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From source to sink: complex dual role of the Kairei hydrothermal plume in deep ocean trace metal cycling at the Central Indian Ridge

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ABSTRACT

Hydrothermal venting represents a significant source of trace metals to the deep ocean, but key aspects of these fluxes remain poorly constrained. Whether high-temperature hydrothermal venting at a particular site represents a net source for fluid-sourced trace metals to the open ocean is determined by complex processes during plume mixing, which can also make them sinks for (seawater-derived) elements. We present a comprehensive dataset of dissolved trace metals (Cd, Co, Cu, Fe, Ga, Mn, Mo, Ni, Pb, U, V, and REY) for endmember fluids and from water column profiles covering the buoyant plume and the non-buoyant plume up to 30 km away from the mixed ultramafic/mafic-hosted Kairei Hydrothermal Field (KHF) at the Central Indian Ridge and a background station at 56 km distance. The non-buoyant plume was sampled with a newly developed autonomous trace metal rosette (TMR) for contamination-free hydrocasts. The KHF acts as a significant source of Fe, Mn, Co, and to a lesser degree of Ga to the deep Indian Ocean, with size fractionation revealing Fe being present predominantly as small particles (53 % at 0.2–0.8 μm) and large colloids (28 % at 0.015–0.2 μm) which are removed quickly near the source, while the soluble fraction ($<0.015 \mu\text{m}$) is more stable and exported to the deep ocean. Similarly, Pb was found to be largely present in the small particulate fraction (95 %) close to the source and being rapidly removed as particulate sulfides with little effect on dissolved concentrations, while all other investigated elements were found largely in the soluble fraction ($<0.015 \mu\text{m}$). Conversely, the plume effectively scavenges REY, V, and notably Cd from the water column as well as the fluid-sourced contributions, with near-quantitative Cd removal observed in the plume despite ~ 100 -fold endmember enrichment. Copper and Ni exhibit complex non-conservative behavior, both being depleted relative to background seawater in the near-field, likely reflecting initial sulfide precipitation; Cu is subsequently re-enriched in the far-field via oxidative release during plume aging, while any comparable Ni release likely falls below our detection limit given its lower endmember concentration, making the plume an apparent net sink for Ni. The relatively low $\text{H}_2\text{S}/\text{Fe}$ ratio of 0.90 at Kairei compared to other hydrothermal systems likely favors greater metal transport to the water column. These findings demonstrate that hydrothermal contributions to marine trace metal budgets are highly system-specific, controlled by endmember chemistry and plume processes, highlighting the need for detailed multi-element investigations across diverse hydrothermal settings.

1. Introduction

During hydrothermal circulation, seawater penetrates fractures in the oceanic crust in the vicinity of magmatically active areas where it is heated and convectively rises to the seafloor as a hydrothermal fluid

with temperatures that can exceed 400 °C (Koschinsky et al., 2008). The chemical composition of these hydrothermal fluids is changed significantly by interaction with the host rock, the addition of volcanic gases, and, in some cases, the separation of vapor and brine phases (e.g. Seyfried Jr. et al., 2003; Reeves et al., 2011). Typical alterations of the fluid

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include depletion of magnesium (Mg) through precipitation of smectite and chlorite, a reaction that also generates acidity and lowers the fluid pH together with a strongly reduced redox state (low oxidation reduction potential (ORP) and elevated H_2) controlled by Fe-bearing mineral equilibria during fluid-rock reaction, such as ferrous-iron oxidation and magnetite formation (e.g. Gallant and Von Damm, 2006). For example, ultramafic-hosted systems such as Rainbow and Logatchev on the Mid-Atlantic Ridge produce fluids markedly enriched in Fe, Cu, and H_2 relative to typical basalt-hosted mid-ocean-ridge fluids, owing to serpentinization of olivine-rich host rocks (Charlou et al., 2002; Schmidt et al., 2007). By contrast, magmatically influenced back-arc and arc systems such as those of the NE Lau Basin generate H_2S -rich, strongly acidic fluids, where sulfide precipitation more strongly governs the fate of Fe (Fouquet et al., 1991; Wang et al., 2022). Within the upflow zone the hydrothermal fluid is typically hot (up to ~ 350 – 400 °C), acidic, reducing, and chloride-rich. These conditions strongly enhance metal solubility, directly through high temperature and low pH as well as through the formation of aqueous chloride complexes that stabilize base metals in solution. The fluid therefore efficiently leaches metals from the host rock, most prominently iron (Fe) and manganese (Mn), together with chalcophile elements such as cobalt (Co), copper (Cu) and lead (Pb), and to a lesser degree cadmium (Cd), nickel (Ni), and the rare earth elements and yttrium (REY, or REE when explicitly excluding Y). In ambient deep-sea conditions at mid-ocean ridges (cold, alkaline, and oxygenated) most of these elements occur at very low dissolved concentrations relative to crustal abundance as well as to endmember vent fluids, because oxidative precipitation of Fe and Mn, and scavenging of the other elements onto the resulting particles, remove them from solution. Endmember vent fluids are consequently enriched in these metals by several orders of magnitude over background seawater. This enrichment is transient: on mixing with cold, oxygenated seawater at the seafloor the same elements are rapidly removed from the dissolved phase, precipitating as metal sulfides (e.g. Cu, Pb, Fe) and, in the buoyant plume, as Fe-Mn oxyhydroxides. Because Mn(II) oxidizes more slowly than Fe(II), however, a larger fraction of Mn remains dissolved through the buoyant plume before it too precipitates as oxide, and REY (particularly Ce) are progressively scavenged onto these newly forming Fe and Mn oxide phases rather than behaving conservatively (e.g. German et al., 1990; James and Elderfield, 1996). This scavenging behavior, especially pronounced for Ce, is well documented in hydrothermal plumes (Mitra et al., 1994; Ludford et al., 1996; Bau and Dulski, 1999; Sherrell et al., 1999). Hydrothermal fluid composition is governed by controls operating at different scales: the broader geological setting (e.g. tectonic context and host-rock composition) together with more local conditions such as temperature, water-rock ratio, phase separation, and reaction progress. Fluid compositions therefore vary among different hydrothermal systems as well as among vents within a single system or setting. This variability in turn strongly affects the hydrothermal flux of these metals to the ocean on regional and global scales (Resing et al., 2015; Diehl and Bach, 2025).

Overall, the hydrothermal flux of elements such as Fe to the ocean is estimated to range from 2.8 – 23×10^{10} mol year $^{-1}$ compared to a riverine flux of 2.3×10^{10} mol year $^{-1}$, while for Mn the hydrothermal flux is around 1.4 – 4.2×10^{10} mol year $^{-1}$ compared to a 0.49×10^{10} mol year $^{-1}$ riverine flux (Alt, 2003). The largest fraction of these metals, however, does not contribute to the dissolved pool of trace metals in the ocean basin (e.g. Mottl and McConachy, 1990; Feely et al., 1994). A large part is rapidly precipitated and removed from solution as the hydrothermal fluids mix with seawater, forming the characteristic precipitates that create the visually appealing “black smoker” chimneys. These precipitates also generate the black plume emerging from the vents and accumulate around hydrothermal fields as mineral deposits. In the past, this created the assumption that hydrothermal venting could not significantly contribute as inputs to marine trace metal cycles. It is known now, however, that an important fraction of hydrothermal Fe is more stable in the water column than previously expected due to, for

example, transport as nanoparticles (Yücel et al., 2011) and stabilization by organic ligands (Hoffman et al., 2024). This leads to the formation of hydrothermal plumes in the ocean that are detected up to thousands of kilometers from the source vents (Sander and Koschinsky, 2011; Fitzsimmons and Steffen, 2024). The distance and direction over which this dissolved and particulate hydrothermal Fe is dispersed are ultimately governed by the advection of the deep water masses transporting the non-buoyant plume, so that regional deep-ocean circulation shapes the far-field distribution of hydrothermally derived metals (Nishioka et al., 2013; Resing et al., 2015).

When the hot hydrothermal fluid is vented into the cold deep ocean, it is highly buoyant and rises in the density-stratified water column, where it keeps mixing with seawater, until its density reaches equilibrium with the surrounding seawater. At this point, the buoyant plume becomes non-buoyant and transitions from rapid vertical movement to slowly spreading horizontally through further mixing with seawater and advective transport by ocean currents (Baker et al., 1995). Depending on the temperature of the source fluid and the stratification of the water column, a hydrothermal plume will typically rise from tens to hundreds of meters above the vent site (e.g. Baker et al., 1995).

Because hydrothermal plumes are far easier to detect than the vents themselves – indeed the Galápagos vents were located only after their plume signal was recognized (Weiss et al., 1977; Corliss et al., 1979) – water-column plume surveys remain the primary tool for locating and characterizing venting.

Understanding the processes affecting trace metals during transport in the non-buoyant plume is essential for quantifying hydrothermal metal fluxes to the ocean, which are likely to play a key role in controlling ocean biogeochemical cycles (Tagliabue et al., 2010; Resing et al., 2015). We use ocean biogeochemistry here in the basin-to-global sense, meaning a perturbation of the regional or whole-ocean dissolved inventory once an element is dispersed beyond the local plume into the general circulation; this need not reach the surface ocean and can occur thousands of kilometers downstream in the deep sea, as distinct from the plume-local scale within tens of kilometers of the vent. Plume microbial communities also participate directly in these cycles, coupling the oxidation of reduced hydrothermal species to carbon fixation and modulating trace-metal speciation (Dick, 2019; Hoffman et al., 2024). Our current understanding of these trace-metal processes is based largely on studies of early mixing in buoyant plumes with limited sample sets and low-resolution spatial coverage of non-buoyant plumes (e.g. Mottl and McConachy, 1990; Findlay et al., 2019; Fang and Wang, 2021). Only a few studies published trace metal concentrations at often limited sample resolution and number of analytes in non-buoyant plumes with increasing distance from the vent sites (James and Elderfield, 1996; González-Santana et al., 2020; Kleint et al., 2022). Basin-scale studies of trace metals in the ocean within the GEOTRACES program have demonstrated that with increasing distance from the vents in the far-field plume, the transport of these elements is controlled by processes different to those close to the source shifting from precipitation and oxidation, to ad-/desorption, and biological cycling (Resing et al., 2015; Gartman and Findlay, 2020). The transition from the near-field to the far-field non-buoyant plume falls between these two bodies of work: it is under-resolved both by buoyant-plume studies that focus on early mixing and by basin-scale surveys that sample the already oxidized far-field. Yet it is an interval over which important redox transitions take place: reduced species are progressively oxidized, metal sulfides precipitate and subsequently begin to oxidize, and scavenging, organic complexation, and sorption can strongly influence whether hydrothermal metals are retained near the source or exported to the wider ocean (Gartman and Findlay, 2020). With this study, we aim to provide more insight into the complex processes that control the fate of hydrothermally affected trace metals during the evolution of a hydrothermal plume with increasing distance from the vent. We discuss these processes using the example of the Kairei Hydrothermal Field (KHF) in the central Indian Ocean. Kairei is well suited to this question. It is a

hybrid, ultramafic-influenced basalt-hosted system whose fluids combine characteristics of both settings, giving rise to unusually high H_2 and metal concentrations (see Study Area). It also lies on the Central Indian Ridge, a spreading center that remains comparatively under-sampled in trace-metal studies of hydrothermal plumes. To resolve

this transition within a single system, we sampled the Kairei plume from the high-temperature endmember fluids through the buoyant and non-buoyant plume to the dilute far-field, at stations up to 56 km from the vent, following the same plume from source to dispersal.

This study investigates trace metals depending on their geochemical

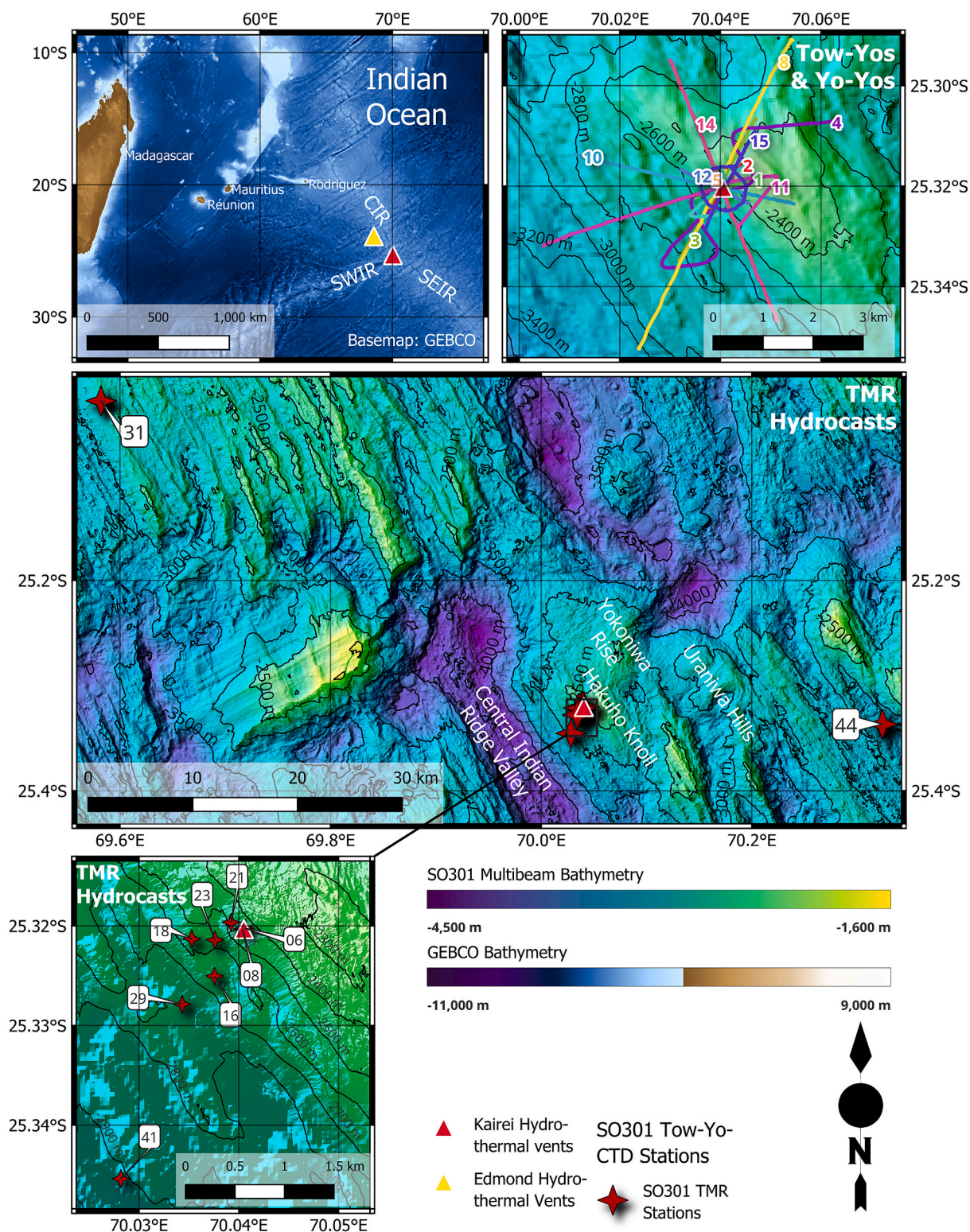


Fig. 1. Location of the Kairei hydrothermal vent field in the Indian Ocean at the Rodriguez Triple Junction of the Central Indian Ridge (CIR), the Southeast Indian Ridge (SEIR), and the Southwest Indian Ridge (SWIR). Tracks of the Tow-Yo CTD stations that mapped the Kairei hydrothermal plume during cruise SO301 (RV Sonne, 2023), and locations of hydrocasts using the MARUM trace metal rosette (TMR) during SO301. Maps produced in QGIS 3.4. based on bathymetric data collected during research cruise SO301 (Engels et al., 2024) and the GEBCO 2025 General Bathymetric Chart of the Oceans.

behavior in the ocean and hydrothermal plumes in particular. The elements showing the highest enrichment in hydrothermal fluids and plumes relative to the seawater background concentrations are Fe and Mn (e.g. Feely et al., 1994; Edmonds and German, 2004). Hydrothermal plumes disperse these elements well beyond the vent sites, supplying hydrothermally derived Fe and Mn to the deep ocean over distances of tens to thousands of kilometers (e.g. González-Santana et al., 2020; Bühring et al., 2025) and the formation of Mn oxides and Fe oxides and sulfides plays a key role in controlling the fate of other metals emitted by hydrothermal systems (Feely et al., 1994; Edmonds and German, 2004). Gallium (Ga) is a trace element whose hydrothermal cycling remains poorly studied, but it is enriched in vent fluids and can impart a small but distinct hydrothermal signal to the plume close to the source (Ho et al., 2019). Chalcophile elements, such as Cu, Cd, Co, Pb, and Ni are predominantly incorporated in sulfide minerals (Metz and Trefry, 1993). Depending on the concentrations in the source fluid and the mineralogy of the particles formed during plume mixing, hydrothermal plumes can be a source of these elements or remove them by sulfide formation leading to net removal from the oceanic water column (Mottl and McConachy, 1990; Jacquot and Moffett, 2015; Roshan and Wu, 2015). Particle-reactive elements like the rare earths, Y, and scandium (Sc), are commonly scavenged by adsorption to surfaces of mineral particles, and hydrothermal plumes have been shown to be sinks for these elements in the deep sea (German et al., 1990). This expected behavior of the transition metals and REY follows the framework German et al. (1990) summarized for a Mid-Atlantic Ridge plume (TAG). This scavenging signature has since been confirmed directly in the Rainbow hydrothermal plume, where Haalboom et al. (2020) found particulate REE/Fe molar ratios to increase with distance from the vent, indicating continuous REY scavenging onto Fe-oxyhydroxides as the plume ages. Kairei, a hybrid ultramafic-influenced basalt-hosted system with lower end-member Fe than strongly ultramafic-hosted Rainbow (Edmonds and German, 2004), may differ in the balance between seafloor sulfide precipitation and Fe oxyhydroxide formation, and so in how chalcophile metals and REY partition between dissolved and particulate phases. Vanadium (V) is likewise removed by scavenging onto Fe-oxyhydroxide particle surfaces, so that hydrothermal plumes act as an effective sink for dissolved V in seawater (Trefry and Metz, 1989; Coale et al., 1991).

1.1. Study area

The KHF is located at the Central Indian Ridge (CIR) north of the Rodriguez Triple Junction (RTJ) of the CIR, the Southeast Indian Ridge (SEIR), and the Southwest Indian Ridge (SWIR) at 25.32033°S, 70.0405°E and 2455 m depth (Fig. 1) where it was discovered in 2000 (Hashimoto et al., 2001). During research cruise SO301 (Engels et al., 2024), we extensively mapped and sampled the vertically and horizontally spreading hydrothermal plume by tow-yo and yo-yo conductivity-temperature-depth (CTD) deployments as well as vertical hydrocasts using a newly constructed trace metal rosette (TMR).

1.2. Geological background

The KHF is located on the eastern wall of the Central Indian Ridge rift valley, at the western flank of Hakuho Knoll more than 7 km off-axis and approximately 1800–2000 m above the valley floor (Hashimoto et al., 2001; Gallant and Von Damm, 2006; Kumagai et al., 2008). Tectonic uplift and step-faulting have exposed older basaltic crust in this area (Van Dover et al., 2001; Kumagai et al., 2008). The seafloor directly beneath the vents consists entirely of basaltic lithologies, including massive and porphyritic basalts, sheet flows, and pillow remnants (Van Dover et al., 2001; Fujii and Okino, 2018). Collectively, these form a broad talus apron that blankets portions of the underlying volcanic basement and obscures parts of the sulfide system. Even though the field is basalt-hosted at the surface, the wider lithospheric context is heterogeneous. Several nearby oceanic core complexes, such as the

Uraniwa Hills and Yokoniwa Rise, expose serpentinized troctolites, olivine gabbros, plagioclase dunites, and mantle peridotites. This indicates that olivine-rich lower-crustal and mantle-transition rocks lie unusually close to the seafloor beneath a correspondingly thin basaltic crust around Kairei (Kumagai et al., 2008; Nakamura et al., 2009; Okino et al., 2015).

The hydrothermal system itself is found to be strongly influenced by fault architecture: Kairei and the adjacent inactive mound are located at the intersection of a ridge-parallel structure and an NE-trending cross-fault that offsets the mound crest. This configuration focuses fluid ascent along a fractured ridge-top and into the talus-covered mound below. The resultant sulfide accumulation forms a composite block-mound structure, with black smoker complexes rising up to ~20 m above the seafloor, comprising massive Cu-rich cores, Zn-rich outer zones, chimney edifices and debris, siliceous and talc-bearing breccias, and extensive weathered sulfide rubble that continues downslope into the surrounding talus (Van Dover et al., 2001; Wang et al., 2014). The presence of large volumes of reworked sulfides, along with U–Th ages of massive sulfides, indicates the persistence of hydrothermal activity for a minimum of tens of thousands of years (Wang et al., 2012; Adam et al., 2020). The observations presented herein collectively support the hypothesis of a hybrid subsurface configuration, in which seawater reacts with serpentinizing troctolites and related ultramafic to mafic rocks. This reaction produces abundant hydrogen (Nakamura et al., 2009), yielding fluids that retain a predominantly basalt-hosted chemical signature, but clearly reflect deep ultramafic influence. In this sense, Kairei represents a magma-assisted, ultramafic-influenced basalt-hosted system that is structurally and lithologically comparable to other off-axis, oceanic core complex (OCC)-related vent fields such as Aurora in the Arctic Ocean at 82°53.83'N, 6°15.32'W (Walter et al., 2025). The geological framework of Kairei exerts a first-order control on fluid geochemistry and trace-metal distribution in the overlying water column.

1.3. Fluid composition

The hydrothermal fluids of the KHF have been sampled repeatedly since its discovery in 2000 (Hashimoto et al., 2001; Gamo et al., 2001) including in 2001 (Gallant and Von Damm, 2006), in 2002, and in 2006 (Takai et al., 2004; Kumagai et al., 2008).

The hydrothermal fluids at Kairei display a geochemical composition that reflects the field's geological setting. Measured temperatures reach 365–369 °C at the primary vents, with pH values between 3.3 and 3.6, consistent with typical basalt-hosted systems (Gamo et al., 2001; Gallant and Von Damm, 2006; Kumagai et al., 2008). However, several compositional features distinguish Kairei fluids from conventional mid-ocean ridge (MOR) hydrothermal systems. Hydrogen (H₂) concentrations in Kairei fluids range from 2.5 to 8.5 mmol kg⁻¹, approximately an order of magnitude higher than typical basalt-hosted systems (Van Dover et al., 2001; Takai et al., 2004; Kumagai et al., 2008). These H₂ levels are comparable to those found in ultramafic-hosted systems along the Mid-Atlantic Ridge such as Nibelungen (Schmidt et al., 2011). The discovery of serpentinized troctolites at the nearby Uraniwa Hills provided insight into this enrichment. Geochemical modeling by Nakamura et al. (2009) indicated that serpentinization of olivine-rich rocks at temperatures above 400 °C could produce the observed H₂ concentrations. Subsequent interaction with basalt during upflow maintains elevated H₂ while generating the high silica concentrations (~17 mmol L⁻¹) measured in the fluids. Subseafloor precipitation of metal sulfides may contribute minor additional H₂ and acidity, through reactions such as $\text{Fe}^{2+} + 2\text{H}_2\text{S} \rightarrow \text{FeS}_2 + 2\text{H}^+ + \text{H}_2$ (Gallant and Von Damm, 2006).

Gallant and Von Damm (2006) report that the individual Kairei vents differ in fluid composition, which they attribute to differing subsurface processing of a single, shared hydrothermal source. Across these vents, metal concentrations are elevated, with Fe at 5 mmol L⁻¹, Mn at 0.8 mmol L⁻¹, and Cu near 100 μmol L⁻¹ (sampled in 2001: Gallant and Von Damm, 2006; sampled in 2006: Kumagai et al., 2008). The relatively

high Fe compared to other vent systems has been related to multiple factors: chlorinity enrichment of 14 ‰ above seawater values indicating brine-phase separation, interaction with ultramafic rocks, and pH conditions that enhance metal solubility. The high Fe/Mn ratios of 4.4–7.0 indicate that little of this Fe is removed by sulfide precipitation in the seafloor, consistent with its efficient transport to the seafloor (Gallant and Von Damm, 2006). Gallant and Von Damm (2006) further note that the total Fe/Mn of the Kairei plume (approximately 15) is higher than that of the discrete vent fluids they sampled (4.4–9.7), which they attribute to hotter, more Fe-rich fluids that were not directly sampled rather than to additional vent fields, implying that the fluids feeding the plume are more Fe-rich than the sampled endmember.

Despite high H_2 concentrations, methane (CH_4) levels remain relatively low at $\sim 0.2 \text{ mmol L}^{-1}$, contrasting with ultramafic-hosted systems where CH_4 typically exceeds 2 mmol L^{-1} (Kumagai et al., 2008). This high H_2/CH_4 ratio has been attributed to lower Ni content in troctolites compared to mantle peridotites, which limits catalytic methane production (Nakamura et al., 2009).

1.4. The Kairei Hydrothermal Plume

The water column at the KHF is influenced by regional circulation patterns characteristic of the Central Indian Ocean. Background waters at vent depths consist primarily of Circumpolar Deep Water (CDW) that enters the CIR rift valley through fractures in the SWIR. It spreads northward into the Indian Ocean from the Southern Ocean (You, 2000), and its advection sets the direction and distance over which the non-buoyant plume and its dissolved and particulate trace-metal load are carried away from the vents, while continued mixing dilutes the plume signal. The oxygen content, nutrient load, and background trace-metal concentrations of the carrier water in turn set the local baseline against which plume anomalies are measured and shape the redox and scavenging conditions experienced by the metals during transport. This water mass, identified by slightly reduced salinity within the axial valley, creates the density structure that controls plume dispersion (Rudnicki and German, 2002).

Hydrothermal activity at Kairei was first detected in 1993 through water column anomalies in dissolved Mn, methane, and particulate matter (Gamo et al., 1996). Subsequent surveys have documented a non-buoyant plume extending from approximately 2150 to 2300 m depth, indicating a rise height of 290–300 m above the seafloor vents. This plume height has remained consistent across nearly two decades of observations (Gamo et al., 1996; Rudnicki and German, 2002; Noguchi et al., 2015).

Time-series measurements of the non-buoyant plume have documented temporal variability of tidal and higher frequencies, with particle anomalies varying in intensity and vertical distribution, while remaining bounded by isopycnal surfaces (Rudnicki and German, 2002). Dissolved Fe concentrations in the non-buoyant plume reach several hundred nmol L^{-1} (Statham et al., 2005). Recent surveys within the INDEX project of the Federal Institute for Geosciences and Natural Resources (BGR) in 2016 measured dissolved Fe up to $41 \mu\text{mol L}^{-1}$ in the buoyant plume 4 m above vents, decreasing to $\sim 500 \text{ nmol L}^{-1}$ in the non-buoyant plume (Noowong, 2022).

Chemical gradients within the plume reflect the source fluid composition and subsequent reactions. Hydrogen concentrations up to 88 nmol L^{-1} occur in the proximal plume but decrease rapidly, with anomalies restricted to within several hundred meters of the vent field. This distribution indicates rapid oxidation, with estimated half-lives of less than one day. Methane shows more conservative behavior, with concentrations reaching 12 nmol L^{-1} and anomalies extending several kilometers (Noguchi et al., 2015).

Microbiological studies have identified chemolitho(auto)trophic SUP05 (Thioglobus) phylotypes and Epsilonproteobacteria proliferating in the mixing zone, while methanotrophic populations develop in distal plume regions (Noguchi et al., 2015). These microbial processes can

influence trace metal speciation through organic ligand production and redox modifications (Dick, 2019; Hoffman et al., 2024). Physical dilution and the stabilization of dissolved metals by strong organic ligands favor conservative behavior, while chemical precipitation, particle formation, and scavenging drive non-conservative removal. The net behavior of an individual metal reflects the degree of influence of these processes, which for many elements is dominated by removal close to the source. This complicates quantitative estimates of the KHF's contribution to the regional marine trace-metal budget and highlights the need for detailed sampling of the Kairei hydrothermal plume. Such sampling is essential for improving our understanding of the plume processes that influence trace metals after they are released into the water column.

2. Materials & methods

Water samples and hydrographic data were collected from the KHF plume as an ancillary user project during RV *Sonne* expedition SO301 from November 2023 to January 2024. To map the hydrothermal plume and characterize trace metal distributions, we employed a combination of in-situ sensor measurements and discrete water sampling using both conventional CTD-rosette systems and a specialized TMR to minimize trace metal contamination. In total, we deployed 11 CTD tow-yo stations, 2 CTD yo-yo casts of 12.5 h each at the vent site and 10 TMR hydrocast stations (Engels et al., 2024).

Hydrothermal fluid samples from the Kairei vent field, used to characterize the endmember fluid source, were collected during the INDEX 2013 cruise (RV *Sonne*, December 2013) and the INDEX 2016 cruise (RV *Pourquoi pas?*, January to February 2016) by BGR.

2.1. Sensor measurements

Hydrothermal plumes can be detected in real time at several kilometers' distance using in-situ measurements of turbidity (a proxy for hydrothermally sourced particles) and ORP, tracing reduced chemical species (Gamo et al., 1996; Rudnicki and German, 2002), which guided our tow-yo and yo-yo CTD surveys of the Kairei plume. We obtained in-situ hydrographic measurements during SO301 using the on-board CTD rosette system in tow-yo deployments. The system is equipped with a SBE11Plus CTD (Sea-Bird Scientific) that includes sensors for conductivity, temperature, pressure, and oxygen concentration. For detection of hydrothermal plumes, we additionally deployed miniature autonomous plume recorders (MAPR) by NOAA (Baker, 1997; Walker, 2023) mounted to the CTD-hydrowire. The MAPR uses a temperature sensor, a boosted-gain backscatter sensor (Seapoint Inc.) to measure turbidity, and an ORP sensor measuring a platinum electrode against an Ag/AgCl reference potential. Identical turbidity and ORP sensors were added to the vessel's CTD for online detection of hydrothermal plume anomalies in the water column alongside an additional ORP sensor (AMT GmbH).

2.2. Plume sampling (SO301)

During cruise SO301, we acquired samples using the TMR to avoid contamination. Since the TMR used for this study operates autonomously without a data connection during deployment, it can only be used for vertical hydrocasts after previously acquiring a sensor profile with a regular CTD system. This approach to obtain plume samples is impeded by the strong temporal variability of the non-buoyant plume: the fluctuations on sub-tidal timescales down to the buoyancy frequency mean in practice that it is difficult to target the strongest plume signals, as the timespan between the two casts is of the same order as the natural variability. Therefore, we additionally took samples close to the vent field using the vessel's CTD rosette to acquire water samples for trace metal analysis from the buoyant and the young non-buoyant plume close to the vent field, where high concentrations of metals in the samples make contamination from the sampling system and hydrowire much less

of a concern than for samples from the far-field plume and the background water column.

2.2.1. CTD-Tow-Yos & time series stations

For the detailed mapping and sampling of the Kairei hydrothermal plume, we used the vessel's onboard CTD-rosette in a tow-yo deployment mode, where during the deployment the ship was slowly moving (0.3 to 0.8 kn) and the CTD was lowered and heaved with 0.5 to 1 m s⁻¹, resulting in a zig-zagging up-and-down cross-section along the ship track for a total of 11 tow-yo profiles (Fig. 1, Table 1). In addition, we conducted two time series stations of the plume, where the CTD-rosette was lowered and heaved while the ship remained in position above the vent site (so-called yo-yo deployment). RV *Sonne*'s CTD rosette is equipped with 24 12 L Niskin samplers. For cruise SO301, two of those were removed for an Aquadopp current profiler, and the internal metal springs of the samplers were replaced with latex springs to avoid contamination.

Immediately after CTD recovery, water samples from the CTD-rosette system were collected in acid-clean containers for trace metal analyses and in gas-tight copper tubes for concentrations and isotopic ratios of the helium isotopes ³He to ⁴He, and neon to be determined post cruise.

2.2.2. TMR-hydrocasts

To acquire contamination-free samples of the (non)-buoyant plume as well as background waters above and below the plume and in the far-field, we deployed the newly constructed autonomous TMR of MARUM (Fig. 2) at nine stations from the non-buoyant and one station from the buoyant plume (Fig. 1, Table 4). The system is constructed with a titanium frame by K.U.M. Umwelt- und Meerestechnik Kiel GmbH. Samples are triggered by a G.O. Model 1018 Intelligent 12-position control unit manufactured by General Oceanics. The frame can support up to 12 5 L water samplers. During cruise SO301, we deployed four externally sprung O.T.E. Model 114 5 L contamination-free samplers (Ocean-TestEquipment, like G.O. "Go-Flo" samplers). These samplers were used primarily for background samples where trace-metal contamination is particularly critical. In the remaining eight positions of the TMR, we deployed metal-free O.T.E. Model 110 5 L ("Niskin") samplers with internal latex springs and internal PTFE-spray. Due to contamination from the internal latex springs particularly for Zn (Garçon et al., 2017), this means that unfortunately, the sample set collected in this study is not suited for analysis of Zn. Before first deployment, all samplers were acid-cleaned (0.01 mol L⁻¹ HCl, 48 h) and rinsed three times with ultrapure water, repeated between deployments for samplers used on high-turbidity plume samples to avoid carry-over contamination (see Supplementary Material for the full procedure). We used veering/heaving speeds of up to 0.7 m s⁻¹, slowing down to 0.25–0.3 m s⁻¹ between 200 m below and above the expected plume depth to avoid smearing effects, as during autonomous operation, it is not possible to

stop the system for closing water samplers. The 1018 intelligent control unit can operate autonomously, allowing deployment on a simple aramid rope without a data connection and triggering samples at pre-programmed times or at pre-determined depths using the integrated pressure sensor. Although upcast sampling is generally preferred to minimize contamination, at the first stations of SO301, operational troubleshooting required triggering the bottles during the downcast. For later stations, all samples were taken during the upcast. Using such an autonomous system avoids the need for a separate deck winch, which would be a significant additional cost factor in acquisition and shipping as well as requiring additional technical personnel for operation. To determine appropriate sampling depths, a standard CTD deployment is conducted prior to deploying the TMR. Sampling depths were chosen based on the ship's CTD real-time sensor profile and pre-programmed before the TMR deployment immediately following the vessel's CTD cast. As accurate depth information is crucial to avoid contamination from seafloor contact, we mounted a Sonardyne WSM6 + 4 k MF ultra-short baseline (USBL) positioning transponder to the frame to precisely track the position of the TMR in the water column.

2.3. Onboard trace metal sample processing

All samples were processed in the onboard laboratory under filtered air using a class 1000 laminar-flow bench (Colandis). Samples for trace metal analysis were stored in low-density polyethylene (LDPE) bottles and acidified using ultrapure hydrochloric acid (HCl, Rotipuran Ultra, 34 %) at a ratio of 1.5 µL acid/mL sample (final concentration ~16 mmol L⁻¹, pH ~1.8). Prior to the cruise, all LDPE sample bottles were cleaned following the standard trace-metal protocol of Constructor University, comprising sequential acid leaching in dilute HNO₃/HF and then HCl at 45 °C with ultrapure water rinses between steps; immediately before sampling, each bottle was rinsed three times with the water to be collected (see Supplementary Material for the full procedure).

2.3.1. CTD samples

To acquire samples from the vessel's CTD-rosette, samples were directly filtered from the Niskin samplers on deck using pre-cleaned tubing and cartridge filters (Pall Life Sciences AcroPak 500 with 0.8/0.2 µm Supor polyethersulfone (PES) membrane). Before first use, each AcroPak cartridge filter was rinsed with 5 L of 0.01 mol L⁻¹ HCl (Rotipuran suprapure) followed by 5 L of ultrapure water; after each sample the filter was rinsed again with 5 L of ultrapure water, and filters used for high-turbidity samples were reserved for subsequent samples of similarly high turbidity (see Supplementary Material for the full procedure). For the sequential filtrations later used to investigate particle size fractionation effects, unfiltered water samples were collected from the Niskin samplers and stored in 1 L LDPE bottles for further processing in the onboard laboratory.

Table 1

Overview of stations used for mapping the Kairei hydrothermal plume during cruise SO301 with CTD Yo-Yo and Tow-Yo deployments.

Station ID	Date/Time Start [dd/mm/yyyy hh:mm UTC]	Date/Time End [dd/mm/yyyy hh:mm UTC]	Lat. Start [°N]	Lon. Start [°E]	Lat. End [°N]	Lon. End [°E]	Station Type
SO301_5	27/11/2023 04:13	27/11/2023 18:48	-25.320	70.040	-25.321	70.040	CTD Yo-Yo
SO301_7	28/11/2023 01:35	28/11/2023 11:41	-25.316	70.043	-25.325	70.039	CTD Tow-Yo
SO301_9	28/11/2023 21:07	29/11/2023 05:34	-25.316	70.045	-25.317	70.040	CTD Tow-Yo
SO301_10	29/11/2023 08:54	29/11/2023 12:14	-25.317	70.033	-25.324	70.046	CTD Tow-Yo
SO301_15-1	02/12/2023 13:52	03/12/2023 01:41	-25.307	70.062	-25.325	70.037	CTD Tow-Yo
SO301_17-1	03/12/2023 09:05	03/12/2023 16:37	-25.325	70.038	-25.315	70.045	CTD Tow-Yo
SO301_20-1	18/12/2023 16:07	18/12/2023 22:26	-25.315	70.016	-25.324	70.055	CTD Tow-Yo
SO301_22-1	19/12/2023 05:30	19/12/2023 13:41	-25.306	70.047	-25.334	70.032	CTD Tow-Yo
SO301_24-1	19/12/2023 20:39	20/12/2023 00:50	-25.319	70.046	-25.322	70.035	CTD Tow-Yo
SO301_28-1	22/12/2023 09:12	22/12/2023 21:35	-25.320	70.040	-25.320	70.040	CTD Yo-Yo
SO301_40-1	29/12/2023 21:49	30/12/2023 05:22	-25.295	70.053	-25.353	70.024	CTD Tow-Yo
SO301_42-1	30/12/2023 12:32	30/12/2023 18:24	-25.347	70.052	-25.301	70.032	CTD Tow-Yo
SO301_43-1	30/12/2023 21:32	31/12/2023 01:37	-25.319	70.050	-25.332	70.005	CTD Tow-Yo

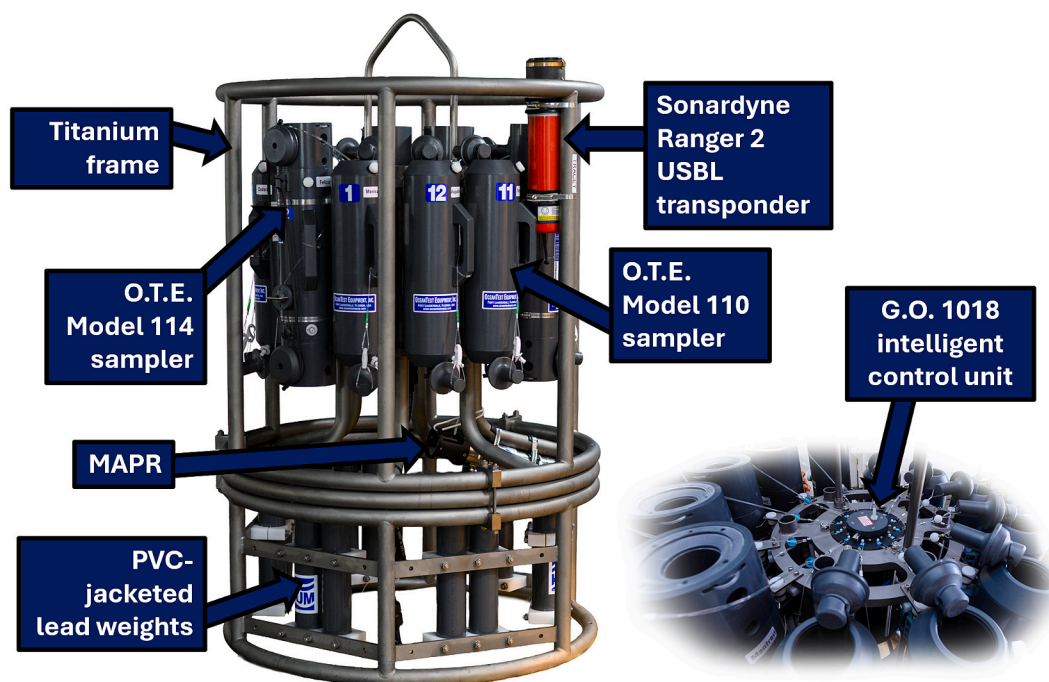


Fig. 2. Overview of the components of the MARUM trace metal rosette (TMR) as deployed during research cruise SO301.

2.3.2. TMR samples

After recovering the TMR, all water samplers were removed from the TMR and immediately transferred to the onboard laboratory for further processing under filtered air. Water samples for measurements of dissolved concentrations ($<0.2 \mu\text{m}$) were filtered using pre-cleaned cartridge filters ($0.8/0.2 \mu\text{m}$ AcroPak 500, Pall Corp.).

2.3.3. Sequential filtration

To investigate the effects of particle size fractionation on trace metal concentrations and speciation, water samples were additionally filtered with pore sizes of 0.8 , 0.2 , and $0.015 \mu\text{m}$ at selected depths in the plume as well as in the water column above and below the plume (a maximum of three samples per station). For the 0.8 and $0.2 \mu\text{m}$ fractions, 47 mm diameter Supor PES membrane filters were used, while the $0.015 \mu\text{m}$ fraction was filtered through 47 mm diameter Nuclepore polycarbonate (PC) membranes using acid-cleaned PC filter towers under filtered air in the horizontal flow-bench. Between samples, the PC filter towers were acid-cleaned ($10 \text{ \% HNO}_3$) and the O-rings cleaned with Mucosol detergent, each followed by ultrapure water rinses; after reassembly, the towers and membranes were rinsed with $0.5 \text{ mol L}^{-1} \text{ HCl}$, then ultrapure water, and finally a discarded sample aliquot before the subsamples were collected (see [Supplementary Material](#) for the full procedure).

2.4. ROV sampling of hydrothermal fluids

Hydrothermal fluid samples had been taken during cruise INDEX 2013 with RV *Sonne* by means of the inert fluid-sampling system KIPS (Garbe-Schönberg, 2006; Schmidt et al., 2007) mounted into the sampling module of the remotely operated vehicle (ROV) *Kiel 6000* (GEO-MAR, Kiel, Germany). The same system was used for sample acquisition during cruise INDEX 2016 with RV *Pourquoi pas?* and the ROV *Victor 6000* (IFREMER, Brest, France). Immediately after recovery of the ROV on deck, all KIPS sample flasks filled with hydrothermal fluid were transferred to the ship's laboratory for sub-sampling within a clean bench following a standardized protocol. Each sample was rehomogenized by shaking and transferred via nitrogen overpressure directly into sample flasks or filtration units. All hot black smoker fluids were not filtered following the rationale that all particles in these

samples are assumed to have precipitated in situ during cooling and mixing with seawater and represent part of the formerly dissolved metal load of the fluid.

2.5. Analysis

2.5.1. Trace metal composition of plume samples – SeaFAST-Apex-ICP-MS/MS

We determined concentrations of Cd, Co, Cu, Fe, Ga, Mn, Ni, Pb, and V as well as REY using a tandem inductively coupled plasma mass spectrometer (ICP-MS/MS; Thermo Fisher iCAP-TQ) after automated online pre-concentration and matrix separation using the SeaFAST SP2 (Elemental Scientific Inc.). Additionally, an Apex 2Q desolvating nebulizer (Elemental Scientific Inc.) was used prior to sample injection into the ICP-MS/MS to increase sensitivity.

The analytical procedure was modified after Hollister et al. (2024) and Kraemer et al. (2024) and is outlined in detail in the [supplementary material](#). In summary, in the SeaFAST SP2 system, two Nobias PA1 resin columns ($200 \mu\text{L}$) are utilized for pre-concentration and matrix separation through chelation with automatic loading, washing and elution procedures with syringe pumps. This procedure results in a pre-concentration factor of approximately 15. All surfaces in contact with samples and reagents in the system are made from high-purity perfluoroalkoxy alkane (PFA) material to eliminate contamination. We used exclusively ultra-high-purity reagents for SeaFAST analysis in this study that were prepared using ultra-pure de-ionized (DI) water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$ resistivity) from an Arium Pro (Sartorius AG) water purification system. The buffer solution used in this procedure is a 4 mol L^{-1} ammonium acetate buffer at pH 6.20 (adjusted to ± 0.05) and we used a $5 \text{ \%}$ nitric acid (HNO_3) eluting solution and a hydrochloric acid (HCl) solution adjusted to pH 1.7 as a carrier/diluent for autocalibration and autodilution. Indium was used as an internal standard and loaded onto the column together with the samples (In , $10 \mu\text{g L}^{-1}$ in $5 \text{ \% HNO}_3$). This represents a modification of the method described in Kraemer et al. (2024), replacing the $10 \text{ \% NaCl}$ matrix-matching step. The ICP-MS/MS system was operated in oxygen mode and was tuned to CeO/Ce ratios of around $1 \text{ \%}$.

For detailed quality-control evaluation of the NASS-7, SLRS-6

certified reference materials (CRMs), refer to [supplementary material](#).

2.6. Trace metal composition of plume samples – direct ICP-MS

For measurements of cesium (Cs), molybdenum (Mo), and uranium (U), pre-filtered sample aliquots (0.8/0.2 μm , AcroPak capsule filters) were 100 times diluted with 0.5 mol L⁻¹ HNO₃ (suprapure, Roth). An internal standard including Ru was added to 2 ppb to correct potential drift during the MS measurement.

We used a quadrupole inductively coupled plasma-mass spectrometer (Perkin Elmer NEXion 350x) in normal mode to measure dissolved U and Cs in marine matrices. The kinetic energy discrimination (KED) mode with helium gas was selected for the detection of Mo to reduce polyatomic interferences.

In order to fit the saline matrix of the samples, three calibration standards were prepared in 6 mmol L⁻¹ NaCl (suprapure, Merck) – 0.5 mol L⁻¹ HNO₃. A multielement spike was added to reach final concentrations of 0.21 nmol kg⁻¹ (0.05 ppb), 2.10 nmol kg⁻¹ (0.5 ppb), and 8.40 nmol kg⁻¹ (2 ppb) for U, Mo, and Cs.

For quality control, two certified seawater reference standards were measured along with the samples: NASS-7 (NRCC), which provides certified values for U and Mo, and IAPSO, providing a certified value for Cs. The same procedure as described for preparing the samples was used here. Both reference standards were measured repeatedly, with one standard analyzed alongside each batch of four samples.

2.7. Major element composition of plume samples – ICP-OES

The major element composition of a selection of the 20 plume samples with the strongest hydrothermal influence (indicated by the turbidity) was determined using an inductively coupled plasma optical emission spectrometer (ICP-OES, Spectro Ciros Vision). The analytes include boron (B), calcium (Ca), potassium (K), magnesium (Mg), sodium (Na), sulfur (S), silicon (Si), and strontium (Sr), and measurements were validated by analysis of the IAPSO standard seawater.

An overview of the limits of detection and quantification (LOD, LOQ, calculated as 3.3 and 10 times the standard deviation of the blanks, respectively) as well as recoveries of the included certified reference materials for the analytical methods described above is available in the [supplementary material](#).

2.8. Trace metal composition of hydrothermal fluid samples – ICP-SF-MS

All non-filtrated but acidified samples (nf/a) carrying insoluble particulates that precipitated during cooling after sampling were filtrated and re-unified with the (dissolved) particulates after mixed acid digestion. The hot-plate mixed-acid digestion procedure involved a multi-step procedure with HF-aqua regia in PFA screw-top vials (Savillelex™) and subsequent repeated evaporation and re-dissolution with dilute subboiled nitric acid. Particle-laden filters (Nuclepore™ polycarbonate, Sartorius™ cellulose acetate) were leached following the same protocol. Filter and procedural blanks always had very low concentrations, 1–2 orders of magnitude below those of the samples. All work was done with pre-cleaned lab ware and ultra-pure reagents in a Class 100 clean room environment.

Dissolved concentrations of Fe and Mn were determined in non-filtrated, non-acidified (nf/na) original samples by means of ICP-optical emission spectrometry (Spectro Ciros SOP, Ametek). Samples were 10-fold diluted with 2 % (v/v) nitric acid and spiked to 1 mg kg⁻¹ Y for internal standardization. Seawater NaCl matrix-matched multi-element standard solutions were used for external calibration, and IAPSO and NIST 1643 reference materials served as external consistency standards. Precision of results as estimated from multiple analyses of IAPSO and replicate sample analyses was typically better than 1 % relative standard deviation (RSD). Samples with re-dissolved particulates were analyzed in the same way. Concentrations of minor and trace

elements V, Co, Ni, Cu, Pb, Cd, Ga, Mo, U, and REY were determined by high-resolution inductively coupled plasma sector-field mass spectrometry (ICP-SF-MS; Element XR, Thermo Scientific) after 25-fold dilution and spiking with Y and Re for internal standardization using appropriate mass resolution settings. Precision is typically better than 3–10 % RSD for concentrations 10-fold above the respective limit of detection of an element. Accuracy was monitored by analyzing IAPSO, NIST 1643, NIST 1640 and an in-house standard (“Anna-Louise”) that had been prepared from mixed hydrothermal fluids from Logatchev. Further details of calibration and analytical quality control (AQC) strategies can be found in [Schmidt et al. \(2007, 2011\)](#). The final tabulated compilation of analytical results represents blank-subtracted averages of 3 replicate runs. Samples stabilized with ZnAc + gelatine were analyzed for dissolved H₂S by photometry following the methylene blue method ([Fonselius et al., 1999](#)).

2.9. Helium isotopic composition

Helium concentrations and isotopic ratios of the helium isotopes ³He to ⁴He, and neon were determined in the Bremen Mass Spectrometer Laboratory ([Sültenfuß et al., 2009](#)). The excess ³He from the hydrothermal sources is here reported as $\delta^3\text{He}$ in percent, defined by the isotopic ratio (R) between ³He and ⁴He compared to the atmospheric ratio (R_A) of ³He to ⁴He, with $R_A = 1.39 \times 10^{-6}$ Eq. (1).

Equation 1: Definition of excess ³He.

$$\delta^3\text{He} = 100 \left(\frac{R}{R_A} - 1 \right)$$

3. Results

The comprehensive sampling and analytical approach described above yielded a detailed geochemical dataset spanning from the high-temperature vent fluids to the dilute far-field plume at distances up to 56 km from the vent field. We present these results following the plume's evolution from source to dispersal, beginning with the endmember composition of the hydrothermal fluids, through buoyant rise to non-buoyant dispersion and dilution as traced by sensor anomalies and trace metal distributions.

3.1. Hydrothermal fluid endmember concentrations

Here, we report the endmember composition of the Kairei hydrothermal fluid in [Table 2](#) by extrapolation of the measured dissolved concentrations to zero Mg; temperature and pH are reported as directly measured values and are not extrapolated. Values for INDEX 2013 are based on the mean concentrations for samples 31-ROV and 35-ROV-A, while the values for INDEX 2016 are based on the concentrations of sample 006-ROV-3. For comparison, we include the available data from [Gamo et al. \(2001\)](#) (sampled in 2000, based on samples 168A, 168A1, and 168A2) and [Gallant and Von Damm \(2006\)](#) (sampled in 2001, based on samples from Vent 4, Vent 5, and Vent 6). As the endmember composition of the hydrothermal fluids at the KHF showed stable values over 4 samplings and 16 years, we calculated a mean concentration of all available data for the elements investigated in this study and assume this composition to likely be representative for the venting fluid during the 2024 plume sampling campaign of cruise SO301. For reference of the seawater endmember during mixing of the hydrothermal plume, we include the mean concentrations of samples acquired at the reference station 31-TMR between 2250 and 2547 m depth, representing the average water column from the vent to the maximum plume height without hydrothermal influence. We calculated the enrichment of the hydrothermal fluid by dividing the average endmember concentrations by the corresponding values for the background seawater. In [Table 3](#), we report the REY-composition of two endmember samples from the INDEX 2013 campaign and their average (no full REY data are available for the

Table 2

Comparison of the composition of the hydrothermal endmember (Mg-extrapolated) of the Kairei hydrothermal vent field with the bottom seawater (average total conc. for station SO301-31 at 2250–2547 m depth).

	pH	T °C	H ₂ S mmol L ⁻¹	Cd nmol kg ⁻¹	Co nmol kg ⁻¹	Cu μmol kg ⁻¹	Fe μmol kg ⁻¹	Ga nmol kg ⁻¹	Ni nmol kg ⁻¹	Mn μmol kg ⁻¹	Mo nmol kg ⁻¹	Pb nmol kg ⁻¹	U nmol kg ⁻¹	V nmol kg ⁻¹	ΣREE nmol kg ⁻¹
Gamo et al. (2001) (sampled 2000)	3.5	360	4.00				5268			820					
Gallant and Von Damm (2006) (sampled 2001)	3.4	343	3.99	98		213	4717			832		369			
INDEX 2013			4.54	68	580	28	4775	19.3	166	826		164	<LOD		9.56
INDEX 2016	3.3	360	3.95	72	2081	344	4922	34.6	23.7	838	54.3	264	<LOD	12.7	
Ø Endmember	3.4	354	4.12	79	1331	195	4921	27	95	829	54.3	266		12.7	9.56
Seawater	7.8	2	0	0.8	0.03	0.003	0.004	0.028	9	0.002	108	0.008	13.1	37.7	0.096
Enrichment Factor				10 ²	10 ⁴	10 ⁴	10 ⁶	10 ³	10 ¹	10 ⁵	0.5	10 ⁴		0.33	10 ²

2016 sampling).

3.2. Hydrographic results

Background currents were observed with the ship's vessel-mounted 38 kHz ADCP down to a depth of 1500–1600 m. The current strength declines sharply below 1000 m depth, with a very weak flow of less than 0.05 m s⁻¹ mostly coming from the east. The most prominent signal in this layer between 1000 m and 1500 m is the tidal modulation, which has an amplitude of 5 to 10 cm s⁻¹, and is very much in phase with the barotropic tidal forcing (see ADCP data in [supplementary material](#)). While our observations do not cover the depth range of the non-buoyant plume, they are very much in agreement with the observed distribution of the particle plume, which shows a patchy dispersal centered around the vent site ([Fig. 3](#)). The tidal 'sloshing' of the plume is also evident during the 12-h time-series station ([Fig. 4](#)), where buoyant and non-buoyant plume signals were observed from the seafloor up to the upper plume boundary at $\sigma_2 = 36.987 \text{ kg m}^{-3}$ ([Fig. 5](#)) during the first 6 h of the station, while during the second half at first the non-buoyant plume was still present, and then totally disappeared towards the end of the deployment.

3.3. Buoyant plume samples from CTD tow-yos

Contamination of seawater samples with low metal concentrations by the sampling device and hydrowire used for regular CTD-deployments and tow-yos makes these samples unsuitable for determination of background levels and non-buoyant plume mixing. Therefore, we chose only a limited number of samples from these tow-yos for trace metal analysis, specifically where the strong sensor plume signal (i.e., in the buoyant and early non-buoyant plume) led us to expect concentrations high enough to be unaffected by contamination. For visualization, we show the measured concentrations in relation to turbidity ([Fig. 6](#)) as an indicator for the input of mineral particles to the water column by the KHF, and hence plume strength ([Fig. 7a](#)). The use of helium isotopes as a true chemically conservative tracer for fluid dilution was unfortunately not possible for trace metal samples, as the helium samples taken during SO301 were predominantly from different Niskins, and hence due to the high spatial and temporal variability of the plume occurrence not suitable as an indicator for dilution. Correlating $\delta^3\text{He}$ to turbidity ([Fig. 7b](#)) validates the use of turbidity as a tracer for hydrothermal input in this sample set.

The major ion composition did not show any deviation from background levels with the high dilution of the source fluid in the plume samples investigated here, but as expected, the major hydrothermally derived metals Fe and Mn are highly enriched in the rising plume of the KHF. We found maximum dissolved concentrations of 833 nmol kg⁻¹ Mn and 293 nmol kg⁻¹ Fe in the sample with the strongest hydrothermal input (28-CTD-4) indicated by the measured turbidity of 19.8 NTU. This represents a significant enrichment over the marine background

concentrations of these elements but is already significantly lower compared to the hydrothermal endmember concentrations of 829 μmol kg⁻¹ Mn and 4921 μmol kg⁻¹ Fe, a reduction of roughly three to four orders of magnitude relative to the endmember. The concentrations of both elements further decline rapidly with decreasing turbidity. We observe similar behaviors for both Co and Ga, which showed maximum concentrations of 0.49 nmol kg⁻¹ and 64 pmol kg⁻¹ in sample 28-CTD-4, respectively, compared to 1331 nmol kg⁻¹ Co and 27 nmol kg⁻¹ Ga in the KHF endmember followed by a rapid decline with decreasing turbidity approaching background seawater concentrations. Conversely, the REY, here represented by Tb, show significantly reduced concentrations compared to the background seawater in the rising plume samples with a minimum concentration of 1.1 pmol kg⁻¹ in sample 28-CTD-4, which represents 13 % of the background seawater concentration of 8.3 pmol kg⁻¹, despite the KHF endmember being enriched ~100-fold on average for REY compared to the marine background concentrations. In a similar fashion, both Cd and Cu, despite being enriched ~100-fold to 79 nmol kg⁻¹ Cd and ~10,000-fold to 195 μmol kg⁻¹ Cu in the KHF endmember, display reductions in their dissolved concentrations in the rising plume sample 28-CTD-4 to 1.49 nmol kg⁻¹ Cu and 0.34 nmol kg⁻¹ Cd representing 50 % and 43 % of the background seawater concentrations, respectively. Another element that shows a reduced concentration in the rising plume of 28.3 nmol kg⁻¹ (75 % of the seawater background) is V, which is also depleted in the KHF endmember to a concentration of 12.7 nmol kg⁻¹ (33 % compared to the background seawater). Molybdenum and U, both being reduced by 50 % and fully depleted in the KHF endmember, do not show any significant deviation from the background seawater concentration in the investigated water samples. Finally, Pb, despite being ~10,000-fold enriched in the KHF endmember, does not show any significant deviation from dissolved seawater concentrations in the CTD plume samples except for some scattered higher concentrations at mid-turbidity that we attribute to contamination during the sampling procedure.

3.4. TMR Stations – (Non)-buoyant Plume

We sampled the non-buoyant plume of the Kairei vent field with vertical TMR-Hydrocasts to study the reactions affecting trace metals during the mixing of the plume with seawater at increasing distance to the vent field. Since the rise of the buoyant plume is slanted by the flow field, the spreading direction of the non-buoyant plume changes dramatically with the tidal currents. This makes the geographic distance to the vent field an unsuitable quantity to study the progression of plume processes. However, we measured depth profiles of temperature, turbidity, and ORP with every TMR deployment using a MAPR. Both the turbidity as an indicator of particle load, and the ORP anomaly (ORP Delta, defined as the difference of ORP at the plume peak and the plume shoulder in the water column above) caused by the emission of reducing species like Fe(II), Mn(II), and reduced gases can be used to trace the degree of mixing of the hydrothermal fluid with the surrounding

Table 3
Rare earth element and yttrium (REY) concentrations (total, Mg-extrapolated) in endmember samples from the INDEX 2013 campaign at the Kairei hydrothermal field.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu
	nmol kg ⁻¹	nmol kg ⁻¹	nmol kg ⁻¹	nmol kg ⁻¹	nmol kg ⁻¹	nmol kg ⁻¹	nmol kg ⁻¹	nmol kg ⁻¹	nmol kg ⁻¹	nmol kg ⁻¹	nmol kg ⁻¹	nmol kg ⁻¹	nmol kg ⁻¹	nmol kg ⁻¹	nmol kg ⁻¹
31-ROV	0.82	2.01	0.3	1.38	0.54	3.48	0.56	0.07	0.35	6.92	0.07	0.2	0.03	0.17	0.02
35-ROV-A	0.77	1.93	0.29	1.32	0.54	3.24	0.56	0.07	0.36	8.15	0.08	0.21	0.03	0.18	0.02
Ø	0.80	1.97	0.30	1.35	0.54	3.36	0.56	0.07	0.36	7.54	0.08	0.21	0.03	0.18	0.02

seawater (Fig. 7a). Turbidity as a tracer for the hydrothermal contribution in plume samples is further validated by the linear relationship with $\delta^3\text{He}$ in CTD bottle samples collected during SO301 (Fig. 7b). Therefore, in the following, results from TMR stations will be presented in the order of decreasing plume signal strength according to Table 4.

3.4.1. Cd, Cu, Co, Fe, Ga, Ni, Mn, Mo, Pb, U, V

The effect of local hydrothermal input or excess removal on trace metals in the water column via plume dispersal from the KHF is assessed by deviations in elemental distribution from the “background” reference station sampled during SO301 at a distance of 56.3 km “upstream” from the KHF, where the least influence of the KHF hydrothermal plume is expected based on the prevailing deep currents (31-TMR). The typical profiles of the investigated elements through the water column in the central Indian Ocean can be seen in Fig. 11d–f.

The depth distributions of Ni and Cd through the water column at 31-TMR follow typical nutrient-type patterns with gradually increasing concentrations with depth, and nearly constant concentrations below 2200 m. Copper, an essential micronutrient but also known to be prone to (reversible) scavenging (e.g. Little et al., 2013; Liang et al., 2023) only starts to increase below 1400 m and down to 2200 m, and then slightly decreases again down to the bottom. Cobalt shows a concentration increase from surface waters in the upper 1000 m and then nearly constant concentrations, with a slight decrease in the lowermost samples at 2400–2500 m, a distribution that can be attributed to nutrient or hybrid nutrient-scavenging type behavior in the water column (e.g., Malla and Singh, 2024). Lead shows gradually decreasing concentrations from surface water to about 2150 m, typical for scavenged type elements (Bruland et al., 2013), and nearly constant concentrations below. Manganese, another typical scavenged-type element in the ocean, shows high concentrations in surface water and lower concentrations in intermediate water down to 1400 m, consistent with internal biogeochemical cycling dominated by scavenging removal (e.g., Malla and Singh, 2025). However, we observe significantly enhanced Mn concentrations between 2000 m and the bottom station at 2500 m (up to 2 nmol kg⁻¹). Iron, which often shows hybrid nutrient-scavenged type behavior during cycling throughout the water column, its distribution controlled by biotic Fe uptake, recycling, regeneration and scavenging removal processes (Nishioka et al., 2013; Vu and Sohrin, 2013; Chinni et al., 2019), increases from low surface water concentrations to higher concentrations in intermediate waters in 31-TMR. Similar to Mn, a sharp concentration increase of Fe up to 4.3 nmol kg⁻¹ is observed between 2000 m and the bottom water station at 2500 m, which is not to be expected when solely governed by internal cycling in the deep water column, even when release from particles is considered. Gallium concentrations decrease from surface water to minimum concentrations in intermediate water down to 1000 m, typical for a scavenged-type trace element, but show a slight increase further below. Uranium, V, and Mo are typically not affected by biological activity or scavenging and show conservative depth profiles with constant concentration throughout the water column as observed in 31-TMR.

In the horizontally spreading non-buoyant plume with the strongest turbidity and ORP plume signal (station 23-TMR, 300 m geographical distance to KHF, sample 6 at 2224 m depth), we measured max. dissolved transition metal concentrations of 1.42 nmol kg⁻¹ Cu, 0.09 nmol kg⁻¹ Co, 233 nmol kg⁻¹ Fe, 7.8 nmol kg⁻¹ Ni, 142 nmol kg⁻¹ Mn, and 38.1 nmol kg⁻¹ V and for the post-transition metals, concentrations of 0.17 nmol kg⁻¹ Cd, 32.8 pmol kg⁻¹ Ga, and 13.1 pmol kg⁻¹ Pb. This station showed the greatest hydrothermal influence of all TMR stations during this cruise with a turbidity maximum of 0.116 NTU at 2221 m depth accompanied by deviation in the redox potential ΔORP of -107.1 mV (see Table 4). These concentrations represent a significant enrichment over the background seawater concentrations for Co, Fe, Mn, and Ga, while Cd and V are depleted compared to the background. Copper and Ni show typical nutrient-type concentration profiles (surface depletion and enrichment at depth) through the water column very

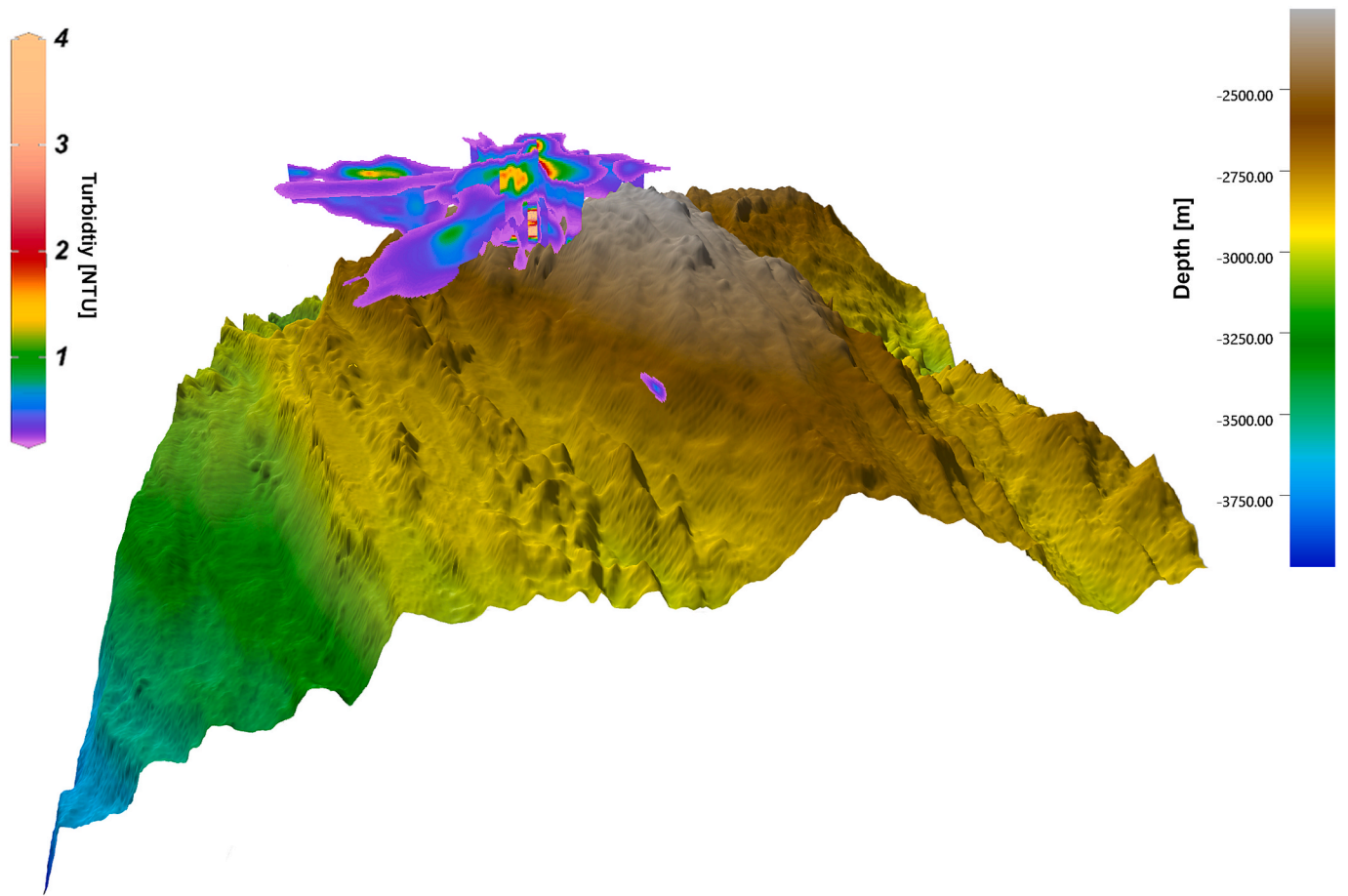


Fig. 3. Three-dimensional view of the hydrothermal plume at Kaiei by visualization of the turbidity signal measured during CTD-Tow-Yo deployments after background removal. The figure shows the view from the South of Hakuho Knoll with a 3.5x vertical exaggeration of depth and bathymetry. An orbiting animation is available as a video file in the supplementary material.

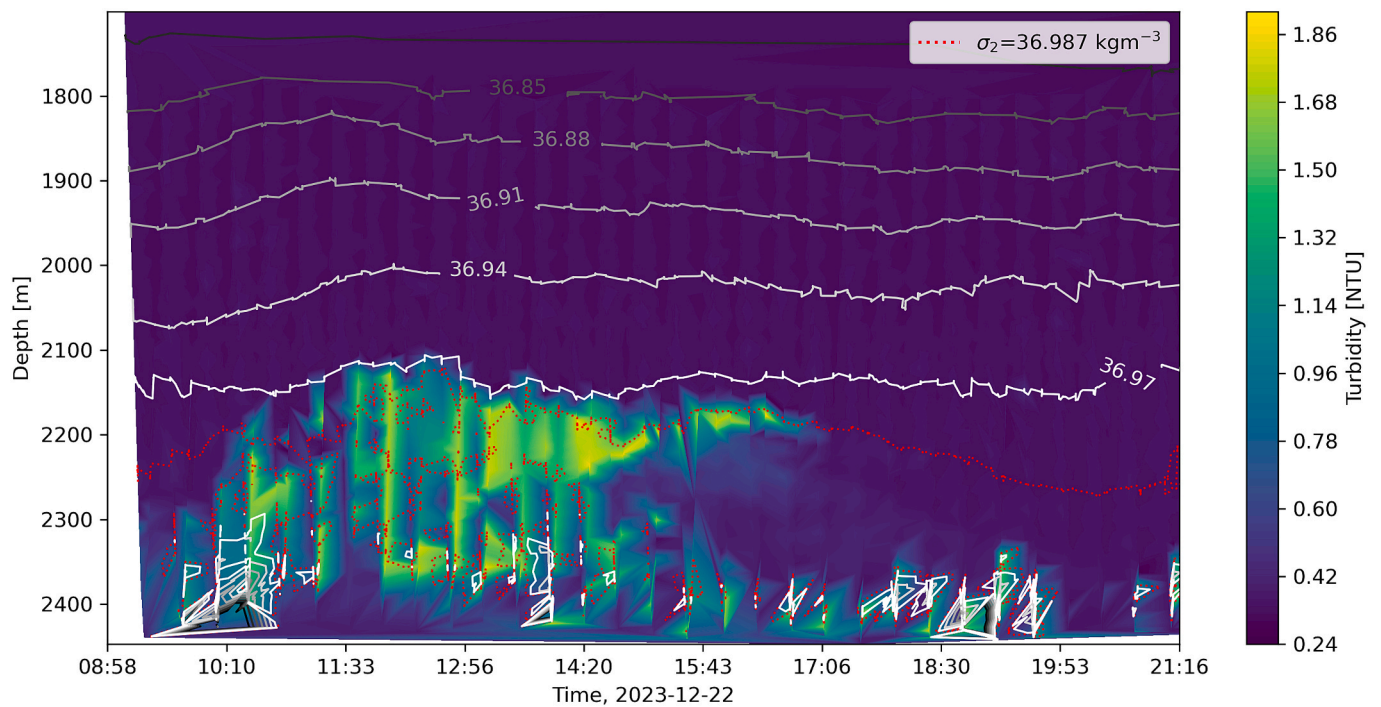


Fig. 4. Time Series of turbidity profiles at the Kaiei hydrothermal vent field at station 28 during cruise SO301.

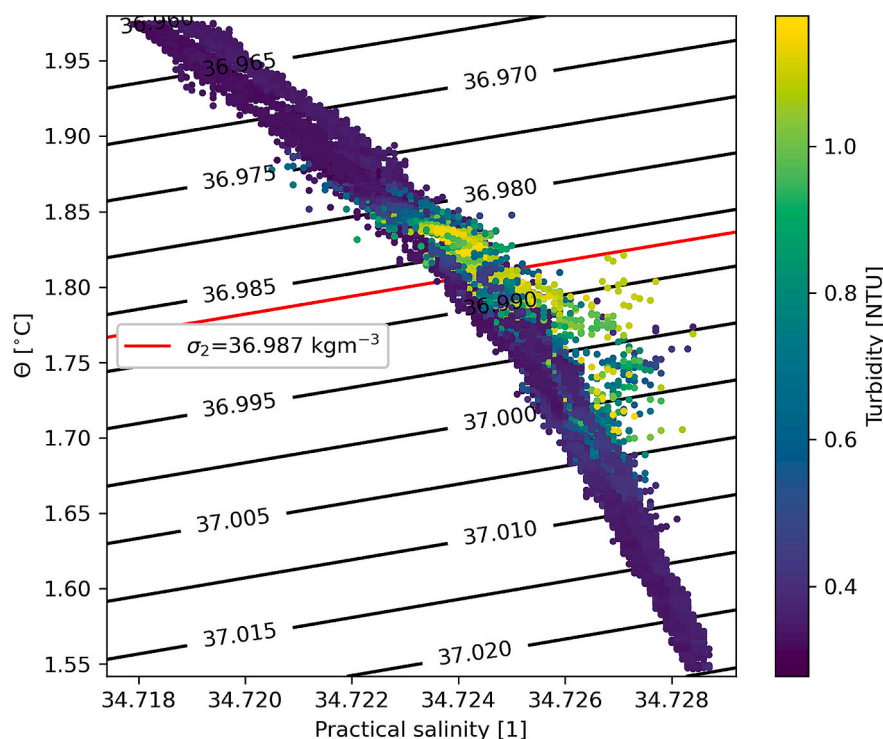


Fig. 5. T/S (temperature/salinity) diagram of station 22 during cruise SO301 showing the turbidity anomaly in the water column at the Kaiei hydrothermal field. The non-buoyant plume with elevated turbidity is located again at the reference density level found by Rudnicki and German (2002).

similar to the background profile acquired at station 31-TMR (Fig. 8) with surface depletion to 2.4 nmol kg^{-1} Ni and 0.5 nmol kg^{-1} Cu increasing to $\sim 8 \text{ nmol kg}^{-1}$ Ni and $\sim 2 \text{ nmol kg}^{-1}$ Cu in the deep water. Neither Mo, U, nor Pb showed significant deviation from the background profiles in the water column here.

Similar profiles with smaller positive deviations at the plume depth are apparent for Co, Fe, and Mn at station 21-TMR, which is located closer to the KHF with 150 m geographical distance but shows weaker hydrothermal influence with a turbidity maximum of 0.088 NTU (no ORP profile was recorded at this station due to technical issues). This profile, however, shows a second distinct plume signal below the “main” plume with 0.031 NTU at 2343 m depth (80 m below the maximum at 2263 m). As seen in Fig. 9, this turbidity signal is reflected in the measured metal concentrations as well. In contrast to station 23-TMR, we see a depletion in Cu and Ni of ~ 1.2 and $\sim 5 \text{ nmol kg}^{-1}$, respectively, compared to their concentrations in the hydrothermally unaffected water column above the plume of the KHF.

Station 18-TMR at 530 m geographical distance from the KHF showed a very similar sensor profile to station 21-TMR with a maximum turbidity peak of 0.075 NTU accompanied by a redox-anomaly ΔORP of -46.7 mV and a distinct second plume signal of 0.034 NTU at 2323 m depth (125 m below the main plume at 2198 m depth). However, only 4 water samples were collected from this station that do not allow for the interpretation of plume processes (see supplementary material).

Station 8-TMR (Fig. 10a–c) was located directly above the vent field at Kaiei but did not show the greatest hydrothermal influence on the water column as the origin of the non-buoyant plume is shifted horizontally from the source by ocean currents during the rising of the buoyant plume. We measured a maximum turbidity signal of 0.021 NTU and ΔORP of -41.1 mV at the non-buoyant plume depth of 2190 m. At this station, we observe several narrow additional peaks in the turbidity signal at 2289 m (0.034 NTU), and 2307 m (0.065 NTU) without a significant deviation in the ORP signal as well as a 0.024 NTU signal with an additional ΔORP of -90 mV at the maximum depth of the profile at 2420 m. This suggests brief contact of the instrument with the

buoyant plume that rises through a horizontally narrow area. The short contacts with the buoyant plume during the descent of the TMR did not create an ORP signal due to the longer response time of that sensor compared to the turbidity sensor. Unfortunately, owing to technical issues with the newly commissioned TMR sampling system during these early deployments, we did not get a sample from the non-buoyant plume depth at this station, but the samples potentially affected by the rising plume show elevated Fe concentrations up to $16.8 \text{ nmol kg}^{-1}$ in sample 8 at 2326 m depth. All analyzed trace metals show variable deviations from their background concentrations across this depth range, with enrichments in the profiles of Fe, Mn and Co and depletion of Cu, Ni, and V.

At station 6-TMR, also located directly above the KHF, the high baseline of the turbidity sensor masks any potentially significant turbidity signal, but a ΔORP of -21.2 mV and maximum Fe concentration of $133.7 \text{ nmol kg}^{-1}$ indicate a significant hydrothermal influence. The concentration profiles of the other analyzed trace elements resemble those of station 21-TMR (see supplementary material) with Mn and Co following the enrichment of Fe at plume depth while Cd, Cu, Ni, and V show depletion.

At station 29-TMR (Fig. 10d–f) at 1 km distance from the KHF, the hydrothermal signal is already significantly diluted but clearly detectable with a maximum turbidity peak of 0.019 NTU and ΔORP of -8.2 mV . Here again, we observe additional plume signals below the main plume depth of 0.005 NTU at 2310 m and 0.007 NTU at 2360 m depth. These signals correlate with increased Fe concentrations up to $27.7 \text{ nmol kg}^{-1}$ as well as elevated Mn levels. Vanadium shows depletion at the plume depth as observed at the previous station but also below the plume. Additionally, Ni and Cd show background levels at plume depth but depletion below. Copper, on the other hand, shows a small enrichment at plume depth.

Station 16-TMR at 600 m geographical distance to the KHF showed very little hydrothermal influence in the sensor data with a maximum turbidity signal of 0.007 NTU and ΔORP of -1 mV . But no water samples were acquired at the depth of the plume to investigate whether this

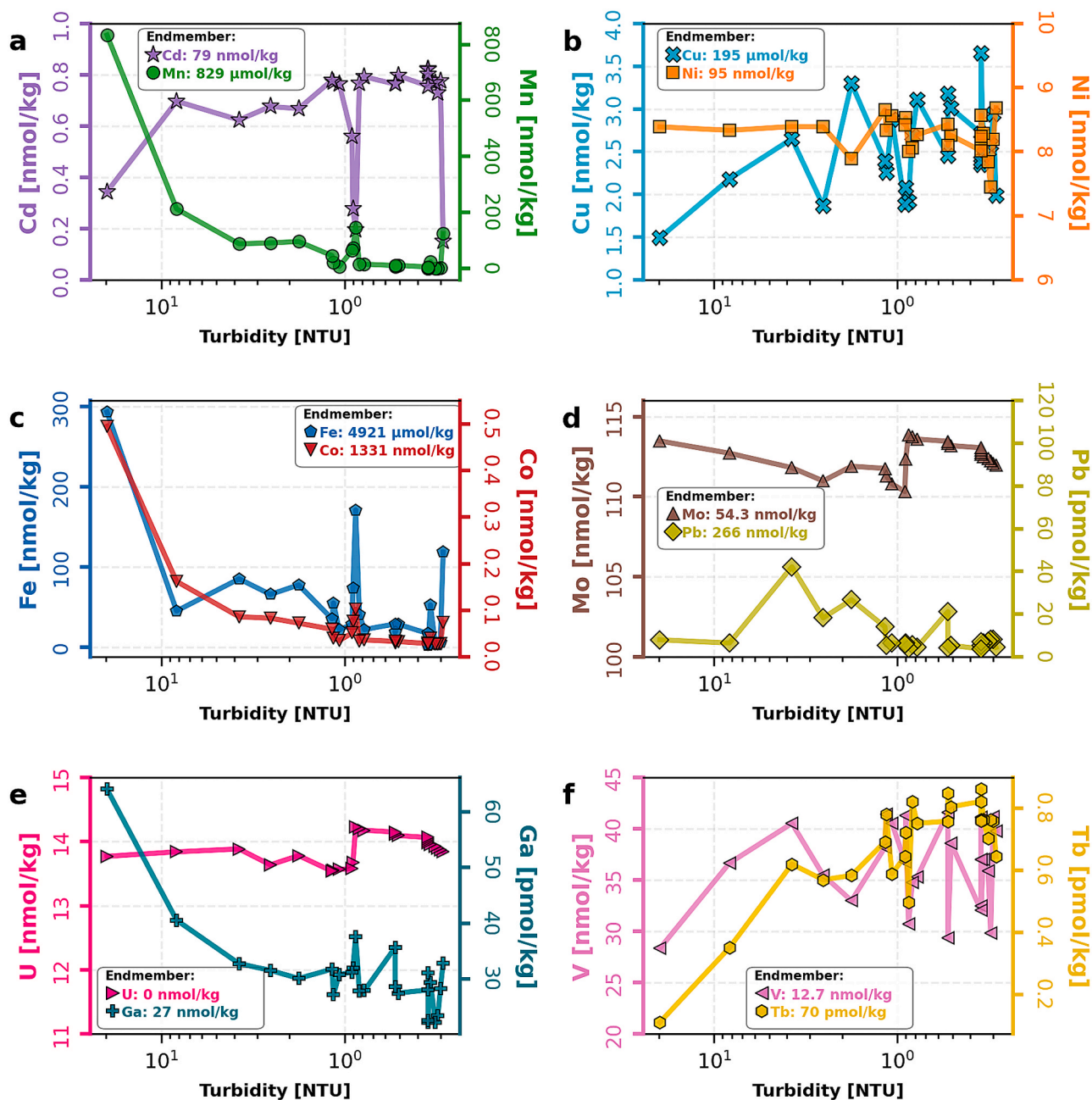


Fig. 6. Trace metal concentrations ($<0.2 \mu\text{m}$) in samples from the Kaiei Hydrothermal plume obtained through CTD Tow-Yo deployments during research cruise SO301. Trace metals are plotted against turbidity on an inversed logarithmic x-axis to correlate their concentrations to the contribution of hydrothermal influence.

dilute signal has an influence on the trace metal composition of the water column (see [supplementary material](#)). Similarly, both stations 41-TMR at 3 km distance and 44-TMR at 28.6 km distance had no measurable turbidity or redox signal that would indicate hydrothermal influence. At station 44-TMR, only 4 samples were collected, which do not represent a depth profile suited for interpretation of hydrothermal plume processes but have concentrations that are consistent with those measured at the corresponding depths at the background station 31-TMR (Fig. 11d-f), which was located at 56.3 km distance from the KHF without any hydrothermal influence. Station 41-TMR, despite its closer proximity to the KHF and higher sample resolution, did not show a significant hydrothermal influence on the trace metal profiles either.

3.4.2. REY

At the background reference station, the REY show a nutrient-like

depth distribution, with generally low concentrations at the surface and increasing concentrations with depth. As the REY are not essential micronutrients, this nutrient-like profile reflects not biological uptake but continuous regeneration of REY from sinking particles at depth via desorption and remineralization, as documented for dissolved REY in seawater (Elderfield and Greaves, 1982; de Baar et al., 1985; Sholkovitz et al., 1994; Alibo and Nozaki, 1999). At station 23-TMR, however, all measured REY show depletion with a small negative deviation from the background profile at the depth of the hydrothermal plume with a significantly more pronounced depletion at station 21-TMR. At station 29-TMR, with 1 km distance from the vent field and reduced hydrothermal influence indicated by the turbidity and ORP profiles, any deviation of the REY from the background at plume depth is minor and lies within the combined uncertainty introduced by sampling and processing, so it cannot be confidently attributed to a hydrothermal depletion,

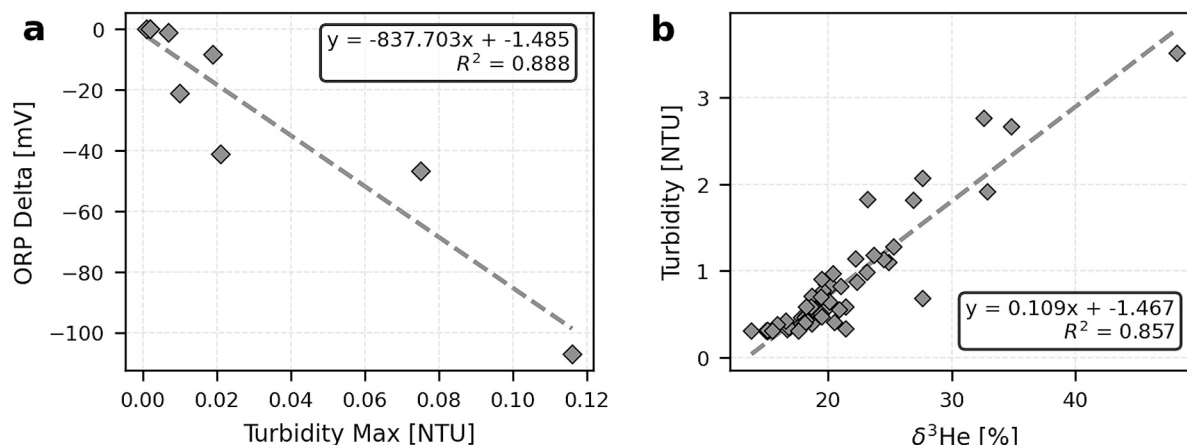


Fig. 7. (a) Turbidity maxima and ORP delta peaks for TMR and (b) Turbidity vs. $\delta^3\text{He}$ as indicators for hydrothermal influence in CTD bottle samples in the plume of the Kaiei hydrothermal field from cruise SO301.

Table 4

Table of TMR stations from research cruise SO301 with their locations, distances to the Kaiei vent field and turbidity/ORP maxima. Sorted according to strength of plume signal.

Station ID	Lat [°N]	Lon [°E]	Distance to Kaiei [m]	Turbidity Max [NTU]	ΔORP [mV]
23-TMR	-25.321	70.037	300	0.116	-107.1
21-TMR	-25.320	70.039	150	0.088	no data
18-TMR	-25.321	70.035	530	0.075	-46.7
06-TMR	-25.320	70.041	0	no data	-21.2
08-TMR	-25.320	70.040	0	0.021	-41.1
29-TMR	-25.328	70.034	1,050	0.019	-8.2
16-TMR	-25.325	70.037	600	0.007	-1.0
41-TMR	-25.345	70.028	3,000	0.002	0
44-TMR	-25.337	70.324	28,600	0.001	0
31-TMR	-25.029	69.582	56,300	0.002	0

while the profile at station 41-TMR with 3 km distance matches the background profile (Figs. 8–11).

3.4.3. Size fractionation

To investigate the effects of particles on trace metal transport and their distribution in different particle sizes, we used sequential filtration with 0.8 μm , 0.2 μm , and 0.015 μm membrane filters to separate the different size fractions. Here, we define the size fractions operationally as small particles (0.2–0.8 μm), large colloids (0.015–0.2 μm), and soluble ($<0.015 \mu\text{m}$). A selection of samples with measurable hydrothermal influence is displayed in Fig. 12 with increasing distance from the source. In this figure, each size fraction is shown as an absolute concentration, stacked to the total, from which the percentage contributions given below are derived. Further samples with less hydrothermal influence did not show differences between the size fractions larger than the analytical error. These measurements reveal a significant size fractionation for Fe, which in sample 23–7 was present as 53 % small particulate, 28 % large colloidal, and 19 % soluble. The particulate and colloidal contribution to the Fe pool rapidly declines in the following samples. While Mn follows a similar trend in total concentrations, our data show no particulate or large colloidal Mn as it is present fully in the soluble size fraction. Similarly, Co follows the trend of decreasing total concentrations with only a minor contribution of “large colloidal” Co at high concentrations. Nickel, Mo, U, Ga, and V show no significant trend in concentration over the investigated sample set and are all present fully in the soluble size fraction. Cadmium shows no significant trend of total concentrations in this sample selection either but has a small contribution of small particulate Cd closer to the vent while at greater distance, it is also fully soluble. Copper shows no consistent partitioning

across the sample set, with a minor small particulate contribution (0.2–0.8 μm) in the sample nearest the source and a minor large colloidal contribution (0.015–0.2 μm) in one more distal sample, while it is otherwise present in the soluble fraction. The REY, here again represented by Tb, increase in concentration with distance from the KHF and show only minor contributions from the large colloidal and particulate fractions to their total concentrations. While Pb showed no significant elevation in concentration over the seawater background in the 0.2 μm filtered samples from the buoyant and non-buoyant plume presented above, the size fractionated samples showed a significant hydrothermal contribution of Pb to the small particulate pool at 0.2–0.8 μm . Considering the composition of the fractions themselves, the particulate and large colloidal pools in the early plume are dominated by Fe, with Pb the only other element contributing a marked particulate fraction, although at concentrations too low to affect the bulk particulate pool.

4. Discussion

The data presented in this study reveal highly dynamic spreading of the Kaiei hydrothermal plume coupled with complex geochemical processes affecting the trace metals emitted with the hydrothermal fluids of the KHF.

4.1. Hydrography/physical plume behavior

Our observations of the particle plume of the Kaiei site show remarkably stable venting compared to the earlier data from 2000 published by Rudnicki and German (2002): Rise height of the plume as well as the core density of the non-buoyant plume layer are unchanged compared to a quarter of a century ago, consistent with a relatively stable heat flux of the Kaiei system over this period. More directly, repeated sampling of the KHF over this interval has shown no obvious change in major vent fluid characteristics (see Table 2), which supports the use of the INDEX fluid endmember here, since vent metal concentrations can shift with subtle changes in temperature, pH, or subsurface flow paths without a corresponding change in heat flux. Closer to the vent field, stations 21- and 18-TMR also resolved a second, distinct plume signal 80 to 125 m below the main non-buoyant layer (Fig. 9). While our data cannot establish its origin, plume signals at different depths could reflect venting from sites of differing temperature and buoyancy flux, which reach different neutral-buoyancy heights; the Kaiei field is known to host several vents of differing fluid composition (Gallant and Von Damm, 2006).

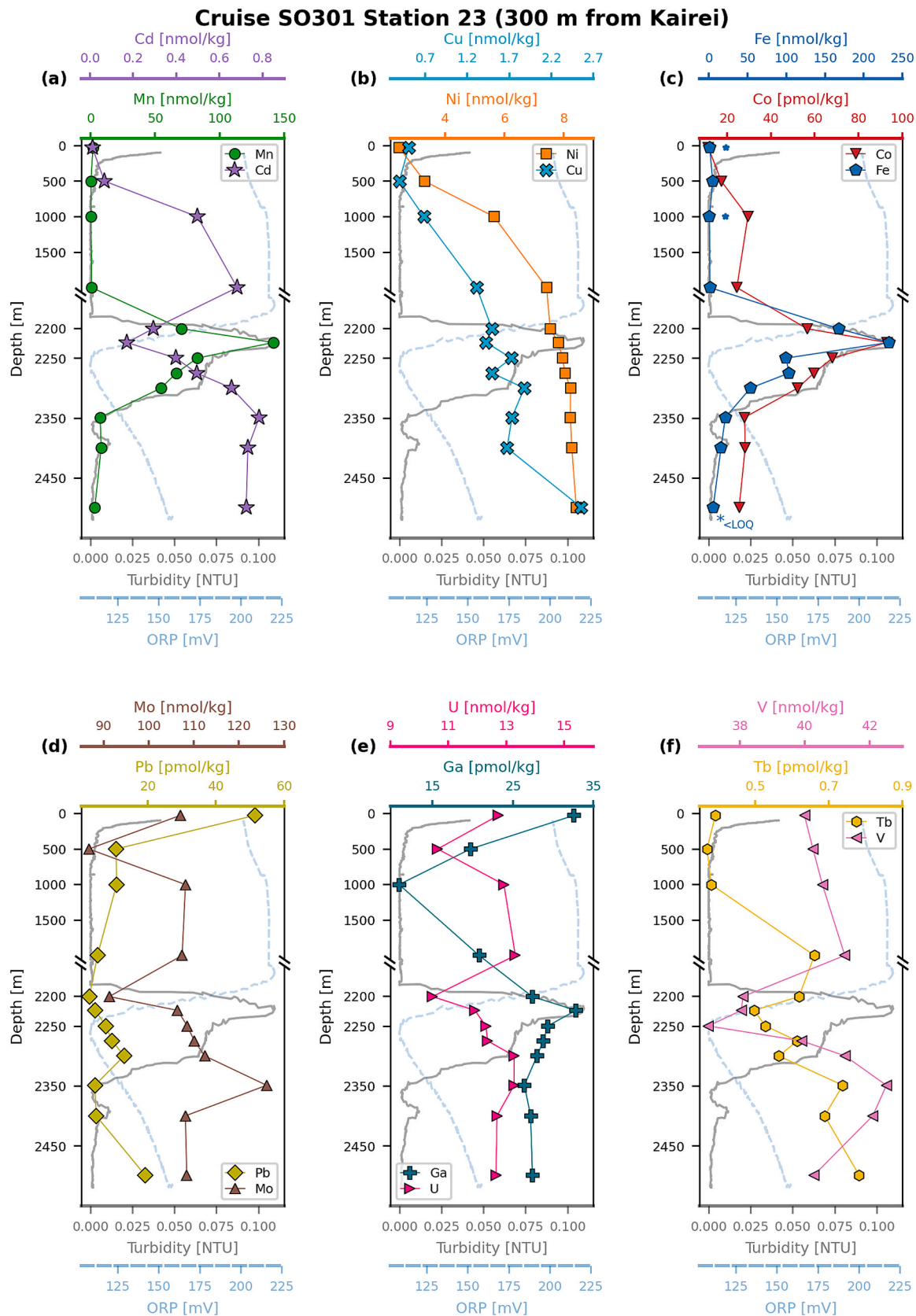


Fig. 8. Depth profiles at station 23-TMR during cruise SO301 of trace metal concentrations ($<0.2 \mu\text{m}$) in the water column around the Kairei hydrothermal field with turbidity and ORP data as tracers for hydrothermal input. The y-axis of all subplots is broken at 2150 m depth to magnify the hydrothermally affected zone of the water column.

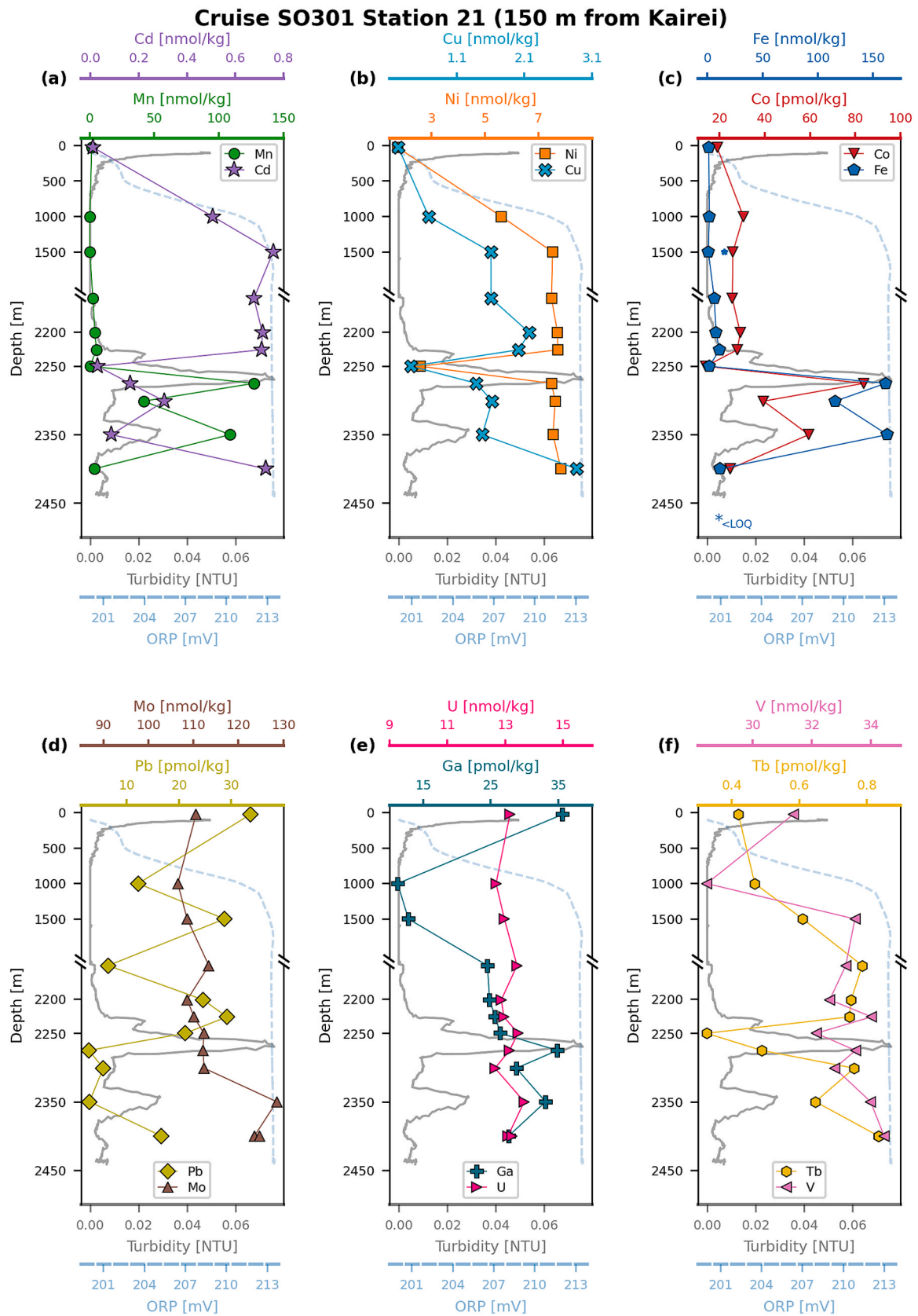


Fig. 9. Depth profiles at station 21-TMR during cruise SO301 of trace metal concentrations ($<0.2 \mu\text{m}$) in the water column around the Kairei hydrothermal field with turbidity and ORP data as tracers for hydrothermal input. The y-axis of all subplots is broken at 2150 m depth to magnify the hydrothermally affected zone of the water column.

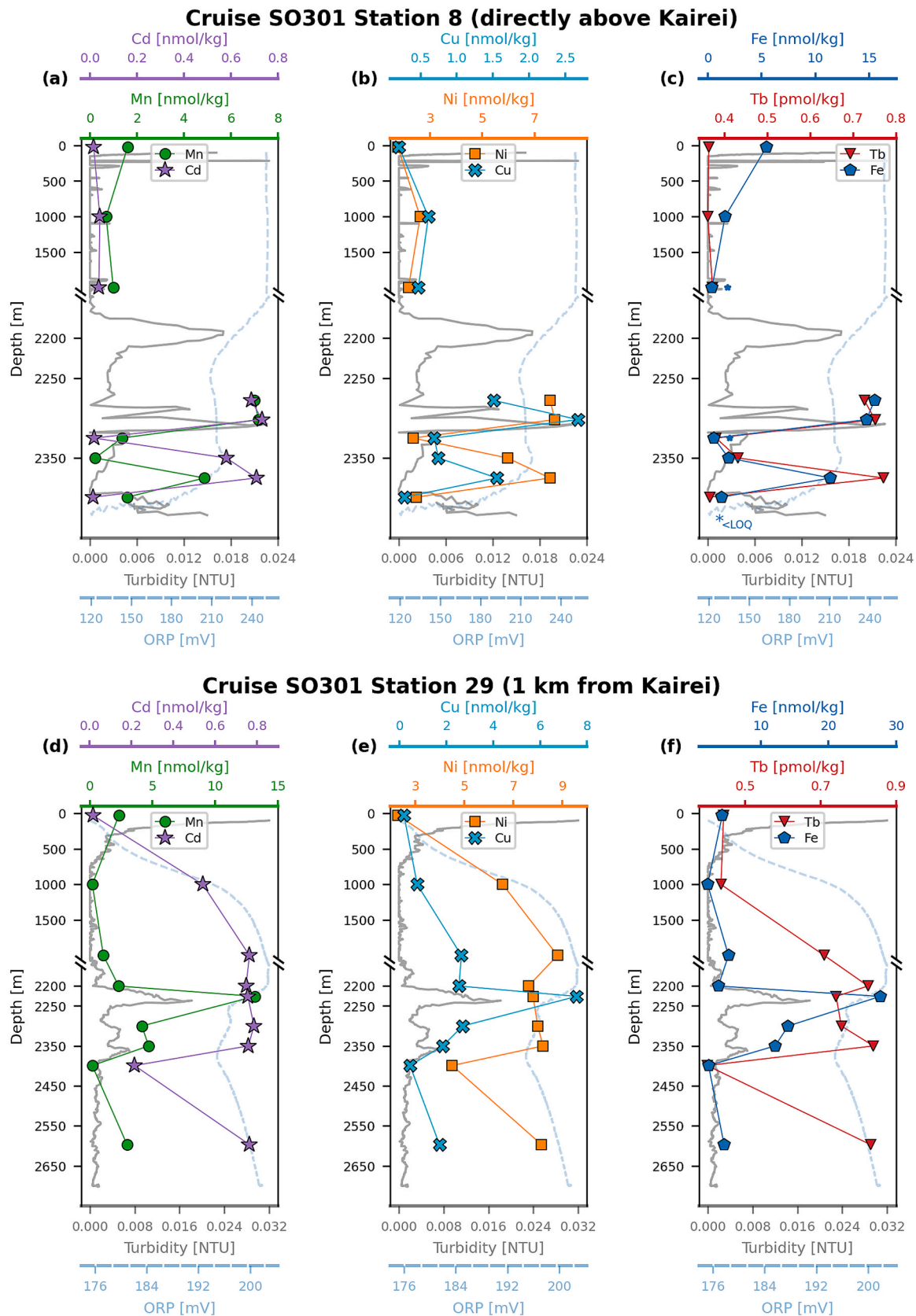


Fig. 10. Depth profiles at stations 8 and 29 during cruise SO301 of trace metal concentrations ($<0.2 \mu\text{m}$) in the water column around the Kairei hydrothermal field with turbidity and ORP data as tracers for hydrothermal input. The y-axis of all subplots is broken at 2150 m depth to magnify the hydrothermally affected zone of the water column.

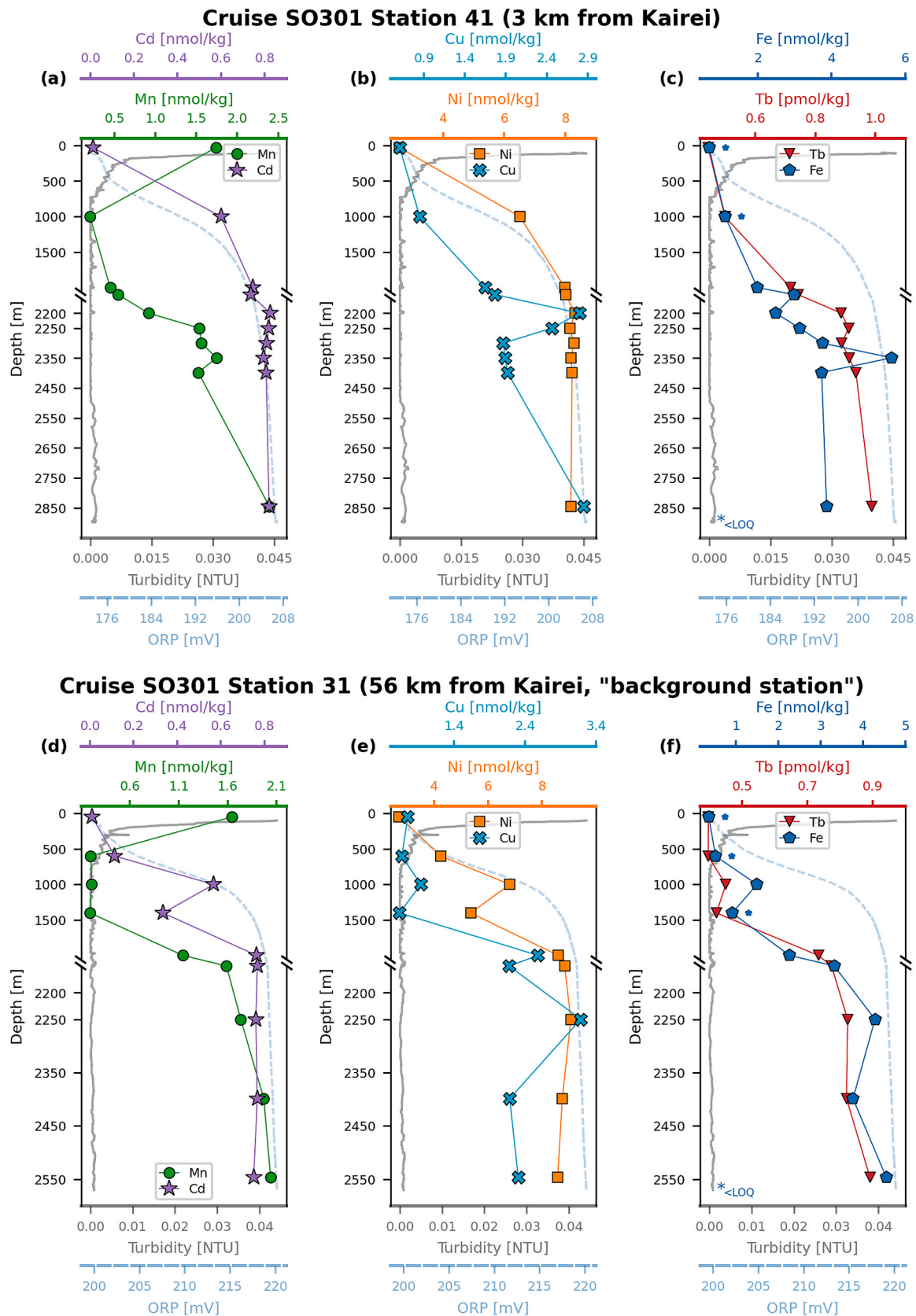


Fig. 11. Depth profiles at stations 41-TMR and 31-TMR during cruise SO301 of trace metal concentrations ($<0.2 \mu\text{m}$) in the water column around the Kairei hydrothermal field with turbidity and ORP data as tracers for hydrothermal input. The y-axis of all subplots is broken at 2150 m depth to magnify the hydrothermally affected zone of the water column.

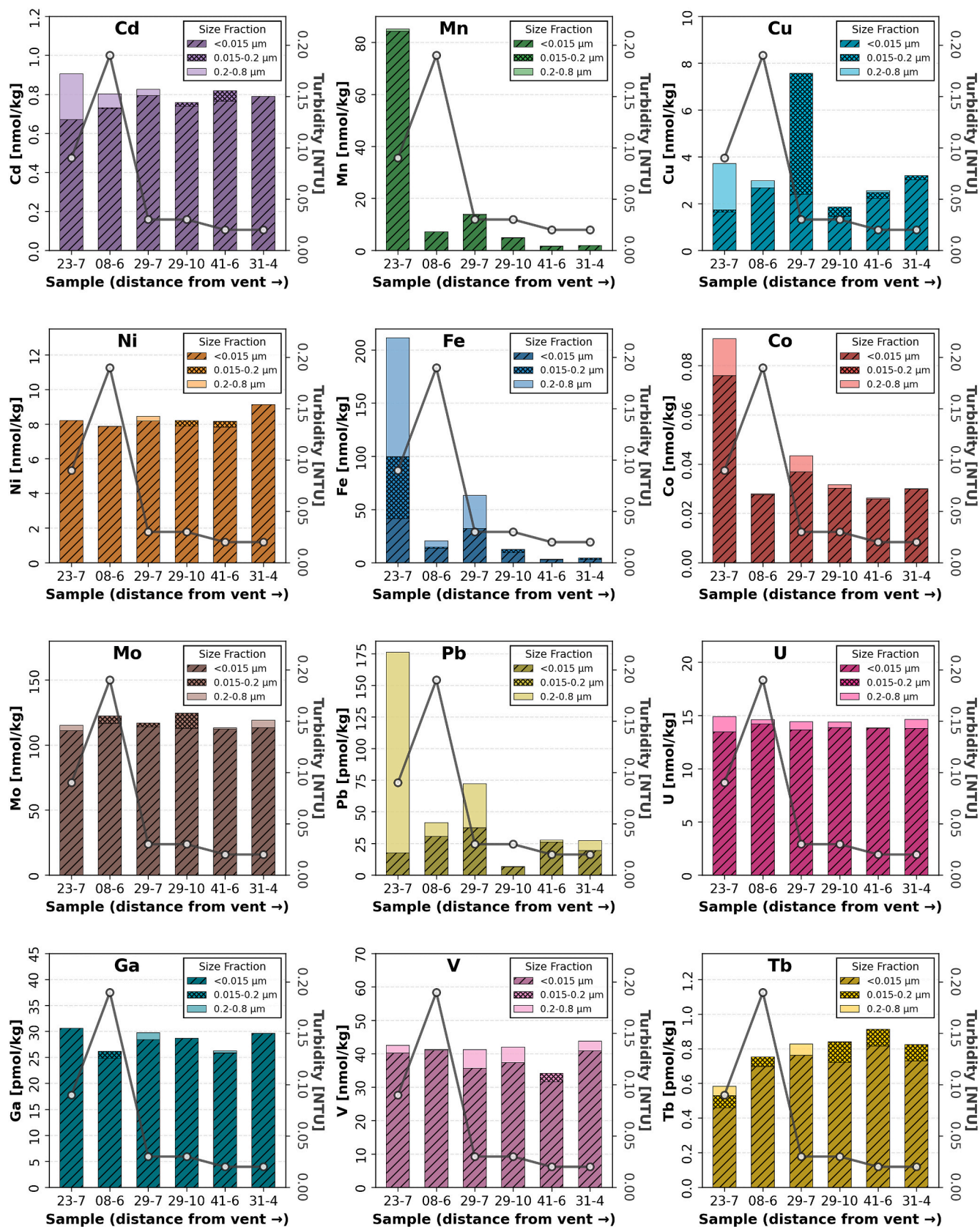


Fig. 12. Stacked bar chart of the concentrations of trace metals in the size fractions <0.015 µm (“soluble”), 0.015–0.2 µm (“large colloidal”), and 0.2–0.8 µm (“small particulate”) acquired by sequential filtration of samples from the plume of the Kaiei hydrothermal field during research cruise SO301 with increasing distance from the source going from left to right on the x-axis. Note that the x-axis is categorical: samples are ordered by their distance from the vent field (nearest at left, background station 31-TMR at right) but are not spaced to scale. Turbidity of the samples is included as an indicator for the hydrothermal contribution to these samples.

4.2. “Background” levels of trace metals for the Kairei plume

Elemental distribution through the water column is shaped by internal biogeochemical cycling, external sources (such as benthic and hydrothermal), and lateral (related to water mass movements) processes. Comparing the concentrations of Cd, Co, Cu, Mn, Ni, Pb, and Fe at 31-TMR (Fig. 11d–f) to data available from GEOTRACES sections in the Indian Ocean (Nishioka et al., 2013; Vu and Sohrin, 2013; Chinni et al., 2019; 2019; Malla and Singh, 2024, 2025, 2026; Yadav et al., 2025; GEOTRACES Intermediate Data Product Group, 2025), the profiles

match prior observations from the Central Indian Ocean Basin close to the CIR (GI04 full water column stations ER10 and ER11 at 20°S/72.5°E, and GI09 full water column stations 16 and 18), with additional dissolved Fe reference data from stations GI01-16 and GI02-8. This comparison is shown in Fig. 13, covering all elements for which published reference profiles are available for the region. These span the contrasting depth behaviors discussed below: nutrient-type Cd, Co, and Ni; scavenging-type Mn and Pb; and the deep enrichment of Mn and Fe. At all sites, Cd, Co, Cu, and Ni follow a nutrient-type distribution as a result of biological uptake at the surface and remineralization of biogenic

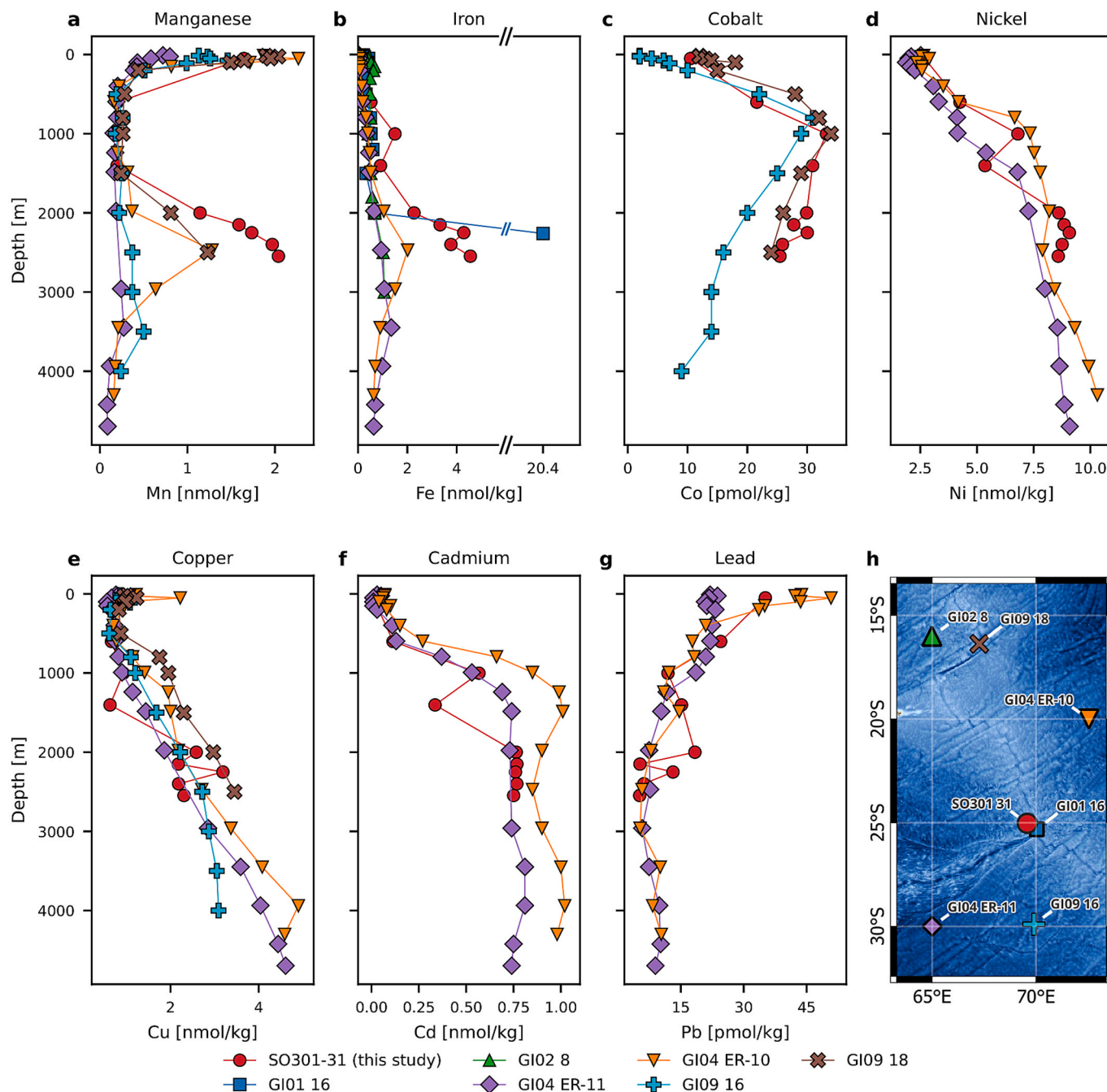


Fig. 13. Depth profiles of dissolved ($<0.2 \mu\text{m}$) Mn (a), Fe (b), Co (c), Ni (d), Cu (e), Cd (f), and Pb (g) at station 31-TMR of cruise SO301 (the background station, 56 km from the Kairei hydrothermal field), compared to previously published GEOTRACES measurements from the surrounding region. Comparison data derive from Vu and Sohrin (2013; Mn, Ni, Cu, Cd, Pb) and Nishioka et al. (2013; Fe) at stations GI04 ER-10 and GI04 ER-11; from Chinni et al. (2019; Fe) at stations GI01-16 and GI02-8; and from Malla and Singh (2024; Co), Malla and Singh (2025; Mn), and Malla and Singh (2026; Cu) at stations GI09-16 and GI09-18. Data for the GI01, GI02, and GI04 stations were accessed through the GEOTRACES Intermediate Data Product 2025. Locations of stations plotted in (h). The x-axis of the Fe subplot (b) is broken at 6 nmol kg^{-1} to accommodate the elevated near-bottom value at station GI01-16 (located at the KHF), indicative of hydrothermal Fe input.

particles in intermediate waters. Copper may additionally be affected by scavenging outbalancing remineralization down to 1400 m. Manganese and Pb follow the typical scavenging-type profile with decreasing concentrations from surface to intermediate waters. From 2000 m downwards, however, Mn shows a significant enrichment (up to 2 nmol kg^{-1} at 31-TMR), and also the Fe concentrations exceed 2 nmol kg^{-1} below this depth.

The observed enrichment of Fe and Mn in the deep water layer of our reference station (below 2000 m; Fig. 13a, b) points to an external source and is most likely related to widespread hydrothermal plume dispersal. Hydrothermal input of Fe and Mn into the ocean can be extensive, with persistent, long-range transport of dissolved Fe over more than 1000 km (e.g. Fitzsimmons et al., 2017). This long-range export reflects the deep circulation itself: the hydrothermally enriched layer at the CIR sits within the Circumpolar Deep Water that ventilates the ridge (see Study Area), and its advection disperses the dissolved Fe and Mn signal along the ridge and into the wider Central Indian Ocean Basin sampled by the regional GEOTRACES sections (Nishioka et al., 2013; Vu and Sohrin, 2013). Hydrothermal sources have been shown to influence the basin-wide Fe distribution in the Central Indian Ocean, with enhanced dissolved Fe concentrations between 2000 m and about 3500 m close to the central rifts up to 2 nmol kg^{-1} Fe (Nishioka et al., 2013; Vu and Sohrin, 2013; Chinni et al., 2019; Moffett and German, 2020), and decreased concentrations in the water column below. Global ocean biogeochemical models indicate that a hydrothermal dissolved Fe source is required to reproduce these deep-ocean Fe distributions, raising the simulated deep-ocean dissolved Fe inventory by roughly 14 % globally (Tagliabue et al., 2010). Indian Ocean ridges account for about 9 % of the gross global hydrothermal Fe input in these models (Tagliabue and Resing, 2016). The comparatively low endmember $\text{H}_2\text{S}/\text{Fe}$ ratio of 0.90 at Kairei implies that little of the vented Fe is lost to sulfide precipitation, leaving a larger dissolved and colloidal Fe pool available for stabilization and transport; in the same modeling framework, more efficient Fe stabilization lengthens the residence time of hydrothermal Fe and amplifies its downstream impact (Tagliabue and Resing, 2016). Similarly, hydrothermal activity at the CIR has also been shown to contribute significantly to the dissolved Mn budget of the deeper waters between 2000 and 3500 m, with enrichments of dissolved Mn above the CIR up to 1.3 nmol kg^{-1} Mn (Vu and Sohrin, 2013; Malla and Singh, 2025; GEOTRACES Intermediate Data Product Group, 2025). The elevated Fe and Mn concentrations at our reference station are therefore consistent with widespread hydrothermal influence on the deep water column above and around the CIR. Beyond Fe and Mn, Co shows a weaker deep enrichment at 31-TMR as well as at station G109 18 at the CIR, which may indicate a limited net export of hydrothermally derived Co, although with only limited regional reference data available we regard this as tentative. Overall, the reference station Fe and Mn concentrations used in this study (as well as potentially Co) should not be considered representative of the deep Indian Ocean unaffected by hydrothermal input on a large scale but as local reference for the assessment of the KHF plume.

Cadmium, Cu, Ni, and Pb do not appear to show signatures of hydrothermal input or excess removal via plumes from active spreading ridges of the Indian Ocean at the background reference station, with concentrations similar to their background levels reported for the Central Indian Ocean Basin. Similarly, U, V, and Mo concentrations do not deviate from their conservative distribution pattern. As no published Ga data are available for the Indian Ocean, it remains unclear whether this distribution reflects background concentration levels controlled by scavenging and particle release in areas unaffected by hydrothermal activity or if it indicates an external (hydrothermal) source contributing to the small deep layer enrichment observed at 31-TMR. The contrasting behaviors of these element groups follow from the oceanic residence times of the elements (Bruland et al., 2013). Conservative-type metals interact only weakly with particles and have residence times far longer than the ocean mixing time, so their concentrations stay uniform and a

single ridge cannot perturb them; Mo is the typical example, with a residence time of about 8×10^5 years (Bruland et al., 2013). Uranium is likewise well mixed and conservative, with a residence time of $3.2\text{--}5.6 \times 10^5$ years (Dunk et al., 2002). Vanadium is near-conservative, showing only a slight surface depletion from biogenic particle uptake and a residence time of about 5×10^4 years (Collier, 1984), so its deep-water concentrations remain effectively uniform. Cadmium, Cu, and Ni all follow nutrient-type distributions, depleted at the surface and re-generated at depth. Nickel tracks phosphate at shallow depths and silicate in deep water, with an oceanic residence time of about 10^4 years (Sclater et al., 1976; Bruland et al., 2013); its deep concentrations increase along the flow path as water masses age and are set by basin-scale circulation and biological cycling, not by local hydrothermal input. Copper's profile shape is similarly nutrient-type, but its oceanic residence time is markedly shorter than Cd's or Ni's, reflecting a greater influence of particle scavenging alongside biological regeneration (Bruland et al., 2013). Lead belongs to the scavenged-type class, with a short residence time (decades to about a thousand years) and concentrations governed by particle scavenging and proximity to sources (Bruland et al., 2013). In each case, the regional, water-mass-controlled signal dominates over any local plume contribution, which is why these elements match the Central Indian Ocean Basin reference profiles.

4.3. Geochemical plume processes

When comparing the concentrations of trace metals in the end-member hydrothermal fluid of the KHF measured by Gamo et al. in 2000 and by Gallant and Von Damm in 2001 as well as in 2013 and 2016 within the INDEX project (see Table 2) to the surrounding bottom seawater (here represented by the mean concentrations of three samples acquired between 2250 and 2547 m depth at station 31-TMR without measurable hydrothermal influence), we see a wide range with very significant enrichments up to a factor of 10^6 for Fe, 10^5 for Mn, and 10^4 for Co, Cu, and Pb, and more moderate enrichments of 10 to 10^3 for Cd, Ni, and REY. All these trace metals are leached from the host rock by the fluid during hydrothermal circulation due to their increased solubility at high temperature and low pH and ORP. On the other hand, U, Mo, and V are highly immobile under reducing conditions and are therefore depleted in the KHF source fluid relative to seawater by factors of 0.5 for Mo, 0.33 for V and to zero for U. While the concentrations and discharge volumes of the hydrothermal fluid are crucial parameters for estimating trace metal fluxes and their contribution to marine (bio)geochemical cycles, the complex processes affecting these metals during mixing of the hydrothermal plume with the surrounding seawater severely complicate any attempts at quantifying the overall global marine hydrothermal trace metal budget. Here, the global budget refers to the whole-ocean dissolved inventory considered at steady state over the oceanic mixing and residence timescale (10^3 years and longer), so that the hydrothermal term is the globally integrated net flux weighed against riverine, atmospheric, and sedimentary inputs and outputs. At this scale the role of venting differs between elements: for Fe, Mn, and Co the plume is a net source to the deep ocean, while for the conservative elements V, U, and Mo hydrothermal systems act as a net sink (V by scavenging onto plume Fe-oxyhydroxides, U and Mo by uptake within the hydrothermal system, consistent with their endmember depletion), even though far-field seawater concentrations remain conservative. This challenge is even greater when attempting to estimate the contributions of individual hydrothermal systems such as the KHF plume examined in this study.

With sulfide minerals being a major pathway for the removal of dissolved hydrothermal metals, the emission of H_2S by the hydrothermal fluid is one of the major controlling factors for the fate of the metals emitted by the hydrothermal fluids. At $4.12 \text{ mmol kg}^{-1}$ H_2S , the Kairei endmember is rich in sulfide but it is also highly enriched in metals including on average 4.6 mmol kg^{-1} Fe (Table 2) creating a relatively low $\text{H}_2\text{S}/\text{Fe}$ ratio of 0.90 when compared for example to the endmember fluids of the Logatchev hydrothermal field with $\text{H}_2\text{S}/\text{Fe} = 1.02$ (Schmidt

et al., 2007), Pacmanus F3, Manus Basin with $H_2S/Fe = 1.29$ (Reeves et al., 2011), or an even higher average $H_2S/Fe = 14.9$ at the Main Endeavour Field, Juan de Fuca Ridge (Seyfried Jr. et al., 2003). While at systems like Logatchev, sulfide precipitation can be expected to remove most of the dissolved metals early on in the plume mixing process, the KHF fluids show a relative excess of dissolved Fe and other metals over sulfide. Therefore, we expect increased transport to the water column and a higher importance of oxidation and related scavenging on Fe oxides and organic complexation processes for the transport of these elements.

Only few multi-element trace metal studies of hydrothermal plumes comparable to the dataset presented here have been published in the literature; Fitzsimmons and Steffen (2024) have compiled a thorough review on studies of the input of hydrothermal fluxes on marine trace metal budgets within the GEOTRACES program and Kleint et al. (2022) have investigated the influence of shallow hydrothermal plumes on a wide range of elements at the volcanoes of Macauley (330–680 m depth) and Brothers (1200–1600 m depth) in the Kermadec Arc. We have compiled a comparison of the net effects of hydrothermal plumes on the elements investigated in this study to the published data in Table 5.

4.3.1. Plume source (Fe, Mn, Co, Ga)

Hydrothermal contributions to the marine Co, Fe, and Mn cycles have been well established, and particularly hydrothermal Fe inputs to the ocean have been studied intensely over the past decades due to its role as an essential micronutrient for marine phytoplankton (e.g. Tagliabue et al., 2010; Sander and Koschinsky, 2016; Tagliabue and Resing, 2016; Holmes et al., 2017).

Fitzsimmons and Steffen (2024) list 37 studies for Fe and 8 studies for Mn, demonstrating hydrothermal plumes to be significant sources of these elements to the water column. The four studies of hydrothermal Co, on the other hand, showed mixed behavior, and the two sites investigated in the Kermadec Arc also showed heterogeneous behavior

Table 5

Observed influence of the Kairei hydrothermal plume on trace metals (this study) compared to results obtained within the GEOTRACES program (Fitzsimmons and Steffen (2024)) and a multi-element study of shallow hydrothermal plumes in the Kermadec Arc (Kleint et al. (2022)).

Element	Fitzsimmons and Steffen (2024)	Kleint et al. (2022)	This Study
Cd	Significant scavenging (1 study)	Plume source at Macauley, no plume influence at Brothers	Significant scavenging
Co	Mixed behaviour (4 studies)	Plume source at Macauley, small plume source at Brothers	Significant plume source
Cu	Mixed behaviour (5 studies)	Plume source at Macauley, no plume influence at Brothers	Complex behavior
Fe	Significant plume source (37 studies)	Significant plume source	Significant plume source
Ga	Small plume source (1 study)	Not covered	Small plume source
Mn	Significant plume source (9 studies)	Significant plume source	Significant plume source
Mo	Scavenging (1 study)	Not covered	No plume influence
Ni	Not covered	Plume source at Macauley, no plume influence at Brothers	No plume influence
Pb	Scavenging/Mixed (4 studies)	Plume source	No plume influence
REY	Scavenging (4 studies)	Plume source at Macauley, no plume influence at Brothers	Significant scavenging
U	Not covered	Not covered	No plume influence
V	Scavenging (1 study)	Not covered	Moderate scavenging

with the Macauley plume being a significant Co source to the water column while the Brothers plume only showed a small positive deviation from background concentrations. An additional hydrothermally sourced element that would be relevant to investigate is Zn. As outlined in the methods section, unfortunately, contamination from the internally sprung water samplers that were available for sampling in this study makes this sample set unsuitable for analysis of Zn. Future studies with the MARUM TMR will deploy only externally sprung samplers to allow for investigation of more contamination-prone trace elements and Zn in particular.

While the hydrothermal endmember at Kairei is highly enriched in trace metals relative to seawater with enrichment factors up to 10^6 (Fe), their concentrations decrease rapidly in the buoyant plume immediately after venting from the hydrothermal chimneys. The plume concentrations measured at station 23-TMR (Fig. 8) represent a reduction factor (combining dilution and removal) of 4×10^6 of the endmember concentration for Fe, 4.5×10^5 for Mn, and 8.8×10^4 for Co. At station 21-TMR (Fig. 9), these reduction factors increase to 5×10^6 for Fe, 2.7×10^6 for Mn, and 4.8×10^5 for Co. These reduction factors are calculated from the sampled vent endmember; because the plume appears to integrate hotter, more Fe-rich fluids than the discrete vents sampled 2006. The endmember Fe, and hence the Fe reduction factors, are likely lower bounds. These numbers highlight significantly faster precipitation and oxidation kinetics for Fe than Mn during mixing of the hot, reduced plume with the cold oxic seawater, leading to a much smaller fraction of the source concentration of Fe remaining in the buoyant (station 8-TMR, Fig. 10a–c) and early non-buoyant plume compared to Mn and Co (station 23-TMR, Fig. 8). We also observe this in the size fractionation data (Fig. 12) that show a significant colloidal contribution to total Fe concentrations in samples very close to the vent that will be removed faster from the water column than the “truly dissolved fraction”; in contrast, we found Mn and Co to barely have any colloidal contribution to their total concentrations. This partitioning agrees with observations at the nearby Edmond field, where colloids accounted for 14–50 % of total Fe in the young non-buoyant plume while Mn resided almost entirely in the truly dissolved fraction with negligible colloidal or particulate contribution (Sands et al., 2012). Findlay et al. (2015) likewise found Mn residing almost entirely in the $< 0.2 \mu m$ fraction within the first 1.5 m of the rising plume at three Mid-Atlantic Ridge vents (Rainbow, TAG, and Snakepit), a result they explicitly attribute to the same control documented for Edmond. As a consequence, the Fe/Mn ratio of the plume depends on the size fraction considered. Because Mn is entirely soluble, the soluble Fe/Mn ratio equals the total Fe/Mn ratio scaled by the soluble share of Fe, which in sample 23-7 (19 % soluble Fe) places it roughly a factor of five below the total ratio. With distance from the vent the particulate and colloidal Fe pools shrink and the two ratios converge, so that the Fe/Mn ratio of the aged plume reflects the small portion of Fe that escaped early particle formation and no longer records the endmember ratio. This size dependence arises only upon mixing with seawater; in the vent fluid itself both metals are dissolved. The opposite trend can be observed when comparing the ratios during the further mixing with significantly lower remaining concentrations relative to the source fluid for both Co and Mn compared to Fe. This indicates faster removal of Co and Mn or better stabilization of hydrothermal Fe in solution during far-field mixing of the hydrothermal plume of the KHF which is consistent with the findings of for example Nishioka et al. (2013); Resing et al. (2015); and Gartman and Findlay (2020). In addition to its colloidal behavior, dissolved Fe is stabilized in solution by complexation with strong organic ligands (Hoffman et al., 2024). Dissolved Co is likewise strongly organically complexed in seawater, although much of the hydrothermal Co appears to be scavenged during plume aging, consistent with the limited persistence of dissolved Co plumes (Noble et al., 2017). While the data presented here cannot attribute a hydrothermal signal specifically to the KHF at distances beyond 20 km, we do observe elevated Fe, Mn, and Co in the deep water column as far as our background station at 56 km (see

“Background” Levels of Trace Metals for the Kairei Plume), consistent with a broader regional hydrothermal influence rather than one traceable to the KHF plume individually. The near-field trends shown above are nonetheless consistent with the KHF acting as a source of these elements to the water column, despite the removal of most of the original fluid concentration during early mixing in the immediate vicinity of the vent field. A full quantification of this contribution is not possible with the present dataset. Because the helium isotope and trace metal samples were not collected from the same water parcels, dilution and chemical removal cannot be fully disentangled, and the non-linearity of the removal processes (oxidation, mineral precipitation, and particle settling) means the near-field trends should be projected toward the far-field with some caution.

The comparatively low endmember $\text{H}_2\text{S}/\text{Fe}$ of the Kairei fluid (0.90) favors Fe-(oxyhydr)oxide formation and oxidative scavenging over early sulfide removal, consistent with the buoyant-plume observations of Stewart et al. (2021), who found that particulate Fe shifts from Fe-sulfide toward metastable Fe-(oxyhydr)oxide phases as the fluid sulfide-to-Fe ratio decreases. At the low-sulfide extreme of this spectrum, the ultramafic-hosted Rainbow field on the Mid-Atlantic Ridge ($\text{H}_2\text{S}/\text{Fe} \approx 0.05$; Charlou et al., 2002) develops a plume dominated by Fe-(oxyhydr)oxides in which dissolved Fe is exported over exceptional distances (Edmonds and German, 2004). The neighboring Edmond field on the Central Indian Ridge, with even more Fe-rich brine fluids ($\text{H}_2\text{S}/\text{Fe} \approx 0.1\text{--}0.35$, Fe/Mn 7.2–9.7) (Gallant and Von Damm, 2006), lies between Rainbow and Kairei in this respect, and its non-buoyant plume accordingly carries Fe in the dissolved, colloidal and particulate fractions while Mn remains almost entirely dissolved (Sands et al., 2012). At the opposite, sulfide-rich extreme lie the magmatically influenced back-arc and rear-arc volcanoes of the NE Lau Basin, where high- H_2S , low-pH source fluids drive near-source removal of Fe as Fe-sulfide. At Mata Fitu and Mata Ua, where the vent fluids carry $\text{H}_2\text{S}/\text{Fe}$ of roughly 3–10, Fe is lost from the rising plume through Fe-sulfide precipitation (Wang et al., 2022); comparably H_2S -rich, acidic fluids at Niutahi (Klose et al., 2022) and Maka (Klose et al., 2021) record the same control. Such near-source sulfide loss, however, need not preclude efficient distal export: Cohen et al. (2021) traced dissolved Fe and Mn several hundred kilometers with the surviving Fe inferred to be ligand- and colloid-stabilized. With its intermediate $\text{H}_2\text{S}/\text{Fe}$, the ultramafic-influenced but basalt-hosted Kairei fluid falls between these more sulfide-rich systems and the Rainbow endmember, with Fe in its plume carried presumably predominantly as Fe-(oxyhydr)oxide, not as Fe-sulfide.

Gallium concentrations in the Atlantic and Pacific Oceans have been reported to show scavenged depth profiles with surface enrichment, minimum concentrations in intermediate waters (~300–1500 m), and conservative behavior in deeper waters (Ho et al., 2019; Liu et al., 2025). We observe similar behavior in the data acquired in this study, which to our knowledge represents the first data on Ga depth distribution in the Indian Ocean (Fig. 8/9 and supplementary material). With maximum surface concentrations of 32–40 pmol kg^{-1} , the concentrations observed here are generally higher than most profiles for the Pacific Ocean, where Liu et al. (2025) reported surface maximum concentrations of 10–17 pmol kg^{-1} , but within the range reported for the Atlantic Ocean by Shiller (1998), who observed maximum surface concentrations of 15–45 pmol kg^{-1} in the temperate and tropical Atlantic Ocean. While little is known about hydrothermal inputs of Ga into the ocean, a small but distinctly measurable hydrothermal contribution to the plume of the southern East Pacific Rise has been reported in the GEOTRACES East Pacific Zonal Transect GP16 (Ho et al., 2019), which matches our observation of Ga enrichment in the KHF source fluid to 27 nmol kg^{-1} (10^3 -fold enrichment over background seawater) and a small but distinct hydrothermal input at plume depth close to the KHF that is lost quickly with increasing distance to the field.

4.3.2. REY, V, Mo, U, Cd (scavenged/depleted)

We normalized the patterns of REY concentrations in the endmember

to chondrite (Fig. 14a), two buoyant plume samples (28-CTD-4 and 20-CTD-22) and six samples from the non-buoyant plume to shale (Fig. 14b). To visualize inputs into the ocean, we normalized the measured data as well as a theoretical conservative mixing model of seawater and the hydrothermal fluid to the average background concentrations of seawater in the area (at station 31-TMR) (Fig. 14c and d). In the fluid endmember when normalized to seawater, we observe REY enrichment most significantly for the middle rare earth elements (MREE) and less for the heavy rare earth elements (HREE) with a pronounced positive Eu anomaly that is typical for high-temperature hydrothermal fluids (e.g. Klinkhammer et al., 1994) while the apparent positive Ce anomaly is an artifact of normalizing to seawater, which itself has a typical negative Ce anomaly (Ce depleted relative to neighboring La and Pr, i.e. $\text{Ce}/\text{Ce}^* < 1$) in both shale- and chondrite-normalized patterns (e.g. Alibo and Nozaki, 1999; Zocher et al., 2024). Overall, the pattern is quickly diluted to resemble background seawater, but during early plume development shows levels below seawater concentrations despite the high concentrations of the KHF endmember.

The REY are well known to be particle-reactive due to scavenging to mineral particle surfaces in the water column, and hydrothermal plumes have been well established as a sink for REY in the marine system (German et al., 1990; Haalboom et al., 2020; Mitra et al., 1994; Sherrell et al., 1999; Bau and Dulski, 1999). While the endmember concentration is enriched in REY relative to seawater by factors of 10 to 10^3 , the plume concentrations are lower than in the water column below and above the plume as well as in the background profile. The buoyant plume of the KHF shows the strongest overall depletion of REY relative to seawater in sample 28-CTD-4 (Fig. 14b and c) with the MREE being more depleted than the HREE. Europium is less depleted than its neighboring elements due to the positive anomaly inherited from the source fluid (Fig. 14a), while Y is scavenged less than Ho, i.e. behaving more conservatively (Bau and Dulski, 1999), which leads to a positive anomaly in the seawater-normalized profile. Because the Eu anomaly is inherited from the source fluid, its weaker apparent depletion does not by itself indicate less efficient scavenging. Because the anomaly is a ratio of neighboring REY, uniform scavenging removes Eu and its neighbors in the same proportion and cancels in the ratio, so the anomaly can still be used to approximate the conservative volume fraction of hydrothermal fluid, ϕ , in each sample. On this basis, sample SO301-28-CTD-04 with the strongest Eu anomaly corresponds to approximately 0.005 % endmember fluid, and the remaining samples with a measurable anomaly to approximately 0.001 % (see Supplementary Material S5 for details). Cleanly separating the inherited signal from in-plume removal would require referencing each sample to its conservatively mixed source, which remains limited by the lack of a co-located truly conservative dilution tracer for the trace-metal samples. In the early non-buoyant plume, the depletion of the REY becomes most evident in the medium vicinity of the vent field with the most pronounced negative deviation from the background profile at station 21-TMR.

REY depletion and anomalies can be produced by scavenging to Mn and Fe oxide phases – with HREE less scavenged than MREE, Y less than Ho, and Ce more than its neighbors as seen by the distribution coefficients (K_D) found for leachates of ferromanganese crust samples (Bau and Koschinsky, 2009).

The contrasting oxidation kinetics of Fe and Mn offer a way to separate their respective oxide phases as REY scavengers. Fe(II) oxidises rapidly (Statham et al., 2005), so Fe-oxyhydroxides likely dominate scavenging in the young, near-field plume, whereas the slower oxidation of Mn(II) means Mn oxides, and the elements they preferentially host such as Co, become important only in the older, distal plume. Consistent with this, the negative Ce anomaly typical for seawater is least pronounced in the early plume samples (28-CTD-4, 21-TMR-8, and 23-TMR-6) and appears to deepen with plume age, as expected for the kinetically slow oxidative scavenging of Ce (Takahashi et al., 2007; Bau et al., 2014; Manceau et al., 2026).

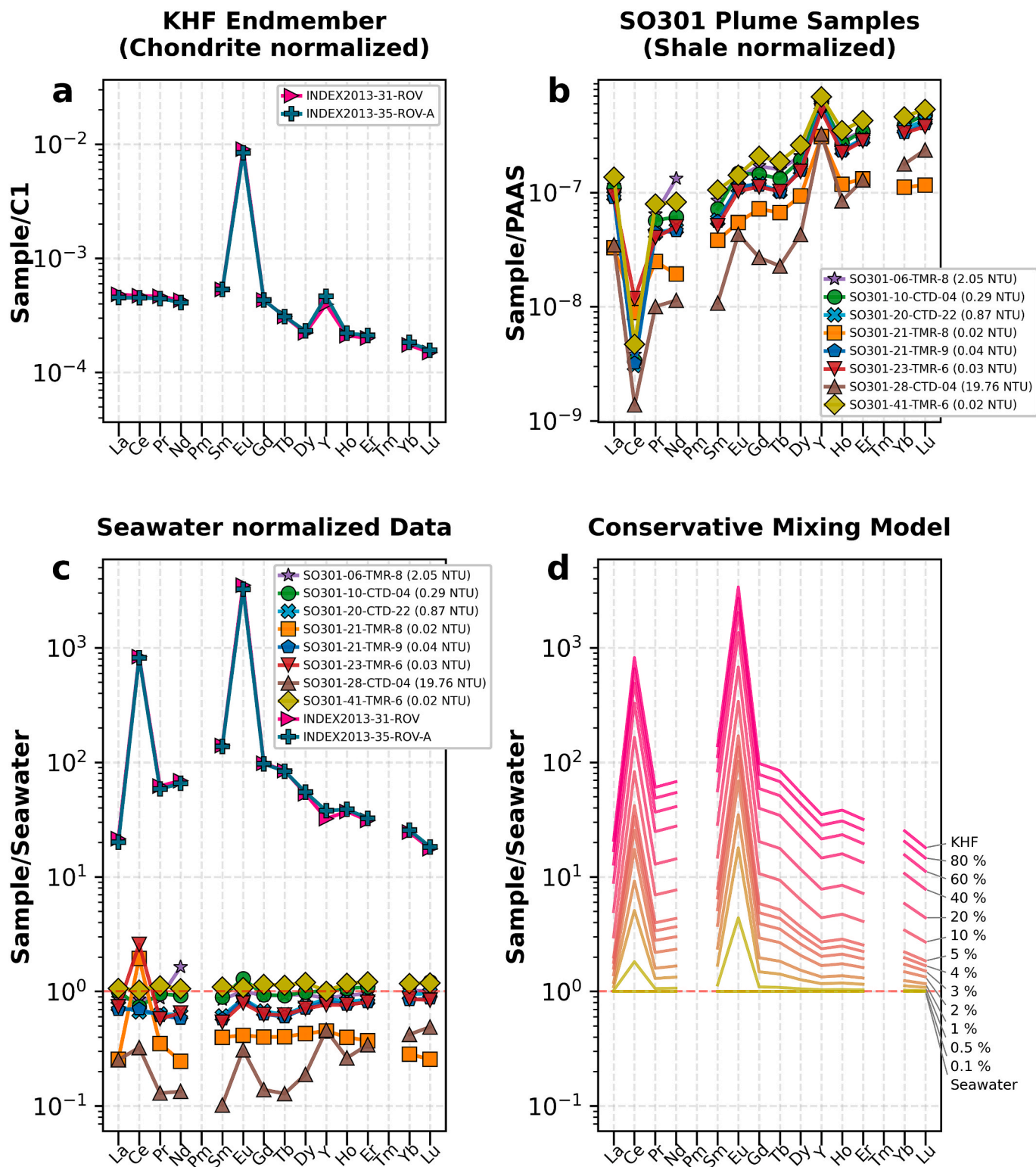


Fig. 14. (a) Rare Earth and Yttrium (REY) patterns from the Kairei hydrothermal endmember (sampled in the INDEX 2013 campaign, Mg-extrapolated total concentrations) normalized against C1 chondrite and (b) shale-normalized plume samples collected during cruise SO301 ($<0.2 \mu\text{m}$). (c) REY concentrations of end-member and plume samples normalized to background seawater concentrations at the corresponding depths and (d) seawater-normalized REY-patterns of a theoretical conservative endmember mixing model using background seawater and the average KHF hydrothermal fluid.

Therefore, the plume of the KHF is a local sink for REY from the water column, depleting the deep ocean of these elements despite the fluid having elevated concentrations. This interpretation is directly supported by observations in the Rainbow plume on the Mid-Atlantic Ridge, where [Haalboom et al. \(2020\)](#) found particulate REE/Fe molar

ratios to increase with distance from the vent over more than 20 km, indicating continuous scavenging of seawater REY onto Fe-oxyhydroxides as the plume ages and disperses. Consequently, we can expect significant deposition of REY alongside Fe/Mn deposits on the seafloor around the KHF ([Hu et al., 2024](#)).

Vanadium is significantly depleted in both the source fluid and the hydrothermal plume of the KHF (see Table 2, Fig. 6, and Fig. 8f). This effect is well-studied and attributed to effective scavenging of V from the water column by Fe-oxide particle surfaces (Coale et al., 1991; German et al., 1991). Hydrothermally sourced Fe oxides are estimated to remove $0.6\text{--}3 \times 10^8 \text{ mol V year}^{-1}$ from seawater, with a best estimate of $1.4 \times 10^8 \text{ mol year}^{-1}$ (Trefry and Metz, 1989), against a riverine V input of about $4\text{--}6 \times 10^8 \text{ mol year}^{-1}$ and a total dissolved V input to the ocean of roughly $8\text{--}10 \times 10^8 \text{ mol year}^{-1}$ (Schlesinger et al., 2017), making hydrothermal plumes including that of the KHF a highly effective sink for marine V. Molybdenum often behaves similarly to V in the marine water column as a chemically conservative trace element and is similarly depleted to half of the seawater concentration in the KHF endmember fluid. Ho et al. (2018) reported depletion for both V and Mo at the Southern East Pacific Rise in samples from the GEOTRACES East Pacific Zonal Transect (GP16) as a result of scavenging to Fe-oxyhydroxides. We, however, do not observe a significant influence of the KHF buoyant or non-buoyant plume on the distribution of Mo in the water column (Figs. 6, 8, and 9). With a higher concentration in seawater and a lower degree of depletion in the KHF endmember for Mo compared to V, potentially occurring scavenging effects may simply be too small to be visible in the data presented here. Uranium is quantitatively removed in the KHF endmember as is commonly observed in hydrothermal fluids. We do not, however, observe an effect of the KHF plume on U distribution as the samples analyzed here are already too dilute with respect to the hydrothermal fluid contribution to show conservative mixing effects at the difference in U concentrations between hydrothermal and seawater endmembers in both non-buoyant and buoyant plume samples (Figs. 6, 8, 9, 10, and 11).

Other than the elements discussed above, Cd is enriched in the endmember fluid of the KHF by a factor of $\sim 10^2$ compared to background seawater. We, however, observe no enrichment of Cd in CTD samples from the non-buoyant plume (Fig. 6) and significant depletion of Cd for hydrothermally affected TMR stations at the depth of the hydrothermal plume with near-complete removal at stations 23-TMR, 21-TMR, and 8-TMR and still a small negative deviation from the background profile at station 29-TMR. Cadmium has been shown to be enriched in hydrothermal deposits and hydrothermally affected sediments, hosted in sulfide minerals such as sphalerites (Zhou et al., 2024), but the behavior of Cd in hydrothermal plumes is still poorly constrained with very limited data availability. While, for example, Metz and Trefry (1993) have suggested hydrothermal sulfide particles to be sources of dissolved Cd upon oxidation, our data show near-quantitative removal of the background Cd in the plume of the KHF making it a significant local sink. Similarly, measurements from the GEOTRACES GA03 transect of the North Atlantic Ocean revealed the plume of the Mid-Atlantic Ridge to be a significant Cd sink that the authors propose to be a result of scavenging by Fe-oxyhydroxide particles (Conway and John, 2015). While sulfides may cause removal of Cd during early plume development where sulfides are stable, scavenging of Cd by oxidized Fe particles can affect seawater-sourced elements including Cd in the far-field hydrothermal plume as well. Both processes may be acting in the plume of the KHF. The colloidal Fe-oxyhydroxide phases documented here provide a substrate for this scavenging, and earlier plume studies show that Cd is scavenged onto hydrothermal Fe-oxyhydroxide particles and coprecipitated with sulfides (German et al., 1991; Metz and Trefry, 2000). In the Rainbow plume, Cd showed the greatest preferential loss of the chalcophile elements examined ($\text{Cd} > \text{Zn} > \text{Co} > \text{Cu}$; Edmonds and German, 2004). Cadmium also follows a nutrient-type distribution in the open ocean, closely coupled to phosphate, so part of its background structure reflects regeneration of biogenic particles. We did not measure macronutrients on this cruise and therefore cannot directly compare Cd with phosphate or silicate, but because the plume signal is evaluated as the deviation from the local background profile (station 31-TMR), this regenerative baseline is already accounted for and the depletion at plume depth can be attributed to hydrothermal scavenging. While we

lack measurements of particulate Fe and Cd to confirm this hypothesis or differentiate between sulfide incorporation and oxide scavenging, our observations of dissolved Cd concentrations are consistent with oxide scavenging in the far-field and potentially additionally sulfide incorporation in the early rising plume. If Cd adsorption to Fe oxyhydroxides is common among hydrothermal plumes throughout the ocean, they could present the primary sink for the ocean's global Cd budget. Both Cd sulfide precipitation and scavenging on Fe oxide phases have been shown to enrich the light Cd isotope on the solid phases, implying that hydrothermal Cd sinks would also influence Cd isotopic signatures in the ocean (Guinoiseau et al., 2018; Chen et al., 2021).

4.3.3. Cu, Ni, Pb (complex behavior)

Copper is highly enriched in the source fluid of the KHF by a factor of $\sim 10^4$, but we observe no enrichment in the buoyant plume in CTD samples (Fig. 6), or TMR samples (station 8-TMR, Fig. 10a–c). The non-buoyant plume close to the vent site visible at station 23-TMR (Fig. 8) also shows essentially the same profile as the background at station 31-TMR (Fig. 11d–f) with no significant deviation at plume depth. Station 21-TMR (Fig. 9), however, shows depletion of Cu at the depth of the hydrothermal plume while we see enrichment in the plume at station 29-TMR (Fig. 10d–f) and even at 3 km distance from the KHF at station 41-TMR (Fig. 11a–c) where we see little to no influence of the plume on the other elements investigated in this study. Copper must therefore be controlled by different processes in the far-field plume compared to the near-field of the KHF. Removal of dissolved Cu to the particulate phase by precipitation of chalcopyrite is likely the dominant process affecting Cu concentrations in the buoyant plume (e.g. German et al., 1991; Sands et al., 2012). At Edmond, Sands et al. (2012) found Cu to reside predominantly in the particulate phase, with particulate Cu tracking particulate Fe at a Cu:Fe ratio ~ 0.013 close to the vent-fluid value, whereas our size fractionation finds Cu to be largely soluble with only a minor particulate contribution near the source (Fig. 12). This is consistent with the near-source loss of Cu-bearing sulfides documented at Edmond, with the far-field release of Cu (Metz and Trefry, 1993) to the dissolved pool inferred here from our more distal stations. Findlay et al. (2015) similarly found Cu to be carried mainly in the particulate phase within the first 1.5 m of the rising plume at three Mid-Atlantic Ridge vents, coprecipitating with Fe as chalcopyrite and incorporating Co, which reinforces that near-source removal of Cu is governed by sulfide precipitation. The depletion of Cu in the depth profile visible at station 21-TMR indicates further removal of background Cu despite the low H₂S availability from the KHF endmember, suggesting a significant effect of adsorption of dissolved Cu to particle surfaces, as also observed for arc-volcano plumes of the Northeast Lau Basin (Wang et al., 2024). In the far-field, however, we see a release of Cu to the dissolved fraction, which is coherent with the release of Cu during transformation of sulfide particles to oxides in the aging hydrothermal plume that has been observed in the field and validated through laboratory experiments before (Metz and Trefry, 1993; Sarradin et al., 2009). At the basin scale, dissolved-Cu speciation in the deep tropical South Pacific shows a similar soluble-dominated, partly colloidal partitioning, and Roshan and Wu (2018) found a small excess dissolved-Cu component near the East Pacific Rise that weakly tracks hydrothermal ³He ($R^2 = 0.41$), which they tentatively attribute to dissolved Cu being continuously solubilized from far-field-transported hydrothermal particles. They stress that this signal is small. More broadly, hydrothermal regions have been suggested to act as either a source (Roshan and Wu, 2018) or a sink (Jacquot and Moffett, 2015; Roshan and Wu, 2015) of dissolved Cu, depending on the efficiency of particulate transport and the solubilization of Cu-bearing particles. Hydrothermal Cu does not easily scavenge to oxide minerals (compared to Cd that is scavenged to oxide phases in the non-buoyant plume), and similarly to Fe, as discussed above, has been shown to be strongly bound by organic ligands allowing further transport of Cu in the far-field plume (Sander and Koschinsky, 2011). Therefore, while the complexity of the processes affecting Cu in the plume of the KHF

complicates the quantification of Cu fluxes, our data suggest the KHF plume to overall be a local net source of Cu to the deep ocean. The complex behavior of Cu in the KHF plume is in line with the published data showing mixed net effects in the 5 GEOTRACES studies reviewed by [Fitzsimmons and Steffen \(2024\)](#), and [Kleint et al. \(2022\)](#) finding a significant plume source at Macauley with no significant plume influence at Brothers. Given the major importance of Cu for marine microbiological cycles, there appears to be a need for more detailed studies on the behavior of hydrothermal Cu in the near- and far-field of hydrothermal systems in different geological and hydrographic settings.

Lead is similarly enriched in the KHF as Cu to a factor of 10^4 compared to seawater, but we do not observe any significant enrichment in dissolved concentrations of the plume. Our size fractionation measurements, however, reveal the hydrothermal input of Pb to be present predominantly in the small particulate (and potentially large particulate $>0.8\ \mu\text{m}$, not measured) fraction, which is rapidly removed in early mixing of the buoyant rising plume by precipitation as sulfide minerals ([Estes et al., 2022](#)). We would therefore expect significant deposition of Pb-bearing minerals in the immediate vicinity of the vent field, but the KHF appears to have little impact on regional Pb concentrations in the water column. Consistent with this, [Yadav et al. \(2025\)](#) report uniformly low, scavenging-controlled dissolved Pb of 4.7–15.8 pM in the deep waters of the southern Indian Ocean (25–30°S) without any hydrothermal signature from the CIR, a range that encompasses our plume maximum of 13.1 pmol kg⁻¹ at station 23-TMR. The existing literature shows variable effects of the influence of hydrothermal plumes on the marine Pb budgets with the four studies within the GEOTRACES program reporting scavenging effects ([Fitzsimmons and Steffen, 2024](#)), while [Kleint et al. \(2022\)](#) found a plume source for Pb at both Brothers and Macauley. This is likely related to typically much higher Pb concentrations in the endmember fluid at these island arc settings that are a result of the feldspar-rich dacitic/rhyolitic host-rock composition that contains much higher leachable Pb ([Zhang et al., 2003](#)). Mid-ocean ridge systems like Kairei, by contrast, are hosted in basaltic crust that supplies little leachable Pb, consistent with the low Pb concentration of the endmember fluid and with the intrinsically Pb-poor composition of the mafic-ultramafic oceanic crust that hosts the system ([Workman and Hart, 2005](#)).

Nickel is less enriched in the KHF endmember than Cu and Pb, at only ~10-fold enrichment over seawater. In the near-field of Kairei, the depth profiles of Ni match those of Cu with no enrichment in the rising plume in CTD samples ([Fig. 6](#)) or at station 8-TMR ([Fig. 10a–c](#)), essentially a background profile at station 23-TMR ([Fig. 8](#)) and depletion in the non-buoyant plume at station 21-TMR ([Fig. 9](#)). At the further stations, however, we see no significant hydrothermal impact on the depth profiles of Ni concentrations. Few studies on the fate of Ni in hydrothermal plumes have been published so far, but particle scavenging has been suggested as a controlling factor for hydrothermal Ni, for example, by [Mottl and McConachy \(1990\)](#). That would be consistent with our observations, where the enriched Ni from the KHF endmember is scavenged early in the plume mixing process and hydrothermal particles appear to further scavenge Ni from the background seawater. Contrary to Cu, however, we do not observe a later release of Ni to the water column in the KHF plume. If oxidative release from particles were occurring, however, the signal would be too diluted to be detected here due to the significantly lower Ni endmember input. We therefore suggest that for Ni, while it is affected by similar geochemical processes during plume mixing like Cu, the Kairei plume is likely an overall small net local sink as the lower enrichment of dissolved Ni in the endmember is not sufficient to compensate for the scavenging of Ni from the water column. The effects of hydrothermal plumes on marine Ni distributions have only recently been addressed within the GEOTRACES program: [Bian et al. \(2024\)](#) found that hydrothermal influence on Pacific seawater Ni can act as either an addition or a removal depending on vent geochemistry and proximity to the source. [Kleint et al. \(2022\)](#) observed similar behavior for Ni as for Cu in the Kermadec arc with a significant plume

source at the shallower Macauley and no effect of the Brothers plume on Ni in the water column. The controls behind these contrasting net budgets remain speculative. One possibility is that the balance between a metal's endmember supply and the Fe-Mn scavenging substrate is decisive: Kairei's high Fe and Mn load may generate enough particle surface to scavenge its modest Ni input along with background Ni (net sink), while a higher Ni-to-(Fe + Mn) ratio or a shallower, less diluted plume could tip a system such as Macauley towards export. Lead and Ni would then be limited by different processes, Pb by sulfide supply and Ni by scavenging capacity. This severely complicates estimation of global hydrothermal inputs of Cu, Ni, and Pb to the deep ocean as ratios of their concentrations to other endmember components including Fe, Mn, and H₂S will control whether an individual system acts as a source or sink for these elements.

5. Conclusion

This study provides a detailed assessment of trace metal behavior in the Kairei hydrothermal plume, demonstrating the complex and element-specific processes that control the fate of hydrothermally derived metals during plume evolution from source to far-field dispersal. Our high-resolution sampling approach, combining CTD tow-yos for buoyant plume characterization with contamination-free TMR hydrocasts for non-buoyant plume analysis, reveals that the KHF acts simultaneously as both a source and sink for different trace metals in the deep Indian Ocean.

The successful deployment of our newly developed autonomous TMR system demonstrates its utility for contamination-free sampling of hydrothermal plumes. With its compact design, minimal personnel requirements, and compatibility with aramid cable winches available on most research vessels for autonomous operation, this system enables high-quality trace metal sampling to be incorporated into focused studies alongside conventional oceanographic operations. This accessibility is particularly important given the need for more detailed investigations of hydrothermal systems across diverse geological and oceanographic settings.

The hydrothermal plume of the KHF represents a significant source of Fe, Mn, Co, and to a lesser degree also Ga to the water column, despite rapid removal of most of the endmember concentrations during early mixing. The size fractionation data demonstrate that while Fe is transported predominantly in colloidal phases that are progressively removed during plume aging, Mn and Co remain primarily in the truly dissolved fraction, facilitating their far-field transport. Conversely, the plume acts as an effective sink for REY, V, and notably Cd, with near-quantitative removal of background Cd concentrations observed in the proximal non-buoyant plume. This finding adds to the limited existing data on Cd behavior in hydrothermal systems and suggests that if common among global hydrothermal plumes, this scavenging effect could represent a major sink in the marine Cd budget that has been previously underappreciated.

Perhaps most significantly, our data reveal complex, non-conservative behavior for Cu, Ni, and Pb that varies with distance from the vent field. The observed depletion of Cu and Ni in the near-field plume followed by Cu enrichment in the far-field suggests a combination of initial sulfide precipitation and particle scavenging followed by oxidative release during plume aging. The released Cu probably combines hydrothermally sourced and scavenged seawater Cu, which our data cannot distinguish. This complexity, combined with the element-specific enrichment factors in the endmember fluid, indicates that individual hydrothermal systems may act as either sources or sinks for these metals depending on their specific fluid chemistry, particularly the ratios of metal concentrations to H₂S and Fe. The relatively low H₂S/Fe ratio of 0.90 at Kairei, intermediate between the Fe-(oxyhydr)oxide-dominated Rainbow endmember (≈ 0.05) and the sulfide-rich back-arc and arc systems such as the NE Lau Basin volcanoes (≈ 3 –10) and the Main Endeavour Field (14.9), could favor greater metal transport away

from the vent field, although our data do not allow this to be quantified. Kairei thus represents the ultramafic-influenced, basalt-hosted hybrid systems that occupy the middle of this range. More broadly, the fate of each metal is set by its endmember enrichment and by the ratios of metal to H_2S , Fe, and Mn. Sulfide precipitation removes chalcophile elements such as Cu, Pb, and Cd near the vent; Fe-Mn oxyhydroxide scavenging depletes the REY and V in the aging plume, while Mn, Co, and ligand-stabilized Fe are exported to the deep ocean.

The highly dynamic nature of the Kairei plume, shifting horizontally with tidal currents, leads to a spatial disconnect between the distance to the vent location and maximum plume influence, which presents significant challenges for flux quantification. This dynamic behavior underscores the need for time-series observations and adaptive sampling strategies to accurately capture plume processes and estimate hydrothermal contributions to regional trace metal budgets.

While an impressive body of research on hydrothermal metal fluxes to the ocean already exists in the literature, our findings highlight critical gaps in understanding hydrothermal trace metal cycling, particularly for elements exhibiting complex behavior like Cu, Ni, and Pb. The contrasting behaviors observed between elements and the evolution of their distributions with distance from the vent field confirm that simple extrapolations from endmember compositions cannot adequately predict hydrothermal contributions to marine trace metal cycles. Our high-resolution study of the diverse behavior of different elements in the hydrothermal plume also invites comparison with well-characterized systems such as the Rainbow vent plume at the MAR, which shares a comparable ultramafic-influenced setting and metal-rich, high- H_2 fluid character but contrasts in its sulfur systematics, with a much lower H_2S /Fe that favors a more Fe-oxyhydroxide-dominated plume. Future studies should focus on high-resolution spatial and temporal sampling of hydrothermal plumes, coupled with particulate phase analysis and speciation measurements, to better constrain the processes controlling metal fate during plume evolution. Particularly promising directions include resolving how Cu is adsorbed and then released during the progressive oxidation and aging of plume particles, and finer size fractionation, in particular the addition of ultrafiltration, to separate truly dissolved metals from the small colloids that the present scheme does not fully resolve. Element-specific speciation measurements could further constrain the chemical forms involved; for example, because the redox state of V governs its affinity for particle surfaces, spectroscopic determination of its oxidation state (Kurahashi et al., 2024) would help to interpret its scavenging behavior. Vanadium stable isotopes offer a complementary tool: fractionation of V isotopes during hydrothermal sediment accumulation (Wu et al., 2022) could help trace the sedimentary footprint of hydrothermal plume dispersal around the KHF. Only through such detailed investigations across a range of hydrothermal systems can we develop the process-based understanding necessary to accurately quantify the role of hydrothermal venting in global marine trace metal budgets and its impact on ocean biogeochemistry.

CRediT authorship contribution statement

Nico Fröhberg: Conceptualization; Data curation; Formal analysis; Investigation; Project Administration; Resources; Software; Visualization; Writing – original draft; Writing – review & editing. **Katja Schmidt:** Data curation; Formal analysis; Investigation; Methodology; Resources; Validation; Writing – review & edit. **Sandra Poehle:** Data curation; Investigation; Methodology; Writing – review & editing. **Ignacio Pedre:** Investigation; Methodology; Writing – review & editing. **Maren Walter:** Data curation; Formal analysis; Funding acquisition; Project Administration; Resources; Writing – review & editing. **Jonathan Mette:** Data curation; Formal analysis; Investigation; Visualization; Writing – review & editing. **Sebastian Fuchs:** Formal analysis; Writing – review & editing. **Dieter Garbe-Schönberg:** Investigation; Methodology; Resources; Writing – review & editing. **Charlotte Kleint:** Formal analysis; Writing – review & editing. **Andrea Koschinsky:**

Conceptualization; Funding acquisition; Project administration; Resources; Supervision; Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Further figures including depth profiles of trace element concentrations at all TMR stations from cruise SO301, and further oceanographic illustrations are available in the [supplementary material](#).

The full dataset of major, minor, and trace element concentrations of plume samples acquired during cruise SO301 has been published in the PANGAEA database: <https://doi.pangaea.de/10.1594/PANGAEA.989559>.

The physical oceanographic data and He isotopic compositions are available in the PANGAEA Database under the following links:

<https://doi.pangaea.de/10.1594/PANGAEA.988334> (CTD data)

<https://doi.pangaea.de/10.1594/PANGAEA.989411> (MAPR data)

<https://doi.pangaea.de/10.1594/PANGAEA.989377> (MAPR data)

<https://doi.pangaea.de/10.1594/PANGAEA.989376> (MAPR data)

<https://doi.pangaea.de/10.1594/PANGAEA.989354> (CTD bottle data including He isotopic composition).

Declaration of generative AI and AI-assisted technologies in the manuscript preparation process

During the preparation of this work, the authors used a large language model (Claude Sonnet and Opus 4/5) in order to improve the language/readability of individual sections. After using this tool/service, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

Supplementary material

The supplementary materials include trace element method details and analytical quality information, cleaning protocols for sampling materials used for trace metal sampling during cruise SO301, additional depth profiles of trace element concentrations at all TMR stations during SO301, additional figures of physical oceanographic data, a table of analytical quality data, an approximation of conservative mixing ratios based on the seawater-normalized europium anomaly in the plume samples, and an orbiting animation of the turbidity plume at Kairei.

Appendix A. Supplementary material

Supplementary material to this article can be found online at <https://doi.org/10.1016/j.gca.2026.09.018>.

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