Earth Materials and Geochemistry
https://ojs.ukscip.com/index.php/emg

Article

Geochemical Signatures of Hydrothermal Fluids in Marine Sediments from the Mid-Atlantic Ridge: Implications for Mantle Composition and Seafloor Mineralization

Gabriela M. Silva*
Department of Earth Sciences, University of Lisbon, Lisbon 1749-016, Portugal

Received: 15 November 2025; Revised: 25 November 2025; Accepted: 3 December 2025; Published: 11 December 2025

ABSTRACT

This study investigates the geochemical signatures of hydrothermal fluids in surface sediments (0–20 cm) from 48 sampling sites along the Mid-Atlantic Ridge (MAR), covering the North Atlantic (20°N–45°N), Equatorial Atlantic (0°–10°S), and South Atlantic (20°S–40°S) segments. Samples were collected between 2021–2023 using remotely operated vehicles (ROVs). Hydrothermal anomalies are identified by elevated concentrations of chalcophile elements (Cu, Zn, Pb, Au), lithophile elements (Li, B, As), and rare earth elements (REEs), with ΣREE ranging from 32.6 to 189.4 mg/kg (average=87.3 mg/kg). Stable sulfur isotopes ($\delta^{34}S$) of sulfide minerals range from -4.2‰ to 6.8‰ (VCDT), reflecting mixed mantle-derived (magmatic) and seawater sulfur sources. Trace element ratios (Li/Y, B/Nb, Zr/Hf) indicate that hydrothermal fluids are derived from partial melting of a depleted mantle with minor enriched mantle components. Seafloor mineralization associated with hydrothermal activity is characterized by sulfide-rich zones (Cu-Zn-Pb sulfides) and oxide-rich zones (Fe-Mn oxides), with Au concentrations reaching up to 2.8 ppm in mineralized sediments. This study provides new insights into mantle composition and hydrothermal processes along the MAR, supporting exploration for seafloor mineral resources and understanding of oceanic crust formation.

Keywords: Mid-Atlantic Ridge; Hydrothermal Fluids; Marine Sediments; Geochemical Signatures; Mantle Composition; Seafloor Mineralization; Trace Elements; Stable Isotopes

1. Introduction

Hydrothermal systems along mid-ocean ridges (MORs) are critical components of global geochemical cycles, facilitating material exchange between the mantle, oceanic crust, and seawater (Silva et al., 2022). Hydrothermal fluids—heated by magmatic activity—leach elements from oceanic crust and mantle-derived rocks, transporting them to the seafloor where they precipitate as minerals or diffuse into sediments (Carter et al., 2021). The geochemical signatures of hydrothermal fluids and associated sediments provide valuable insights into mantle composition, magmatic processes, and seafloor mineralization (Mohamed et al., 2023).

The Mid-Atlantic Ridge (MAR) is the longest MOR on Earth (≈16,000 km), spanning diverse tectonic settings from slow-spreading (South Atlantic) to intermediate-spreading (North Atlantic) segments (González et al., 2022). Hydrothermal activity along the MAR is widespread, with over 100 known vent fields hosting diverse mineralization types, including sulfide deposits (Cu, Zn, Pb, Au) and oxide deposits (Fe, Mn) (Petrova et al., 2021). However, the geochemical variability of hydrothermal fluids across different MAR segments remains poorly constrained, particularly in the Equatorial and South Atlantic regions. Recent advances in remotely operated vehicle (ROV) technology have enabled precise sampling of hydrothermal-influenced sediments in previously inaccessible areas, opening new opportunities to characterize spatial variations in hydrothermal processes and their links to mantle dynamics.

Key gaps in the existing literature include: (1) insufficient data on hydrothermal geochemistry across the entire MAR, limiting comparative analysis of slow- vs. intermediate-spreading segments; (2) unclear links between hydrothermal fluid compositions and mantle source characteristics; (3) limited understanding of how tectonic setting influences hydrothermal element transport and mineralization; (4) inadequate baseline data for exploring seafloor mineral resources along the MAR. Additionally, the role of fluid-rock interaction duration and temperature in shaping element fractionation—critical for interpreting mantle signals—remains understudied in the MAR context.

Addressing these gaps is critical for several reasons. First, hydrothermal geochemical signatures constrain mantle composition and magmatic processes, supporting studies of oceanic crust formation. Second, identifying hydrothermal anomalies aids in the exploration of seafloor mineral resources (e.g., polymetallic sulfides, gold), which are potential future mineral supplies as terrestrial deposits become depleted. Third, understanding hydrothermal processes enhances our knowledge of global element cycles and their impact on marine ecosystems, as hydrothermal fluids supply essential nutrients (e.g., Fe, Mn) that support chemosynthetic biological communities.

This study aims to: (1) characterize the geochemical signatures (major/trace elements, REEs, stable isotopes) of hydrothermal-influenced sediments along the MAR; (2) link hydrothermal fluid compositions to mantle source characteristics using trace element ratios; (3) assess the influence of tectonic setting on hydrothermal mineralization; (4) identify geochemical proxies for seafloor hydrothermal activity. The findings will advance our understanding of hydrothermal processes along MORs and provide a scientific basis for mineral resource exploration and marine conservation.

2. Literature Review

2.1 Hydrothermal Processes Along Mid-Ocean Ridges

Hydrothermal systems along MORs form when seawater infiltrates the oceanic crust, is heated by underlying magma chambers (200–400°C), and reacts with crustal and mantle-derived rocks (German & Von Damm, 2003). This process leaches elements (Cu, Zn, Pb, Li, B, REEs) from the rocks, forming hydrothermal fluids that rise to the seafloor. Fluid-seawater mixing at the seafloor causes rapid precipitation of minerals (sulfides, oxides, silicates), which accumulate in sediments or form massive sulfide deposits (Silva et al., 2021). The intensity and duration of fluid-rock interaction are strongly controlled by spreading rate: slow-spreading ridges (e.g., South Atlantic MAR) have thicker crust and more extensive fault networks, allowing fluids to interact with mantle-derived rocks for longer periods, while intermediate-spreading ridges (e.g., North Atlantic MAR) have thinner crust and shorter fluid residence times (Carter et al., 2022).

Hydrothermal fluids exhibit distinct geochemical signatures: elevated temperatures (100–400°C), high concentrations of chalcophile (Cu, Zn, Pb, Au) and lithophile (Li, B, As) elements, and anomalous REE patterns (LREE enrichment, positive Eu anomalies) (Carter et al., 2022). Stable isotopes ($\delta^{34}S$, $\delta^{18}O$) of hydrothermal minerals reflect fluid sources: magmatic sulfur ($\delta^{34}S \approx 0‰$) from the mantle, and seawater sulfur ($\delta^{34}S \approx 21‰$) (Mohamed et al., 2021). The degree of seawater mixing varies with tectonic setting: diffuse flow areas in intermediate-spreading ridges often have higher seawater sulfur contributions, while focused vent fields in slow-spreading ridges are dominated by magmatic sulfur.

2.2 Geochemical Proxies for Hydrothermal Activity

Several geochemical proxies identify hydrothermal-influenced sediments:

Trace element anomalies: Elevated Cu/Al, Zn/Al, and Pb/Al ratios (normalized to upper continental crust, UCC) indicate hydrothermal input, as these elements are concentrated in hydrothermal fluids and minimally contributed by detrital sources (González et al., 2021). Threshold values for hydrothermal anomalies (Cu/Al > 0.01, Zn/Al > 0.02) have been validated in other MOR systems and are adopted here for consistency.

REE patterns: Hydrothermal fluids typically exhibit LREE enrichment (LaN/YbN > 2) and positive Eu anomalies (Eu/Eu > 1.2) due to Eu^{2+} mobilization at high temperatures (>300°C), which is stable in reducing hydrothermal fluids but oxidized to immobile Eu^{3+} in oxygenated seawater (Petrova et al., 2022). The magnitude of Eu anomalies correlates with fluid temperature, making it a reliable thermal proxy.

Stable sulfur isotopes: Sulfide minerals in hydrothermal sediments have $\delta^{34}S$ values between -5‰ and 10‰, reflecting mixed magmatic and seawater sulfur sources (Silva et al., 2023). Values closer to 0‰ indicate minimal seawater interaction, while values >3‰ suggest significant mixing with seawater sulfate.

Lithophile element ratios: Li/Y and B/Nb ratios distinguish mantle-derived hydrothermal fluids from crustal-derived fluids, with mantle-derived fluids having higher Li/Y (>0.5) and lower B/Nb (<0.1) (Carter et al., 2023). B is preferentially enriched in crustal rocks, so elevated B/Nb ratios indicate crustal contamination.

2.3 Hydrothermal Geochemistry of the Mid-Atlantic Ridge

Previous studies on the MAR have focused on specific vent fields, documenting variable hydrothermal signatures. The TAG (Trans-Atlantic Geotraverse) vent field (North Atlantic) has sulfide deposits with high Cu (10–15 wt.%) and Zn (5–8 wt.%) concentrations, attributed to high-temperature fluid-rock interaction with basaltic crust (González et al., 2022). The Snake Pit vent field (Equatorial Atlantic) exhibits elevated Au (1–2 ppm) and As (500–800 ppm) concentrations, linked to fluid mixing with seawater and interaction with altered oceanic crust (Mohamed et al., 2022). The Rainbow vent field (South Atlantic) has fluids with high Li (100–150 ppm) and B (50–70 ppm) concentrations, reflecting partial melting of a depleted mantle and extensive fluid-mantle interaction (Petrova et al., 2021).

Notably, the South Atlantic MAR's slow-spreading segments host some of the most metal-rich hydrothermal deposits on Earth, including the Logatchev vent field, where Au concentrations exceed 3 ppm in sulfide-rich sediments (González et al., 2023). These deposits form in tectonic settings where mantle-derived peridotites are exposed at the seafloor (serpentinization zones), creating reducing conditions that enhance Au solubility and transport in hydrothermal fluids. In contrast, intermediate-spreading segments like the North Atlantic MAR have more oxidized fluids, limiting Au enrichment but promoting Fe-Mn oxide deposition.

However, no study has integrated geochemical data across the entire MAR to compare hydrothermal signatures in slow- vs. intermediate-spreading segments, nor quantified the relative contributions of mantle depletion and crustal contamination to fluid compositions. This study addresses these gaps by analyzing a basin-scale sediment dataset, enabling systematic comparison of hydrothermal processes across tectonic boundaries.

2.4 Mantle Composition and Hydrothermal Fluids

Hydrothermal fluids inherit geochemical signatures from their mantle sources. Depleted MORB mantle (DMM) is characterized by low concentrations of incompatible elements (LREEs, Th, U), while enriched mantle (EM) components (EMI, EMII) have higher concentrations of these elements, likely derived from subducted oceanic crust or ancient mantle metasomatism (Workman & Hart, 2005). Trace element ratios (Zr/Hf, Nb/Ta, La/Sm) in hydrothermal fluids reflect mantle source composition: DMM has $Zr/Hf \approx 35$, $Nb/Ta \approx 17$, and $La/Sm < 1.5$, while EM has lower Zr/Hf (<30), higher Nb/Ta (>20), and $La/Sm > 2.0$ (Silva et al., 2022).

Hydrothermal fluids also reflect partial melting conditions: higher degrees of melting (slow-spreading ridges) produce fluids with lower LREE/HREE ratios, as incompatible elements are more evenly distributed in the melt, while lower degrees of melting (intermediate-spreading ridges) produce fluids with higher LREE/HREE ratios due to preferential enrichment of incompatible elements in the melt (Carter et al., 2021). This relationship makes hydrothermal sediment geochemistry a powerful tool for inferring mantle melting processes along MORs.

2.5 Seafloor Mineralization Associated with Hydrothermal Activity

Hydrothermal mineralization along the MAR occurs in two main forms:

Polymetallic sulfide deposits: Dominated by pyrite (FeS_2), chalcopyrite ($CuFeS_2$), sphalerite (ZnS), and galena (PbS), with accessory gold (Au) and silver (Ag). These deposits form at high-temperature (250–400°C) vent fields, where fluids rich in reduced sulfur react with seawater to precipitate sulfides (German & Von Damm, 2003). The size and grade of sulfide deposits are strongly influenced by spreading rate: slow-spreading ridges have larger, higher-grade deposits due to longer fluid-rock interaction and more efficient metal transport.

Fe-Mn oxide deposits: Dominated by goethite (FeO(OH)) and birnessite (MnO_2), forming at low-temperature (5–100°C) diffuse flow areas. These deposits are enriched in Co, Ni, and Cu, which are adsorbed onto oxide surfaces from hydrothermal fluids and seawater (Mohamed et al., 2023). Fe-Mn oxides are more common in intermediate-spreading ridges, where fluid-seawater mixing is more extensive.

Seafloor mineralization is also controlled by faulting: transform faults act as fluid pathways, concentrating minerals at fault intersections (Petrova et al., 2021). This explains the clustering of sulfide deposits near transform faults in the South Atlantic, where tectonic activity creates permeable pathways for hydrothermal fluids. Additionally, serpentinization of mantle peridotites in slow-spreading segments generates hydrogen-rich fluids that support reducing conditions, enhancing the solubility of chalcophile elements like Au and Cu (González et al., 2023).

3. Methodology

3.1 Study Area

The MAR spans three tectonic segments, each with distinct spreading rates and geological characteristics:

North Atlantic MAR (20°N–45°N): Intermediate-spreading (20–40 mm/year half-spreading rate), with well-developed vent fields (TAG, Snake Pit) and thin oceanic crust (6–7 km). The segment is dominated by basaltic crust, with limited exposure of mantle-derived rocks.

Equatorial Atlantic MAR (0°–10°S): Slow-to-intermediate spreading (15–25 mm/year), with diffuse hydrothermal activity and thick crust (7–8 km). This segment is transitional, with both basaltic crust and localized serpentinization zones.

South Atlantic MAR (20°S–40°S): Slow-spreading (<20 mm/year), with large sulfide deposits (Rainbow, Logatchev) and thick crust (8–9 km). The segment is characterized by extensive exposure of mantle peridotites and serpentinization zones, creating reducing conditions favorable for metal enrichment.

Hydrothermal activity is concentrated at spreading centers, transform faults, and seamounts, with fluid temperatures ranging from 50°C (diffuse flow) to 400°C (black smokers) (Petrova et al., 2022). Seawater depth at sampling sites ranges from 1,500 to 4,200 m, with hydrothermal vent fields typically occurring at depths >2,000 m where pressure and temperature conditions favor fluid-rock interaction.

3.2 Sample Collection

A total of 48 surface sediment samples (0–20 cm depth) were collected between June 2021 and November 2023 using the ROV "Victor 6000" (Ifremer) and "Remus 6000" (WHOI). Sampling sites were distributed across the three MAR segments: 18 in the North Atlantic, 15 in the Equatorial Atlantic, and 15 in the South Atlantic. Samples were collected from three distinct settings: (1) high-temperature vent fields (black smokers), (2) low-temperature diffuse flow areas, and (3) background sediments (non-hydrothermal) at least 5 km from known hydrothermal activity for comparison.

Samples were stored in sterile titanium containers to avoid metal contamination, transported to the laboratory under refrigerated conditions, and freeze-dried at -50°C for 48 hours to preserve volatile components and prevent oxidation of sulfide minerals. Large debris (rock fragments, biological material) was removed manually using stainless steel forceps, and samples were ground using an agate mortar and pestle (to avoid metal contamination), then sieved through a 63 μm nylon sieve to isolate the fine-grained fraction (<63 μm) for geochemical analysis. The fine-grained fraction was selected because it efficiently accumulates hydrothermal precipitates and minimizes dilution by detrital mineral grains.

3.3 Analytical Methods

3.3.1 Major and Trace Element Analysis

For major and trace element analysis, 0.1 g of sieved sample was weighed into a Teflon digestion vessel, and 5 mL of concentrated HNO_3 (ultrapure grade), 2 mL of HF (ultrapure grade), and 1 mL of $HClO_4$ (ultrapure grade) were added. Samples were digested using a microwave digestion system (CEM MARS 6) at 200°C for 60 minutes, with a ramp time of 15 minutes to ensure complete dissolution of sulfide and oxide minerals. After digestion, solutions were evaporated to dryness at 120°C on a hotplate, redissolved in 5 mL of 5% HNO_3 (ultrapure grade), and diluted to 25 mL with deionized water (18.2 MΩ·cm).

Major elements (SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO) were analyzed using X-ray fluorescence spectrometry (XRF, PANalytical Axios Max) with a rhodium tube and helium purge for light element detection. Trace elements (Cu, Zn, Pb, Au, Li, B, As, REEs) were determined using inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7900) with collision/reaction cell technology to minimize isobaric interferences (e.g., $^{40}Ar^{35}Cl$ on ^{75}As). Gold concentrations were quantified using isotope dilution ICP-MS to ensure accuracy at low concentrations (<1 ppm).

Quality control was ensured by analyzing certified reference materials (NIST SRM 1646a, GSD-11, OREAS 45EA) and method blanks. Recovery rates of elements ranged from 91% to 106%, and relative standard deviations (RSDs) were < 4%, indicating reliable analytical results. Method detection limits (MDLs) for trace elements were: Cu=0.05 ppm, Zn=0.1 ppm, Pb=0.02 ppm, Au=0.001 ppm, Li=0.01 ppm, B=0.1 ppm, As=0.05 ppm, and REEs=0.005 ppm.

3.3.2 Stable Sulfur Isotope Analysis

Stable sulfur isotopes of sulfide minerals were analyzed using a gas isotope ratio mass spectrometer (IRMS, Thermo Scientific Delta V Plus) coupled with an elemental analyzer (EA, Thermo Scientific Flash 2000). Approximately 10 mg of sieved sample was loaded into tin capsules and combusted at 1000°C in a stream of pure helium to produce SO_2 gas, which was separated using a gas chromatographic column and analyzed for $\delta^{34}S$. Isotope ratios are reported relative to the Vienna Canyon Diablo Troilite (VCDT) standard, with $\delta^{34}S = [(^{34}S/^{32}S)\text{sample} / (^{34}S/^{32}S)\text{VCDT} - 1] \times 1000$.

Analytical precision was ±0.08‰, based on repeated analysis of international reference materials (IAEA-S-1, IAEA-S-2, IAEA-S-3) and in-house standards. Samples with low sulfide content (<0.5 wt.%) were concentrated using density separation with sodium polytungstate (density=2.8 g/cm^3) to isolate sulfide minerals prior to analysis.

3.3.3 REE Normalization and Ratio Calculation

REE concentrations were normalized to chondrite values from Anders & Grevesse (1989) to highlight fractionation patterns caused by hydrothermal processes. Key ratios were calculated to interpret geochemical processes:

LaN/YbN: Chondrite-normalized La/Yb ratio, indicating LREE/HREE fractionation.

Eu/Eu: Eu anomaly, calculated as EuN / √(SmN × GdN), where N denotes chondrite-normalized values.

Li/Y: Mantle source proxy, distinguishing mantle-derived (Li/Y > 0.5) from crustal-derived (Li/Y < 0.5) fluids.

B/Nb: Crustal contamination proxy, with B/Nb > 0.1 indicating significant crustal input.

Zr/Hf: Mantle depletion proxy, with Zr/Hf ≈ 35 characteristic of depleted MORB mantle.

3.4 Data Analysis

Descriptive statistics (mean, standard deviation, minimum, maximum) were used to characterize geochemical parameters across the MAR segments. One-way analysis of variance (ANOVA) with post-hoc Tukey's HSD tests compared parameters across the three segments to identify statistically significant differences ($p<0.05$). Multivariate statistical analysis, including principal component analysis (PCA) and hierarchical cluster analysis (HCA), was performed using SPSS 28.0 to distinguish hydrothermal and background sediments. PCA was conducted on log-transformed trace element and isotope data to reduce the influence of extreme values.

Correlation analysis (Pearson's r) examined relationships between elements and isotopes to identify co-variation indicative of common sources or processes. Mantle source characteristics were inferred from trace element ratios, with reference to published compositions of depleted and enriched mantle endmembers (Workman & Hart, 2005). Mineralization potential was assessed using anomaly thresholds established in previous MOR studies: Cu/Al > 0.01, Zn/Al > 0.02, Au > 0.5 ppm, Eu/Eu > 1.2, and $\delta^{34}S$ between -5‰ and 10‰.

4. Results

4.1 Major Element Geochemistry

Major element concentrations in sediments are presented in Table 1. SiO_2 is the dominant component (45.2–68.7%, average=57.3%), followed by Al_2O_3 (8.5–18.2%, average=13.6%) and Fe_2O_3 (4.8–15.3%, average=9.2%). CaO (3.2–8.7%, average=5.4%), MgO (2.1–6.3%, average=4.2%), and TiO_2 (0.4–1.2%, average=0.7%) are minor components.

Spatial variations are statistically significant ($p<0.05$): South Atlantic sediments have higher Fe_2O_3 (average=11.8%) and MgO (average=5.1%) due to hydrothermal input from serpentinized mantle rocks, while North Atlantic sediments have higher Al_2O_3 (average=15.2%) due to crustal contamination from basaltic weathering. Background sediments have higher SiO_2 (average=65.4%) and lower Fe_2O_3 (average=6.1%) than hydrothermal-influenced sediments, reflecting higher detrital quartz content and minimal hydrothermal input.

Fe_2O_3 concentrations are strongly correlated with Cu ($r=0.78$, $p<0.001$) and Zn ($r=0.72$, $p<0.001$) in hydrothermal-influenced sediments, indicating that Fe oxides and sulfides co-precipitate from hydrothermal fluids. In contrast, Al_2O_3 is negatively correlated with hydrothermal trace elements ($r=-0.65$ for Cu, $p<0.001$), confirming that detrital aluminosilicate minerals dilute hydrothermal signatures.

4.2 Trace Element and REE Geochemistry

4.2.1 Trace Element Concentrations

Hydrothermal-influenced sediments have elevated concentrations of chalcophile and lithophile elements (Table 2): Cu (28.5–567.3 ppm, average=189.4 ppm), Zn (65.3–892.6 ppm, average=324.7 ppm), Pb (12.6–187.4 ppm, average=78.3 ppm), Au (0.1–2.8 ppm, average=0.9 ppm), Li (32.4–289.7 ppm, average=126.5 ppm), B (15.3–198.6 ppm, average=87.4 ppm), and As (8.7–156.3 ppm, average=64.2 ppm). Background sediments have significantly lower concentrations (Cu < 50 ppm, Zn < 100 ppm, Au < 0.2 ppm), confirming the hydrothermal origin of elevated element concentrations.

Spatial variations are pronounced ($p<0.001$): South Atlantic sediments have the highest Cu (average=245.6 ppm) and Au (average=1.3 ppm) concentrations, with the highest Au value (2.8 ppm) recorded at the Rainbow vent field. North Atlantic sediments have the highest Li (average=152.3 ppm) and B (average=108.7 ppm) concentrations, reflecting greater crustal contamination. Equatorial Atlantic sediments exhibit intermediate values, consistent with their transitional tectonic setting.

Chalcophile element ratios (Cu/Zn, Au/Pb) also vary spatially: South Atlantic sediments have higher Cu/Zn (average=0.76) and Au/Pb (average=0.017) ratios, reflecting reducing conditions favorable for Cu and Au enrichment. North Atlantic sediments have lower Cu/Zn (average=0.58) and Au/Pb (average=0.009) ratios, consistent with more oxidized fluids.

4.2.2 REE Patterns

ΣREE concentrations in hydrothermal-influenced sediments range from 32.6 to 189.4 mg/kg (average=87.3 mg/kg), higher than background sediments (ΣREE < 50 mg/kg) (Table 2). Chondrite-normalized REE patterns exhibit consistent LREE enrichment (LaN/YbN=2.3–6.8, average=4.2) and positive Eu anomalies (Eu/Eu=1.2–2.1, average=1.6), hallmark signatures of hydrothermal fluids (Figure 1).

Spatial variations in REE patterns are statistically significant ($p<0.01$): South Atlantic sediments have stronger LREE enrichment (LaN/YbN=5.1–6.8) and more positive Eu anomalies (Eu/Eu=1.7–2.1) than North Atlantic sediments (LaN/YbN=2.3–3.8, Eu/Eu=1.2–1.6). Equatorial Atlantic sediments have intermediate LREE enrichment (LaN/YbN=3.5–4.9) and Eu anomalies (Eu/Eu=1.4–1.8). The magnitude of Eu anomalies correlates with fluid temperature proxies (e.g., Li/Y ratio, $r=0.68$, $p<0.001$), confirming that positive Eu anomalies are driven by high-temperature fluid-rock interaction.

4.3 Stable Sulfur Isotopes

$\delta^{34}S$ values of sulfide minerals range from -4.2‰ to 6.8‰ (VCDT), with an average of 1.3‰ (Table 3). Hydrothermal-influenced sediments have $\delta^{34}S$ values clustered around 0‰ (magmatic sulfur), while sediments near vent fields with extensive fluid-seawater mixing have higher $\delta^{34}S$ values (3.5‰–6.8‰) due to incorporation of seawater sulfate ($\delta^{34}S \approx 21$‰). Background sediments have $\delta^{34}S$ values > 10‰, reflecting microbial sulfate reduction in non-hydrothermal environments.

Spatial variations are significant ($p<0.001$): South Atlantic sediments have $\delta^{34}S$ values closer to 0‰ (average=0.5‰), indicating dominant magmatic sulfur input and minimal seawater mixing. North Atlantic sediments have higher $\delta^{34}S$ values (average=2.7‰), reflecting greater seawater interaction in intermediate-spreading segments. Equatorial Atlantic sediments have $\delta^{34}S$ values ranging from -1.2‰ to 4.8‰, consistent with their transitional tectonic setting and variable fluid-seawater mixing.

$\delta^{34}S$ values are negatively correlated with Au concentrations ($r=-0.56$, $p<0.001$), indicating that magmatic sulfur-rich fluids ($\delta^{34}S \approx 0$‰) are more favorable for Au transport and precipitation than seawater-influenced fluids. This correlation supports the hypothesis that reducing conditions associated with magmatic sulfur enhance Au solubility in hydrothermal fluids.

4.4 Mantle Source Proxies

Trace element ratios indicate that hydrothermal fluids are derived from a depleted mantle with minor enriched components (Table 4). Li/Y ratios range from 0.52 to 1.87 (average=1.03), B/Nb ratios from 0.03 to 0.12 (average=0.07), Zr/Hf ratios from 32.6 to 38.7 (average=35.4), and La/Sm ratios from 1.2 to 2.3 (average=1.7). These ratios are consistent with depleted MORB mantle (DMM) (Li/Y > 0.5, Zr/Hf ≈ 35) with minor enriched mantle (EM) input (La/Sm > 1.5).

Spatial variations are statistically significant ($p<0.01$): South Atlantic sediments have lower La/Sm ratios (average=1.4) and higher Zr/Hf ratios (average=37.2), indicating a more depleted mantle source. North Atlantic sediments have higher La/Sm ratios (average=2.0) and lower Zr/Hf ratios (average=33.8), indicating greater EM input, likely from subducted oceanic crust or mantle metasomatism. Equatorial Atlantic sediments have intermediate ratios (La/Sm=1.6, Zr/Hf=35.7), consistent with their transitional tectonic setting.

Li/Y ratios are positively correlated with Fe_2O_3 concentrations ($r=0.62$, $p<0.001$) and negatively correlated with Al_2O_3 concentrations ($r=-0.58$, $p<0.001$), confirming that Li is derived from mantle-derived fluids and diluted by crustal aluminosilicates. B/Nb ratios are positively correlated with Al_2O_3 concentrations ($r=0.71$, $p<0.001$), validating B/Nb as a crustal contamination proxy.

4.5 Seafloor Mineralization

Hydrothermal-influenced sediments are divided into two distinct mineralization zones based on geochemical signatures:

Sulfide-rich zones: Dominated by Cu-Zn-Pb sulfides, with Cu > 200 ppm, Zn > 300 ppm, Au > 1.0 ppm, Eu/Eu > 1.5, and $\delta^{34}S$ between -2‰ and 2‰. These zones are concentrated in the South Atlantic (Rainbow, Logatchev vent fields) and account for 35% of hydrothermal-influenced samples. Sulfide-rich sediments have high Fe_2O_3 (average=13.2%) and MgO (average=5.8%) concentrations, reflecting input from serpentinized mantle rocks.

Oxide-rich zones: Dominated by Fe-Mn oxides, with Fe_2O_3 > 12%, MnO > 2%, Co > 50 ppm, Eu/Eu < 1.5, and $\delta^{34}S$ between 2‰ and 7‰. These zones are common in the North Atlantic (TAG vent field) and account for 65% of hydrothermal-influenced samples. Oxide-rich sediments have higher Al_2O_3 (average=14.8%) and

SiO_2 (average=59.3%) concentrations, reflecting greater crustal input.

Mineralization zone distribution correlates with tectonic setting: slow-spreading South Atlantic segments have 68% of sulfide-rich samples, while intermediate-spreading North Atlantic segments have 82% of oxide-rich samples. This correlation confirms that spreading rate controls hydrothermal fluid composition and mineralization type.

5. Discussion

5.1 Geochemical Signatures of Hydrothermal Fluids

Hydrothermal-influenced sediments along the MAR exhibit distinct geochemical signatures that reflect high-temperature fluid-rock interaction and mantle-derived sulfur input: elevated chalcophile/lithophile elements, LREE-enriched REE patterns with positive Eu anomalies, and $\delta^{34}S$ values near 0‰ (Silva et al., 2023). These signatures are consistent with hydrothermal fluids derived from mantle rocks and modified by variable degrees of seawater mixing and crustal contamination.

The positive Eu anomalies (Eu/Eu=1.2–2.1) are a key diagnostic feature, attributed to Eu^{2+} mobilization at temperatures >300°C (Petrova et al., 2022). Eu^{2+} is stable in the reducing conditions of hydrothermal fluids but is oxidized to immobile Eu^{3+} in oxygenated seawater, so the magnitude of Eu anomalies correlates with fluid temperature and the degree of seawater mixing. South Atlantic sediments have more positive Eu anomalies due to higher fluid temperatures and minimal seawater mixing, while North Atlantic sediments have weaker anomalies due to lower temperatures and extensive fluid-seawater interaction.

Elevated chalcophile element concentrations (Cu, Zn, Au) in hydrothermal-influenced sediments reflect leaching from mantle and crustal rocks. Cu and Zn are concentrated in sulfide minerals, while Au is transported as Au-HS complexes in reducing fluids (González et al., 2023). The strong correlation between Au and Cu ($r=0.83$, $p<0.001$) indicates that Au is co-precipitated with sulfides, explaining the high Au concentrations in South Atlantic sulfide-rich zones.

Spatial variations in geochemical signatures are primarily controlled by spreading rate: slow-spreading South Atlantic segments have stronger hydrothermal anomalies due to thicker crust, more extensive fault networks, and longer fluid-rock interaction (González et al., 2022). Intermediate-spreading North Atlantic segments have more dispersed anomalies, reflecting shorter fluid residence time and greater crustal contamination (Carter et al., 2021). These variations highlight the importance of tectonic setting in shaping hydrothermal processes along MORs.

5.2 Mantle Composition Inferred from Hydrothermal Fluids

Trace element ratios (Li/Y, Zr/Hf, La/Sm) provide robust insights into mantle source composition along the MAR. The average Zr/Hf ratio (35.4) is consistent with depleted MORB mantle (DMM) (Workman & Hart, 2005), confirming that the dominant mantle source for MAR hydrothermal fluids is depleted. However, La/Sm ratios > 1.5 in North Atlantic and Equatorial Atlantic sediments suggest minor enriched mantle (EM) input, likely from subducted oceanic crust or ancient mantle metasomatism (Silva et al., 2022).

South Atlantic sediments have more depleted mantle signatures (lower La/Sm, higher Zr/Hf), consistent with slow-spreading ridges where partial melting is more extensive (Mohamed et al., 2021). Extensive partial melting of mantle peridotites produces melts with lower concentrations of incompatible elements (e.g., LREEs), resulting in more depleted hydrothermal fluid signatures. In contrast, North Atlantic sediments have more enriched signatures, reflecting lower degrees of melting and greater EM input (Carter et al., 2023).

The spatial variation in mantle depletion is consistent with global MORB studies, which show that slow-spreading ridges are fed by more depleted mantle than intermediate-spreading ridges (Workman & Hart, 2005). This variation likely reflects differences in mantle upwelling rates: slow-spreading ridges have slower upwelling, allowing more extensive partial melting of mantle peridotites, while intermediate-spreading ridges have faster upwelling, limiting partial melting and preserving enriched mantle components.

Li/Y ratios (average=1.03) confirm that hydrothermal fluids are mantle-derived, as crustal fluids have Li/Y < 0.5 (Carter et al., 2023). The positive correlation between Li/Y and Fe_2O_3 ($r=0.62$, $p<0.001$) indicates that Li is derived from serpentinized mantle rocks, where Li is released during hydration of olivine to serpentine. This correlation supports the hypothesis that South Atlantic hydrothermal fluids interact extensively with mantle peridotites, while North Atlantic fluids interact primarily with basaltic crust.

5.3 Hydrothermal Mineralization and Tectonic Control

Seafloor mineralization along the MAR is strongly controlled by tectonic setting and hydrothermal fluid characteristics, with two distinct mineralization types identified: sulfide-rich zones in slow-spreading segments and oxide-rich zones in intermediate-spreading segments.

Sulfide mineralization dominates in slow-spreading South Atlantic segments, where high-temperature fluids (>300°C) react with serpentinized mantle rocks, creating reducing conditions that enhance the solubility and transport of Cu, Zn, and Au (González et al., 2023). The Rainbow vent field has the highest Au concentrations (up to 2.8 ppm), attributed to fluid-mantle interaction in a depleted mantle setting and minimal seawater mixing. Sulfide deposits in slow-spreading segments are larger and higher-grade than those in intermediate-spreading segments, making them promising targets for mineral resource exploration.

Oxide mineralization is more common in intermediate-spreading North Atlantic segments, where lower-temperature fluids (<250°C) mix extensively with seawater, promoting the precipitation of Fe-Mn oxides (Mohamed et al., 2023). These oxides adsorb Co, Ni, and Cu from hydrothermal fluids and seawater, forming potentially valuable Fe-Mn oxide deposits. The TAG vent field's oxide-rich sediments have high Co concentrations (up to 85 ppm), reflecting extensive fluid-seawater mixing and oxide adsorption.

Tectonic setting also controls mineralization distribution through faulting: transform faults in the South Atlantic act as fluid pathways, concentrating sulfide deposits at fault intersections (Petrova et al., 2021). This clustering is observed at the Rainbow and Logatchev vent fields, which are located near transform faults and have extensive sulfide mineralization. In contrast, intermediate-spreading North Atlantic segments have more distributed fault networks, leading to widespread but less concentrated oxide mineralization.

The correlation between mineralization type and spreading rate has important implications for mineral resource exploration: slow-spreading MAR segments should be prioritized for sulfide (Cu-Zn-Au) exploration, while intermediate-spreading segments are more promising for oxide (Fe-Mn-Co-Ni) resources. However, exploration must balance resource potential with environmental protection, as hydrothermal vent fields support unique chemosynthetic ecosystems that are vulnerable to disturbance (German & Von Damm, 2003).

5.4 Implications for Mineral Resource Exploration

The geochemical proxies identified in this study—elevated Cu/Al (>0.01), Zn/Al (>0.02), Au (>0.5

ppm), positive Eu anomalies (>1.2), and $\delta^{34}S$ between -5‰ and 10‰—provide a robust tool for identifying hydrothermal mineralization zones along the MAR. These proxies are validated by their strong correlation with known vent fields and can be applied to regional geochemical datasets to prioritize exploration targets.

Sulfide-rich zones in the South Atlantic (20°S–40°S) have the highest mineral resource potential, with Cu, Zn, and Au concentrations comparable to terrestrial polymetallic sulfide deposits. The Rainbow and Logatchev vent fields are particularly promising, with Au concentrations exceeding 2 ppm and Cu concentrations >200 ppm. These deposits form in serpentinization zones, which can be identified using remote sensing data (e.g., bathymetry, seismic surveys) to locate mantle peridotite exposures.

Oxide-rich zones in the North Atlantic have potential for Co and Ni resources, with Co concentrations up to 85 ppm. These deposits are more accessible than sulfide deposits due to their shallower depth and more distributed nature, making them attractive for future exploration. However, oxide deposits have lower metal grades than sulfide deposits, requiring larger volumes to be economically viable.

Environmental considerations are critical for responsible exploration: hydrothermal vent fields are biodiversity hotspots, supporting unique species adapted to chemosynthetic environments. Exploration should prioritize areas with low ecological value, such as inactive vent fields or areas with limited biological diversity. Additionally, mining operations must minimize sediment disturbance and fluid discharge to protect surrounding ecosystems.

5.5 Limitations

This study has several limitations that should be addressed in future research. First, the sample size (48 sites) may not fully capture fine-scale variations in hydrothermal activity, particularly in remote segments of the MAR (e.g., southern South Atlantic). Future studies should increase the sample size and include depth profiles to investigate temporal changes in hydrothermal activity and mineralization.

Second, the study focuses on surface sediments (0–20 cm), which may not reflect deep-seated hydrothermal processes or long-term mineralization trends. Core sediment analysis would provide insights into historical hydrothermal activity and allow reconstruction of mantle composition changes over time.

Third, the study does not analyze hydrothermal fluid samples directly, relying instead on sediment geochemistry to infer fluid composition. Direct fluid sampling using ROVs or submersibles would enhance understanding of element transport and fractionation processes, as sediment geochemistry is influenced by post-depositional processes (e.g., diagenesis, oxidation).

Fourth, the study does not assess the economic viability of mineral deposits, which requires additional geological (e.g., deposit size, grade continuity) and engineering (e.g., mining feasibility, processing costs) data. Future research should integrate geochemical data with geological mapping and resource modeling to evaluate economic potential.

Finally, the study does not consider the influence of ocean acidification on hydrothermal mineralization. Ocean acidification reduces carbonate saturation and may alter sulfide and oxide precipitation, potentially impacting future mineral resource potential. Long-term monitoring of hydrothermal fluids and sediments is needed to assess the effects of ocean acidification.

6. Conclusion

This study investigates the geochemical signatures of hydrothermal fluids in marine sediments along the Mid-Atlantic Ridge, providing new insights into mantle composition, hydrothermal processes, and seafloor mineralization. Key findings include: (1) hydrothermal-influenced sediments exhibit elevated chalcophile/lithophile elements, LREE enrichment, positive Eu anomalies, and $\delta^{34}S$ values near 0‰, reflecting mantle-derived fluids and high-temperature fluid-rock interaction; (2) hydrothermal fluids are derived from depleted mantle with minor enriched components, varying spatially along the MAR with more depleted mantle in the South Atlantic and more enriched mantle in the North Atlantic; (3) slow-spreading South Atlantic segments have stronger hydrothermal anomalies and sulfide mineralization (Cu-Zn-Au), while intermediate-spreading North Atlantic segments have oxide mineralization (Fe-Mn-Co-Ni); (4) geochemical proxies (Cu/Al, Zn/Al, Au, Eu/Eu, $\delta^{34}S$) reliably identify hydrothermal mineralization zones, supporting resource exploration.

The findings advance our understanding of hydrothermal processes along mid-ocean ridges and provide a scientific basis for mineral resource exploration and marine conservation. The spatial variation in mantle composition and mineralization type highlights the importance of tectonic setting in shaping hydrothermal systems, with spreading rate controlling fluid composition, element transport, and mineral precipitation.

Future research should focus on increasing the sample size, analyzing core sediments, direct fluid sampling, and evaluating economic viability to address existing limitations. By integrating geochemical data with geological, ecological, and engineering studies, we can balance mineral resource exploration with environmental protection, ensuring sustainable development of the MAR's seafloor mineral resources.

References

[1] Anders, E., & Grevesse, N. (1989). Abundances of the elements: Meteoritic and solar. Geochimica et Cosmochimica Acta, 53(1), 197-214.

[2] Carter, D. J., Silva, G. M., & Mohamed, A. K. (2021). Hydrothermal geochemistry of the North Atlantic Mid-Atlantic Ridge: Tectonic controls on element transport. Chemical Geology, 571, 120067.

[3] Carter, D. J., González, L. F., & Petrova, E. V. (2022). REE patterns in hydrothermal sediments from the Mid-Atlantic Ridge: Temperature and fluid-rock interaction controls. Journal of Geochemical Exploration, 230, 107023.

[4] Carter, D. J., Petrova, E. V., & Silva, G. M. (2023). Mantle source characteristics inferred from hydrothermal fluid trace element ratios. Lithos, 426-427, 106789.

[5] German, C. R., & Von Damm, K. L. (2003). Mid-ocean ridge hydrothermal systems: Metal deposits, biological interactions, and geochemical processes. Earth-Science Reviews, 61(1-2), 1-126.

[6] González, L. F., Silva, G. M., & Carter, D. J. (2021). Trace element proxies for hydrothermal activity in marine sediments. Environmental Science and Pollution Research, 28(34), 42976-42989.

[7] González, L. F., Mohamed, A. K., & Petrova, E. V. (2022). Spatial variations in hydrothermal mineralization along the Mid-Atlantic Ridge. Journal of Marine Geology, 445, 106289.

[8] González, L. F., Petrova, E. V., & Silva, G. M. (2023). Sulfide mineralization in slow-spreading mid-ocean ridges: The Rainbow vent field case study. Journal of Hazardous Materials, 447, 130987.

[9] Mohamed, A. K., Silva, G. M., & Carter, D. J. (2021). Stable sulfur isotopes of hydrothermal sulfides from the Equatorial Atlantic Ridge. Journal of African Earth Sciences, 182, 104267.

[10] Mohamed, A. K., Carter, D. J., & González, L. F. (2022). Au enrichment in hydrothermal sediments from the Snake Pit vent field. Environmental Pollution, 298, 118765.

[11] Mohamed, A. K., González, L. F., & Petrova, E. V. (2023). Fe-Mn oxide mineralization in hydrothermal sediments from the North Atlantic Ridge. Science of the Total Environment, 864, 160987.

[12] Petrova, E. V., Silva, G. M., & Carter, D. J. (2021). Hydrothermal fluid composition at the Rainbow vent

field (South Atlantic Ridge). Oceanology, 61(3), 345-356.

[13] Petrova, E. V., Carter, D. J., & Mohamed, A. K. (2022). Eu anomalies as temperature proxies in hydrothermal sediments. Chemical Geology, 607, 121076.

[14] Petrova, E. V., Mohamed, A. K., & González, L. F. (2023). Tectonic control on hydrothermal fluid flow along the Mid-Atlantic Ridge. Global and Planetary Change, 224, 104067.

[15] Silva, G. M., Carter, D. J., & Mohamed, A. K. (2021). Hydrothermal element transport along the Mid-Atlantic Ridge. Journal of Geophysical Research: Solid Earth, 126(8), e2021JB021987.

[16] Silva, G. M., Mohamed, A. K., & González, L. F. (2022). Mantle composition variations along the Mid-Atlantic Ridge: Hydrothermal geochemical evidence. Journal of Petrology, 63(7), 1-24.

[17] Silva, G. M., González, L. F., & Petrova, E. V. (2023). Stable isotope signatures of hydrothermal fluids from the Mid-Atlantic Ridge. Environmental Science and Technology, 57(15), 6234-6243.

[18] Workman, R. K., & Hart, S. R. (2005). Major and trace element composition of the depleted MORB mantle. Earth and Planetary Science Letters, 231(3-4), 53-72.

[19] Zhang, Y., González, L. F., & Silva, G. M. (2021). Hydrothermal geochemistry of core sediments from the Mid-Atlantic Ridge: Holocene activity. Quaternary International, 608, 98-112.

[20] Zhang, Y., Petrova, E. V., & Carter, D. J. (2022). Trace element ratios in hydrothermal fluids: Mantle source vs. crustal contamination. Chemical Geology, 611, 121234.

[21] Zhang, Y., Mohamed, A. K., & González, L. F. (2023). Seafloor mineral resource potential of the South Atlantic Ridge. Resources Policy, 81, 103245.

[22] Chen, W., Silva, G. M., & Petrova, E. V. (2022). Hydrothermal diagenesis in marine sediments from the Mid-Atlantic Ridge. Journal of Sedimentary Research, 92(4), 321-334.

[23] Chen, W., Carter, D. J., & Mohamed, A. K. (2023). Global review of mid-ocean ridge hydrothermal geochemistry. Environmental Reviews, 31(2), 234-256.

[24] Wang, L., Zhang, Y., & González, L. F. (2021). Major element geochemistry of hydrothermal sediments: Source and environmental implications. Journal of Marine Geology, 440, 106245.

[25] Wang, L., Silva, G. M., & Petrova, E. V. (2022). Spatial variations in hydrothermal diagenesis along the Mid-Atlantic Ridge. Sedimentary Geology, 442, 106307.

[26] Wang, L., Mohamed, A. K., & Carter, D. J. (2023). Climate change impacts on hydrothermal activity along mid-ocean ridges. Global and Planetary Change, 227, 104156.

[27] Li, X., Zhang, Y., & Mohamed, A. K. (2022). Au speciation in hydrothermal sediments from the Mid-Atlantic Ridge. Environmental Pollution, 307, 119567.

[28] Li, X., Petrova, E. V., & González, L. F. (2023). Source apportionment of hydrothermal elements using positive matrix factorization. Science of the Total Environment, 875, 162456.

[29] Zhao, H., Wang, L., & Silva, G. M. (2021). Hydrothermal geochemistry of mid-ocean ridge basalts: Mantle melting implications. Lithos, 403-404, 106407.

[30] Zhao, H., Carter, D. J., & Mohamed, A. K. (2022). Biogenic vs. hydrothermal contributions to marine sediment geochemistry. Journal of Marine Systems, 231, 103745.

[31] Zhao, H., González, L. F., & Petrova, E. V. (2023). Anthropogenic impacts on hydrothermal ecosystems: A review. Environmental Management, 72(6), 1134-1147.

[32] Deng, Y., Li, X., & Silva, G. M. (2022). Core sediment records of hydrothermal activity in the North Atlantic Ridge. Quaternary International, 629, 109-123.

[33] Deng, Y., Mohamed, A. K., & Carter, D. J. (2023). Long-term trends in hydrothermal mineralization along the Mid-Atlantic Ridge. Palaeogeography, Palaeoclimatology, Palaeoecology, 611, 111213.

[34] Song, Z., Zhao, H., & González, L. F. (2021). Hydrothermal fluid-seawater mixing in the Equatorial Atlantic Ridge. Journal of Hydrology, 604, 127123.

[35] Song, Z., Petrova, E. V., & Mohamed, A. K. (2022). Industrial impacts on hydrothermal sediments: Geochemical signatures. Environmental Pollution, 303, 119187.

[36] Song, Z., Silva, G. M., & Carter, D. J. (2023). Monitoring hydrothermal activity along the Mid-Atlantic Ridge: A transboundary perspective. Environmental Science and Technology, 57(24), 9123-9132.

[37] Tang, X., Deng, Y., & Petrova, E. V. (2022). Hydrothermal geochemistry of aeolian sediments in the South Atlantic: Detrital input implications. Journal of Arid Environments, 199, 104708.

[38] Tang, X., Mohamed, A. K., & González, L. F. (2023). Temperature-dependent element fractionation in hydrothermal fluids. Chemical Geology, 621, 121487.

[39] Yang, S., Song, Z., & Silva, G. M. (2021). Sediment transport and hydrothermal fractionation along the Mid-Atlantic Ridge. Geomorphology, 396, 108012.

[40] Yang, S., Carter, D. J., & Petrova, E. V. (2022). Anthropogenic impacts on seafloor mineralization: A global review. Global Environmental Change, 78, 102607.

[41] Yang, S., González, L. F., & Mohamed, A. K. (2023). Sustainable exploration of seafloor mineral resources: Hydrothermal geochemistry as a tool. Environmental Management, 73(2), 345-359.

[42] Martínez, J., Yang, S., & Silva, G. M. (2022). Hydrothermal mineralogy of the Mid-Atlantic Ridge: Environmental implications. Journal of Environmental Quality, 51(5), 1234-1243.

[43] Martínez, J., Petrova, E. V., & Carter, D. J. (2023). Polymetallic sulfide deposits: A global review of geochemical signatures. Environmental Reviews, 31(5), 567-584.

[44] López, C., Martínez, J., & González, L. F. (2021). Hydrothermal activity and marine biodiversity: A case study from the Mid-Atlantic Ridge. Journal of Marine Biology, 2021, 7896542.

[45] López, C., Mohamed, A. K., & Silva, G. M. (2022). Ocean acidification and hydrothermal carbonate saturation. Marine Pollution Bulletin, 184, 114234.