly washed in de-ionized water for the acid neutralization, then wet-sieve analysis will follow to separate the sand size from the silt and clay size. The investigation of isolated mineral grain will be focused on the sand size fractions, hence, concentration will be shifted on this fraction (>63μm). Binocular microscope in conjunction with Standard Electron Microscope (SEM), attached with Energy Dispersive Spectrometer (EDS) wil further be utilized for qualitative spot investigations. Additionally. Sulfide aliquots with respect to specific gravity, termed ethanol elutriation can also be used separate the denser minerals (e.g., sulfides) from the less dense non sulfide grains (e.g., amorphous silica, and others), Popoola et al., 2019a,b. Then the hydrothermal mineral grains of interest such as sulfides (e.g., pyrite, chalcopyrite, bornite, covellite), sulfate (barite, gypsum, anhydrite), and Fe-oxyhydroxides will be handpicked under the binocular microscope (Fig.2 and 3). The selected mineral-grains will further be impregnated with epoxy resin, after the elimination of bubbles, grounded and polished ready for Electron Probe Micro Analysis (EPMA) and Laser Ablation Inductively Coupled Plasma Mass Spectrometer (LA-ICPMS) investigation. The EPMA investigation can give detailed major and minor elements with minimum detection limit of > 0.01 wt. %, whereas, the LA-ICPMS have the ability to probe further into the trace elements to ppm level.

Fig-2. Typical hydrothermal mineral-grains separated from bulk sediments (A) secondary Cu-sulfide minerals (B) Reddish-brown Fe-oxy-hydroxide minerals (C) pyrite minerals (D) anhydrite minerals, Source Popoola, 2019 unpublished

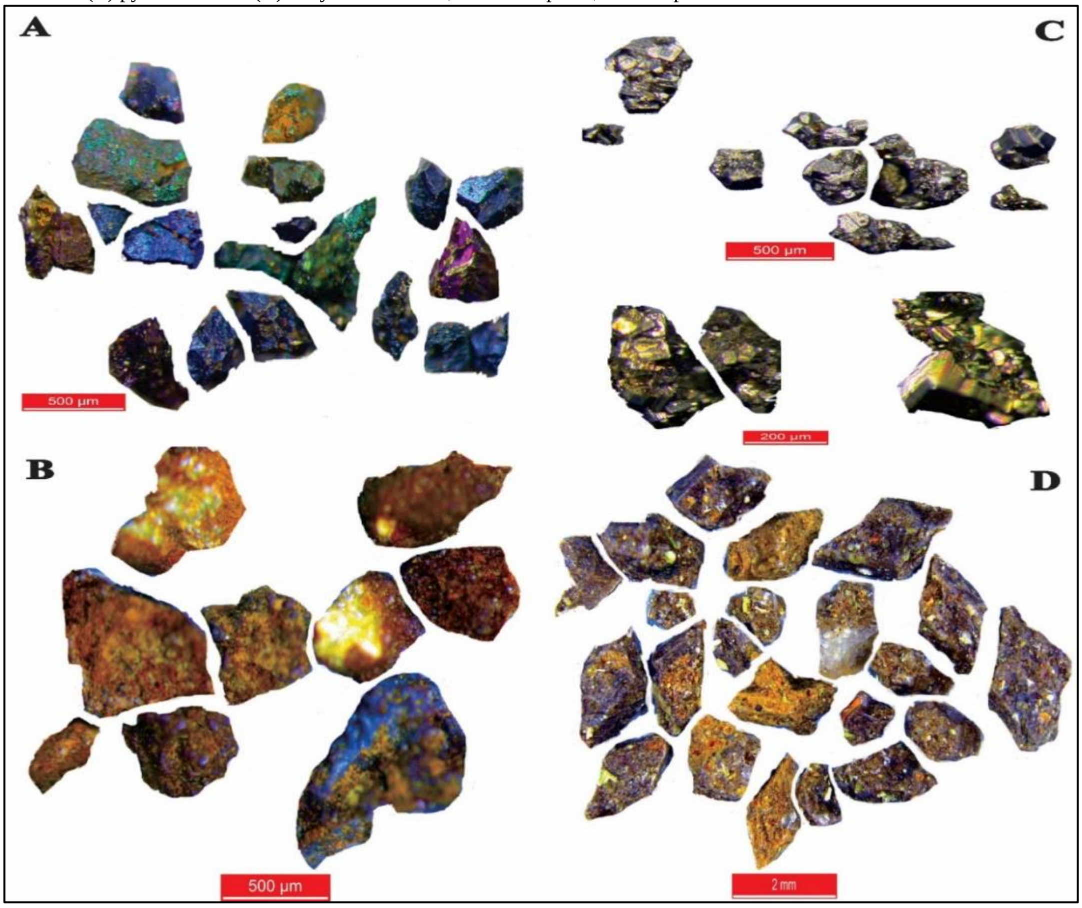
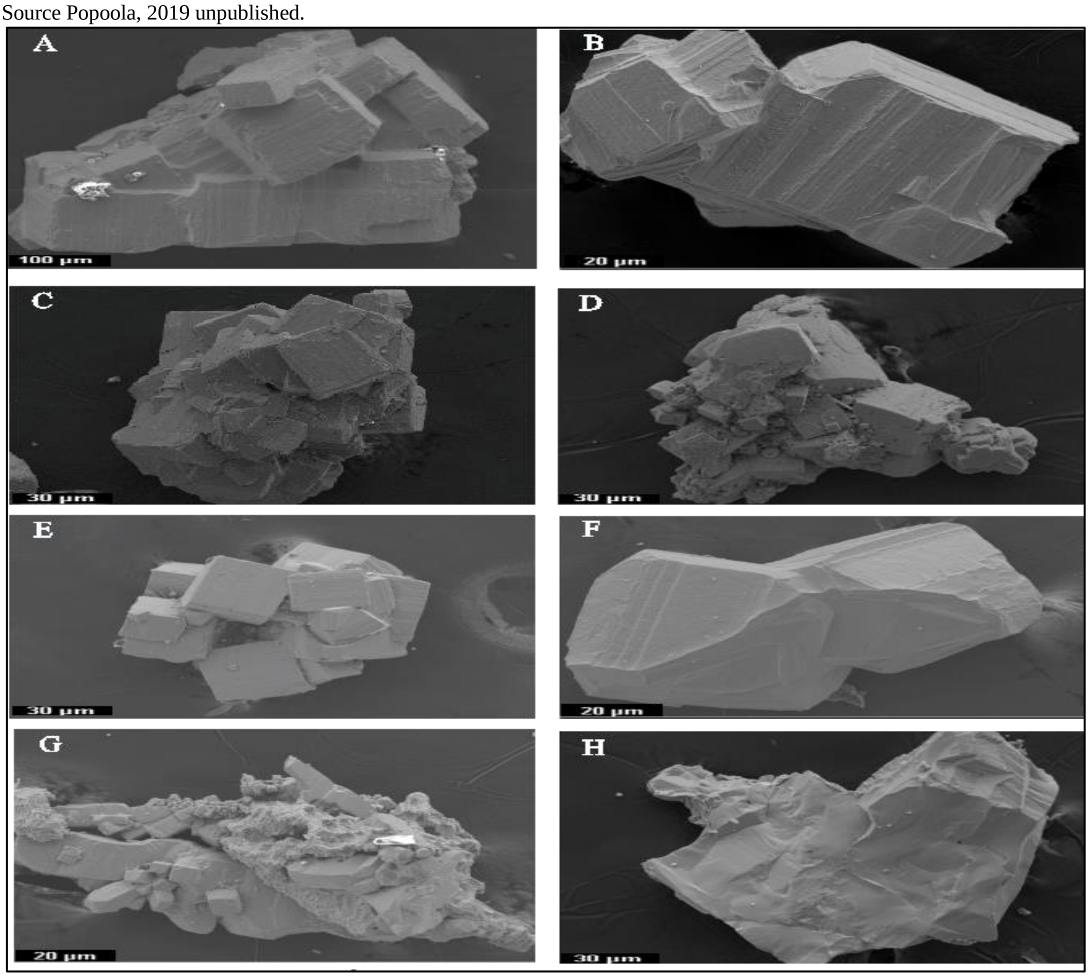


Fig-3. Standard Electron Microscope (SEM) image of separated hydrothermal components from marine sediments in Indian Ocean Ridge Systems, Source Popoola, 2019 unpublished.



3. Application of Isotopes and REEs Signature on Hydrothermal Sediments

Variability in mineral chemistry, degree of mixing of hydrothermal fluid and sea water, physicochemical parameters (e.g., pH, Eh, chloride ions), and sea-floor rock interactions has been highlighted as the triggering factor of different Rare Earth Element (REE) patterns in hydrothermal vent environments [13, 28-30] Previous studies have suggested that metalliferous sediments with hydrothermal components are unlikely to possess positive Cerium (Ce^{+}) anomaly [31, 32]. Moreover, the equivalent values of Pb, Nd and Sr isotopes in sediments to the non-radiogenic local Mid Ocean Ridge Basalt (MORB) or vent-fluid values have been related to the presence of hydrothermal components [10, 11]. Several studies have been conducted on REEs and isotopes, which few are highlighted in this review.

Dymond, *et al.* [33], Used sulfur (^{32}S) and oxygen ($^{18}O/^{16}O$) isotope compositions to suggest a low temperature depositional conditions of seawater-interaction with basaltic crust from the Central North Pacific Ocean. German, *et al.* [11], used the similarity in the non-radiogenic compositions of Pb isotopes in layered components of core sediments with local basalts and vent fluid to confirm the proximal hydrothermal origin of the Trans Adventure Geotraverse (TAG) sediments (Mid Atlantic Ridge), and its close proximity to the hydrothermal upflow zones. They further used the similarity of the REE patterns of the layered sediments with vent-fluid patterns to infer a hydrothermal vent fluid-minimal seawater interactions in the deposition of the TAG metalliferous sediments. Moreover, German, *et al.* [34], used the similarities in the isotopic compositions of Pb with local MORB to suggest a hydrothermal sourced Pb element in the OBS sediments, 21ºN, in the East Pacific Ridge (EPR). They further utilized light Rare Earth Element (LREE) enrichment, low ΣREE concentrations, pronounced Eu/Eu* (2.6-13.3) and negative Ce anomaly (Ce/Ce*) (0.63-0.83) to suggest vent fluid characteristics. Whereas, the down core enrichment of the REE content was used to infer oxidation and seawater contributions. Zeng, *et al.* [30], conducted a sequential analysis on bulk sediments to discriminate between leached and residual phase components from Rainbow hydrothermal vent sites. The leached components which consist of biogenic carbonates (e.g., foraminifera and cocolithopores) and Fe-oxyhydroxides are Heavy Rare Earth Elements (HREE) enriched with negative Ce/Ce*, which are referred to as seawater related fingerprints. The counterparts in the residual phase, which are made up of detrital materials (e.g., sulfide and sulfate fractions) exhibit positive Europium anomaly (Eu/Eu*) and negative Ce/Ce* related to the mixing of hydrothermal fluid and seawater components, with fragments of MORB and aeolian inputs. Dias, *et al.* [10], integrated the Pb and Nd isotopic compositions of near vent sediment core of the Logatchev hydrothermal site, with data from hydrothermal fluids and basalt. The spatial variations in the REE and neodymium (Nd) concentrations were further used to understand the degree of seawater, vent fluid and detrital influence on the precipitation of sulfide minerals in the Logatchev hydrothermal site. Olivarez [35], used the HREE enrichments in the Pacific sediments to reflect basaltic input into the sediments. Finally, Dias and Barriga [36] used seawater REE patterns of negative Ce/Ce* (0.61), negative Eu/Eu* (0.73) to characterize a low temperature depositional conditions in the Saldanha Hydrothermal Field.

These aforementioned approaches have shown the effectiveness of REEs and isotopic signatures as tracers in the understanding of the source and environmental conditions of hydrothermal processes in Mid Ocean Ridges and environments.

4. Signatures from Mineralogical Assemblages and Chemical Compositions

Different sediment fingerprints are specific to various depositional conditions of precipitations in Mid Ocean Ridge environments [37], (Table 1). Several studies have been conducted on the sediments mineralogical and chemical compositions, with a view to the understanding of the hydrothermal components and depositional conditions in the near vent environments. Few are highlighted in this review. Dymond, *et al.* [33], used the mineral assemblages (e.g., goethite, Fe-montmorillonite, Mn-oxides/hydroxides) to infer a low temperature depositional conditions of the sediments from the Central North Pacific Ocean. German, *et al.* [34], utilized the distinct enrichments of Fe (up to 25wt. %); Cu (up to 22wt. %); Zn (up to 13 wt. %); S (up to 30 wt.%) and low Mn (<300ppm) to distinguish hydrothermal sediments from its pelagic counterparts in the OBS (21°N) vent Field in the EPR. Dias and Barriga [36], used nontronite, smectite, amorphous Mn-Mg oxyhydroxides and manganobrucites mineral assemblages to infer a lower temperature of precipitation in the Mount Saldanha Hydrothermal Field. Additionally, previous researchers had utilized the Fe/Ti versus Al/Al+Fe+Mn ratio of < 0.3-0.4 and > 0.4 to indicate the presence of hydrothermal and detrital components in marine sediments [20, 26]. Yu, *et al.* [38], utilized Zn, Cu, Pb enrichments and K, Rb depletion to identify the hydrothermal components in axial sediments along the Carlsberg Ridge. They further utilized the U/Fe enrichment, low $(Nd/Yb)_N$ and Mn depletion to infer the characteristics of post-depositional oxidation and the limited fluid dilution into the sediments. Popoola, *et al.* [27] further used isolated mineral grain chemistry (e.g., SEM-EDS and EPMA) to reconstruct the relative position, temperature and intensity of hydrothermal process in Wocan-1 and Wocan-2 hydrothermal sites, Carlsberg Ridge, Indian Ocean.

Table-1. Mineral assemblages and precipitating conditions

Mineralogical assemblages	Inference
Goelthite, Fe-rich montmorillonitre and Mn hydoxide	Evidence of low temperature environment of precipitation
High Fe, Cu, Zn and S	The presence of sulfidic input in sediments
Sulfides, nontronite, smectite, Mn-oxyhydroxides, Mg-oxyhydroxides, Manganobrucite	Extensive mixing of hydrothermal fluid with seawater
Enriched Cu, Zn, Fe and low Mn in sediments	Proximal location of the sampling point to hydrothermal vent environments

Finally, the sediments-background ratio of Mn, Fe, Ni, Cu, Zn and Al and Ti, have been used in several studies to indicate the enrichment of hydrothermal and detrital fractions in the near Ridge sediments and hydrothermal vent environments [36, 37, 39].

5. Conclusion and Recommendations

Most of the aforementioned studies had focused on bulk sediments geochemical compositions. There is a need to look in the direction of selective analysis of a specific group of metalliferous mineral assemblages, hydrothermal components and the imprints of hydrothermal particulates in marine sediments [26, 27]. This can be achieved through wet-sieve analysis, with respect to the separation and isolated mineral grains and phases of interest. SEM technique in conjucton with Energy Dispersive Spectrometer (e.g., SEM-EDX) is an important tool at which variations in shape, colour, and internal structures such as; zoning, fractures, streaks within a mineral phase can be carried out to constrain their different mineral abundance and percentages [26, 27, 40-42]. There is a need to give more attention to research on the morphological variations and chemical signatures of near vent marine sediments using single grain geochemical techniques via high resolution approach such as: Electron Microprobe Analysis (EMPA) and Laser ablation Inductively Coupled Plasma Mass Spectrometer (LA-ICPMS) analysis. These suggested approach, coupled with single grain radiogenic and stable isotopic tracers such as, Nd, Sr, Pb and sulfur isotopes will further aid in the hydrothermal altered sediment fingerprints and thermo-tectonic origin [42, 43]. It is also liable to aid in the determination of the variations in the chemical compositions among isolated mineral grains and mineral phases such as Cu, Zn and Pb precipitations in the near vent sediments. These precipitations can be viewed via optical microscopes in the form of sulfide mineral phases (e.g., chalcopyrite, pyrite, bornite, marcasite, chalcocite and covellite). The combined approach is liable to offer more opportunity to supplement and widen the earlier information on hydrothermal mineral assemblages, and create new findings on the mode of precipitation and environmental conditions of marine sediments and hydrothermal processes in Mid Ocean Ridges and its environments [44].

This review has highlighted the previous studies on mineralogy, elemental geochemistry, and isotope applications on hydrothermal components in marine sediments located in close proximity to the Mid Ocean Ridge environments. It has further suggested an important methodological approach to the understanding of the near hydrothermal vent sediments' fingerprint.

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