

Temporal and Spatial Variability in the Geochemistry of Hydrothermal Fluids and Hydrothermal Ferromanganese Deposits at the Mid-Atlantic Ridge

by

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Declaration

I declare that this thesis represents original and independently conducted research that has not been submitted to any other university for the conferral of a degree.

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Bremen, 29.11.2010

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Abstract

Hydrothermal circulation at spreading axes plays a fundamental role for global heat flux and the geochemical cycles between the lithosphere, the hydrosphere, and the atmosphere. Slow- and ultraslow-spreading ridges comprise about 50% of the cumulative global ridge-axis length, and mass, heat, and chemical fluxes at hydrothermal systems along these ridges likely contribute significantly to the overall exchange between lithosphere and hydrosphere. Plate separation at slow-spreading ridges is often accommodated by tectonic spreading, and the oceanic lithosphere is characterized by various lithologies. While hydrothermal activity at fast-spreading ridges has been extensively investigated during the last decades, slow-spreading ridges are only randomly explored for hydrothermal activity, except for the northern Mid-Atlantic Ridge (MAR). This study aimed to (1) characterize the hydrothermal fluid composition of different hydrothermal systems at the slow-spreading MAR, and to investigate the influence of geological setting and physical conditions like water pressure and temperature on the hydrothermal fluid composition, (2) to resolve time scales of hydrothermal activity at slow-spreading ridges in different geological settings, and (3) to investigate the potential of hydrothermal oxide deposits to record hydrothermal export fluxes at high-temperature vent sites.

During this study, the fluid geochemistry of three hydrothermal fields, located in different geological environments at the MAR, has been investigated. The Logatchev-1 field at 14°45'N and the Nibelungen field at 8°18'S are both located several kilometres off-axis in tectonic-controlled settings with heterogeneous lithologies, whereas the vent field area at 5°S is hosted in the neovolcanic zone on the ridge axis and includes the hottest hydrothermal field found so far (Turtle Pits: 407-425°C). The possibility to revisit the target sites several times during numerous cruises allowed investigating the temporal evolution of hydrothermal systems depending on their geological setting and physical conditions.

In the Nibelungen vent field, hydrothermal fluids vent from a single smoking crater at temperatures of about 375°C. The composition of hydrothermal fluids is controlled by the hybrid alteration of mafic and ultramafic rocks, probably at an integrated water-rock ratio of less than 0.5. The fluid composition of Nibelungen in comparison to other high-temperature, ultramafic-hosted hydrothermal systems (Logatchev-1 and Rainbow) is similar with respect to key parameters, which collectively define a unique geochemical fingerprint attributed to mantle rock-fluid interaction in heterogeneous lithosphere at high fluid temperatures: strong enrichments of dissolved hydrogen and methane, low concentrations of dissolved H₂S, Si, Li

relative to basaltic-hosted hydrothermal systems, depletion of B relative to seawater (i.e., sink for seawater B) and an enriched $\Delta^2\text{H}_{\text{H}_2\text{O}}$ signature. The multi-step alteration sequence is determined as (1) low- and medium-temperature alteration of mafic rocks, (2) pervasive serpentinization at moderate to high temperatures, and (3) limited high-temperature interaction with basaltic rocks during fluid ascent. In contrast to Logatchev-1, the seafloor at Nibelungen is covered by altered pillow lava and access to ultramafic rocks is provided via a major fault disrupting and thinning the oceanic crust.

The high mobility of transition metals like Fe and Cu at Nibelungen is related to the relatively high fluid temperatures at the emanation site, which, together with the low dissolved H_2S concentration and other factors limits the precipitation of sulfide minerals in the subseafloor and enhances the metal flux into the ocean. Compositional differences between Logatchev-1 and Nibelungen hydrothermal fluids can be ascribed to lower alteration temperatures and other fluid pathways involving a variety of source rocks, higher water/rock ratios, and sulfide precipitation in the sub-seafloor at Logatchev-1. The stability of vent fluid composition at Logatchev-1 (for 13 years) and Nibelungen (for 3 years) is in agreement with previous time series studies in other MAR vent fields and can be related to the setting of these systems controlled by tectonic faults, and to the limited magmatic activity.

In contrast, hydrothermal activity at 5°S (Turtle Pits, Comfortless Cove, Red Lion) is controlled by mafic rock-seawater interaction, with two of them (Turtle Pits and Comfortless Cove) venting at extremely high temperatures up to 425°C, while Red Lion has more moderate fluid temperatures of about 350°C. The hydrothermal activity of Turtle Pits and Comfortless Cove is related to a recent lava eruption. The fluids are affected by phase separation above the critical point of seawater (407°C, 298 bars), which leads to the emanation of (condensed) vapor-phase fluids with about half the seawater salinity. While vapor-phase fluids formed by subcritical phase separation in shallower mid-ocean ridge settings are strongly depleted in metals, Turtle Pits and Comfortless Cove fluids are characterized by high metal concentrations, especially Fe. The high fluid temperatures enhance metal complexation with Cl, while the relatively high density of the vapor phase formed by brine exsolution controls the high solubility of metals in Cl-depleted fluids. The style and temporal evolution of hydrothermal activity associated with magmatic eruptions differ strongly between fast- and slow-spreading ridges. Repeated fluid sampling between 2005-2009 (Turtle Pits, Red Lion) disclosed stable major element fluid composition and temperature. This temporal stability observed over a period of 6 years in an actively phase-

separating hydrothermal system is likely a function of the physical conditions during hydrothermal convection, in contrast to changes in heat and chemical fluxes within month or years at fast-spreading ridges. Similar systems are favoured at high water depth of the ridge axis, as common for slow-spreading ridges.

The extremely hot vapor-phase fluids emanating from two vent fields at 5°S (Turtle Pits and Comfortless Cove) on the MAR display a unique rare earth element and yttrium (REY) distribution compared to formerly investigated fields along mid-ocean ridges. Independent of the major element composition, the fluids display a strong temporal variability of their REY concentrations and relative distributions at different time scales of minutes to years. As evident by the positive correlation of total REE, Ca, and Sr concentrations, precipitation/dissolution of hydrothermal anhydrite controls the variability in REE concentrations and distributions in these fluids and the transformation of one fluid type to the other. Two conclusive models can explain the unusual type II REY distributions: dissolution of anhydrite in ascending fluids, overprinting a primary signal or, venting of a primary reaction zone fluid due to limited exchange with secondary minerals in the subseafloor during short migration paths.

This study shows that other than previously assumed, hot hydrothermal fluids from mid-ocean ridges are not always characterized by large positive Eu anomalies. The strong compositional variability is supposed to be related to the young, post-eruptive stage of hydrothermal venting at high pressure, and may be a common effect in other hydrothermal systems in similar geological settings.

The second part of the thesis presents a detailed study of the geochemistry of hydrothermal Mn crusts and other Fe-Mn oxide deposits from the ultramafic-hosted Logatchev-1 field, intended to resolve hydrothermal fluxes from the lithosphere into the hydrosphere as reflected in these deposits. Despite close spatial associations, the textures as well as mineralogical and chemical compositions of Fe-Mn oxide deposits in the Logatchev hydrothermal field are highly variable, which can be attributed to different formation environments of the deposits. Mixed Fe-Mn oxide deposits forming thin coatings on rock substrates, are dominated by hydrogenetic scavenging in the open ocean, with Fe oxyhydroxides partly being generated in the hydrothermal plume. Stratified, pure Mn oxide crusts precipitated from rising, low-temperature hydrothermal fluids. Hydrothermal fluid flux is evident by the signatures of radiogenic isotopes Os, Hf, and Nd in Mn crusts, in contrast to Fe-Mn oxide coatings displaying only very limited hydrothermal contributions. The stratified Mn crusts are strongly

enriched in Cu and Co, with variable concentrations of Zn and Ni, which distinguishes them from texturally similar Mn crusts from distal hydrothermal settings. In comparison to hydrogenetic ferromanganese crusts, pure Mn crusts are enriched in Cu, Li, Mo, but depleted in Pb, Co, Ni, and Zn, whereas Fe-rich Fe-Mn oxide coatings are in principle hydrogenetic deposits scavenging elements from the open seawater. The geochemical signature of hydrothermal Mn crusts is clearly linked to high-temperature hydrothermal activity. Strong Cu enrichments are related to the mobilization of Cu by leaching of massive Cu sulfides in the subseafloor, which makes such deposits valuable as tracers for hidden sulfide deposits. A clear fingerprint for ultramafic host rock alteration could not be proven. The relative hydrothermal component in single deposits is variable between individual elements and depends on the relative concentrations in the principle sources (seawater and hydrothermal fluid) and the partition coefficients during adsorption. Compositional variations in the crust profiles of pure Mn crusts indicate changes in source fluid composition during the formation of the crusts over time, but not stringently general changes in the high-temperature fluid circulation.

This study extends the data record for hydrothermal systems at the MAR in space and time and substantiates the relevance of hydrothermal activity at slow-spreading ridges for geochemical exchange budgets. Unique features of slow-spreading MAR hydrothermal systems disclose diverse host rock compositions, highly variable fluid compositions depending on the geological setting, physical conditions and tectonic activity, and striking temperature and compositional stability also in actively phase-separating hydrothermal systems, which have profound implications for global chemical fluxes.

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Framework and Outline of the thesis

The framework of this PhD research project is given by the Special Priority Program 1144 "From the mantle to the ocean: energy-, material-, and life-cycles at spreading axes" funded by the German Science Foundation (DFG). The program has been initiated to investigate different processes like magmatic eruptions, seismic activity, tectonic movements, hydrothermal and biological activity and their time scales in different geological settings at the slow-spreading Mid-Atlantic Ridge (MAR) axis, over a time period of 6 years (2003-2009). The interdisciplinary approach encompassing petrological, volcanological, geophysical, microbiological, zoological, oceanographic, geochemical, and convection modeling studies, allowed to investigate relationships and interactions among the different processes. Two target areas were chosen, the area at 15°N, south of the Fifteen Twenty Fracture Zone, which includes the ultramafic-hosted Logatchev I hydrothermal vent field, where a large variety of emanating fluids, mineral precipitates and biotopes is known to exist, and the area between 4-11°S, being nearly unexplored at the beginning of the project except for water-column and seismic data.

One subtopic of the program, initiated by my supervisor Dr. Andrea Koschinsky, dealt with hydrothermal fluids as media for the transport of energy and mass from the lithosphere to the hydrosphere and biosphere and the interrelation with the geological and biological environment in different hydrothermally active areas. For the first time it was possible to investigate hydrothermal activity on a slow-spreading ridge on an annual basis. During the course of the SPP program, four working areas in different tectonic settings and temperature conditions were defined, including newly discovered sites: (1) Logatchev-1 at 14°45'N, (2) 5°S vent area, (3) Nibelungen vent at 8°18'S and (4) Lilliput diffuse vent field at 9°S. While one part deals with the dependency of the fluid and mineral composition on the tectonic activity, the type of basement rock (basalt, peridotite) and the pressure-temperature conditions, another main focus is on geo-bio interfaces and the investigation of chemical species (especially sulfur species and redox speciation and complexation of metals) in the fluids, which is vital for the organisms living in and from the fluids. Interested readers are here referred to the companion PhD thesis by my colleague V. Klevenz, entitled "Geo-bio interactions in hydrothermal fluids from the Mid-Atlantic Ridge: the role of organic ligands", and another recent publication by Koschinsky and Sander (in revision). The Ph.D. project presented here was intended to investigate the composition and temporal evolution of hydrothermal fluids in the ultramafic-hosted Logatchev-1 field and further vent fields in different geological settings along the MAR, coupled to the interdisciplinary research of the SPP1144; with the focus to relate chemical fluid signatures in different settings to geochemical processes in the seafloor. The study aimed to broaden our knowledge about hydrothermal activity at slow-spreading ridges and mass fluxes between the lithosphere and the hydrosphere (and biosphere). At the beginning of the SPP1144 program, no information

about the temporal evolution of hydrothermal flow at the MAR was available. Thus, one major focus was on the short-term as well as medium-term changes in the fluid geochemistry of hydrothermal vent fields investigated during this program, with the latter being performed by the investigation of hydrothermal manganese crusts, which potentially record changes in the fluid geochemistry over the last several thousand years. Further, Fe-Mn oxide deposits may provide information about hydrothermal export and removal fluxes. The working areas were the Logatchev-1 hydrothermal Field, which is located south of the Fifteen Twenty Fracture Zone at 14°45'N at the eastern axial valley of the Mid-Atlantic Ridge in ultramafic rock talus, the newly discovered Nibelungen field at 8°18'S, located about 9 km off axis the presently active rift valley in old pillow lava, and the vent field area at 5°S, spatially linked to fresh volcanic lava flows. Between 2004 and 2008, I participated in four research cruises and was able to obtain scientifically very valuable suites of fluid samples and oxidic Fe-Mn deposits for my project.

Chapter 1: The first chapter provides an introduction into hydrothermal activity at slow-spreading mid-ocean ridges and develops the larger theoretical context by giving an overview on the geology of slow-spreading axes, on water-rock interaction in ultramafic mantle rocks, on the effects of phase separation, and on hydrothermal fluxes (export, removal).

Chapter 2 discusses the fluid elemental and gas composition of high-temperature and low-temperature emanations in the ultramafic Logatchev-1 field and provides an evaluation of the temporal evolution of this field since the first fluid sampling in 1996 (Douville et al., 2002). The fluid and solid samples for this study were obtained during SPP1144 cruise M60/3 in 2003, followed by cruise M64/2 in 2005. The Logatchev-1 field is characterized by different vent architectures and chimney mineral compositions, which intended the evaluation of site-specific differences of fluid compositions within the Logatchev-1 field. The paper further aimed to investigate the uptake of elements and elemental associations in sulfide particles forming in the fluids in the initial mixing zone with seawater. The fluid sampling system KIPS (Kiel Pumping System), which was used to obtain the hydrothermal fluid samples, was developed and handled by Dr. Dieter Garbe-Schönberg, while my supervisor Dr. A. Koschinsky, a college from Brazil, Dr. L. de Cavalho and me, did the sample treatment and first on-board analyses. In the home laboratory, an analytical program for the elemental composition of the hydrothermal fluids was developed, in close cooperation with Dr. D. Garbe-Schönberg. This first paper strongly benefited from repeating discussions with my supervisor A. Koschinsky and with D. Garbe-Schönberg, which contributed also the introductory part and the outline of the paper, and with other specialists within the SPP1144 (to name a few: T. Kuhn, S. Petersen, H. Strauss).

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The intention of **Chapter 3** was to investigate the fluid geochemistry and hydrothermal fluxes in an actively phase-separating, post-eruptive hydrothermal system hosted in basaltic rocks in the newly discovered vent field at 5°S. This field, composed of three separate fields venting fluids of different temperatures but at similar water depth, provides the opportunity to evaluate the net effect of temperature and phase separation on the fluid composition. At Turtle Pits, the highest yet reported temperatures for mid-ocean ridge hydrothermal fluid were measured with 425°C and the fluids represent a chloride-depleted vapor phase with a distinct chemical composition. Due to the great water depth of these vent fields (3000 m), fluid temperatures >400°C cause phase separation close to the critical point of seawater, which has important implications on metal solubility and complexation. Further, repeatedly observed releases of vapor blows of extremely high temperatures indicate a highly dynamic hydrothermal circulation in the seafloor. Such systems were not able to be investigated before and strongly improve our understanding of hydrothermal activity in deep-seated settings. Further, the study contributes to the discussion of elemental fluxes from the lithosphere to the hydrosphere. The field work was done by A. Koschinsky and D. Garbe-Schönberg. My contribution to this study was part of the analytical work as well as discussions with the co-authors on the depth of water-rock interaction and the effects of phase separation.

This paper has been published in Geology:

Koschinsky, A., Garbe-Schönberg, D., Sander, S., **Schmidt, K.,** Gennerich, H.-H., Strauss, H., 2008. *Hydrothermal venting at pressure-temperature conditions above the critical point of seawater, 5°S on the Mid-Atlantic Ridge. Geology* 36(8): 615-618.

Chapter 4 is a comprehensive study of the fluid geochemistry of the Nibelungen hydrothermal vent, newly discovered at 8°18'S, MAR in 2006 during the SPP1144 cruise M68/1 and re-sampled in 2009 during SPP1144 cruise M78/2. The Nibelungen field is affected by ultramafic rock alteration, as indicated by dissolved gas data (Melchert et al., 2008). The study reports the first fluid elemental data for Nibelungen and the first oxygen and hydrogen isotopic data for hydrothermal fluids from mantle rock settings, completed by new major and trace element data for Logatchev-1 from 2007 (SPP1144 cruise MSM04/3). The intention for the paper came from the observation of a geochemical fingerprint very similar to

the Logatchev-1 hydrothermal field, which enlarges the number of high-temperature hydrothermal systems located in mantle rocks and led to the definition of an ultramafic fluid signature including trace elements and stable isotopes. The study aimed to quantify geochemical processes defining the elemental and isotopic composition of hydrothermal fluids at Nibelungen with a special focus on alkali metals and stable isotopes. The field work with the collection of samples and first analytical measurements on boards was conducted by A. Koschinsky, V. Klevenz in the Nibelungen field and by me in the Logatchev-1 field. As mentioned before, D. Garbe-Schönberg was in charge of maintenance and handling of the KIPS fluid sampling system, while I was in charge of the Major fluid samplers used in the Logatchev field in 2007. Dr. Wolfgang Bach introduced me into the field of geochemical reaction path modeling of stable isotopes with the code GWB and was of great help for the discussion of fluid pathways in the host rocks of the Nibelungen field. The analytical work was done in the home laboratory by me as well as by D. Garbe-Schönberg at CAU Kiel. Prof. Harald Strauss from the Wilhelms-Universität Münster in collaboration with P. Königer (LIAG) provided the oxygen and hydrogen isotopic data. All co-authors contributed with their experience in scientific writing to the quality of the paper.

This paper is in press in Chemical Geology:

Schmidt, K., Garbe-Schönberg, D., Koschinsky, A., Strauss, H., Jost, C.L., Klevenz, V., Königer, P., *Fluid elemental and stable isotope composition of the Nibelungen hydrothermal field (8°18'S, Mid-Atlantic Ridge): Constraints on fluid-rock interaction in heterogeneous lithosphere. Chemical Geology In Press, Accepted Manuscript.*

Chapter 5: High-temperature hydrothermal fluids venting along the ridge axis are different in their absolute REY (rare earth elements and yttrium) content, but are characterized by similar distributions with strong positive Eu anomalies and LREE (light rare earth elements) over HREE (heavy rare earth elements) enrichments in chondrite-normalized pattern. The idea for this paper developed after observing unusual, highly heterogeneous REY compositions in extremely hot, vapor phase hydrothermal fluids from the 5°S vent system and first discussions with my college D. Garbe-Schönberg. The REY content of hydrothermal fluids is controlled by temperature, solution complexation, Eh, and secondary mineral formation. The Turtle Pits and Comfortless cove vent fields at 5°S represent young, post-eruptive hydrothermal systems and are characterized by phase separation at temperatures >400°C, and the distinct REY distribution in the emanating fluids might be related to the specific physico-chemical conditions and/or limited water-rock interaction. The question arose if the REY distribution in the fluids is related to the specific physico-chemical conditions and might offer new insights into the controlling parameters of REY distribution of fluids venting at such conditions or not. The finding of chimney anhydrite minerals at Turtle Pits and anhydrite particles filtered from the analyzed fluids displaying broadly similar REY distributions as determined in the

hydrothermal fluids further pushed the progress paper. The discussions with Dr. M. Bau and Dr. D. Garbe-Schönberg strongly improved my understanding of REY geochemistry in solution and during mineral uptake and improved the quality of the manuscript. The REY separation method for low-REY solutions has been developed by my supervisor Michael Bau. Dieter Garbe-Schönberg analyzed the chimney anhydrites and provided an independent REY separation method check, while the fluid analytical work and the chemical analyses of fluid particles have been done in the home lab at JUB. The determination of particle mineralogy was done in collaboration with Dr. S. Petersen from IfM Geomar Kiel.

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Schmidt, K., Garbe-Schönberg, D., Bau, M., Koschinsky, A., 2010. Rare earth element distribution in >400 C hot hydrothermal fluids from 5°S, MAR: The role of anhydrite in controlling highly variable distribution patterns. *Geochimica et Cosmochimica Acta* 74(14): 4058-4077.

Chapter 6, entitled “*Manganese and Fe-Mn mineralization in the Logatchev I hydrothermal field, Mid-Atlantic Ridge: implications for elemental fluxes at low-temperature emanation sites in active high-temperature vent fields*”, focuses on the mineralogy and geochemistry of oxidic deposits found in and close to the Logatchev-1 hydrothermal vent field and represent the second part of the thesis. The intention for this study came up by the finding of stratified Mn crusts and other Fe-Mn deposits during the first research cruise M60/3 in 2003 by my supervisor A. Koschinsky and her colleges from Kiel (T. Kuhn, S. Petersen). The formation of stratified Mn crusts is known to be related to the by upwelling diffuse fluids, which represent an important source of elements in oxide deposits in proximal settings. Such deposits have the potential to represent archives of the evolution of the high-temperature fluid circulation. Furthermore, Stratified Mn crusts and other oxidic deposits in high-temperature hydrothermal systems can provide information on hydrothermal export and removal fluxes. The collaboration with colleges from other institutions allowed me to follow a multidisciplinary approach: X-ray diffraction (XRD) analyses for mineralogical studies were conducted in collaboration with the Christian-Albrechts-Universität Kiel (Dr. D. Garbe-Schönberg), while Dr. J. Hein from USGS did microscopic work with Secondary Emission Microscope (SEM). Dr. P. Andersson (Natural History Museum, Stockholm) provided isotopic analyses for Nd and Dr. M. Brauns (Universität Gießen) for Os, and the determination of Hf isotopes was done together with Dr. C. Münker in Westfälische Wilhelms-Universität Münster. The analytical work for the determination of major and trace elements was done in collaboration with the Christian-Albrechts-Universität Kiel (first analyses) and later in the home laboratory at JUB. The concept of the chapter developed after the chemical data were complemented by isotopic data, resolving variable hydrothermal contributions to the oxide deposits. The manuscript strongly benefited from discussions with my supervisors A. Koschinsky and M.

Bau on trace metal accumulation including REY and HFSE (high field strength elements) in Fe and Mn oxides, as both have a strong background in this research. The idea for another manuscript dealing with the HFSE composition in hydrogenetic ferromanganese crusts was born by M. Bau. Further, helpful discussions with J. Hein and S. Petersen (IfM Geomar Kiel) improved the quality of the chapter.

A condensed version of this chapter will be submitted, with the co-authors A. Koschinsky, M. Bau, J. Hein, P. Andersson, and M. Brauns.

Chapter 7: This chapter summarizes my further contributions as co-author to other relevant studies conducted within the SPP1144 research, which are related to the general field of hydrothermal fluid geochemistry.

Chapter 8 provides the conclusions derived from this study in the broader context of hydrothermal research.

1. Introduction

[1] Hydrothermal circulation in young oceanic crust along mid-ocean ridges has long been recognized to play a fundamental role for global heat flux and the geochemical cycles between the lithosphere, the hydrosphere, and the atmosphere (German and Von Damm 2004, Elderfield and Schultz, 1996). The interaction between seawater and oceanic lithosphere buffers the composition of the oceans and alters the composition of the lithospheric rocks, which in turn controls magmatic processes in subduction zones. It is been calculated that the mass of the ocean is recycled through the crust every 30 Ma. Hydrothermal activity is mainly driven by magmatic heat and hydrothermal convection of seawater plays an important role to balance the magmatic heat input. About 50% of the total hydrothermal heat flux released from mid-ocean ridge axes is extracted by high-temperature hydrothermal fluids (German et al., 2010a) while the rest of the hydrothermal heat loss occurs by low-temperature fluid flow on-axis and off-axis in ridge-flank crust up to roughly 65 million years in age. Global chemical fluxes are strongly modified by axial high-temperature export fluxes, on- and off-axis export and removal fluxes, and biogeochemical processes in hydrothermal plumes (Elderfield and Schultz, 1996).

1.1 Slow-spreading Mid-ocean ridges

[2] During the first decade of research on hydrothermal systems at mid-ocean ridges, scientists focused dominantly on fast-spreading ridges like the East Pacific Rise (EPR). In the last two decades, more interest in slow- and ultraslow spreading ridges (<60mm/yr full rate) aroused and the relevance of hydrothermal systems at these classes of spreading axes became clear (Bach and Früh-Green, 2010). About 50% of the cumulative global ridge-axis length is comprised by slow- and ultraslow spreading ridges (Sinha and Evans, 2004) and extends from the Arctic Ocean, along the entire Mid-Atlantic Ridge (MAR) and into the Indian Ocean (Southwest Indian Ridge, SWIR) which implies that hydrothermal activity at slow- and ultraslow spreading ridges, if common, plays a significant role for global heat and geochemical fluxes.

[3] Contrasting modes of plate separation determine the differences in ocean crust architecture, ridge morphology, and alteration history (Fig. 1). Fast-spreading ridges are characterized by continuous magma supply in accordance with plate extension, while plate separation at slow-spreading ridges is often accommodated by tectonic extension with only episodic magma supply. This results in contrasting crustal architecture: While fast-spreading ridges show a relatively uniform “layer cake” structure with a sequence of basalt, diabase, sheeted dyke complexes and gabbro, slow- and ultraslow-spreading ridges are characterized by an irregular lithosphere with variable thickness and heterogeneous composition. The composition of the lithosphere at slow-spreading ridges range from pure amagmatic (i.e.

mantle lithosphere exposed at the seafloor) to a continuous magmatic crust formed by episodic intrusion and extrusion of magma. According to recent models the ridge structure varies along-axis, with more typical mafic oceanic crust at segment centers and core complex formation related to detachment faults at segment ends (Searle and Escartin, 2004; Cannat et al., 1995). Upper mantle sequences are exposed at detachment faults and often accompanied by plutonic rocks, and are common in many places along the MAR (Smith et al., 2008). As a result of plate separation, the brittle lithosphere is commonly disrupted by axial-parallel, deep-reaching normal and detachment faults extending 10-30 km off-ridge axis, thinning the magmatic crust and possibly exhuming mantle lithosphere, which offers pathways for circulating fluids (Gràcia et al., 2000; Escartin et al., 2008). Caused by the plate separation mode, slow- and ultraslow spreading ridges are characterized by deep axial valleys with typical water depth below 3000 m, which is in contrast to generally lower water depth of fast-spreading ridges.

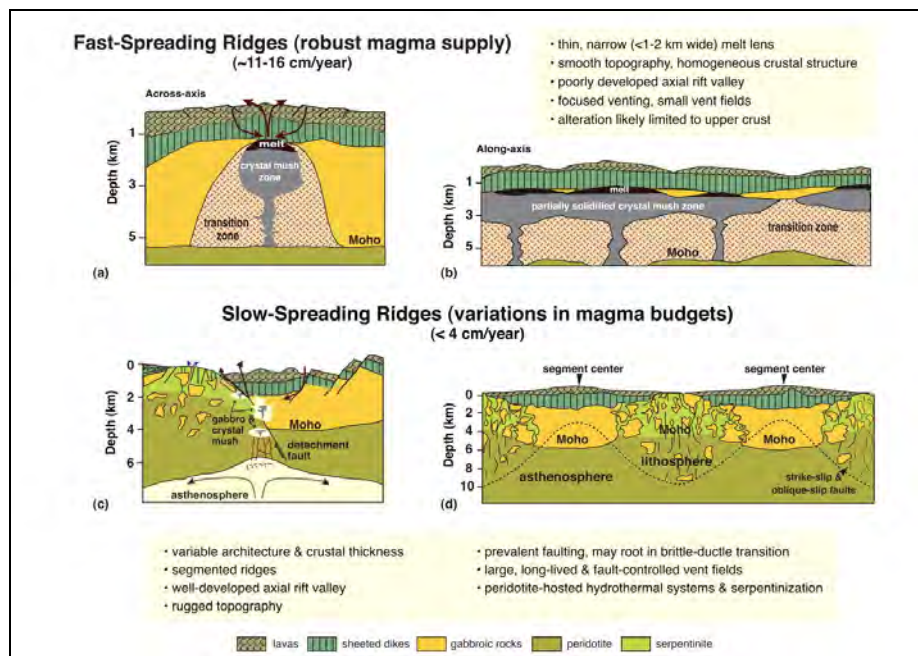


Figure 1: Schematic cross-sections (across and along axis) of the oceanic lithosphere at fast-(a) and slow-(b) spreading ridges, demonstrating the contrasting modes of plate separation, taken from: Bach and Früh-Green (2010).

[4] Slow- and ultraslow spreading ridges are characterized by frequent hydrothermal activity (Fig. 2). While the heat supply is the first-order control on the global distribution of hydrothermal activity, as evident from a positive correlation of site frequency and spreading rate, ultraslow-spreading ridges are much more efficient in supporting active vent fields than fast-spreading ridges, inferred from the higher magmatic delivering rate-normalized site frequency (Baker et al., 2004). This may indicate direct cooling of upper mantle, heat supplied by exothermic serpentinization, deep-mined heat, and magma focusing at volcanic centers. On average, high-temperature hydrothermal systems on slow- and ultraslow-

spreading ridges occur with a frequency of about 100 km (German et al., 2010). As has been discussed in Devey et al. (2010), however, the potential of the ridge axis to host high-temperature or low-temperature hydrothermal systems will depend on the tectonic and magmatic activity on the individual segments. At fast-spreading ridges the distribution of hydrothermal systems is mainly controlled by magmatic processes, while the activity of the hydrothermal fields at slow- and ultraslow spreading ridges is probably linked to the existence of the deeply penetrating faults, providing fluid pathways with access to the host rocks and efficient heat extraction (e.g., McCraig et al., 2007; Schroeder et al., 2007).

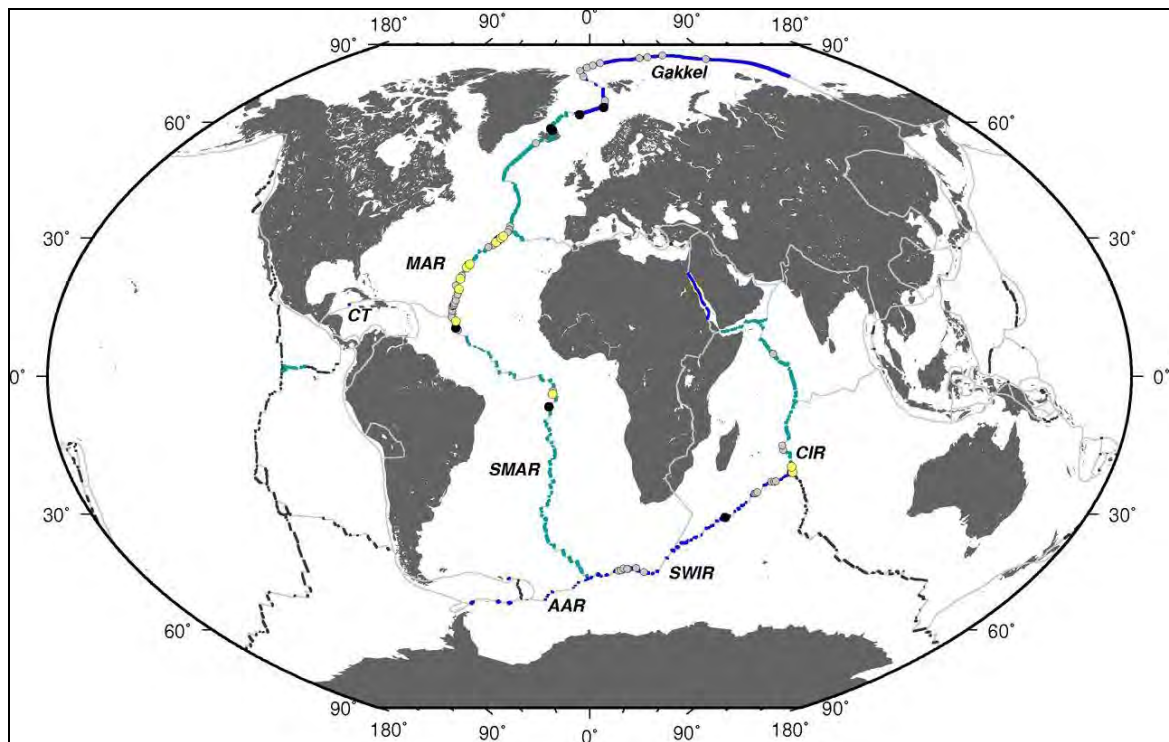


Figure 2: Inferred (grey circles), confirmed (black circles) and sampled (yellow circles) hydrothermal vent systems at slow- and ultraslow spreading ridges (not included: Cayman Trough, German et al., 2010), taken from: Edmonds (2010)

[5] Heterogeneous lithosphere rocks make up at least 25% of slow-spread crust composed of ultramafic rock containing gabbro intrusions (Cannat et al., 1995; Teagle et al., 2009). The diverse composition of the oceanic lithosphere at slow-spreading ridges, ranging from altered mantle rocks to thick-layered mafic crusts has a strong impact on chemical and heat fluxes between the hydrosphere and lithosphere in associated hydrothermal systems and likely plays an important role for the ocean chemistry.

[6] Considering the geological settings, the following effects and consequences for hydrothermal alteration at slow-spreading ridges can be assumed:

1. Hydrothermal systems at slow- and ultraslow spreading ridges can be active for longer periods, leading to the deposition of large ore bodies.

2. Greater depths of rift valleys imply the possibility for higher vent fluid temperatures and for phase separation by brine condensation above the critical point of seawater 298 bar/407°C; Bischoff and Rosenbauer, 1988).
3. Different lithologies lead to a greater variety of hydrothermal alteration and different hydrothermal fluxes.
4. Common occurrence of prevalent axial-parallel faults makes off-axis localities possible and favors the alteration down to lower oceanic crust and in mantle rocks lithologies along detachment faults.

[7] The vent fields discovered so far along the MAR, including recent discoveries within the SPP1144 program and on other, ultraslow-spreading ridge axes, display a high variety of hydrothermal activity compared to fast-spreading ridges, encompassing: low- and high-temperature venting influenced by peridotite rock alteration, hydrothermal systems affected by the alteration of exposed lower oceanic crust, high-temperature off-axis hydrothermal venting, hydrothermal systems indicating the presence of highly altered oceanic crust in the subseafloor, the deepest systems (up to 5000 m) located so far, and also hydrothermal systems being characterized by active phase separation above the critical point of seawater, associated with volcanic activity (see below). Furthermore, the MAR hosts the largest massive sulfide ore deposits at modern spreading axes. Hydrothermal systems on slow-spreading ridges have a tendency to be longer-lived than their fast-spreading counterparts, as evident by long histories of focused high-temperature flow (Lalou et al., 1993). Hydrothermal systems on fast-spreading ridges are characterized by shorter activity periods related to repeated magmatic activity and changes of heat and mass flux at time scales of days to decades. This stability is in general agreement with suggestions made by Fontaine et al. (2008) who proposed that along-axis variations in lithosphere thickness associated with the magmatic and tectonic segmentation of slow-spreading ridges should favor the formation of large and centrally located vent fields, mining heat on several kilometers along axis and leaching the lithosphere up to a few tens of kilometers along axis. However, this model does not explain the stability of off-axis hydrothermal fields like Logatchev. The fault-controlled setting of many hydrothermal systems possibly allows a more constant hydrothermal convection compared to hydrothermal systems driven by magmatic eruptions, with the heat being mined from heat sources further away (Petersen et al., 2009).

1.2 Hydrothermal activity at slow-spreading ridges – spatial and temporal characteristics

[8] At present, 14 hydrothermally active vent fields have been discovered along the slow-spreading Mid-Atlantic ridge, encompassing both low- and high-temperature venting at the seafloor (Fig. 3). Besides the well known vent fields TAG (26°N, Rona et al., 1986), Broken Spur (29°N, Murton et al., 1995), Menez Gwen (37°50'N, Fouquet et al., 1995), Menez Hom

(37°10'N, Fouquet et al., 2002), Lucky Strike (37°17'N, Langmuir et al., 1997), Saldhana (36°N, Barriga et al., 1998), Rainbow (36°14'N, Fouquet et al., 1998), Lost City (30°N; Kelley et al., 2001), Logatchev 1-4 (14°45'N, Krasnov et al., 1995), and Snakepit (23°N, Detrick et al., 1986), this also includes the recently discovered fields on the southern MAR – 5°S (Haase et al., 2007), Nibelungen (8°18'S, Devey et al., 2005), and Lilliput (9°33'S, Koschinsky et al., 2006) and the Ashadze vent fields 1-4 (13°N, Beltenev et al., 2003). A fluid data compilation is given in Edmonds et al. (2010), not including the newly discovered fields Ashadze, Nibelungen, and Lilliput.

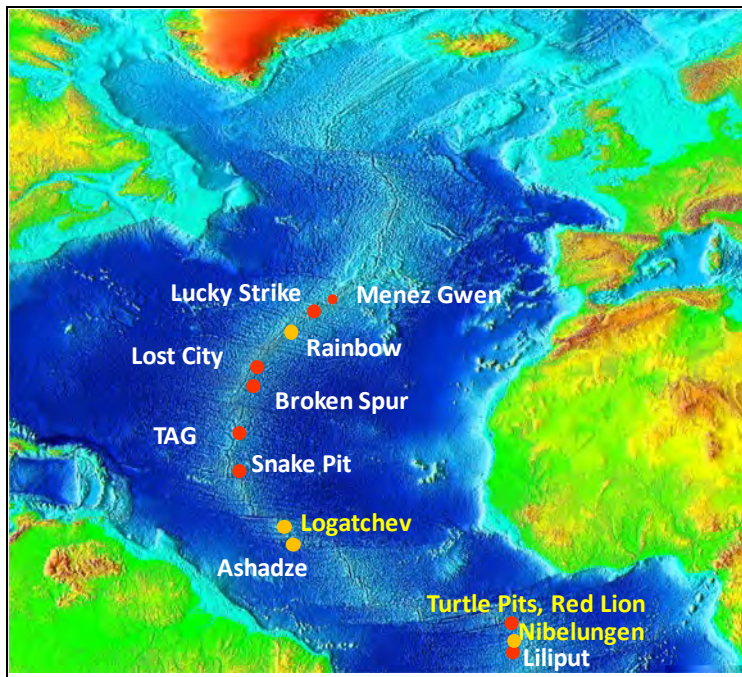


Figure 3: Positions of hydrothermal vent fields at the Mid-Atlantic Ridge, orange coloured circles indicate ultramafic host rocks, the low-temperature vent field “Saldhana” is not shown on this map

[9] Of these, Saldhanha (warm, CH₄-rich fluids), Rainbow (>350°C, above seawater salinity), Logatchev-1 (350°C, seawater salinity), and Logatchev-2, Ashadze-1 and -2 (310-375°C, variable salinity) and Lost City (70-90°C, alkaline pH) are hosted in ultramafic, serpentinized mantle rocks, and characterized by strong enrichments of H₂ and CH₄, low Si activities and strongly reducing conditions (Douville et al., 2002; Charlou et al., 2002, 2008; Kelley et al., 2005). The fluid geochemistry of the newly discovered Nibelungen field is part of the present study; first indications refer to ultramafic-rock-seawater interaction (Melchert et al., 2008). Many more hydrothermal ore deposits have been discovered by dredging especially by Russian scientists, including the largest sulfide deposit at the MAR – Krasnov at 16°38'N (e.g., Beltenev et al., 2006). More than 30 more active vent fields are inferred by plume studies (c.f., Edmonds et al., 2010), many of them probably located in ultramafic mantle rocks (e.g., Charlou and Donval, 1993; Charlou et al., 1998).

[10] Along the Central Indian Ridge (CIR), two hydrothermal fields were discovered and sampled – Kairei and Edmond (Gamo et al. 2001; Van Dover et al. 2001; Gallant and Von Damm, 2006; Nakamura et al., 2009). High-temperature hydrothermal activity has been inferred from water column anomalies indicating hydrothermal plume dispersal and from dredging at the South West Indian Ridge (SWIR; Bach et al., 2002; Baker et al., 2004, Tao et al., 2007), the Gakkel Ridge (Edmonds et al., 2003; Baker et al., 2004), in the Lena Trough (Snow et al., 2001), at Knipovich Ridge (Donnelly et al., 2007), and the Cayman Trough (German et al., 2010). From the results obtained so far, a high diversity of hydrothermal activity is indicated: Knipovich Ridge and SWIR host ultramafic hydrothermal systems; while Cayman Trough host ultramafic-hosted but also TAG-type hydrothermal systems. At the CIR, lower oceanic crust is altered. Based on the frequency of ultramafic rock outcrops at the seafloor along the MAR and other slow-spreading ridges (see Früh-Green et al., 2004 and references therein), ultramafic-hosted hydrothermal systems can be expected to be common.

[11] Long hydrothermal activity is evident at TAG (for more than 120 000 years; Lalou et al., 1993), at Logatchev I with 58 000 years and from Ashadze I with 35 000 years (Cherkashev et al., 2008), while the age of the extinct massive sulfide deposits at Krasnov is as old as 119 000a (Cherkashev et al., 2008).

[12] Many of the hydrothermal systems localized to far along slow- and ultraslow-spreading ridges are very deep-seated systems: Ashadze (3300-4530 m), Broken Spur, TAG (>3000 m), Cayman hydrothermal field (>5000 m), and also the hydrothermal systems-hosting spreading axes Gakkel Ridge and SWIR have deep rift valleys with water depth >3000m up to 5000 m (Baker et al., 2004).

[13] For those systems from which information about a temporal evolution is available, hydrothermal activity remains rather stable (TAG, MARK (Snakepit): Edmonds et al., 2010 and references therein). At the fast-spreading EPR, hydrothermal fluids are often affected by changing compositions at short time scales (Butterfield et al., 1994), which is related to common magmatic activity. Before the discovery of 5°S vent fields, hydrothermal systems in similar geological settings have not been observed at the MAR and the temporal response to magmatic events remained unclear. The stability of heat and chemical fluxes due to hydrothermal venting, as often observed at MAR hydrothermal systems has important implications for the quantification of regional and global heat and mass fluxes.

1.3 Serpentinization of abyssal mantle rocks

[14] Serpentinization conditions in oceanic peridotites range over wide pressure (p)- and temperature (T) conditions, often associated with fluid flow deep into the lithosphere along

prevalent (detachment) faults (Teagle et al., 2009). Mantle rock lithologies outcropping at the seafloor are found at many places along Mid-ocean ridges as well as in transform faults.

Serpentinite-hosted hydrothermal vents differ significantly from basaltic-hosted hydrothermal systems, with distinct fluid chemistry. The occurrence of hydrothermal activity associated with mantle rock alteration is often linked to off-axis tectonic fault zones (Lost City, Logatchev-1, Nibelungen – (Kelley et al., 2001; Melchert et al., 2008; Petersen et al., 2009), which provide fluid pathways and may promote access to, and penetration of, mantle lithologies. At present, two types of hydrothermal systems affected by ultramafic rock alteration can be distinguished: (1) Lost City, emanating fluids with temperatures $<90^{\circ}\text{C}$ and alkaline pH, very low Si activity, high dissolved H_2 and CH_4 concentrations, and very low transition metal concentrations (Kelley et al., 2001, 2005), and (2) Logatchev-1 and 2 at 15°N , MAR (Charlou et al., 2002, 2007; Douville et al., 2002), Ashadze-1 and 2 at 13°N (Charlou et al., 2007) and Rainbow at 36°N , MAR (Douville et al., 2002; Seyfried et al., 2004), emanating fluids with temperatures $>300^{\circ}\text{C}$, and acidic pH, moderate Si activity, high dissolved H_2 and CH_4 concentrations and high transition metal concentrations. During seawater–mantle rock interaction, peridotite is hydrated in a multi-step reaction of olivine to brucite, followed by the breakdown of brucite and the formation of serpentine and magnetite, which is accompanied by the formation of large amounts of hydrogen (e.g., Bach et al., 2006). Iron-Ni alloys form because of strongly reducing conditions (e.g., Klein and Bach, 2009). The formation of high amounts of CH_4 and other hydrocarbons in ultramafic-hosted hydrothermal systems result from the abiotic reduction of CO_2 under strongly reducing conditions which is likely catalyzed by Ni-Fe alloys and/or oxides (Fischer-Tropsch-Type synthesis — Proskurowski et al., 2008; Foustoukos and Seyfried, 2004). At temperatures above 300°C , the alteration of mantle rocks is dominated by the hydration of orthopyroxenes, with the formation of alteration minerals like tremolite and talc (Allen and Seyfried, 2003). The low pH of high-temperature fluids is controlled by the alteration assemblage tremolite-talc-serpentine and has as strong impact on metal solubility (Allen and Seyfried, 2003).

[15] The type of ultramafic rock alteration (serpentinization, rodingitization, staetization) depends on fluid circulation pathways and protolith lithology. For a comprehensive introduction on the history of mantle rock research, the occurrence of mantle rocks at the seafloor and on serpentinization of oceanic peridotites, the reader is referred to the PhD thesis of Klein (2009) and references therein. Detailed experimental and theoretical investigations of serpentinization reactions at different pressure (p)-temperature (T) conditions and protolith composition have been conducted by Bach et al. (2004), Bach and Klein (2008), Klein et al. (2009), Klein and Bach, (2009), McCollom and Bach (2009), Allen and Seyfried (2003, 2004), Seyfried et al. (2007), Seyfried et al. (2004), Jankecky and Seyfried, (1986), Wetzal and Shock (2000), and mineralogical studies of mantle-rock alteration in drill cores are presented in Bach et al. (2006). Type and sequence of serpentinization reactions depend on

the composition of the protolith, conditions of water-rock interaction, fluid-rock reaction pathways and fluid flux, and produce fluids with highly variable pH and silica activities (Alt et al., 2009 and references therein). The work by Bach et al. (2006) and subsequent investigations by his group was critical for a better understanding of the sequences of serpentinization reactions at different p - T conditions and protolith compositions.

[16] The fluid chemical characteristics with enhanced silica activities of the high-temperature vent systems in ultramafic host rocks are not in full agreement with experimental and theoretical studies on serpentinization (Allen and Seyfried, 2003; Wetzel and Shock, 2000). Although the metastable alteration of pyroxene minerals at $T > 350^\circ\text{C}$ buffers enhanced Si concentrations in the alteration fluids relative to olivine alteration (Allen and Seyfried, 2003) and could explain smaller Si enrichments, an additional Si source in these systems is likely. Exothermic serpentinization reactions are not sufficient to produce enough heat to drive a high-temperature hydrothermal circulation (Allen and Seyfried, 2004); thus, the high-temperature hydrothermal systems observed in ultramafic rock settings require an additional (magmatic) heat source and are probably affected by hybrid alteration of both mafic and ultramafic lithologies (Douville et al., 2002, Schmidt et al., 2007, German and Lin, 2004).

[17] Due to the breakdown of serpentinites during subduction, water and fluid-soluble elements are released into the mantle wedge affecting the generation and composition of arc magmas. As a common component of oceanic lithosphere, the subduction of serpentinites has a strong influence on global geochemical processes (Kerrick, 2002).

[18] Further, hydrothermal systems fueled by ultramafic-rock alterations are interesting with respect to the evolution of early life, as such sites may be analogous to those where life may have originated (Martin et al., 2008).

1.4 Geochemical behavior of elements in hydrothermal systems

[19] The elemental and isotopic composition of hydrothermal fluids is determined by the host rock composition and the geochemical behavior of elements during water-rock interaction. Besides the total bulk rock composition, critical for individual elemental concentrations in the fluid are the specific physico-chemical conditions in the reaction zone defining phase equilibria (p , T , pH, redox state), the transport capacity of the fluid during ascent (e.g., available ligands, total Cl content, pH, T , sulfur activity), phase separation, water-rock ratios and sulfide/sulfate precipitation during ascent below and at the seafloor (Hemley et al., 1992; Seewald and Seyfried, 1990; Seyfried and Ding, 1995).

1.5 Temperatures of hydrothermal fluids

[20] The temperature of hydrothermal fluids venting at the seafloor commonly ranges between 350°C and about 400°C, while inferred maximum temperatures in the reaction zone are generally higher and range up to 445°C (e.g., Fontaine et al., 2009; Coumou, 2009 and references therein). Temperatures of circulating hydrothermal fluids are imposed by thermodynamic properties of the solutions, which depend on temperature and pressure. It has been shown by Jupp and Schultz (2000), and Geiger et al. (2005) that upwelling hydrothermal plumes have a natural tendency to form at 400°C (pure water) or at about 420°C (seawater-like salinity) where the advective energy transport of the solutions is maximized (fluxability model), which implies cooling in most of the hydrothermal systems investigated so far. Coumou and coworkers (2008) have shown that the energy transport in hydrothermal convection cells is maximized when upflowing water reaches temperatures of about 400°C and down-flowing water in a proximal recharge zone reaches temperatures of about 200°C. Pure water above the critical point of seawater has been used as closest approximation to seawater in these simulations, while simulations including the full-phase relations of seawater have shown that the overall narrow shape of the upwelling plume remains similar in spite of phase separation in Coumou (2009).

[21] Large hydrostatic pressures due to a greater depth of magma reservoirs cause temperatures of upwelling fluid to be higher. While at 400 bars, the temperature cannot exceed 420°C, at 500 bar temperatures up to 500°C are possible and have been shown to exist in fluid flow simulations (Geiger et al., 2005; Coumou et al., 2009). As fluid expansion and diffusion during long upwelling paths to the seafloor causes heat loss, the hottest fluid temperatures are expected at large seafloor depth but shallow magma chamber, due to limited energy loss during fluid ascent (Geiger et al., 2005). Such conditions are given when magmatic activity associated with magma extrusion happens at deep, slow-spreading ridges.

[22] The fluid temperature strongly affects the solubility of metal complexes in solution and thus, metal mobility and the hydrothermal flux into the hydrosphere. Further, the temperature of a hydrothermal fluid, which crosses the 2-phase boundary of seawater, determines the type of phase-separation with vapor formation below the critical point of seawater (CP_{SW}) or brine condensation above the critical point of seawater. Depending on the physico-chemical conditions, this will modify the chemistry of the venting hydrothermal fluids and thus the hydrothermal export fluxes. In single-phase fluids, the degree of complexation increases with T and decreasing p as conditions above the critical point of seawater are approached, as the complex stability is inversely correlated with water density and dielectric constant. Metal-chloride complexes like $FeCl_3^0$ are thus most stable in low- p , high- T region (Ding and Seyfried, 1992). Close to the critical point of seawater, fluids are characterized by special physico-chemical properties. Metal complexation is strongest at the

critical point, as aqueous charged species should be present as neutral species that permits enhanced metal transport (Von Damm et al., 2003).

1.6 Phase separation of hydrothermal fluids

[23] Boiling and phase separation have a first order effect on the geochemistry of hydrothermal fluids because gases, chloride and metals forming chloride complexes will separate into the respective vapor and brine phases. Hydrothermal systems characterized by phase separation found so far are subject to significant changes with time (e.g., Von Damm et al., 1997).

[24] Phase separation means that a single homogeneous fluid phase splits into two coexisting fluid phases. In two-component systems like NaCl-H₂O, coexisting liquid and vapor differ in physical properties but also in composition. Critical behavior occurs along critical curve, which is defined by the critical points of a given fluid composition and is not uniquely defined in terms of p and T . The critical point of a defined system composition defines the pressure and temperature at which liquid and vapor attain identical physical and chemical properties. Phase separation can either occur by *boiling*, when the p - T evolution of an initially homogeneous fluid intersects the two-phase surface on the liquid side of the critical curve of the system and vapor bubbles nucleate from the liquid, or by *condensation* upon intersection of the two-phase curve on the vapor side, which implies the formation of liquid droplets from the vapor (Liebscher et al., 2007). The p - T conditions at which phase separation of seawater occurs are reflected in the liquid-vapor two-phase boundary of the 3.2 wt% NaCl isosalinity p - T section of the H₂O-NaCl system (Fig. 4). While in the literature the terms "subcritical" and "supercritical" fluid phase separation are used to indicate whether phase separation occurs at p - T conditions below or above the CP_{SW} (298 bars, 407°C; Bischoff and Rosenbauer, 1988), these terms are avoided in this thesis and replaced by boiling or condensation, in agreement with the definitions suggested by Liebscher et al. (2007).

[25] With rising pressure along the liquid-vapor equilibrium curve, the density of the vapor in equilibrium with the brine phase rises. Opposite to phase separation by boiling with the formation of gas-rich vapor of very low chlorinity and density, at conditions above the CP_{SW}, brine condenses and leaves a complementary slightly Cl⁻ depleted and relatively dense vapor phase. Around the CP_{SW}, the differences between vapor and brine are only minor. The degree of partitioning of elements between vapor and brine decreases with increasing temperature, but increases with increasing density difference away from the CP_{SW} (Pokrovski et al., 2002, 2005, Liebscher et al., 2005). Besides the species volatility, a key factor in controlling metal transport by vapor-phase fluids is the density. With increasing density of the vapor phase in equilibrium with the brine phase close to and above the CP_{SW}, the ability of the vapor to hydrate aqueous volatile species and complex metal species increases dramatically (Pokrovski

et al., 2005; Williams-Jones et al., 2002). The formation of ion-water clusters significantly enhances the solubility of elements with low volatility in the vapor phase. Details on the experimentally determined partitioning of elements and gases between vapor and brine phases at different condition can be found in Foustoukos and Seyfried, 2007a; Liebscher et al., 2005; Pokrovski et al., 2005, 2008; Shmulovich et al., 2003).

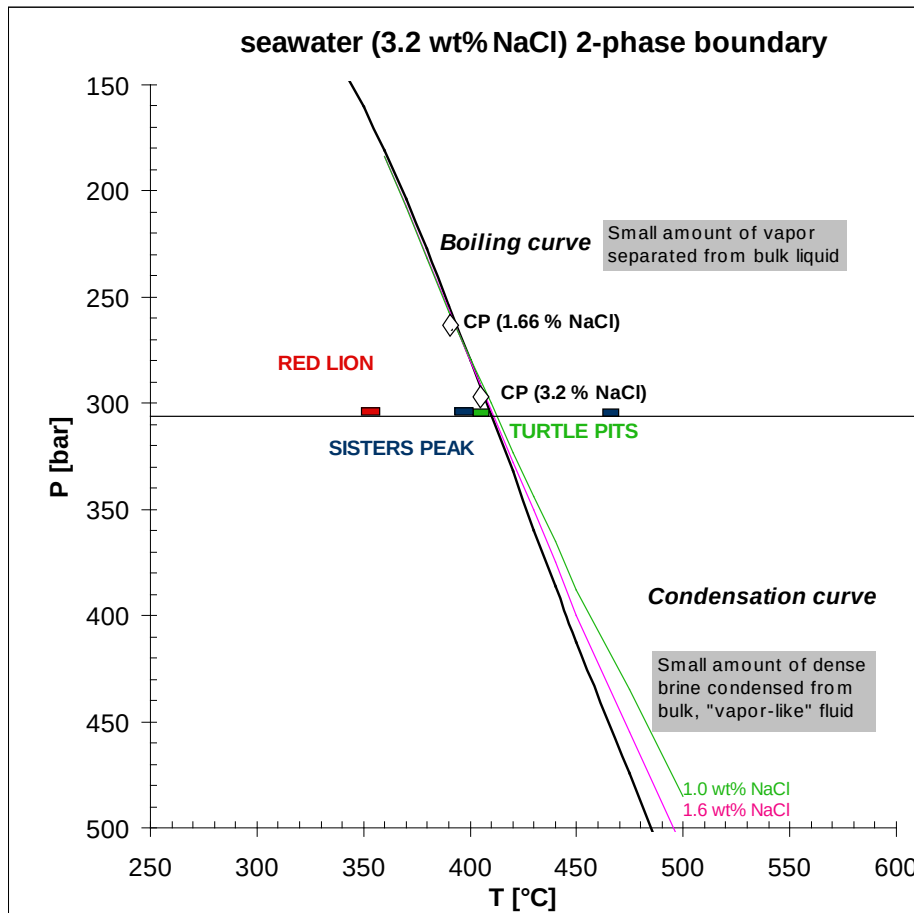


Figure 4: Liquid-vapor two-phase boundary of the 3.2 wt%, 1.6 wt%, and 1.0 wt% NaCl isosalinity p - T sections of the H_2O -NaCl system, and the position of Red Lion, Turtle Pits and Sisters Peak (black smoker at Comfortless Cove) in the pressure-temperature diagram

[26] In recent years, computational fluid-flow simulations had a strong impact on the understanding of hydrothermal circulation dynamics and the physical effects of phase separation processes. Phase separation, and the depth at which this occurs, appear to be first-order controls on the salinity of vent fluids and its variation in space and time (Coumou et al., 2009). As shown in simulations of low-pressure systems, low-salinity vapors and high-salinity brines can vent simultaneously, with boiling occurring over the length of the upflow zone. In contrast, high-pressure systems with phase separation above the CP_{sw} , phase separation is limited to the region close to the underlying magma chamber, and vent fluids consist of a single-phase low-salinity vapor mixed with a seawater-like fluid during ascent, resulting in uniform vent salinities in time and always below seawater salinity. Depending on

the depth of the seafloor and the depth of the magmatic heat source, phase separation may or may not occur by brine condensation.

[27] Phase separation above the CP_{SW} has been inferred for many hydrothermal systems (e.g., Lucky Strike, Broken Spur and TAG at MAR: Coumou et al., 2009 and references therein; Main Endeavor Field on the Juan de Fuca Ridge and 9°50'N on the East Pacific Rise: Butterfield et al., 1994; Seyfried et al., 2003; Foustoukos and Seyfried, 2007b), but the fluids could never be directly sampled under *in situ* p - T conditions above the critical point of seawater (CP_{SW}). In the course of vent site discoveries at the southern MAR and the research activity within the SPP1144, such fluids could be sampled for the first time in the Turtle Pits vent field at a water depth of 3000 m (Koschinsky et al., 2008).

1.7 Hydrothermal fluxes and the value of Fe- and Mn oxide deposits

[28] Hydrothermal circulation has been recognized as important for geochemical cycles between the lithosphere and in the hydrosphere. Altered rocks act either as a source or as a sink for elements dissolved in the oceans, depending on the composition of the lithosphere rocks and alteration conditions. High-temperature hydrothermal fluids are enriched in Ca, SiO_2 , alkalis, base metals, and sulfide but, due to low-temperature alteration, the net effect of the alteration of oceanic crust is the uptake of alkali elements, as well as other elements like B, Mg, P, sulfate and U in the crust (e.g., Elderfield and Schultz, 1996). The alteration of heterogeneous lithologies at slow-spreading ridges including peridotites probably has major consequences for long-term, global geochemical fluxes, differing from those of mafic-rock alteration. The consequences of the alteration of heterogeneous lithosphere on global chemical exchange budgets are poorly constrained. Serpentinization results in uptake of H_2O , C, S, U, B, Cl, LREE and generation of hydrogen and methane, and Ca (Früh-Green et al. 2004), while seafloor weathering of serpentinite acts as a source of Mg for the oceans (Snow and Dick 1995). It is assumed that the total fluxes of B, Sr, Li, Os, H, C may be differently influenced compared to seawater exchange with mafic rocks (Teagle et al., 2009; Alt et al., 2009). The possibility for a net hydrothermal export flux depends in the geochemical behavior of the individual elements during mixing of fluid with seawater.

[29] Hydrothermal fluxes into the open ocean can occur via high-temperature venting or via low-temperature venting. The net effect of high-temperature hydrothermal export fluxes is determined by processes happening at the emanation sites and in the hydrothermal plumes, which modify gross hydrothermal fluxes to the deep ocean. For many elements, hydrothermal plumes act as a net *sink* in the ocean chemical budgets. This is related to the formation of polymetallic sulfides close to the vent sites and to the formation of Fe (III) oxyhydroxide particles in the buoyant and non-buoyant plume, which affectively co-precipitate or scavenge dissolved elements in the plume, which are either sourced from the hydrothermal fluids (e.g.,

Cu, Zn) or dominantly from seawater (oxyanions, REE, Ni – German et al., 1990; German and Von Damm, 2003; Rusakov, 2009). As the ocean water mass is estimated to pass through hydrothermal plume systems once every 10^3 – 10^4 yrs, this particle scavenging may have a significant impact on global geochemical cycles of some elements in the ocean. Except for Mn, net hydrothermal fluxes of dissolved metals are strongly reduced by the formation of sulfides in buoyant plumes and scavenging to particulate Fe oxyhydroxides in buoyant and non-buoyant plumes, which prevents a significant hydrothermal contribution to the dissolved metal budgets in the ocean. However, organic complexation in hydrothermal plumes has recently been recognized as possible pathway to increase the hydrothermal flux of dissolved metals from the lithosphere to the hydrosphere, as it prevents precipitation as sulfides and oxidation. The stabilization of dissolved Fe and Cu by organic ligands could result in increased hydrothermal fluxes of dissolved Fe and Cu in the deep ocean and have estimated with up to 22% (Fe) and 9% (Cu) (Koschinsky and Sander, in revision; Bennett et al., 2008; Toner et al., 2009).

[30] Export fluxes of metals in hydrothermal plumes are mainly associated with Fe oxyhydroxide particles and, as calculated in German et al. (2010), represent fluxes that have been scavenged from seawater (like REE, oxyanions) within the buoyant and non-buoyant plume rather than from hydrothermal fluids while others like Cu and Zn are mainly sourced from fluids. Oxide particles forming in the buoyant and non-buoyant plumes can be transported over long distances into the open ocean away from the vent sites or settle down to the seafloor and are incorporated into the sediments, depending on the ocean currents and the oxidation rate of Fe(II) and aggregation of particles. Plumes can migrate for distances as large as 2000 km (Lupton, 1995), but may be much more restricted in their dispersal in the MAR rift valley (Rusakov et al., 2009).

[31] An important effect of ultramafic rock alteration at high temperatures may have the high metal/sulfide ratio in the venting fluids, which implies that only a small fraction is precipitated as sulfides, while the overwhelming majority of Fe is oxidized and forms Fe(III) particles. This will result in enhanced removal fluxes of scavenged elements sourced from seawater but also from the hydrothermal fluid (German et al., 2010). In the light of organic complexation, limited sulfide precipitation close to the vent sites could then also result in enhanced fluxes of dissolved, fluid-sourced metals.

[32] A plurality of plume studies focusing on chemical fluxes have been conducted, to name a few focusing mainly on slow-spreading ridges: Rusakov, 2009 (TAG, Broken Spur), German et al., 2002 (13°N, EPR), Edmonds and German, 2004 (Rainbow), Cave et al., 2003, German et al., 2010 (Rainbow), Statham et al., 2005 (Karei plume).

[33] Hydrothermal export fluxes are not restricted to hydrothermal plume dispersals resulting from high-temperature venting but may be also important from low-temperature emanations for some elements. Powerful tools to investigate hydrothermal fluxes at high- and low-temperature vent sites are Fe and Mn oxide precipitates. Formed as plume fallout accumulations or as primary precipitates of low-temperature hydrothermal fluids, these precipitates record export hydrothermal fluxes into the ocean in different parts of the system.

1.8 Hydrothermal fields investigated within this project and related scientific questions

While first water column surveys and the deployment of an autonomous underwater vehicle (AUV) led to the localization and visual observation of the Turtle Pits vent at 4°48'S, MAR during a British research cruise in 2005 (German et al., 2008), it was not until the beginning of the SPP1144 program south of the equator that further hydrothermal fields were discovered and sampled at the southern MAR and that vapor phase fluids formed above the critical point of seawater (298 bars, 407°C) could be sampled directly. The PhD project presented here focuses on certain scientific questions within this program, while further results considering the fluid geochemistry and heat fluxes in these systems were published in Keir et al. (2008) and Melchert et al. (2008).

The following hydrothermal fields have been investigated during this project:

- (1) The area at 4°48'S is located at the center of a ridge segment in 2990 m depth and comprises 4 active vent fields named *Turtle Pits (TP)*, *Comfortless Cove (CC)*, *Red Lion (RL)* and *Wideawake* (Koschinsky et al., 2006, Haase et al., 2007, Koschinsky et al., 2008). At TP and CC, low-chlorinity hydrothermal fluids vent at stable temperatures up to 407°C (Koschinsky et al., 2006). The fields are hosted by lava flows, with very fresh lava found at Turtle Pits, which are proposed to be related to the seismic event in 2002 in this area (German et al., 2008; Haase et al., 2007). This recent magmatism probably provides the shallow heat source driving the fluid circulation. In contrast, the Red Lion vent field located north of TP and CC, emanates hydrothermal fluids with seawater-like salinity at temperatures of about 350°C (Haase et al., 2007). The Wideawake site is a diffuse field, which is likely fed by TP high-temperature fluids, as indicated by chemical data (Haase et al., 2007). The region at 5°S not only offers the opportunity to observe the temporal response of a hydrothermal system to an eruptive event on a slow-spreading ridge but also to investigate the effect of phase separation above the critical point of seawater.
- (2) At 8°18'S, the *Nibelungen hydrothermal vent* has been discovered about 9 km off-axis the present ridge axis of the A2 segment, located at a prominent fault scarp in a sedimented pillow-lava area and with fluids venting solely from a single crater-like

structure (Koschinsky et al., 2006, Melchert et al., 2008). First chemical fluid data indicate an unusual composition with low ^3He and strong enrichments of hydrogen and methane (Melchert et al., 2008). While the first may indicate an old, degassed heat source like cumulative gabbro, the latter probably results from the alteration of mantle rocks (Melchert et al., 2008).

- (3) The *Logatchev-1 hydrothermal field* is located at 14°45'N, MAR at 3000 m water depth, situated on a plateau on the eastern flank of the rift valley about 7 km away from the neovolcanic zone (Batuev et al., 1994; Petersen et al., 2009). In this region, uplift of upper mantle sequences occurs along large detachment faults and results in core complex formation (Smith et al., 2008). According to McCaig (2008) and Petersen et al. (2009) the Logatchev I field is, in analogy to the Rainbow field at 36°14'N, located at the ultramafic footwall of a detachment fault, allowing for extensive penetration of seawater into the footwall

The similar water depth in all three within the SPP1144 program investigated high-temperature hydrothermal fluids of about 3000 m, together with variations in host rock composition on one hand and on fluid temperature/ phase separation on the other hand offers the unique possibility to compare the individual effects of different parameters on fluid composition.

The specific questions for this project have been formulated as:

- How are the type of substrate rock and physical conditions including temperature and pressure reflected in the composition of hydrothermal fluids and precipitates (Fe-Mn crusts and plume particles) in the working areas? *Chapters 2,3,4,5,6*
- Which geochemical processes determine the fluid composition in settings with heterogeneous lithosphere, can they be quantified? – *Chapters 2,5*
- Can we identify chemical fingerprints characteristic for the different systems at the MAR, such as basaltic-hosted (Turtle Pits at 5°S) versus ultramafic-hosted (Logatchev at 15°N), high-temperature (Turtle Pits at 5°S) versus moderate temperature (Red Lion at 5°S) *Chapters 2,3,5*
- How do p-T conditions influence the reactivity and the composition of hydrothermal fluids in systems at large water depth? What are the consequences of temperature and phase separation close to and above the CP_{SW} on the hydrothermal fluid compositions? *Chapters 3 and 4*
- What is the medium-term temporal fluid variability (range of several years) in hydrothermal fields depending on the geologic situation? *Chapters 2,3,4,5*
- How does phase separation above the CP_{SW} influence the temporal evolution of a hydrothermal system on the MAR? Do models developed for Pacific systems apply? *Chapter 3*

- How are geochemical signals of hydrothermal activity and temporal evolution preserved in marine chemical precipitates? *Chapter 6*

The SPP1144 program involved numerous research cruises to formerly known and newly discovered vent sites, and the sampling campaigns provided new data every year and added more and more information about the hydrothermal activity at the slow-spreading MAR. Thus, the succession of the individual manuscripts of this dissertation presented in chapters 2, 3, 4, 5, and 6 is partly attributed to the incoming data of the research cruises. While the 5°S vent fields have been firstly sampled in 2005, with repeated sampling in 2006, 2008, and 2009, high-quality fluid samples for the Nibelungen vent field have not been obtained before 2009 (first sampled in 2006), which is reflected in the late publication of chapter 5.

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Chapter 2

Geochemistry of hydrothermal fluids from the ultramafic-hosted Logatchev hydrothermal field, 15°N on the Mid-Atlantic Ridge: Temporal and spatial investigation

Geochemistry of hydrothermal fluids from the ultramafic-hosted Logatchev hydrothermal field, 15°N on the Mid-Atlantic Ridge: Temporal and spatial investigation

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Abstract

Mantle-derived ultramafic rocks commonly occur on the seafloor at slow-spreading axes and are tectonically emplaced along shear zones. Since the early 1990s, a growing number of hydrothermal systems have been detected in ultramafic settings. But chemical data for fluid compositions in active systems are still limited. Besides the Logatchev field at 15°N on the Mid-Atlantic Ridge (MAR), the only other active high-temperature (>300 °C) hydrothermal field known to be strongly influenced by ultramafics is the Rainbow field at 36°N on the MAR. The field at Logatchev consists of six active vent sites at about 3000 m water depth, situated along a NW–SE-trending line with distances of 50–200 m between the individual sites. The vent sites were mapped in detail and re-sampled during two cruises in 2004 and 2005 using a ROV. The geochemical composition of the hydrothermal fluids is characterized by very high concentrations of dissolved methane and hydrogen (up to 3.5 mM and 19 mM, respectively) related to serpentinization processes in the reaction zone. Together with moderate Si concentrations of 9 mM, a depletion in B compared to seawater and Li concentrations lower than in basaltic systems, this fluid composition has been identified as characteristic signature of high-temperature hydrothermal fluids reacting with ultramafic rocks. However, additional alteration of gabbroic intrusions is likely. The fluid composition is very similar at all vent sites, indicating a common source in the reaction zone and little variation during upflow. Spatial differences in fluid composition were observed between smoking craters and the complex chimney system IRINA II, but are restricted to elements with strong temperature-controlled solubility, as Cu and Co. These differences can be related to different exit temperatures (up to 350 °C and <300 °C, respectively). Concentrations of rare earth elements, and chondrite-normalized patterns with LREE enrichment and positive Eu anomalies are comparable to those of basaltic-hosted systems, thus indicating minor influence of host-rock composition. A comparison of published fluid composition data from 1996 [Douville, E., Charlou, J.L., Oelkers, E.H., Bienvenu, P., Jove Colon, C.F., Donval, J.P., Fouquet, Y., Prieour, D., Appriou, P., 2002. The Rainbow vent fluids (36°14'N, MAR): the influence of ultramafic rocks and phase separation on trace metal content in Mid-Atlantic Ridge hydrothermal fluids. *Chemical Geology*, 184: 37–48.] with our own data indicates that the system remained stable over the past nine years. There is no clear indication of phase separation taking place at Logatchev. Mineralogical and

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chemical composition of the rocks, reaction temperature, and partly sub-seafloor mixing with entraining seawater are supposed to be the main controlling parameters of fluid geochemistry in the Logatchev field.

As it is known that more ultramafic-hosted hydrothermal systems exist along slow-spreading ridges, this type of hydrothermal systems might have a significant influence on the elemental budget of the oceans. Detailed information about the fluid geochemistry and its spatial and temporal variations is an important prerequisite for an estimation of elemental fluxes in ultramafic-hosted systems and their relative importance compared to basaltic-hosted systems.

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1. Introduction

Since the discovery of submarine hydrothermal systems it has been recognized that they play an important role for the oceanic cycle of many elements (Butterfield et al., 2003; Lowell et al., 1995). However, the quantification of hydrothermal contributions to the elemental budget of the ocean is restricted because of the lack of knowledge on the number of sites, heat flow, scales and changes of fluid input and chemistry with time. In particular hydrothermal systems characterized by boiling of fluids and phase separation are subject to significant changes with time (e.g., von Damm et al., 1997). Boiling and phase separation have a first order effect on the fluid geochemistry because gases, chloride and metals forming chloride complexes will separate into the respective vapor and brine phases. To our knowledge, no time-dependent investigations have been carried out in systems at great water depth (≥ 3000 m) where phase separation may take place at supercritical conditions (above the critical point of seawater, which is 407 °C at 298.5 bars, Bischoff and Rosenbauer, 1988). Also, not much is known about the temporal variability in hydrothermal fields in which hydrothermal circulation and water–rock interactions are (at least partly) driven by serpentinization reactions of mantle rocks. However, the continuous sampling of hydrothermal fluids at the Rainbow field over 10 years indicates a stable system (pers. comm. Jean-Luc Charlou). Such systems may play an important role for heat and material output into the ocean at slow-spreading ocean ridges (Lowell and Rona, 2002). Along the Mid-Atlantic Ridge, three hydrothermal systems with temperatures above 40 °C are known to be active in serpentinized ultramafic settings: (1) the Rainbow vent field at 36°14'N (Charlou et al., 2002; Douville et al., 2002), (2) the Logatchev vent field at 14°45'N on the MAR (Batuev et al., 1994; Douville et al., 2002), and (3) the low-temperature field Lost City at 30°N (up to 90 °C; Kelley et al., 2001, 2005), which is located 15 km west off-axis and is completely different in its mineralogy, chemistry and associated fauna compared to the other systems.

Further ultramafic-hosted systems (active and inactive) were discovered along slow- and ultra-slow spreading ridges: the Saldanha field (diffuse venting, Dias and Barriga, 2006), Ashadze (sulfide deposits, Beltenev et al., 2003) and the Lena Trough (fresh massive sulfides, Snow et al., 2001). Recent evidence for hydrothermal activity in ultramafic environments has also been reported for the Southwest Indian Ridge (Bach et al., 2002) and the Gakkel Ridge (Edmonds et al., 2003). This increasing number shows, that ultramafic-hosted systems are common along slow- and ultra-slow spreading ridges.

The Logatchev hydrothermal field was discovered in 1993–1994 in about 3000 m water depth on the eastern rift mountain of the MAR south of the Fifteen–Twenty fracture zone at 14°45'N (Batuev et al., 1994). The main characteristic of the spreading ridge segment at 14°45'N is the presence of serpentinized peridotite outcropping on the eastern and western walls of the ridge axis. The Logatchev field offers a high diversity of high- and low-temperature fluid emanations (up to 350 °C, Douville et al., 2002), precipitates, plumes and fauna associations (Sudarikov and Roumiantsev, 2000). The few fluid data from the Logatchev field published so far are, compared to other vent fields from the northern MAR, intermediate for most metals and reflect ultramafic as well as mafic rock influences (Douville et al., 2002; Charlou et al., 2002).

Within the frame of the 6-years Special Priority Program 1144 of the German Science Foundation DFG entitled “From Mantle to Ocean: Energy, Material and Life Cycles at Spreading Axes” two research cruises with R/V Meteor to the Logatchev field were carried out recently: cruise M60/3 (Jan./Feb. 2004; Kuhn and Shipboard Scientific Party, 2004) and cruise M64/2 (April 2005, Lackschewitz and Shipboard Scientific Party, 2005). The principal scientific purpose of these cruises was to elucidate the inter-relationship of geological and biological processes in this active, ultramafic-hosted hydrothermal system, and its medium-term variability within a few years. In addition, the observed spatial heterogeneity in terms of structural setting, morphology, and biological community structure of the

different vent sites was to be substantiated by fluid chemical data. In this paper, we report detailed geochemical investigations of hydrothermal fluid samples recovered at different vent sites during the two cruises and a first assessment of temporal changes and spatial differences within this field.

Compared to the Rainbow vent field which is strongly influenced by phase separation (emanation of high-chlorinity fluids), the Logatchev fluids show no, or no significant, influence of phase separation (see chlorinity data in Douville et al., 2002). This allows a more straightforward interpretation of water–rock interactions in ultramafic systems at very high temperature. Therefore, the detailed fluid geochemistry study presented here can provide an estimate on the importance of this type of vent systems on elemental budgets in the ocean.

2. Geological setting and description of sampling sites

In contrast to the fast spreading East Pacific Rise (EPR), the Mid-Atlantic Ridge (MAR) with its low spreading rates (<3 cm/yr, total rate) consists of ridge segments with a more discontinuous and irregular shaped structure. Tectonic processes dominate in relation to magmatic spreading. Large parts of the lithosphere in

slow-spreading ridge settings are composed of a mixture of partially serpentinized peridotites and gabbroic intrusions (Cannat, 1996). South of the 15°20'N fracture zone abyssal peridotites and gabbroic rocks are exposed on both flanks of the spreading axis due to tectonic faulting, associated with extension and crustal thinning. Ultramafic rocks recovered during drilling project ODP 209 in the 15°20'N area show complex alterations patterns due to hydrothermal alteration at temperatures up to 400 °C, with abundant serpentine, magnetite, relict tremolite and talc (Bach et al., 2004; Paulick et al., 2006). Rock samples obtained in the Logatchev area during research cruises M60/3 and M64/2 include peridotites (mainly harzburgites, some pyroxenites) as well as gabbroic rocks (Kuhn and Shipboard Scientific Party, 2004; Lakschewitz and Shipboard Scientific Party, 2005).

The hydrothermally active Logatchev field is situated at 14°45'N and 44°58' W on a plateau right below a 350 m high cliff at a water depth of 3060 m to 2900 m (Fig. 1). It extends at least 800 m in NW–SE and 400 m in SW–NE direction and shows a high diversity of vent sites and associated fauna (Kuhn and Shipboard Scientific Party, 2004; Lakschewitz and Shipboard Scientific Party, 2005). Two main areas of high-temperature hydrothermal activity make up the central



Fig. 1. Hydrothermal fields along the northern Mid-Atlantic Ridge; location of the Logatchev hydrothermal field.

part of the field: an area of at least three “smoking craters” (ANNA LOUISE, IRINA and Site B), and the large mound of IRINA II with black smoker chimneys at its top as well as the newly discovered QUEST smoking crater further to the NW (Fig. 2). The smoking craters have a 2–3 m deep central depression surrounded by a rim with 1–2 m elevation above the surrounding seafloor and a diameter up to 10 m (Lakschewitz and Shipboard Scientific Party, 2005). Small chimneys (50 cm up to 2 m) occur on the crater rims. Black smoke is intensely venting at all three sites, either from the chimneys on the crater rim or from holes in the ground within the craters (Fig. 3.3 and 3.5). Unfortunately, these holes were inaccessible for the ROV and, hence, this type of venting fluids could not be sampled directly. The maximum measured temperature for the Logatchev field is 350 °C (Douville et al., 2002), however, the authors didn’t mention a vent site. Maximum temperatures measured inside chimney

orifices at IRINA and ANNA LOUISE were 188 °C (station 249 ROV-11) and 210 °C (station 249 ROV-8), respectively, representing minimum temperatures (Lakschewitz and Shipboard Scientific Party, 2005). Measured in-situ temperatures for Site B chimneys are 300 °C (station 266 ROV-10) and 350 °C (station 257 ROV-8), respectively. In this environment the hydrothermal fauna is scarce.

IRINA II consists of a mound with steep slopes rising about 15 m above the surrounding seafloor with a basal diameter of about 60×40 m. Four vertical chimneys, several meters high, mark the top of the mound (Fig. 3.1). Several beehive structures have been observed, characterized by high thermal gradients due to intense mixing of hydrothermal fluid with seawater. The chimneys are densely overgrown with mussels (*Bathymodiolus* cf. *puteoserpentis*), accompanied by crabs, snails and limpets (for detailed description of vent fauna see Kuhn and Shipboard Scientific Party, 2004;

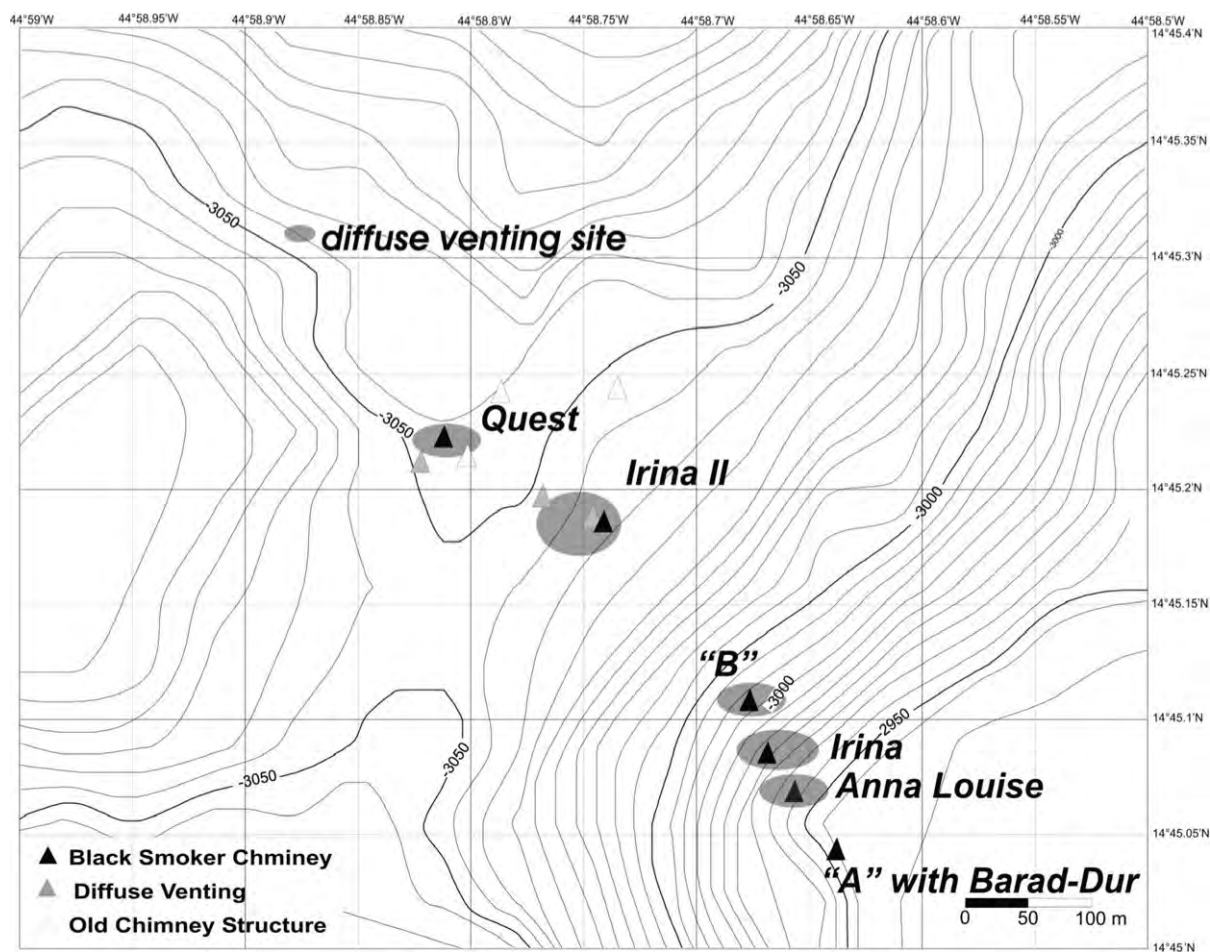


Fig. 2. Sketch map of vent sites in the Logatchev hydrothermal field.

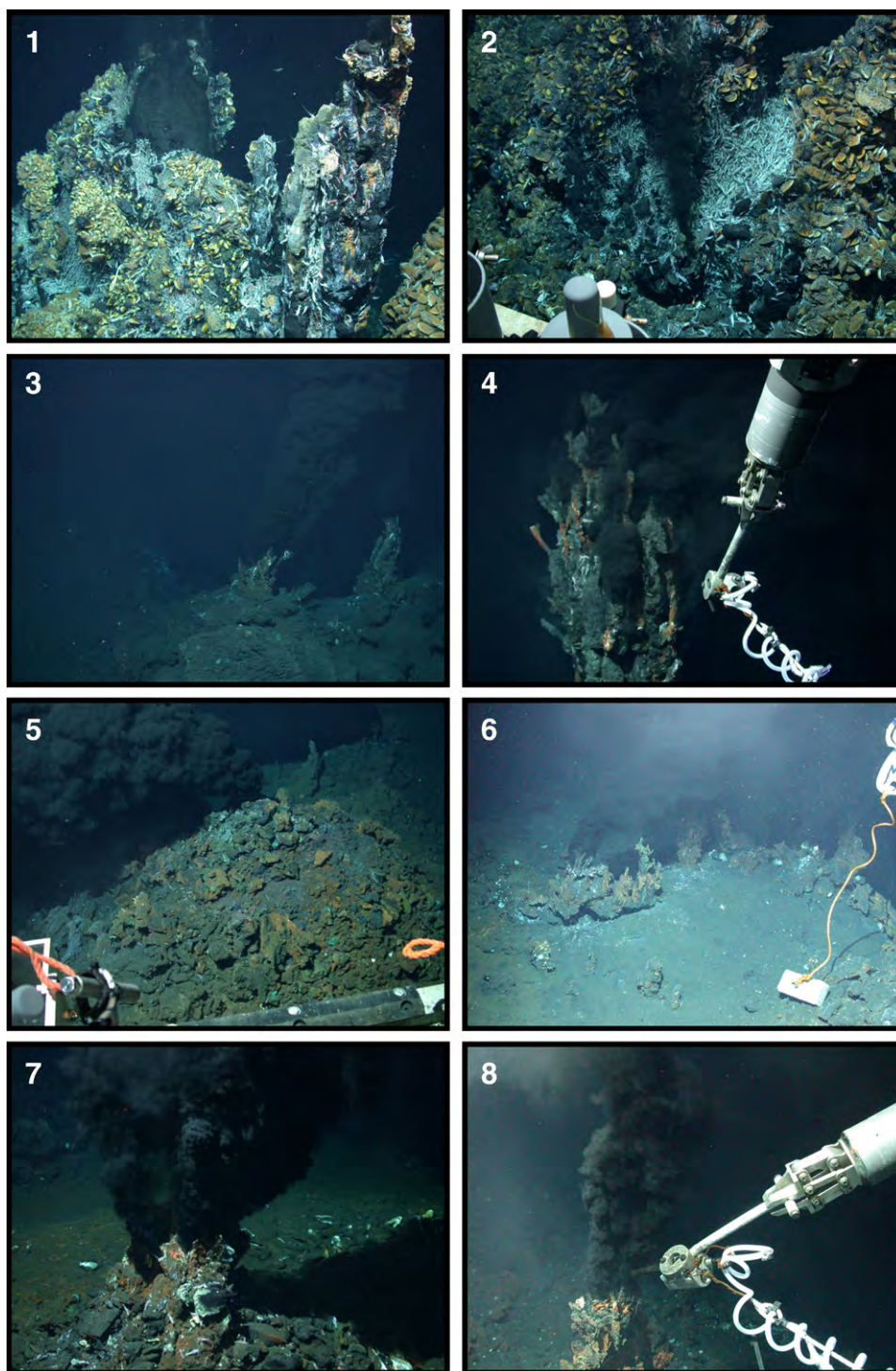


Fig. 3. Photo plate of sampling sites: 1) IRINA II main complex with chimney and beehive structures, dense mussel inhabitation; 2) Sampled fluid emanation at the base of IRINA II main complex (samples 277 ROV-5; 283 ROV-5), dense shrimp mat; 3) Site B smoking crater, sample 257 ROV-8 was taken from the smoker on the left, whereas sample 266 ROV-10 was taken from the smoker on the right; 4) Sampling of Site A chimney tower; 5) IRINA smoking crater with crater wall consisting of oxidized sulfide talus, sample 261 ROV-6 was taken from the emanating black smoke; 6) Site QUEST, sample 281 ROV-5 was taken from the chimney on the right; 7) Single black smoker at IRINA II, sample 224 ROV; 8) Fluid sampling at Logatchev with the KIPS pump system at ANNA LOUISE; copyright by MARUM, Univ. Bremen.

Table 1

Description of the sampling sites for hydrothermal fluids (2005) discussed in this paper; temperature data are minimum values

Vent site	Sample ID	<i>T</i> (°C)	Endmember fluid (%)	Description
IRINA II				
Main complex 3034 m	277 ROV-5	170	20	Emanating grey smoke from a small fissure at the base of the sulfide complex (eastern side), dense shrimp mat
	283 ROV-5		55	
Single black smoker 3034 m	224 ROV	225	75	Free-standing black smoker chimney SE of IRINA II
Mussel bed	232 ROV-3			Diffuse fluids
	232 ROV-7			Diffuse fluids
	266 ROV-7			Diffuse fluids
	277 ROV-4			Diffuse fluids
QUEST 3042 m	281 ROV-5	280	55	Black smoker chimney approx. 1 m high, Marker MC
Mussel bed	281 ROV-2			Diffuse fluids
IRINA 2963 m	261 ROV-6		70	Black smoker chimney at the southeastern crater rim of the smoking crater, Marker MD
Site B 2983 m	266 ROV-10	300	75	Black smoker chimney 1, southeastern crater rim of the smoking crater (right)
	257 ROV-8	350	98	Black smoker chimney 2, southeastern crater rim of the smoking crater (left), Marker MA

Lackschewitz and Shipboard Scientific Party, 2005; Gebruk et al., 1997, 2000). Active venting of grey smoke is restricted to small cracks at the basis of the sulfide structures and one chimney (Fig. 3.2). Measured in-situ temperature is 170 °C (station 183 ROV-5), again representing a minimum temperature due to the difficulty in getting access to the vent. The chimneys are surrounded by densely populated mussel beds and also by inactive chimneys and empty mussel shells further down the slope. A single black smoker a few meters south of the mound top emanates vigorous black smoke, with the in-situ fluid temperature up to 225 °C (station 224 ROV) (Fig. 3.7), again, representing a minimum temperature.

QUEST is a newly discovered high-temperature, black smoke venting site situated about 130 m WNW of the active chimneys of IRINA II (Kuhn and Shipboard Scientific Party, 2004). The formation of a depression, small chimneys and smoking pipes emanating black smoke give the QUEST site a similar appearance as the smoking craters on the main mound. However, QUEST does not show the typical circular crater rim and therefore may represent an early state of a developing smoking crater (Fig. 3.6). While the faunal composition grossly corresponds to that found at the smoking craters on the main mound, QUEST additionally harbored scattered clusters of mussels.

The southeastern end of the field is occupied by a 9 m high black smoker sitting on a 3 m-high mound of chimney

talus at Site A (Gebruk et al., 1997), which we named “Barad-Dûr” (Lackschewitz and Shipboard Scientific Party, 2005). There were no mussel beds at this site, and hydrothermal fauna was restricted to shrimps and crabs on the upper part of the smoker.

Approximately 200 m northwest of the QUEST field a site of diffuse venting was discovered in 2005 (Lackschewitz and Shipboard Scientific Party, 2005). It is characterized by brownish Fe-oxyhydroxide precipitates at the emanation site. Several inactive chimneys and oxidized chimney fragments have been described between IRINA II and Site B, north of IRINA II and around the smoking craters (Schreiber, 2006), thus indicating former hydrothermal activity at different places.

A summary of sampling locations for the hydrothermal fluids discussed in this paper is given in Table 1.

3. Methods

3.1. Fluid sampling

For the direct sampling of hydrothermal fluids from high-temperature vents a pumped flow-through system (Kiel Pumping System, KIPS) entirely made of inert materials (perfluoralkoxy, PFA, polytetrafluorethylene, PTFE, and high-purity titanium) was specially designed for the ROV QUEST. Samples are collected via a

titanium nozzle of 50 cm length, which can be directly inserted into the hot vent orifice. PFA tubing connects the sampling nozzle to 5–15 parallel PFA sampling flasks (675 ml volume each) and a mechanical gear pump mounted downstream to the sampling flasks. In its older version used during M60/3 each sampling flask had mechanical open-close valves with handles, which were operated by the ROV's manipulator. The whole system is contained within a plastic frame, which was mounted on the ROV's equipment sled. During cruise M64/2, a modified version of the system was used. Coiled PFA tubing (5 m length) connects the Ti sampling nozzle to 4 handle-operated open-close valves allowing the distribution of the vent fluids directly to either a series of 3×5 PFA sampling flasks (675 ml volume each, Savillex, USA) mounted in three racks, or to an in-line filter holder, or to a remotely controlled, motor-driven ulportiport valve (PETP/PTFE). The valve control software is fully integrated in the ROV control system (Marum Soft, Bremen). Parallel to the nozzle is an on-line temperature probe monitoring the in-situ temperature at the point of sampling. Before filling the sampling tube and sample bottles, they were first rinsed several minutes with the hydrothermal fluid.

In addition to the KIPS system for direct sampling of hot and diffuse fluids, three standard Niskin bottles mounted at the front of the ROV were used to sample the plume within the first meter above the vent outlet.

Besides hydrothermal fluid samples plume particles have been obtained from different vent sites. During M60/3 in-situ filtration with the KIPS was used to sample precipitates formed due to incipient seawater-fluid interaction at the vent outlet. In 2005 particles were sampled directly in the first meter of the rising plume, either with a slurp gun or a cloth net.

4. Analytical methods

All KIPS and Niskin samples were sub-sampled in the ship's laboratory immediately after recovery of the ROV. For dissolved gas analyses of hydrothermal fluid and seawater, sample was transferred via PVC tubing from KIPS and Niskin samplers into glass bottles and sealed headspace free by Teflon lined screw caps. The bottles were immediately connected to the purge and trap analytical system or a vacuum degassing unit for on-board analysis of methane or hydrogen, respectively. After sub-sampling for dissolved gas analyses, aliquots were taken and pressure-filtrated with Argon (99.999%) at 0.5 bar through pre-cleaned 0.2 µm Nuclepore PC membrane filters by means of polycarbonate filtration units (Sartorius, Germany). The filtrates were further subdivided into

aliquots for voltammetric and ICP analyses and acidified to pH 1 with 100 µl subboiled concentrated HNO₃ per 50 ml (ICP), and with suprapure HCl to pH 2 (voltammetry), respectively. Samples for speciation analyses and anion analyses were kept non-acidified. Another aliquot of the original hydrothermal fluid was acidified with subboiled HNO₃ until the precipitate was re-dissolved. All work was done in a class 100 clean bench (Slee, Germany) using only all-plastic labware (polypropylene, polycarbonate, perfluoralkoxy (PFA)). Ultrapure water (>18.2 MOhm) was dispensed from a Millipore Milli-Q system.

4.1. On-board measurements

The determination of pH and Eh (Mettler electrodes with Ag/AgCl reference electrode) was done in unfiltered sample aliquots immediately after sample recovery. To identify a possible influence of phase separation, all vent fluid samples and some samples from the water column profiles were analyzed for chloride by titration with AgNO₃ after the method of Fajans, using fluoresceine-sodium as indicator.

Methane was analyzed on-board applying a purge and trap technique (Seifert et al., 1999). The water sample is stripped by helium and methane in the outflowing gas stream is concentrated in a cooled trap (activated charcoal) at –84 °C. After degassing, the trapped gas is released to a gas chromatograph (CARLO ERBA GC 6000) equipped with a packed (activated Al₂O₃) stainless steel column and a flame ionization detector (FID) to detect and quantify the component. Recording and calculation of results are performed using a PC operated integration system (BRUKER Chrom Star). Analytical procedures were calibrated daily with commercial gas standards (LINDE). Analyses were generally done within 12 h after sampling.

For on-board measurements of dissolved hydrogen up to 615 ml of sample were connected to a high-grade vacuum in an ultrasonic bath and heated until boiling. Aliquots of the released gas were transferred via a septum from the degassing unit into the analytical system by a gas-tight syringe. A gas chromatograph (THERMO TRACE) equipped with a packed stainless steel column (Molecular sieve 5A, carrier gas: He) and a pulsed discharge detector (PDD) is used to separate, detect and quantify hydrogen. Recording and calculation of results are performed using a PC operated integration system (THERMO CHRO M CARD A/D). The analytical procedures were calibrated daily with commercial gas standards (LINDE).

For on-board speciation and trace metal concentration analyses, the electrochemical method of voltammetry was used. All the voltammetric measurements were performed using two Metrohm (Herisau, Switzerland) equipments:

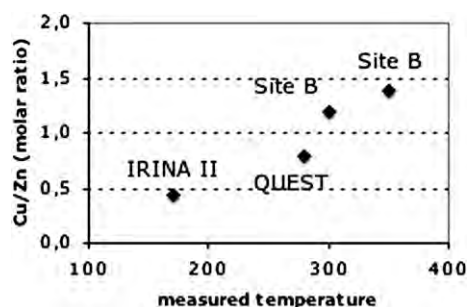


Fig. 4. Cu/Zn ratios in sampled fluids vs measured emanation temperatures for different vent sites; not plotted are Cu/Zn for IRINA (2.2) and IRINA II black smoker (0.8) because of unknown emanation temperatures.

a 693 V A processor in combination with a 694 V A stand and a 757 V A computrace run with a standard PC. For the decomposition of stable metal organic complexes, a UV Digester (Model 705, Metrohm) containing a high pressure mercury lamp (500 W) was used.

The voltammetric determinations of dissolved sulfide concentrations (after Metrohm Application Bulletin,

199/3e) and of the redox speciation of Fe, Cr and As were carried out immediately after sample recovery. The concentrations of active Fe (non-filtered), Fe(II) and Fe (III) were determined in the undigested samples using the cathodic stripping voltammetric method with 1-nitroso-2-naphtol as complexing reagent (Aldrich and van den Berg, 1998) and compared to total Fe concentrations in digested samples. Arsenic speciation was carried out in the undigested samples by cathodic stripping voltammetry (Barra and dos Santos, 2001). In this method, As(III) is determined in a 1 M HCl and 10 mg/l Cu(II) supporting electrolyte. Total As is determined after the UV digestion using the rotating gold electrode (Au-RDE; Application Bulletin Metrohm 226/2), and As(V) is calculated by subtraction of As(III) from total arsenic. The chromium redox speciation was carried out by the catalytic cathodic stripping voltammetric method using diethylenetriamine-pentaacetic acid (DTPA) as complexing reagent (Boussemart et al., 1992, adapted to hydrothermal fluid samples by Sander and Koschinsky, 2000). For Se and Te redox

Table 2

Chemical composition of selected original hydrothermal fluid samples and hydrothermal endmember concentrations (EM); seawater data are from Douville et al., 2002 and Charlou et al., 2002 (except for own data for Na, Cl, Si, SO₄, B, Co); BS: black smoker

	IRINA		Site B				QUEST	
	261 ROV-6		257 ROV-8		266 ROV-10		281 ROV-5	
	Measured	EM	Measured	EM	Measured	EM	Measured	EM
Mg mM		0		0		0		0
SO ₄ mM	10	2.1	4	1.3	9	2.5	16	3.3
H ₂ S mM	1.8	2.5	1.7	1.9	2.5	3.6	0.7	1.4
Cl, mM ^a	552		551		549		545	
Br, μM ^a	836		828		846		840	
B, μm	375	344	347	328	370	360	390	343
Si, mM	6.2	8.9	7.9	8.6	6.5	8.8	4.6	9.1
Al, μm	8.7	12.2	11.7	12.8	9.1	12.3	5.8	12.5
Na, mM ^a	457		440		456		461	
K, mM	18	25	22	23	21	24	17	25
Ca, mM	21	30	27	28	25	30	20	29
Li, μM	193	263	225	243	194	253	144	258
Rb, μM	20.9	29	25	28	19.6	26	12.7	23
Cs, nM	251	348	318	351	263	355	187	347
Sr, μM	117	130	122	125	119	130	107	127
Fe, μM	1700	2420	2200	2350	1830	2470	1220	2400
Mn, μM	244	347	302	330	255	345	180	354
Cu, μM	40.2	75.1	44.3	44.9	30.9	39.9	14	30.4
Zn, μM	18	32.6	32	32.5	26	33.3	18	38.3
Cd, nM	19.4	26.8	25.8	28.6	27.4	36.7	20.4	37.5
Co, nM	0.66	0.91	0.91	1.01	0.56	0.76	0.18	0.33
Pb, nM	67.9	94.5	104	115	139	187	93.6	174
Ag, nM	11.2	15.6	14.6	16.2	15.6	21.1	10.3	19.2
U, nM	6.5	3.4	3.6	2.4	6.5	3.7	7.6	1.8
Sb, nM	5.7	7.4	—	—	7.3	9.4	5.5	9.2
Mo, nM	39.6	14.3	19.4	10.0	30.1	4.1	58.1	18.5

^a Median values.

^b Average of median values.

speciation the simultaneous determination method described in Ferri et al. (1998) was used. Antimony speciation analysis was carried out in HCl medium (Quentel and Filella, 2002).

During cruise M64/2, Fe redox speciation was carried out with a photometric method. An orange–red ferriox complex formed by Fe(II) ions with 1,10-phenantroline in a pH range of 3–5 was measured with a Biochrom Libra S12 spectral photometer at 511 nm. Total Fe was analyzed by reducing all Fe with ascorbic acid. Fe(III) was determined as difference between total Fe and Fe(II).

4.2. Major and trace element analyses in the home laboratories

Major (Na, K, Mg, Ca, Ba, Sr, Si, Fe, Mn, B, Cl) and trace elements (Br, Li, Al, Cs, Ba, Sr, REE–Y, Fe, Mn, Cr, V, Cu, Co, Ni, Pb, U, Mo, As, Sb) were determined by ICP-OES (Spectro Ciros SOP CCD) and ICP-MS using both collision-cell quadrupole (Agilent 7500cs, Perkin Elmer 500 DRCE) and high-resolution sector-field based

instrumentation (Micromass PlasmaTrace2) (Garbe-Schönberg, 1993; Garbe-Schönberg et al., 1998). For the determination of REE–Y in hydrothermal fluids matrix separation with cation exchange columns was applied (Bau and Dulski, 1996). All metals were measured both in filtered and unfiltered aliquots. Insoluble precipitates in unfiltered aliquots were centrifuged and digested with HCl–HNO₃–HF in a pressure digestion system. Sulfate concentrations were determined photometrically with a Technicon Auto Analyzer (ESS method 370.2).

5. Results

5.1. Major elements and dissolved gases in high-temperature fluids

Logatchev high-temperature hydrothermal fluids have been sampled in 2004 and in 2005 at small chimneys in the smoking craters ANNA LOUISE, IRINA and Site B as well as at the single black smoker chimney at IRINA II. In addition, samples from the

IRINA II				Logatchev EM (based on all data)	Seawater
224 ROV-1		283 ROV-5			
Measured	EM	Measured	EM		
	0		0	0	53
8	1.5	14	1.7	1.3	29.5
		0.5	1.0	2.5	0
562		550		551 ^b	560
840		832		837 ^b	838
354	329	392	333	335	450
6.3	8.3	4.6	8.5	8.6	0.036
8.7	11.5	6.5	11.2	12	<0.1
452		464		455 ^b	480
21	24	18	25	24	9.8
23	28	21	30	29	10.2
197	253	152	259	252	26
20.6	26	12.9	23	27	1.3
249	345	195	349	343	2.3
114	122	110	132	127	87
1770	2350	1270	2340	2410	0.0045
250	331	192	355	338	0.0013
26.5	37.0	5.8	16.0	44	0.0033
34	47.9	13	36.2	36	0.028
34	47.0	20.6	36.6	32	0.7
0.51	0.72	0.04	0.07	0.75	<0.015
100	140	94.6	170	138	0.013
26	36.1	8.2	14.8	17	0.023
3.2	<0	8.1	3.1	3	14.3
–	–	6.3	10.4	8	1.2
23	<0	50.1	7.1	4	104

newly discovered smoking crater QUEST and Site A were obtained in 2005. Gray fluids venting more gently were sampled at the main structure of IRINA II, emanating from small fissures within the sulfide structure and from small “smoker fingers”. Analytical results for chemical composition of all samples are listed in Table 2. The results for 2004 samples with higher proportions of seawater entrained during sampling show generally somewhat lower concentrations for most elements, such as Si, Li, Fe, Mn, and H₂S, which is probably caused by non-conservative behavior of these elements during intense mixing with seawater. The data discussed in this paper are, if not stated otherwise, obtained from 2005 samples. Measured exit temperatures at the sampled sites range between 350 °C for Site B and 170 °C for IRINA II main complex, but as pointed out earlier, temperatures are thought to represent

minimum values. The hydrothermal fluids were acidic (pH_(25 °C) 3.8 for Site B) and strongly reducing. Extrapolation of the sample concentrations to a hypothetical hydrothermal endmember was done under the assumption that the hydrothermal endmember fluid does not contain dissolved magnesium (Mg=0 mM) (Mottl and Holland, 1978). Both measured concentrations and calculated endmember concentrations for the fluids from single vent sites are presented in this paper (Table 2). For Na, Cl, and Br no endmember composition have been calculated due to limitations resulting from measured concentrations close to seawater composition and the analytical precision of the measurements. Alternatively, median values are given for the different vent sites.

The different vent sites are very similar in their major element fluid geochemistry for Na, Cl, Si, Ca, K, Fe, Mn, and dissolved gases, indicating a common source in the

Table 3

Endmember composition of hydrothermal fluids from the Logatchev field from 2005 (data for CH₄ and H₂ calculated from 2004 samples), in comparison to data from 1996 (Douville et al., 2002; Charlou et al., 2002) and to data from other vent fields at the MAR (data for Rainbow are from Douville et al., 2002; Charlou et al., 1998, 2002; data for TAG are from Douville et al., 2002; Charlou et al., 1996; data for Snake pit are from Douville et al., 2002; Jean-Baptiste et al., 1991); references for seawater (SW) data see Table 2

	Logatchev 2005	Logatchev 1996	Rainbow	Snake pit	TAG	SW
Temp. (°C)	350	353	365	341	363	4
pH (25 °C)	3.9	3.3	2.8	3.7	3.1	8.1
CH ₄ , mM	3.5	2.1	2.5	n.d.	0.147	0.0003
H ₂ , mM	19	12	16	n.d.	0.37	0.0004
H ₂ S, (aq), mM	2.5	0.8	1	6	3–4	0
Mg, mM	0	0	0	0	0	53
SO ₄ , mM	1.3	n.d.	n.d.	n.d.	n.d.	29.5
Cl, mM	551	515	750	550	650	560
Br, μM	837	818	1178	n.d.	1045	838
HCO ₃ , mM	0.5	n.d.	n.d.	n.d.	n.d.	2.4
B, μM	335	n.d.	n.d.	n.d.	n.d.	450
Si, mM	8.6	8.2	6.9	20	20	0.036
Al, μM	12	4	2	12	10	<0.1
Na, mM	455	438	553	515	550	480
K, mM	24	22	20	23	18	9.8
Ca, mM	29	28	67	11	28	10.2
Li, μM	252	245	340	835	430	26
Rb, μM	27	28	37	12	9.5	1.3
Cs, nM	343	385	333	170	110	2.3
Sr, μM	127	138	200	54	103	87
Fe, μM	2410	2500	24,000	2400	5170	0.0045
Mn, μM	338	330	2250	400	710	0.0013
Cu, μM	44	27	140	35	130	0.0033
Zn, μM	36	29	160	53	83	0.028
Cd, nM	32	63	130	440	66	0.7
Co, μM	0.75	<2	13	<2	<2	<0.015
Pb, nM	138	86	148	265	110	0.013
Ag, nM	17	11	47	31	51	0.023
U, nM	3	n.d.	n.d.	n.d.	n.d.	14.3
Sb, mM	8	<3	3.1	11	3.9	1.2
Mo, nM	4	1	2	3	5	104
Y, nM	3.7	5.6	19	3.4	6.8	0.14
Sum REE, nM	17	n.d.	n.d.	n.d.	n.d.	0.09

reaction zone. Calculated endmember fluids show exceptionally high concentrations of dissolved CH_4 and H_2 (up to 3.9 mM and 19 mM, respectively, based on data from 2004) (Table 3). Dissolved H_2 is produced by oxidation of ferrous Fe-bearing silicate minerals to magnetite in ultramafic rocks (Allen and Seyfried, 2003) and the high concentrations in the Logatchev fluids are most likely produced during the alteration of ultramafic rocks in the reaction zone.

Sodium (455 ± 6 mM Na) and chlorine concentration (515 mM Cl in 2004–540 mM Cl in 2005) of the Logatchev fluids are slightly lowered by approx. 5–10% when compared to seawater concentrations (480 mM Na and 560 mM Cl), while Br/Cl is $1.52 \cdot 10^{-3}$ ($1.50 \cdot 10^{-3}$ in seawater). Phase separation is not evident from these data. Calculated endmember H_2S concentrations range between 1.0 mM (IRINA II main complex) and 3.6 mM (Site B, IRINA) and are lower compared to basaltic systems, which typically range between 4 and 6 mM (Douville et al., 2002). This would be in agreement with lower sulfur availability in ultramafic rocks, but restrictions have to be made because of uncertainties of the measurement due to the possible loss of sulfide during sample recovery. Sulfate endmember concentrations are close to zero in all vent fluids, thus confirming the validity of Mg regression calculation. However, slightly positive values could result from H_2S oxidation during storage and/or anhydrite precipitation and subsequent dissolution.

5.2. Trace metals

Similar to the distribution of major components in the hydrothermal solutions sampled at different vent sites the trace element composition is rather uniform for all vent sites sampled, with the exception of some first row transition metals. Concentrations of Li (252 ± 6 μM), B (335 ± 18 μM), Rb (27 ± 2 μM), Cs (343 ± 2 nM), and Sr (127 ± 3.6 μM) are homogenous within the analytical error between the different vent sites. Results for Ba are erroneous due to sampling artifacts (barite precipitation) and will not be further discussed.

All transition metals have been measured both in filtered and unfiltered aliquots. Differences between filtered and unfiltered samples occur to a variable extent for Cu, Mo, Pb, Zn, Cd, Ag, Co, and Sb. These elements are known to have high tendencies to precipitate as sulfide minerals, which form, caused by cooling and pH change, in the sample flasks during sampling and transport to the ship, and were re-dissolved during acidification. Between 50% and 98% of total metal content is bound in residual precipitates. The highest depletion has been observed in filtered high-temperature fluid samples

of Site B (Table 4). No differences occur for Fe and Mn (<5%). These results are consistent with observations by Trefry et al. (1994) at the Juan de Fuca Ridge and at the EPR. Endmember concentrations for Cu, Zn, Cd, Co, Pb, Ag, U, Sb, and Mo given in Table 2 are calculated from results of unfiltered aliquots. In general, the concentrations of these elements are comparable to basaltic systems not affected by phase separation. This implies similar processes controlling the solubility of these elements independent from different host-rock composition.

Spatial differences in the fluid composition are element-specific and have been observed for Cu and Co. These are depleted in emanating fluids from the complex vent system IRINA II and, to a minor extent, in fluids from Site QUEST, compared to fluids emanating from smoking crater chimneys at IRINA and Site B (Table 2). Measured Cu/Zn ratios (with similar Zn concentrations) are high at IRINA and Site B (>1) and lowest at IRINA II and QUEST (<1), and correlate with measured exit temperatures (Fig. 4). The solubility of Cu and Co has been shown to be strongly temperature-dependent and concentrations decrease drastically in hydrothermal fluids with temperatures below 320 °C (Metz and Trefry, 2000). However, the different sample quality could also explain the differences in endmember concentrations of Cu, as Cu does not behave conservative during mixing with seawater. Samples obtained from IRINA and QUEST are stronger diluted with seawater (around 50%) than samples from IRINA I and Site B.

Some evidence for the precipitation of Cu in or below the sulfide structures comes from sampled particles filtered during fluid uptake with KIPS in 2004. The particles consist of a mixture of fresh and oxidized

Table 4
Percent of total metal content bound in residual precipitates, which formed during sampling and transportation (unfiltered samples), in relation to measured exit temperature and percent endmember fluid in the sample

	QUEST	IRINA II black smoke	IRINA	Site B	Site B
	285 ROV-5	224 ROV	216 ROV-6	266 ROV-10	257 ROV-7
Fe	<1%	<1%	<1%	<1%	<1%
Mn	<5%	<5%	<5%	<5%	<5%
Ba	78%	40%	80%	77%	55%
Mo	95%	60%	80%	90%	90%
Sn	68%	80%	88%	93%	96%
Pb	66%	72%	87%	93%	93%
Zn	67%	75%	87%	93%	91%
Co	50%	55%	50%	80%	60%
Cu	72%	70%	88%	96%	98%
T (°C)	280	?	?	300	350
Fluid %	55	75	70	75	98

sulfide particles (the latter probably as a result of storage), as well as anhydrite and baryte crystals. IRINA II particles obtained from grey smoke fluids are dominated by idiomorphic wurzite (or sphalerite) and pyrrhotite crystals often occurring in aggregates. However, particles sampled from smoking crater fluids at IRINA and Site B consist mainly of Cu sulfides with some minor Fe sulfides. The particles at QUEST are characterized by oxidized Cu sulfides with minor Fe and Zn sulfide particles. Chemical analyses have shown, that the chalcopyrite-dominated vent fluid particles show an enrichment of Co, whereas Zn sulfide-dominated particles are enriched in Mo and Pb. Correlation of Cu and Co in high-temperature precipitates is consistent with described differences in fluid composition between vent sites (see above) and confirms the strong affinity of Co to Cu sulfides. Molybdenum in Zn-rich sulfides is probably obtained from seawater during mixing with vent fluid, as suggested by negative endmember values in filtered hydrothermal fluids (see also Trefry et al., 1994).

The mineralogy and chemical composition of the fluid particles reflect differences in the fluid geochemistry mentioned above and are roughly consistent with the mineralogical composition of sulfide chimneys at the different vent sites. Chimney fragments sampled at the IRINA II main structure are composed of sphalerite- and pyrrhotite-containing sulfides, whereas sulfides from active smoking crater chimneys are characterized

by pure chalcopyrite and isocubanite (Kuhn and Shipboard Scientific Party, 2004).

The REE-Y (rare earth elements plus yttrium) composition of the calculated hydrothermal fluid end-member is generally similar at all sampled vent sites and is characterized by high REE-Y concentrations, similar as in basaltic-hosted systems (Table 5). Chondrite-normalized REE-Y concentrations of the Logatchev fluids show a common pattern with light rare earth element (LREE) enrichment and a positive Eu anomaly, similar to fluid patterns as of basaltic-hosted systems and the Rainbow vent field (Fig. 5a). Fluids from different vent sites exhibit similar REE-Y patterns, except for a slightly stronger HREE/LREE fractionation in fluids from IRINA II and QUEST. The REE-Y concentrations are very similar to those obtained from samples from 1996 (Douville, 1999).

5.3. Composition of diffuse fluids from mussel fields

Emanations of diffuse fluids commonly occur in the Logatchev field at IRINA II and Site QUEST and are mostly marked by dense mussel inhabitation. Enhanced temperatures are indicated by shimmering water. Temperature loggers placed directly above two mussel fields over a period of 1 year revealed maximum temperatures of 6–12 °C (Lackschewitz and Shipboard Scientific Party, 2005). The fluid geochemistry is very similar to seawater except for higher Li and Si

Table 5

Calculated REE-Y endmember concentrations (in nmol/l) in hydrothermal fluids from different vent sites of the Logatchev field, in comparison to data from Snake pit (Douville et al., 1999), Logatchev and Rainbow (Douville et al., 2002), seawater data (SW) are from Douville et al. (1999); Tm was used as internal spike and is therefore missing in the table

nM	SW	224 ROV	281–5	261–6	257–7	283–5	266–10	MS 20 G2	FL 09 G2
		Logatchev						Logatchev	Rainbow
	TAG	IRINA II BS	Quest	IRINA I	Site B	IRINA II	Site B	1996	
La	0.029	4.23	4.94	5.21	5.74	3.88	5.35	9.89	120
Ce	0.0055	6.86	7.26	8.26	9.94	5.37	8.16	10.89	59.6
Pr	0.0044	0.80	0.83	0.96	1.12	0.59	0.96	1.13	3.7
Nd	0.0214	3.96	3.19	3.84	4.69	2.39	4.03	4.42	11.0
Sm	0.0041	0.77	0.65	0.87	0.98	0.51	1.02	1.06	2.0
Eu	0.0011	7.64	8.34	8.34	8.71	7.49	8.77	10.24	30.8
Gd	0.0063	0.69	0.601	0.86	0.96	0.49	1.01	1.03	2.9
Tb	0.0009	0.08	0.07	0.11	0.099	0.058	0.13	0.14	0.3
Dy	0.0064	0.55	0.38	0.53	0.57	0.31	0.63	0.58	1.7
Y	0.1702	4.39	4.63	4.10	4.57	3.29	5.52	4.94	20.4
Ho	0.0017	0.07	0.056	0.08	0.079	0.045	0.11	0.089	0.29
Er	0.0055	0.17	0.15	0.19	0.22	0.11	0.27	0.22	0.71
Tm									
Yb	0.0054	0.11	0.09	0.12	0.14	0.076	0.21	0.14	0.33
Lu	0.0009	<0.02	0.01	0.017	<0.02	<0.02	0.031	0.016	0.035

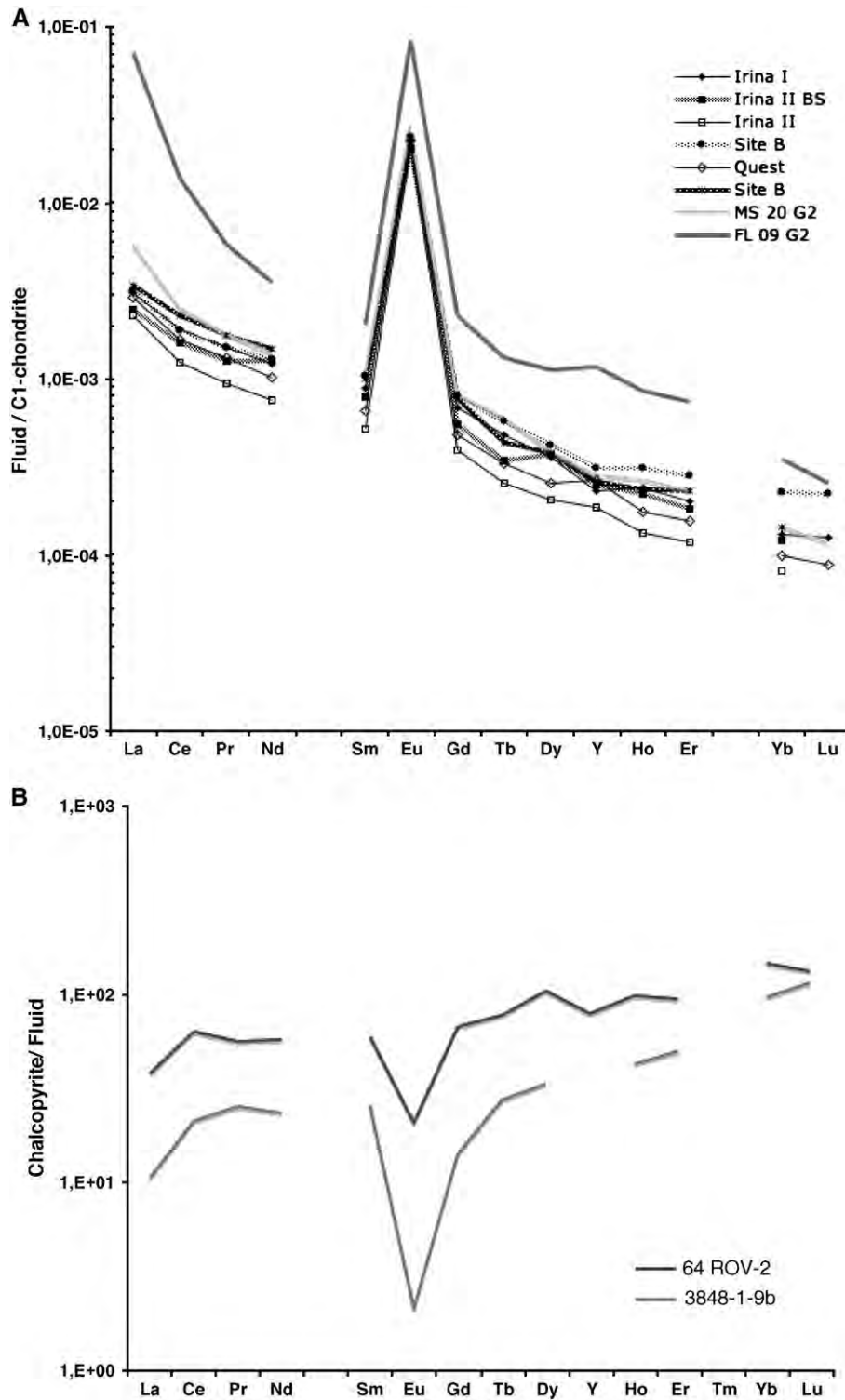


Fig. 5. A) Endmember REE-Y composition for different hydrothermal fluid samples (Site B: 257 ROV-8, 266 ROV-10; black smoker (BS) at IRINA II: 224 ROV, Quest: 281 ROV-5; IRINA I: 261 ROV-6; IRINA II: 283 ROV-5) in the Logatchev field in comparison to endmember data from Douville et al. (2002) for the Logatchev fluids (MS 20 G2) and Rainbow (FL 09 G2) fluids (chondrite-normalized, normalization data are from Anders and Grevesse, 1989); B) REE-Y composition of massive sulfides from Rainbow (3848–1–9b; Rims kaya-Korsakova and Dubinin, 2003) and Logatchev (64 ROV-2), normalized to the host fluid for the Rainbow and Logatchev fields.

Table 6

Measured composition of diffuse fluids emanating in the Logatchev field; the following elements are in the range of seawater composition $\pm 5\%$: Mg, Ca, Na, K, Sr; CH₄ and H₂ were found to be in the μM range, however, data are not given due to high analytical uncertainty

	IRINA II		QUEST	Seawater
	266 ROV-7	277 ROV-4	281 ROV-2	
pH	7.0	7.4	6.5	8.1
H ₂ S (μM)	6.0	0.4	>70	0
Cl (mM)	556	560	567	550
Si (mM)	0.36	0.13	0.17	0.035
Li (μM)	36	29.5	30	26
Fe (μM)	0.05	–	–	<0.01
Mn (μM)	0.014	–	–	<0.01
Cu (μM)	0.65	–	–	<0.01
Zn (μM)	1.1	0.5	0.3	<0.01
Pb (nM)	10.5	0.5	–	<0.01
Cd (nM)	1.25	–	–	<0.01

concentrations together with enhanced concentrations of CH₄, H₂, and H₂S (Table 6). A few samples show higher concentrations of transition metals. The chlorinity is comparable to seawater. As observed for high-temperature fluids filtered aliquots are depleted in most metals compared to unfiltered aliquots, which can be explained by sulfide particle formation during sampling and subsequent dissolution.

5.4. Trace metal speciation of Fe, As, and Cr

Fe is the dominating heavy metal in all fluid samples. The speciation distribution graph (Fig. 6) shows that at least 80% of the total Fe are present in a free reactive form, which includes all inorganic Fe (II and III) and some labile organically complexed Fe (Aldrich and van den Berg, 1998). Time series measurements indicated that the

percentage of reactive Fe decreased to about 60% of total Fe within 5 h after sampling, indicating that free Fe reacts with ligands available in the hydrothermal fluid to form stable complexes and clusters. In samples with a very high contribution of hydrothermal fluid (up to 98%) recovered during cruise M64/2, often all Fe was found to be present as Fe(II), which agrees with the reducing nature of the fluids. However, the dominance of Fe(II) over Fe(III) was also found for diffuse fluids (>80% Fe(II)). It has to be taken into consideration, however, that oxidation of Fe(II) during sample recovery in samples with entrained seawater may also have an influence on the speciation and its determination.

Maximum concentrations of 145 nM total As were measured in unfiltered samples, while the dissolved As (III) concentrations were always below the detection limit of 10 nM. Maximum total dissolved Cr concentrations of 13 nM were found, of which 70–90% were present as Cr (III), and a minor part was Cr(VI). Comparison of UV-digested and non-digested samples confirmed results of earlier Cr speciation work on diffuse hydrothermal fluids in the North Fiji Basin (Sander and Koschinsky, 2000) that most of the Cr(III) appears to be bound in stable organic complexes. Attempts to analyze the redox speciation of Se (IV, VI), Te(IV, VI) and Sb (III, V) were not successful because all values were below or close to the detection limits of 10 nM (Se), 1 nM (Te) and 10 nM (Sb).

6. Discussion

6.1. Common features at all sites

The chlorinity deviation of the Logatchev samples from ambient seawater is in the range of up to 10% depletion in all available datasets. This small depletion is

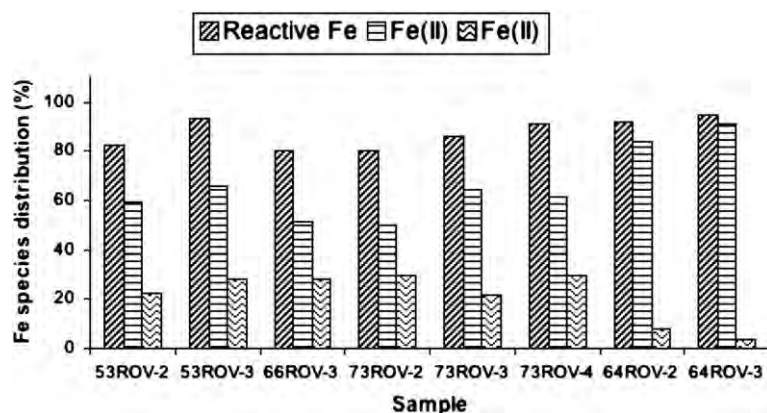


Fig. 6. Distribution of Fe species in hydrothermal fluids taken in 2004 at Sites IRINA (53 ROV-2, 53 ROV-3, 66 ROV-3); IRINA II (73 ROV-2, 73 ROV-3, 73 ROV-4), and ANNA Louise (64 ROV-2, 64 ROV-3).

explainable by water–rock reactions and does not necessarily require phase separation processes to be active (von Damm, 2000; Mevel, 2003). Similar to F and B, Cl is incorporated into serpentine and, to a minor extent, brucite due to isomorphic substitution for OH during serpentinization reactions (Mevel, 2003) and can lead to depletion in the fluid depending on the w/r ratio. The other possible explanation is phase separation in the supercritical region very close to the critical point of seawater (i.e. 298 bar, 407 °C, Bischoff and Rosenbauer, 1988), where the physicochemical differences between two separating phases are only small. The Logatchev fluids would represent the more vapor-like phase, which is characterized by slightly lowered chlorinity compared to seawater. In previous investigations (Sudarikov and Roumiantsev, 2000) the occurrence of very dense brines with negative buoyancy were visually described, but these fluids were never sampled by these authors, and their existence could also not be confirmed during this work. Although we analyzed numerous samples from all known vent sites within the field, we found no high-chlorinity dense fluids that would support the theory of super-critically separated heavy brines flowing downwards. We assume that this phenomenon of descending black smoke fluids is explainable by the strong currents in the field. By video observation during ROV dives we could see the black smoke sometimes being blown away horizontally instead of rising vertically. Sometimes a change of flow directions was observed, which might be related to tidal effects. Taking into account the maximum fluid temperatures and the measured salinity, phase separation seems to be unlikely in the Logatchev hydrothermal field: phase separation in water depths of 3000 m and more require a minimum temperature of ~ 410 °C (Bischoff and Pitzer, 1989), slightly below the critical point of seawater. The measured temperature of 350 °C would therefore imply significant cooling of the phase-separated vapor from 410 °C or more, either due to mixing with cool seawater (in this case the Mg concentration in endmember fluids would not be zero) or caused by mixing with a high-temperature hydrothermal fluid with seawater salinity. Phase separation at greater depth would lead to higher depletions of chloride in the vapor during ascent to the seafloor. To obtain a 350° hot fluid with near seawater chlorinity, again mixing with high proportions of non-separated fluid is needed, which would mask the initial phase separation effect. The Logatchev fluids can therefore not be an endmember vapor phase. If they represent a mixing of a vapor phase with a high-temperature fluid, the effect of element partitioning should be minimal, as seen for Cl concentration. The geochemical composition of hydrothermal fluids from the Logatchev

field is consistent with serpentinization of ultramafic rocks at high temperatures. The concentrations of reduced gases were found to be extremely high in our Logatchev samples compared to basaltic systems, such as TAG or Broken Spur (Douville et al., 2002). Dissolved H₂ is produced by oxidation of ferrous Fe-bearing silicate minerals to magnetite in ultramafic rocks (Allen and Seyfried, 2003), resulting in very reducing conditions. Experimental results by these authors have shown that at temperatures above 350 °C H₂ is produced by hydrolysis of the ferrous component of pyroxene rather than of olivine, which is non-reactive at this high temperature. In a subsequent reaction, CH₄ is formed from the reaction of H₂ with CO₂, explaining the typical high H₂ and CH₄ concentrations in ultramafic-hosted systems (Charlou et al., 2002 and references therein; Holm and Charlou, 2001). Apart from serpentinization processes, the only other way to generate very high concentrations of H₂ are magmatic events, generating redox shifts in the alteration zone together with a temperature increase and pressure decrease. This phenomena has been observed at the “A” vent at 9°N EPR after the eruption in 1991, with maximum H₂ concentrations of more than 30 mM (Lilley et al., 2003). As the concentrations of H₂ (and H₂S) are mainly controlled by temperature- and pressure-dependent fluid–mineral equilibria (Seyfried and Ding, 1995), phase separation itself has only a minor effect. However, high H₂ concentrations caused by a magmatic event in the sub-seafloor would not be stable over a period of 9 years, as observed in the Logatchev and Rainbow fields.

The dissolution of pyroxene minerals releases enough SiO₂ to the solution to stabilize tremolite and talc in the presence of Ca-bearing fluids. Allen and Seyfried (2003) have shown, that significant dissolved Ca concentrations are the result of Mg–Ca exchange during clinopyroxene alteration. As pointed out earlier, peridotitic rocks sampled in the Logatchev area consist mainly of harzburgites and minor pyroxenites, both containing mainly orthopyroxenes rather than clinopyroxenes. One explanation could be, that also a very small amount of clinopyroxene is sufficient to render enhanced Ca concentrations in the fluid. However, orthopyroxenes in abyssal peridotites often contain 4–5 wt.% CaO (GEOROC database) which would be sufficient to enhance the Ca concentration in the fluid during dissolution reaction at given thermodynamic conditions (W. Bach, pers. comm.). The close association of ultramafic rocks with gabbroic intrusions at the MAR including the Logatchev area (Bach et al., 2004; Cannat, 1997), however, support the idea of gabbro alteration, as also assumed by Douville et al. (2002).

Endmember H₂S concentrations are significantly lower than those observed in basaltic systems. Together

with endmember H_2 concentration this indicates a high-temperature fluid in equilibrium with the mineral buffer magnetite, bornite, chalcocite (Seyfried et al., 2004; Allen and Seyfried, 2005). Silica concentrations of 8.6 mM in the Logatchev vent fluids are significantly lower than those in basaltic-hosted systems at similar depth. Opposite to basaltic-hosted systems, where the Si concentration is buffered by fluid–quartz equilibria, Si concentrations in fluids reacting with ultramafic rocks result from the metastable alteration of pyroxene minerals and are buffered by talc and tremolite (Allen and Seyfried, 2003). Boron concentration is depleted compared to seawater (450 μM) in the Logatchev fluids, suggesting that the solubility in high-temperature ultramafic-hosted systems is controlled by B uptake into secondary serpentine and brucite (Mevel, 2003).

Heavy metal speciation in the fluids is characterized by the dominance of free reactive Fe(II) in both focused and diffuse fluids. The decrease of reactive Fe with time probably indicates increasing complexation of Fe, for example with sulfur or organic compounds. This process of changing speciation observed in the lab may also take place for Fe and other metals in the natural system, i.e. in the mixing zone of hydrothermal fluid and seawater (Sander et al., submitted for publication) and may have an influence on the oxidation and precipitation of Fe in the mixing zone. Luther et al. (2001) proposed, that formation of $FeS_{(aq)}$ molecular clusters is a primary mechanism controlling free sulfide detoxification in the mixing zone of hydrothermal fluids and seawater. Reduced forms of Sb, As, Se, and Te, which should from the thermodynamic point of view be the dominating species in reducing fluids (e.g., Price and Pichler, 2005; McPhail, 1995; Pokrovski et al., 2002; Zotov et al., 2003), could rarely be detected. Therefore, the Logatchev fluids are not a significant source of As(III), Sb(III), Se(-II), Se(IV), Te(-II) and Te(IV) to the surrounding water column. Fast oxidation of the reduced species during the sampling procedure could be suspected to be the main reason for low concentrations. However, as also the concentrations of the more oxidized forms As(V), Sb(V), Se(VI) and Te(VI) were very low, a more probably explanation is the inclusion of these metals into precipitating sulfide minerals. Only Cr(III), which does not form sulfides, is stabilized in the fluids by strong organic complexation (Sander and Koschinsky, 2000).

6.2. Comparison of Logatchev vent fluid geochemistry with the Rainbow fluids and hydrothermal fluids from basaltic-hosted systems

Seawater-ultramafic rock interaction at high temperatures ($>300\text{ }^{\circ}C$) produces a characteristic ultramafic

signature: (i) very high concentrations of dissolved H_2 and CH_4 , (ii) a depletion in boron concentration compared to seawater, (iii) lower Li concentrations compared to basaltic systems, (iv) Si concentrations, which are significantly lower than in fluids from basaltic systems at similar depths. Comparable results have been obtained at the Rainbow field (Douville et al., 2002, cf. Table 3) and are in agreement with the work by Allen and Seyfried (2003). Douville et al. (2002) suggested, that the Rainbow hydrothermal system is strongly influenced by phase separation, resulting in the emanation of a high-saline brine phase. This could explain differences between both fields with enhanced concentrations of Cl, Ca, Sr, as well as strong enrichments of most of the transition and heavy metals and REE in the Rainbow fluids, as also pointed out by Douville et al. (2002). However, a chlorine enrichment compared to seawater could also result from very low w/r ratios with intense serpentinization, which results in extensive hydration of the rocks. This process removes water from the fluid and increases its Cl concentration. However, this process is probably not responsible for the extremely high concentrations of Fe, Mn, Cu, Zn, which more likely result from phase separation and high fluid temperatures.

The trace elements Rb, Cs, Cd, Ag, Sb, and Pb were measured in the Logatchev vent fluids. Compared to basaltic-hosted systems, Rb and Cs seem to be more mobile in ultramafic systems, whereas Ag, Cd, Pb are slightly depleted. Similar to the rare earth elements (see below), the concentrations of these elements in the host rocks seem to have only a minor influence to the resulting fluid composition. The concentrations of these elements in the fluid are controlled by temperature- and pressure-dependent fluid–mineral equilibria and the availability of ligands (see Allen and Seyfried, 2005). Phase separation, if taking place beneath the Logatchev field, should have only a minimal effect because of the required dilution of the proposed vapor phase with non-separated fluid.

6.3. Behaviour of rare earth elements in ultramafic-hosted systems

Concentrations and chondrite-normalized patterns of REE-Y in hydrothermal fluids of the Logatchev field are comparable to those of other hydrothermal fluids from basaltic and ultramafic-hosted systems. Both enrichment of light REE (LREE-Y) over heavy REE-Y (HREE-Y) and a positive Eu anomaly seem to be a characteristic signature independently from host-rock composition. Comparing REE-Y data from different hydrothermal fields along the MOR (see compilation in Douville et al.,

1999), concentrations vary only as a function of strong phase separation (e.g. Rainbow field) or different exit temperatures. As discussed by several authors (Allen and Seyfried, 2005; Bau, 1999; Douville et al., 1999; Gammons et al., 1996), REE–Y fractionation in hydrothermal systems is mainly controlled by a combination of reducing conditions at high temperatures, acidic pH, chloride complexation depending on ionic radii and temperature, and incorporation of REE–Y in secondary alteration minerals. Host-rock mineral composition, which has been suggested to be the dominant control by Klinkhammer et al. (1994) seem to be only of minor influence. Investigations of REE–Cl complexes at high temperatures (Gammons et al., 2002) have shown that the complex stability weakly decreases with an increase in atomic number at 200 °C, but that there is no consistent variation with higher atomic number at 300 °C.

By normalizing measured REE–Y data for one fresh chimney piece from ANNA LOUISE (Table 7), consisting of pure chalcopyrite precipitated from the hydrothermal fluid, a preferential uptake of heavy REE–Y compared to LREE is obvious (Fig. 5b), thus reflecting the fractionation of REE–Y during sulfide formation. This is related to the more similar atomic radii of HREE–Y and Cu, Fe, and Zn and the incorporation by substitution into the crystal lattice of the sulfide minerals. This should result in small differences in LREE/HREE ratios between fluids from smoking crater and IRINA II fluids, where Cu-sulfide minerals are thought to be already precipitated. The REE–Y data for the different fluids show a slight tendency to higher LREE/HREE in cooler fluids, but this is not significant. The REE–Y is enriched

in sulfide minerals compared to the fluid, which has also been shown for the Rainbow field (Fig. 5b), (Douville et al., 1999; Rimskaya-Korsakova and Dubinin, 2003). The concentration of REE–Y in hydrothermal fluids from basaltic- and ultramafic-hosted systems is very similar, thus indicating, that the solubility is controlled by similar processes, as also observed for many other elements.

6.4. Spatial variability of fluid composition

Spatial differences in fluid geochemistry between the different vent sites are restricted to elements with strong temperature-controlled solubility like Cu and Co. The generally very similar major and trace element composition suggests a common source in the reaction zone, feeding different vents at distances of approx. 200 m. Lower Cu/Zn ratios in hydrothermal fluids emanating from the IRINA II main complex and QUEST (<1) correlate with differences in the mineralogy of plume particles and chimneys compared to the smoking crater complexes. Thermodynamic calculations by Seyfried and Ding (1995) and compiled data from several hydrothermal systems (Metz and Trefry, 2000) show sharp decreases in concentration of Cu, Co, and Mo for vent fluids as temperatures decrease below 350 °C. In contrast to Cu and Co, Zn concentration is not influenced by cooling between 400 °C and 200 °C. The observed differences in Cu/Zn ratios can therefore clearly be linked to different emanation temperatures. Beehive structures at the IRINA II site indicate stronger cooling of hydrothermal fluids within the chimney complexes. These structures, which consist of complex mineral assemblages of Cu-, Fe- and Zn-sulfides, are probably formed by hot fluids broadly mixing with seawater at more sluggish flow rates (Koski et al., 1994). Lower emanation temperatures at IRINA II are caused by conductive cooling and mixing below the surface of the mound or within the sulfide structure. A large part of the mound structure is covered by a silica cap consisting of silicified mud and talus material. The inner parts of chimneys and beehives at IRINA II are made of chalcopyrite and isocubanite implying that fluids forming these structures have been hotter and contained more dissolved copper than measured in emanating fluids (S. Petersen, pers. comm.). Sampled fluids from the mixing zone with seawater, however, do not carry enough Cu anymore to form these minerals as buoyant plume particles. The latter contain only Zn and Fe sulfides. Copper (and Co) have already been lost, either in the sub-seafloor or within the sulfide structure.

Site QUEST also exhibits Cu/Zn ratios <1 suggesting emanation temperatures below 350 °C. Plume particles

Table 7
REE–Y concentrations (in ppm) in two hydrothermal chalcopyrite (cp) samples from the Logatchev field (Cruise M64/2) and the Rainbow field (Rimskaya-Korsikova and Dubinin, 2003)

ppm	64 ROV-2	3848–1–9b
	Active cp chimney	cp Rainbow
La	0.028	0.174
Ce	0.072	0.177
Pr	0.0075	0.013
Nd	0.033	0.037
Sm	0.0090	0.0077
Eu	0.0274	0.01
Gd	0.0106	0.0065
Tb	0.0016	0.0013
Dy	0.0106	0.0092
Y	0.0380	
Ho	0.0017	0.002
Er	0.0042	0.0059
Tm	0.00044	0.0008
Yb	0.0054	0.0055
Lu	0.00071	0.0007

consist of both Cu sulfides and Fe and Zn sulfides. Conductive cooling below the surface can be assumed due to the existence of silicified rocks recovered from this location. However, chimney mineralogy is comparable to smoking crater sites where chimneys are composed of pure massive chalcopyrite and isocubanite.

6.5. Temporal variability

On the basis of the dataset from 1996 (Douville et al., 2002) and our own data from 2004 samples (gas data) and 2005 samples, it is possible for the first time to investigate the temporal evolution of an ultramafic system.

Comparing all available datasets for the Logatchev field we cannot find a major change in the composition of the fluids within 9 years (c.f. Table 3). Both datasets (the data from Douville et al., 2002 and our data from 2005) are in remarkable good agreement for the major and most trace elements. The standard deviation for Na, Cl, K, Ca, Si, Sr, Li, Fe, and Mn is between 1 and 7%, which is just within analytical error for most of these elements. This compositional stability points to continuous serpentinization in the sub-seafloor without significant changes in alteration patterns and heat supply. Significant differences between both datasets have only been observed for the sulfide-forming metals Cu, Pb, Sb, Mo, Tl, being higher concentrated in 2005 samples. This is more likely the result of sampling artifacts in the samples from 1996 (Douville et al., 2002) than real temporal changes in fluid geochemistry. These elements easily tend to form sulfide particles in contact with seawater or during cooling, and exactly the same elements were depleted in our filtered sample aliquots compared to unfiltered samples. Douville et al. (2002) described their samples as clear solutions even though they were neither filtered nor acidified. As has been seen in the samples taken during our research cruises sulfide particles immediately start to precipitate after sampling which is due to cooling and pH change rather than mixing with seawater. But transparency and the extremely low accretion of particles to smooth PFA surfaces on the sample flasks used here made the complete recovery of the fluid sample more satisfactory. As described for fluid samples from the Juan de Fuca Ridge by Trefry et al. (1994), certain elements (Ag, Cd, Cu, Mo, Pb, Sb, and Zn) easily form residual precipitates in the titanium samplers during sampling and transfer to the ship which later will not be recovered during subsampling from the titanium samplers. This highlights the importance of using un-sedimented, unfiltered, homogeneous samples to obtain correct concentrations.

The chlorinity data for 1996 and 2005 show the same trend to slightly reduced concentrations. The differences

in the chlorine concentration between 1996 and 2005 are within our own analytical error.

Besides differences in trace element concentration, we can also observe a discrepancy in the H_2S concentration. As we have no information on the sample handling and analytical process of Douville et al. (2002) and because of difficulties in the determination of this very unstable compound, we cannot clearly state, whether the differences between Douville's data and our own data are real, or may be caused e.g. by the formation of $FeS_{(aq)}$ clusters (Luther et al., 2001).

7. Conclusions

For the first time the Logatchev hydrothermal field has been systematically sampled with regard to spatial and temporal variability. The fluid geochemistry is very similar at all vent sites and shows signatures characteristic of ultramafic-hosted systems, namely high dissolved hydrogen and methane concentrations resulting from serpentinization reactions of pyroxene-bearing ultramafic rocks, lower silica, lithium, and hydrogen sulfide concentrations compared to basaltic systems, and depletion in boron concentration compared to seawater. The temporal stability of the fluid chemistry over nine years indicates a stable system with continuous serpentinization in the sub-seafloor without significant changes in alteration patterns and heat supply. Possible heat sources, may be gabbroic intrusions and the lithospheric mantle (e.g. German and Lin, 2004). Exothermic serpentinization reactions cannot contribute significantly to the required heat. Boiling which is one of the major factors for short- to medium-term changes in fluid emanations, is not evident in the Logatchev field. As ultramafic systems are generally less frequently affected by strong events such as eruptions and intrusions, which can induce major changes in heat flow and changes in fluid chemistry, we can hypothesize from our results that ultramafic-hosted systems on slow-spreading ridges may generally be more stable systems than basalt-hosted systems. Therefore, detailed investigations in such a field, as they are presented here, contribute to the estimation of elemental fluxes from this spatially and temporally rather uniform field, and the relative role of ultramafic systems on elemental budgets in the ocean compared to mafic systems.

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Chapter 3

Hydrothermal venting at pressure-temperature conditions above the critical point of seawater, 5°S on the Mid-Atlantic Ridge

Hydrothermal venting at pressure-temperature conditions above the critical point of seawater, 5°S on the Mid-Atlantic Ridge

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ABSTRACT

Hydrothermal circulation within oceanic crust depends on pressure (P) and temperature (T); the critical point (CP) of seawater at 298 bar and 407 °C represents the threshold between subcritical and supercritical conditions. Here we present data from the first hydrothermal system in which the sampled fluids fall on and above the CP. The vent system discovered at 5°S on the Mid-Atlantic Ridge is characterized by multiple fluid emanations at variable temperatures in water depths of ~3000 m. Vigorous vapor phase bubbling, stable emanation of superhot fluid at 407 °C, and decreased salinity indicate phase separation at conditions above the CP at one site. At another site the measured maximum T of 464 °C during a 20 s interval is by far the hottest fluid ever measured at the seafloor and falls into the vapor-phase supercritical region of seawater. Besides these two separate fields with ongoing phase separation and extremely hot fluids, a third vent field emanates non-phase-separated fluids at 349 °C and is used as a reference site. Fluid chemistry shows that supercritical fluids evolve differently than subcritical fluids, making this vent system a unique natural laboratory to investigate processes at high P - T conditions. The stability of the high temperature and fluid geochemistry measured in 2005 and 2006 after the assumed seismic trigger event in 2002 supports this as an exceptional site along the Mid-Atlantic Ridge.

Keywords: hydrothermal, fluids, critical point of seawater, supercritical, phase separation.

INTRODUCTION

Hydrothermal systems in the ocean play an important role in the composition of seawater, the formation of valuable ore deposits, the support of exotic ecosystems, and perhaps even for the development of life on early Earth (e.g., Hein et al., 2003; Nisbet and Sleep, 2001). Processes that take place in a hydrothermal circulation cell depend on depth, pressure, and temperature conditions; a pressure of 298 bar and a temperature of 407 °C define the so-called critical point of seawater (CP), representing the threshold between subcritical and supercritical conditions (Bischoff and Rosenbauer, 1988). Above the CP, physico-chemical properties of the fluid change from polar to nonpolar behavior, associated with strong changes in the dielectric constant and self-ionization (e.g., Hack et al., 2007). Opposite to subcritical phase separation with the formation of gas-rich vapor of very low chlorinity and density, at conditions above the CP, a brine phase is produced, and a complementary slightly Cl^- depleted and relatively dense vapor phase. These vapor phase fluids separating above the CP with relative high densities have a high ability to hydrate ions, which is, besides the species volatility, a key factor in controlling metal transport by vapors (Pokrovski et al., 2005). Around the CP, the differences between vapor and brine

are only minor. These properties affect metal solubility, fractionation, and transport in the respective vapor phases. It can reasonably be assumed that hydrothermal processes that take place at supercritical conditions will leave an imprint on the fluids that can be distinguished from purely subcritical fluids. However, until recently, the seafloor venting of fluids at or above the CP had not been observed.

Many hydrothermal systems in the Pacific and Atlantic Oceans characterized by phase separation are placed within the subcritical region on a pressure-temperature (P - T) diagram, i.e., the vents are situated at water depths shallower than 2940 m (corresponding to 298 bar) with fluid temperatures of <407 °C (e.g., 9–10°N, 21°N, and 17–19°S on the East Pacific Rise; Fornari et al., 1998; Von Damm et al., 1985; Charlou et al., 1996; and on the Juan de Fuca Ridge; Butterfield and Massoth, 1994; Lilley et al., 2003). Although in some of these systems, fluids may have undergone supercritical conditions during their ascent, including supercritical phase separation, as discussed for the Main Endeavor Field on the Juan de Fuca Ridge and for 9°50'N on the East Pacific Rise (Butterfield et al., 1994; Seyfried et al., 2003; Foustoukos and Seyfried, 2007), they could not be sampled at those conditions. So far, the only fluid vent-

ing at vapor-phase conditions (403 °C at 2600 m water depth) has been found on the East Pacific Rise (Von Damm et al., 1995).

Phase separation in hydrothermal systems can be related to tectonic or magmatic events that cause rapid temperature increases (Butterfield et al., 1997). So far, all vent systems with post-eruptive $T > 390$ °C were found on the fast-spreading East Pacific Rise, on which seismic, volcanic, and magmatic activities are widespread. Brandon vent, at 21°S on the East Pacific Rise, produced the hottest fluid reported so far, 405 °C at 287 bar, which is close to the CP (Von Damm et al., 2003). However, von Damm et al. (2003) were not able to determine whether the fluids phase separated at subcritical or supercritical conditions.

A few vent systems occur deeper than 3000 m, especially on the slow-spreading Mid-Atlantic Ridge (sites Broken Spur, TAG, MARK; James et al., 1995; Campbell et al., 1988). However, all of those vents have fluid temperatures of <400 °C and, therefore, no fluids could be sampled at supercritical P - T conditions.

Here we report the highest temperatures (≥ 407 °C) measured in deep-sea hydrothermal fluids and the first fluids sampled at supercritical conditions. The superhot vent system was discovered and first sampled in March–April 2005 (cruises CD169 and M64/1) and was revisited in May 2006 (cruise M68/1). It represents a diverse area with fluids of various temperatures emanating at water depths of ~3000 m (Haase et al., 2007; Fig. 1). In the Turtle Pits (TP) field, boiling and phase separation are evident at several black smokers, while in the Comfortless Cove field, just one active smoker named Sisters Peak (SP) vents extremely hot-phase-separated fluid. The Red Lion (RL) vent field emanates non-phase-separated fluids with a maximum temperature of 349 °C from four individual chimneys and is used as a reference site, representing high-temperature water-rock interaction without overprinting by phase separation.

METHODS

Sampling of the hydrothermal fluids was performed with the ROV *Quest* (MARUM [Zentrum für Marine Umweltwissenschaften],

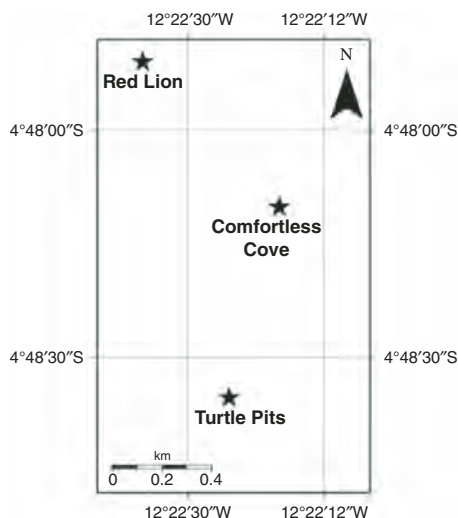


Figure 1. Positions of individual high-temperature hydrothermal fields in the area at 5°S on Mid-Atlantic Ridge. The 407 °C hot smoker Two Boats is located in Turtle Pits field, whereas ≥400 °C hot vent Sisters Peak is in Comfortless Cove field.

Bremen) using a pumped flow-through system (Kiel Pumping System, KIPS) made of inert materials. Located at the sampling nozzle is an online temperature probe for in situ measurements based on a high-temperature negative temperature coefficient (NTC) resistor. Determination of chemical compounds in the fluids included onboard measurements of pH, Eh, dissolved Fe and sulfide by photometry, dissolved Cu and Zn by voltammetry, and shore-based inductively coupled plasma–optical emission spectroscopy (ICP-OES) and ICP–mass spectrometry (MS) determinations of major, minor, and trace elements. The anions Br and Cl were determined in filtered, nonacidified aliquots; Na, Ca, K, Mg, Li, Sr, Fe, Mn, Cu, Zn (ICP-OES), Co, Pb, Mo, and U (ICP-MS) were measured in nonfiltered, acidified aliquots, following a complete dissolution of solid particles. More details on the methods used are provided in the GSA Data Repository.¹

RESULTS AND DISCUSSION

Temperatures of the Superhot Fluids

During the first sampling campaign in 2005, stable maximum temperatures of 400 °C were measured at site Turtle Pits. Short-term temperature maxima as high as 420 °C (in the range of seconds; S. Petersen, 2005, personal commun.)

¹GSA Data Repository item 2008149, method descriptions and measured concentration of individual hydrothermal fluid samples, and Tables DR1 and DR2, is available online at www.geosociety.org/pubs/ft2008.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

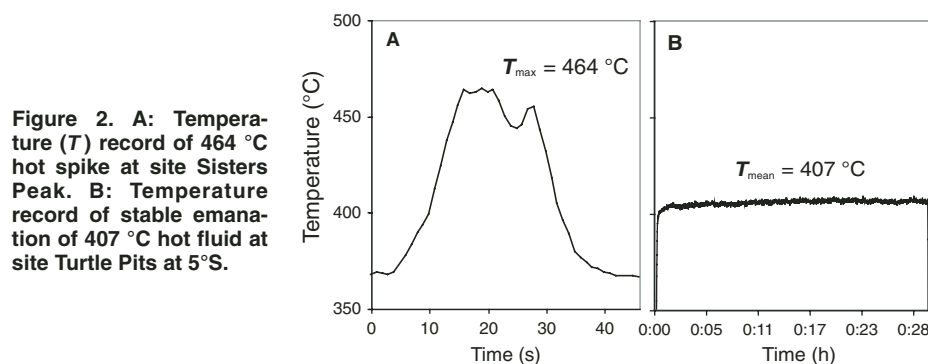


Figure 2. A: Temperature (T) record of 464 °C hot spike at site Sisters Peak. B: Temperature record of stable emanation of 407 °C hot fluid at site Turtle Pits at 5°S.

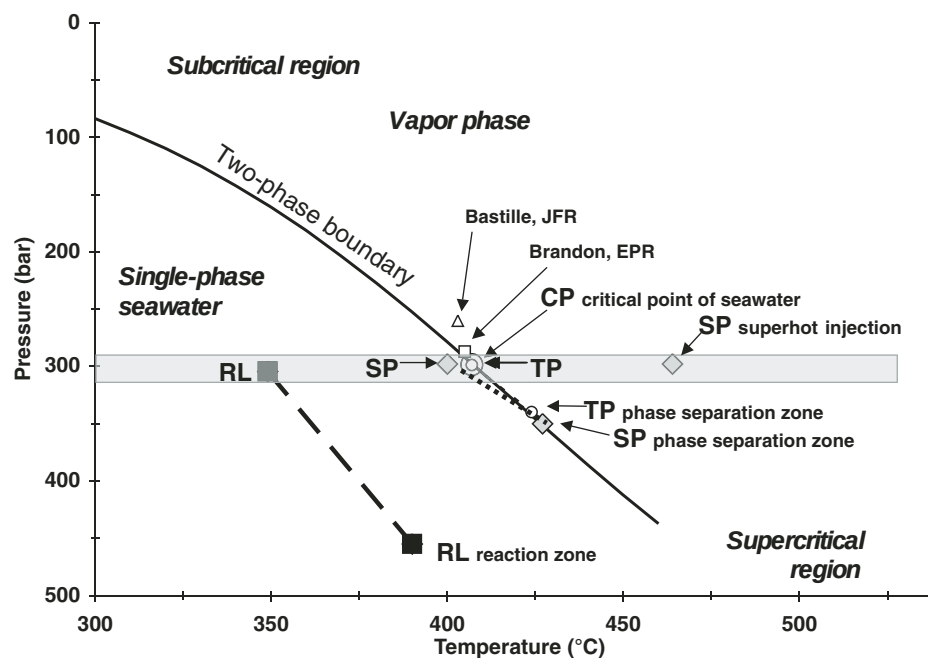


Figure 3. Two-phase boundary of seawater and positions of the 5°S vent fluid samples from sites Turtle Pits (TP), Sisters Peak (SP), and Red Lion (RL) in the pressure-temperature diagram. CP is critical point of seawater. Data points for Brandon (Von Damm et al., 2003) and Bastille (Seyfried et al., 2003) vents from the Pacific are shown for comparison. Depths of zone of phase separation at TP and SP and depth of reaction zone at RL were calculated based on Cl and Si concentration, respectively (after Foustoukos and Seyfried, 2007; Von Damm et al., 1991; a detailed explanation is given in GSA Data Repository; see footnote 1). Gray shaded area represents range of seafloor pressures at 5°S. JFR—Juan de Fuca Ridge; EPR—East Pacific Rise.

were not considered valid at that time. During a revisit to the area in May 2006, the system was found to have similar venting activity and fluid temperatures. The nozzle of the KIPS fluid sampling and temperature sensor system was inserted deep into the vent outlet of the Turtle Pits vent smoker named Two Boats, and a stable temperature of 407 °C was measured for several minutes during fluid sampling (Fig. 2A). In the newly discovered hot vent Sisters Peak, ~1 km away from Turtle Pits, a stable temperature of 400 °C was measured. However, for a period of 20 s a venting temperature of 464 °C was recorded (Fig. 2B) that clearly is in the vapor-phase supercritical region for seawater (Fig. 3). Similar observations of short-term maxima to

405 °C in an otherwise stable 353 °C hot emanation on the Juan de Fuca Ridge have been related to two fluid sources of different temperatures (Tivey et al., 1990).

Geochemistry of the Superhot Fluids

Both Turtle Pits and Sisters Peak vent sites emanate a chlorinity-depleted fluid with 271 and 224 mM Cl, respectively (Table 1), which is evidence for phase separation at P - T conditions above the CP. On a Cl-normalized basis, Turtle Pits and Sisters Peak fluids are clearly enriched in K, Ca, and Na compared to seawater (Table 1), similar to fluids from Red Lion 2 km farther north. Despite lower Cl concentration, the transition metals Fe, Cu, Co, and Mo are

TABLE 1. VENT FLUID CHEMISTRY GIVEN AS END-MEMBER CONCENTRATIONS

Site	Turtle Pits	Turtle Pits	Sisters Peak	Red Lion	Brandon Bd5, EPR	Bastille, JFR	Seawater
Year sampled	2005	2006	2006	2005			
$T_{\max}$ (°C)	405	407	400 (464)	349	405	368	2
Cl (mM)	291 (8)	271 (2.4)	224 (2.6)	552 [†] (3.8)	330	208	552
Br (μM)	494 (5)	482 (14)	392 (15)	873 [†] (29)	550	340	831
B (μM)	536 (11)	547 (5)	591 (4)	520 (3.9)	432	800	425
Si (mM)	11.3 (0.6)	11.6 (0.13)	14.4 (0.23)	21.8 (1.1)	9.5	9.2	0.06
Na (mM)	230 (5)	237 (2.3)	209 (4.5)	480 [†] (3.1)	270	166	474
K (mM)	7.94 (0.15)	8.6 (0.06)	7.4 (0.014)	19.8 (0.13)	7.7	10.0	10.4
Ca (mM)	7.7–10.7	8.8 (0.13)	11.6–17.4	18.6 (0.16)	21.3	12	10.5
Li (μM)	416 (7)	427 (6)	343 (4)	1217 (13)	309	160	25
Sr (μM)	28.2 (1.3)	25.4 (1.0)	35–52	63.1 (0.56)	63.1	63	87
Mn (μM)	454 (6.7)	473 (9)	704 (12)	730 (9.4)	702	550	0.0013
Fe (μM)	3120 (449)	3940 (50)	3380 (6)	803*	7570	2200	0.0045
Co [§] (μM)	1.50*	0.5–0.88	0.44–1.62	0.029*	N.D.	0.14	<0.015
Cu [§] (μM)	111*	9–76	110–347	5.2*	54	25	0.0033
Zn [§] (μM)	55*	28–69	50–155	60*	78	32	0.028
Mo [§] (nM)	101*	15–57	80–270	15.7*	N.D.	68	0.10
Pb [§] (nM)	187*	56–184	126–422	418*	N.D.	100	0.013
H ₂ S (μM)	N.D.	4200*	8310*	N.D.	7950*	22000	0
Na/Ca	<21	26.9	<18	25.8	12.6	13.8	45.1
K/Cl	0.027	0.032	0.033	0.035	0.023	0.048	0.019
Ca/Cl	>0.026	0.032	>0.052	0.034	0.064	0.058	0.019
Fe/Cl × 1000	10.7	14.5	15.1	1.45	22.9	10.6	<<
Fe/Mn	6.9	8.3	4.8	1.1	10.8	4.0	<<

Note: Calculated based on the assumption of Mg = 0 in the end-member fluid for the different vent sites at 5°S sampled in 2005 and 2006. Data in parentheses are relative uncertainties of regression. Data from the Brandon (Von Damm et al., 2003) and Bastille (Seyfried et al., 2003) vents from the Pacific are shown for comparison. Seawater data for Mn, Fe, Cu, Zn, Mo, and Pb are from Douville et al. (2002). EPR—East Pacific Rise; JFR—Juan de Fuca Ridge. *T*—temperature; mM—mmol/Kg; μM—μmol/Kg; nM—nmol/Kg.

N.D.: Not determined.

*Based on one sample.

†Median value.

§As the measured data for Co, Cu, Zn, Mo, and Pb do not lie on a single mixing line, end-member concentrations were calculated based on single data points, thus giving a range of end-member values.

enriched in phase-separated fluids compared to Red Lion fluids, which can be attributed to the high fluid temperatures and the specific properties of supercritical fluids close to the CP. Complex formation constants increase with increasing temperature and decreasing water density (Ding and Seyfried, 1992), and at *P-T* conditions above the CP the relative stability of chloride complexes (mainly neutral complexes) is strongly enhanced. Very high Fe concentrations, up to 4 mM (Table 1), and high Fe/Cl and Fe/Mn ratios compared to Red Lion, reflect this increased Fe mobility in fluids in the low pressure–high temperature region around the CP with an almost complete formation of Fe chloride complexes (Helgeson, 1992; Ding and Seyfried, 1992; Von Damm et al., 2003). Hydrogen sulfide concentrations are as high as 8.3 mM (Table 1).

Zinc and Pb are similarly concentrated at the three sites (Sisters Peak, Turtle Pits, Red Lion), indicating that factors other than pressure and temperature control the solubility of these elements. As shown in experimental work by Pokrovski et al. (2005), the fractionation of elements between vapor and brine is zero at the CP and increases with increasing density difference (i.e., away from the critical curve). Close to the CP, elements like Fe and Zn should partition similarly to Cl. Some metals like Cu, however, seem to be dominated by sulfide com-

plexation, which could lead to the fractionation of elements into the vapor (Cu) and the brine (e.g., Zn) phases (Nagaseki and Hayashi, 2008).

Although the general composition of the 5°S fluids seems to fit into the range of data from other very hot vent fluids (Table 1), a closer look at individual samples and compounds in the extremely hot fluid samples indicates some unusual properties. The major elements and Fe in individual samples from the same vent orifice at Turtle Pits plot on a single mixing line between hydrothermal fluid and seawater, i.e., they seem to represent different dilutions of the same end-member fluid (see Table DR1). However, some transition metals display a high variability among samples despite very similar chlorinities and high fluid percentage (Table 1, Table DR2). Copper, Co, and Mo covary, suggesting a similar control on their mobility, with the lowest concentrations in the hottest fluid sample, whereas Zn and Pb are decoupled from this group of elements. Mixing of the vapor phase with a brine phase or evolved seawater as discussed for the vent Bastille (Seyfried et al., 2003) is unlikely because of chemical constraints such as constant Cl and Fe concentrations. A comparison of total, dissolved, and free plus labile fractions of different metals indicates extremely low free Cu and low free Zn concentrations in the hottest fluids, in contrast to Fe

(Table DR2). We interpret the variable behavior of Cu as the result of Cu being present in the extremely hot single-phase fluid in a different chemical form than in lower-temperature fluids, as previous investigations had shown that Cu complexation is highly sensitive to temperature (e.g., Mavrogenes et al., 2002).

Temporal Evolution of the 5°S Vent System

The hydrothermal system at 5°S on the Mid-Atlantic Ridge is remarkable not only for its absolute fluid-temperature record. More important, and completely unexpected, is the association of these hot vents with recent volcanic eruptions on a slow-spreading ridge. Hydrothermal vent systems on the East Pacific Rise driven by volcanic eruptions are known to show strong temporal variations in heat flow and fluid chemistry. According to the model developed based on these observations (Butterfield et al., 1997; Von Damm et al., 1995), the high heat flow at the beginning of an event is often associated with an onset of boiling of the circulating fluids, and the subsequent venting of the more buoyant gas-rich and initially also Fe-rich vapor phase. Thereafter, the system will cool, boiling will end, and the heavy and cooler brine stored in the subsurface will start to vent.

If we assume that this response model from Butterfield et al. (1997) applies to our young post-eruptive system at 5°S on the Mid-Atlantic Ridge, and that a seismic event recorded in 2002 was the trigger event (Haase et al., 2007), our data from 2005 and 2006 provide a temporal frame for the 5°S system. Accordingly, the high temperature, high Fe concentrations, and constantly low Cl contents in both 2005 and 2006 clearly indicate that the 5°S system, even 4 yr after the eruption, was still in an early stage with high heat flow. Only one other vent system with continuous phase separation for several years following an eruption has been observed (9°46'N, East Pacific Rise; Von Damm et al., 1995). Hydrothermal circulation at the hot Turtle Pits and Sisters Peak vents is probably caused by a diking and an eruption event like those that typically occur on fast-spreading ridges. The stability of the high-heat-flow vapor-emanation phase for at least 4 yr calls for an unusually large and constant heat source beneath this area (Haase et al., 2007). This will enable us to study supercritical fluids in more detail during upcoming cruises and to adapt the response model to systems venting at supercritical pressure-temperature conditions.

SUMMARY AND CONCLUSIONS

Chemical data and exit temperatures for the 5°S hydrothermal vent field are extremely diverse, displaying non-phase-separated hot fluids, phase-separated fluids representing a supercritical vapor-type phase with venting tem-

peratures of ≥ 400 °C, and episodic eruptions of a superhot supercritical phase at 464 °C. The high-temperature vapor-phase fluids apparently vent over unusually long durations (≥ 4 yr) compared to high-temperature sites in the Pacific. This has important implications for heat-flow models of hydrothermal systems. The different solution properties of fluids below and above the CP, and the different speciation of metals under the respective pressure-temperature conditions, will control mineral-formation processes, and possibly also biogeochemical interactions in the mixing zone of the rising plume. Heretofore, information on metal behavior in saline fluids above the CP was deduced indirectly from fluid-inclusion studies and laboratory experiments at high temperatures and pressures (e.g., Audéat et al., 1998; Mavrogenes et al., 2002). Turtle Pits and Sisters Peak are the only vent sites known where supercritical vapor emanations can be observed directly at supercritical conditions. Foustoukos and Seyfried (2007) pointed out that according to their experiments on quartz solubility in the two-phase and critical region, supercritical phase separation might be more common than previously thought. This finding emphasizes the special role of the 5°S field on the Mid-Atlantic Ridge as a model system to investigate processes that likely operate within many other hydrothermal systems occurring at great water depth, but in which the processes become overprinted by cooling and/or dilution before the fluids reach the seafloor.

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Chapter 4

Rare earth element distribution in >400 °C hot hydrothermal fluids from 5°S, MAR: The role of anhydrite in controlling highly variable distribution patterns



Rare earth element distribution in >400 °C hot hydrothermal fluids from 5°S, MAR: The role of anhydrite in controlling highly variable distribution patterns

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Abstract

Two submarine hydrothermal vent fields at 5°S, Mid-Atlantic Ridge (MAR) – Turtle Pits and Comfortless Cove – emanate vapor-phase fluids at conditions close to the critical point of seawater (407 °C, 298 bars). In this study, the concentration and distribution of rare earth element (REE) and yttrium (Y) has been investigated. Independent of the major element composition, the fluids display a strong temporal variability of their REE + Y concentrations and relative distributions at different time scales of minutes to years. Chondrite-normalized distributions range from common fluid patterns with light REE enrichment relative to the heavy REE, accompanied by positive Eu anomalies (type I), to strongly REE + Y enriched patterns with a concave-downward distribution with a maximum enrichment of Sm and weakly positive or even negative Eu anomalies (type II). The larger the sum of REE, the smaller Ce_{CN}/Yb_{CN} and Eu/Eu^* . We also observed a strong variability in fluid flow and changing fluid temperatures, correlating with the compositional variability.

As evident by the positive correlation of total REE, Ca, and Sr concentrations in Turtle Pits and Comfortless Cove fluids, precipitation/dissolution of hydrothermal anhydrite controls the variability in REE concentrations and distributions in these fluids and the transformation of one fluid type to the other. The variable distribution of REE can be explained by the accumulation of particulate anhydrite (with concave-downward REE distribution and negative Eu anomaly) into a fluid with common REE distribution (type I), followed by the modification of the REE fluid signature due to dissolution of incorporated anhydrite. A second model, in which the type II fluids represent a primary REE reaction zone fluid pattern, which is variably modified by precipitation of anhydrite, can also explain the observed correlations of total REE, fractionation of LREE/HREE and size of Eu anomaly as well as Ca, Sr. The emanation of such a fluid may be favored in a young hydrothermal system in its high-activity phase with short migration paths and limited exchange with secondary minerals. However, this model is not as well constrained as the other and requires further investigations.

The strongly variable REE fluid signature is restricted to the very hot, actively phase-separating hydrothermal systems Turtle Pits and Comfortless Cove at 5°S and has not been observed at the neighboring Red Lion vent field, which continuously emanates 350 °C hot fluid and displays a stable REE distribution (type I).

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1. INTRODUCTION

Rare earth elements and yttrium (REE + Y) systematics have been investigated in a variety of submarine hydrothermal vent fluids emanating in mid-ocean ridge (MOR) settings (Michard et al., 1983; Michard and Albarede, 1986; Michard, 1989; Mitra, 1991; Mitra et al., 1994; James

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et al., 1995; Bau and Dulski, 1999; Douville et al., 1999) and back-arc basins (Fouquet et al., 1993; Douville et al., 1999) enhancing the knowledge about controls on REE mobility in aqueous systems, in different geological settings and under different pressure (p) and temperature (T) conditions. Although hydrothermal fluids may be strongly enriched in REE by several orders of magnitude compared to seawater, hydrothermal systems act as a net sink for REE in the modern ocean, caused by intense scavenging onto hydrothermal Fe oxide particles at the emanation sites (German et al., 1990; Bau and Dulski, 1999).

The major source of REE in submarine hydrothermal systems is the host rock; back-arc hydrothermal systems may additionally be affected by a direct input from magmatic fluids (Douville et al., 1999). Despite varying host rock compositions (mafic and ultramafic rocks), temperatures (215–360 °C), and fluid salinities (190–713 mM Cl) in MOR settings, reported data on the REE + Y composition of emanating high-temperature (>200 °C) hydrothermal fluids document a remarkably similar distribution of these elements. Typically, chondrite-normalized (CN) distribution patterns display a smooth decrease from Ce to Yb, a positive Eu anomaly and, sometimes, positive La anomalies. However, studies of REE composition of MOR hydrothermal vent fluids are restricted to evolved systems with maximum venting temperatures of 360 °C, emanating either non-phase-separated fluids with seawater chlorinity (Snakepit), vapor-type fluids (e.g., Lucky Strike, Broken Spur, Menez Gwen) or brines (e.g., TAG, Rainbow) under subcritical pressure p – T conditions. The relatively uniform REE + Y distribution has been attributed to the partitioning of REE + Y between alteration minerals and the co-existing fluid being primary factors controlling the REE distribution in MOR hydrothermal fluids as determined by the relative concentration of ligands, temperature, pH, and redox conditions (Douville et al., 1999; Allen and Seyfried, 2005). The precipitation/dissolution of sulfides and sulfates (like anhydrite) in the sub-seafloor may further influence the REE distribution in fluids, as suggested for TAG (Mitra et al., 1994; Humphris and Bach, 2005).

In the absence of potentially stronger ligands like F^- and OH^- , chloride plays a dominant role as the complexing agent for REE at conditions typical for MOR hydrothermal systems (Gammons et al., 1996; Douville et al., 1999; Mayanovic et al., 2002a,b, 2005, 2007a,b; Migdisov and Williams-Jones, 2002, 2006; Allen and Seyfried, 2005). Recently, Mayanovic et al. (2008) and Migdisov and Williams-Jones (2008) demonstrated that the Cl complex stabilities in low pH aqueous solutions at elevated temperatures decrease from the light to the heavy REE (HREE) at temperatures above 200 °C, suggesting a greater stability of aqueous light REE (LREE) complexes compared to heavy REE–chloride complexes. The positive Eu anomaly in hot MOR vent fluids has been attributed to the redox sensitivity of Eu and the stability of reduced Eu^{2+} in acidic aqueous solution above 250 °C (Sverjensky, 1984; Bilal, 1991), leading to the decoupling and subsequent fractionation of Eu^{2+} from trivalent REE as a consequence of the combined effects of enhanced Cl complexation and discrimination during incorporation into alteration minerals (Haas et al., 1995; Douville et al.,

1999; Allen and Seyfried, 2005). The influence of phase separation, i.e., the separation of single-phase fluids into vapor- and brine-phases (and halite) of different density and salinity on the distribution of REE in hydrothermal fluids is poorly constrained. Hydrothermal systems triggered by active magmatism are often influenced by phase separation, and new pulses of magmatic activity may change conditions within the hydrothermal convection system due to a shift in fluid temperatures and/or reaction zone depths. While during subcritical phase separation (i.e., boiling) a gas-rich vapor phase with very low salinity and density is formed, at conditions above the critical point of seawater ($CP_{SW} = 298$ bars/407 °C, Bischoff and Rosenbauer, 1988) a brine phase is produced by condensation, separating from a slightly Cl-depleted and relatively dense vapor phase. The special physico-chemical conditions of hydrothermal fluids at such high temperatures and pressures – low dielectric constant, low density – with small changes of p/T having a strong impact on ion association – and the process of phase separation above the CP_{SW} may have an impact on REE + Y mobilization, solubility, transportation, and fractionation. However, nothing is yet known about the behavior of REE in natural vapor-phase fluids formed under p – T conditions close to or above the CP_{SW} . Although only three hydrothermal systems have been found so far venting at p – T conditions near or above the CP_{SW} (Brandon vent, 21°N, EPR; 5°S MAR; Ashadze 1 + 2, MAR), similar conditions are likely to be common in hydrothermal systems along mid-ocean ridges, considering the high water depth of especially slow-spreading ridges (Foustoukos and Seyfried, 2007b; Coumou et al., 2009).

Here, we report REE + Y data for two hydrothermal vent sites in 3000 m water depth at 5°S, Mid-Atlantic Ridge (MAR) which are characterized by the vigorous emanation of vapor-phase fluids at extremely high venting temperatures of 400–410 °C, i.e., close to the CP_{SW} (Koschinsky et al., 2008). Geological evidence indicates a recent magmatic event in 2002 associated with effusive lava flows, possibly leading to the recharge of a pre-existing hydrothermal system (Haase et al., 2007). The special state of this high-temperature hydrothermal system provides a rare opportunity to investigate the early evolution of REE distribution in such fluids which may be different compared to more evolved hydrothermal systems. Sampling intervals varying from years to minutes are specifically aimed at resolving compositional variations on different time scales in these highly dynamic vent systems.

2. GEOLOGICAL SETTING

At 4°48'S MAR, four active hydrothermal vent fields (Red Lion, Comfortless Cove, Turtle Pits, and Wideawake) are located in close proximity to each other at a water depth of ~3000 m. Abundant sheet flows and pillow lavas forming a ridge plateau 5 × 10 km wide characterize this ridge segment.

The vent system was first discovered and sampled in March–May 2005 (Haase et al., 2007) and is characterized by diverse hydrothermal emanations including focused black smoker vent sites of different temperatures and diffuse

venting sites. The northernmost vent field Red Lion has four single chimney structures separated by only 10–15 m (Tannenbaum, Mephisto, Sugarhead, and Shrimp Farm), with an average emanation temperature of 350 °C (except for the lower-T vent Shrimp Farm, (Haase et al., 2007). Only 1 km further south, the Comfortless Cove vent field is situated on sheet flow lava, and consists of a single black smoker chimney (Sisters Peak, about 10 m high during sampling in 2008) growing on a 4 m high, blocky mound of cemented massive sulfides and venting fluids at 400–410 °C. Two diffuse vent sites are located within 150 m distance of the hot emanation site. A prominent pillow lava mound to the north of the Sisters Peak chimney characterizes the area, overlying the older sheet flow. The Turtle Pits vent field, about 2 km SSW of Comfortless Cove, is located on top of laminated and jumbled sheet flows and lies within a small depression representing a lava collapse pit. The field consists of two separate sulfide debris mounds with several active black smokers on top. A 13 m high single chimney (Southern Tower) is located between these two mounds (One Boat, Two Boats). Ancient hydrothermal activity is evident from inactive chimneys at the edge of the collapse pit (Haase et al., 2007). Massive blocks of white material containing anhydrite and minor talc are exposed along the northwestern side of the Two Boats site and in the pit itself. A fourth, diffuse venting field called Widewake, without high-temperature vent sites, is located about 200 m to the west of Turtle Pits, characterized by densely inhabited mussel fields. Here, a very young, lobate lava flow with a black, glassy luster partly covers mussel beds, indicating a pre-existing hydrothermal activity. The recent lava eruption can be related to a recent seismic event recorded in June 2002 (Haase et al., 2007).

The black smoker vents at Turtle Pits and Comfortless Cove constantly emanate vapor-phase fluids with 230–270 mM Cl at temperatures of 400–410 °C. Intermittent temperature spikes of up to 464 °C have been related to this recent magmatic activity (Haase et al., 2007; Koschinsky et al., 2008). For the first time, a hydrothermal fluid emanating at *p*–*T* conditions above the CP_{SW} has been sampled directly. With the exception of some trace metals the vapor-phase fluid composition is constant since 2005/2006 (Koschinsky et al., 2008; this study). This is in marked contrast to “post-eruptive” systems at shallower water depths along the EPR where short-term changes in temperature and fluid composition have been reported (Von Damm et al., 1997; Von Damm, 2000; Seyfried et al., 2003).

3. SAMPLES, ANALYTICAL METHODS, AND DATA PROCESSING

Hydrothermal fluids were sampled from the vent fields Turtle Pits, Comfortless Cove and Red Lion during three research cruises, which took place in 2005 and 2006 with F/S Meteor and ROV Quest (cruises M64/1 and M68/1), and in 2008 with N/O Atalante and ROV KIEL6000 (cruise Ata-2). One liter of Atlantic deep water was collected at 3000 m water depth from an area not affected by hydrothermal activity in order to determine the background REE composition of seawater in this area.

Two different sampling devices were used to collect the fluids, both carried by the ROVs: (1) an inert, all-plastic flow-trough pump system (Kiel pumping system, KIPS) (Garbe-Schönberg et al., 2006) with an aligned on-line high-precision temperature probe for *in situ* measurements at the point of sampling, and (2) titanium syringe water samplers (“Majors”) after (Von Damm et al., 1985), manufactured by Brest Meca, France.

On board, aliquots of the original, re-homogenized fluid samples were acidified to pH 2 with ultrapure HNO₃ (MERCK suprapur™) and stored until analysis. Further aliquots were filtered through 0.2 μm polycarbonate membrane filters (Nuclepore™) and subsequently acidified. In the home laboratory, non-filtered aliquots were further treated to dissolve all remaining particles formed prior, during, or after sampling by applying a pressure digestion of particles centrifuged from solution in screw-top PTFE Teflon™ beakers with HCl, HNO₃, and HF at 160 °C, followed by re-homogenization.

A modified method (after Shabani et al., 1992) was applied for matrix separation and pre-enrichment of REE + Y in hydrothermal fluids (Bau and Dulski, 1996a): between 10 and 20 ml of the sample were diluted to about 1 L with de-ionized water, subsequently acidified to pH 2 with ultrapure HCl (MERCK suprapur™) and spiked with 1 ml of 250 ppb Tm. A small aliquot was taken for the determination of the Tm reference concentration, before the sample was passed over an ion exchange column (Sep-Pak C18 cartridges™, BioRad) loaded with a mixture of ethyl-hexyl-phosphates. To remove major alkali and alkali earth elements, the cartridge was washed with 0.01 M HCl; the REE + Y were eluted with 40 ml of 6 M suprapure HCl. The eluates were evaporated in Teflon beakers to incipient dryness and finally taken up in 10 ml of 0.5 M HNO₃. Procedural blanks and certified reference material were processed along with the samples for analytical quality control.

All subsequent measurements of the eluates and the reference aliquots were performed with a quadrupole ICP-MS (PerkinElmer DRC-e) using Ru, Re, and Bi as internal standards. The REE yield for each individual sample has been calculated from the Tm single spike: $Tm (mg/l)_{eluate} \times 100 / Tm (mg/l)_{original}$. The recovery of Tm ranges between 95% and 105% for most samples. The inter-element REE fractionation during the separation procedure is less than 5%, as tested with REE spiked de-ionized water and spiked seawater. The method precision as estimated from duplicate REE + Y matrix separation and measurement of water reference sample SLRS-4 is better than 2% RSD (relative standard deviation) for all REE except Eu (<3% RSD) and Y (<5% RSD). The method precision for a hydrothermal fluid sample duplicate is better than 3% RSD for Pr, Nd, Sm, Eu, Gd, and Dy, better than 6% RSD for Ce, Tb, Ho, and Er, and better than 9% RSD for Yb, Lu, and Y. The procedure has been validated using two natural water standards (seawater: CRM-NASS-5; river water: CRM-SLRS-4; reference data are given in Lawrence and Kamber, 2007), and results are given in Table 1. For NASS-5, the accuracy (defined here as deviation from reference values) is within the analytical uncertainty of reference data (<5% for Nd, Sm, Eu, Dy, Y, Er, Yb, Lu, <8% for La, Ce, Pr, and Ho, and

Table 1

Details on cruises and samples, sequence of sampling, size of Eu anomaly and total REE + Y concentration of filtered aliquots, TB, Two Boats; SP, Sisters Peak.

Cruise	Date	Sample ID	Time	Eu/Eu*	REE + Y _{TOTAL} (nM)	Site/orifice	Sampling device	Temperature	Remarks
M64/1	15.04.2005	141 ROV	15:00	1.41	44.8	TB, exact pos. Not known	KIPS		
M68/1	09.05.2006	3 ROV-10	21:16	2.16	28.7	TB, base of chimney	KIPS	395	Top of a pipe removed
	11.05.2006	12 ROV-B2	19:09	3.49	16.3	Same	KIPS	405–407, stable	
	11.05.2006	12 ROV-B5	19:26	3.3	21.1	Same	KIPS	405–407, stable	
Ata-2	14.01.2008	35 ROV-8	14:34	2.23	32.3	TB, base of chimney	Ti-Major	451–425, after sampling	Clear venting
	18.01.2008	46 ROV-7	16:58	0.81	81.8	Same	KIPS	412, variable	New chimney, 20 cm high, re-opening at base, less vigorous
	21.01.2008	57 ROV-4	15:43	3.55	15.7	Same	KIPS	371 max	Re-opening failed, no clear venting
	21.01.2008	57 ROV-5	15:46	2.93	22.4	Same	KIPS	371 max	
M68/1	13.05.2006	20 ROV-5	18:20	1.13	363	SP, plump-like pipe at the base	KIPS	355–378	Big opening, emanating black smoke
	13.05.2006	20 ROV-6	18:26	2.39	97.5		KIPS	380	
Ata-2	16.01.2008	42 ROV-3	13:05	7.98	22.9	SP, plump-like pipe at the base	KIPS	367, stable	Removal of the top, big opening, several small channels feeding orifice
	16.01.2008	42 ROV-4	13:10	9.05	19.4	Same	KIPS	367, stable	
	16.01.2008	42 ROV-5	13:16	9.43	19.2	Same	KIPS	367, stable	
	16.01.2008	42 ROV-7	15:22	1.47	113	Same	Ti-Major	Failed	

<12% for Tb concentrations) and within 5% for element ratios. For SLRS-4, the deviation from the reference data is <1% for Ce, Nd, Tb, Dy, Y, Er, <4% for Sm and Gd, <6% for Pr, Ho, Yb, and Lu, and <9% for La. Aliquots of all samples were taken in duplicate for subsequent analysis in the ICPMS laboratories at University of Kiel, and digested in a similar way as described above if necessary. REE concentrations in hydrothermal fluid samples with low degrees of admixed seawater are high enough to be analysed directly with ICPMS after 12.5-fold dilution with ultrapure water. An Agilent 7500cs instrument was used with In and Re for internal standardization. The instrument was optimized for low oxide formation (LaO/La <1%), and an interference correction was applied for BaO on mass ¹⁵¹Eu and CeOH on mass ¹⁵⁷Gd. A weak signal suppression due to high abundances of easily ionisable elements in the seawater matrix was identified and corrected for. Results for the most REE-enriched fluid sample compare very well with the data obtained after matrix separation and are within 3% RSD (relative standard deviation) for La, Ce, Pr, Nd, Sm, Gd, Dy, and Er, and within 6% RSD for La, Tb, and Ho. Ytterbium and Lu could only be determined after matrix separation. The good agreement of results obtained with two independent methods reduces the possibility that our data are affected by systematic errors.

The concentrations of Cl, Na, K, Ca, Li, Si, Fe, Mn, Cu, and Zn in filtered and non-filtered fluid aliquots were determined according to the methods described in Schmidt et al. (2007).

3.1. Calculation of REE endmember concentrations and quantification of the anomalous behavior of europium and lanthanum

In most cases, hydrothermal fluid samples represent variable mixtures of pure hydrothermal fluid and admixed seawater. Assuming that Mg is quantitatively removed in hot hydrothermal fluids (Mottl and Holland, 1978), the percentage of entrained seawater can be calculated from: $Mg_{\text{sample}} \times 100 / Mg_{\text{seawater}}$. Endmember concentrations for the individual samples can be calculated as: $((100 \times REE^X_{\text{sample}}) - (\% \text{ seawater} \times REE^X_{\text{seawater}})) / \% \text{ fluid}$, where REE^X_{sample} is the measured concentration of a rare earth element or yttrium in the fluid sample and REE^X_{seawater} is the concentration of this element in the seawater (reference values are taken from Douville et al. (1999)) for 3000 m deep water in the TAG area; our own seawater data generally confirm the uniformity of Atlantic deep bottom water, but seem to be influenced by hydrothermal fluids, as indicated by slightly positive Eu anomalies. An approach combining Mg concentration and Y/Ho ratios to determine REE + Y endmember concentrations as suggested by Bau and Dulski (1999) is not required, as the almost chondritic Y/Ho ratios in all our samples (see below) prove a conservative behavior for both elements during the initial mixing with seawater.

Normalized REE data refer to Cl-chondrite (subscript CN, Anders and Grevesse, 1989). The anomalous behavior of Eu is quantified as Eu/Eu* of normalized data, where Eu

is the actual concentration and Eu^* is the predicted concentration based on interpolation of neighboring REE; the anomaly is defined as $\text{Eu}/\text{Eu}^* = \text{Eu}_{\text{CN}} / (0.67\text{Sm}_{\text{CN}} + 0.33\text{Tb}_{\text{CN}})$ following the method of (Bau and Dulski, 1996b). The fractionation between light, middle and heavy REE is expressed as $\text{Pr}_{\text{CN}}/\text{Gd}_{\text{CN}}$, $\text{Gd}_{\text{CN}}/\text{Yb}_{\text{CN}}$, and $\text{Pr}_{\text{CN}}/\text{Yb}_{\text{CN}}$. Lanthanum anomalies are quantified as $\text{La}/\text{La}^* = (3\text{Pr}_{\text{CN}} - 2\text{Nd}_{\text{CN}})$ after Bolhar et al. (2004).

4. RESULTS

In the following section, the REE compositions of vent fluids collected at Turtle Pits, Comfortless Cove and Red Lion are presented. Concentration data are presented as endmember values to allow for easier comparison between individual samples, independent of seawater admixture during sampling. In Table 1, details on the sequence of sampling for the cruise campaigns, on the type of sampler used for individual fluid samples, the exit temperature and brief site descriptions are given. Fluid data for filtered and original aliquots are given in Tables 2 and 3.

4.1. REE distribution in phase-separated hydrothermal fluids from Turtle Pits and Comfortless Cove

The two vent fields constantly emanate chloride-depleted vapor-phase fluids, formed by phase separation at P–T conditions above the critical point of seawater (Koschinsky et al., 2008). The following results refer to filtered aliquots.

The Two Boats chimney at Turtle Pits was sampled for the first time in 2005 with one sample (M64/1), then re-sampled in 2006 with three samples (M68/1) and in 2008 with four samples (Ata-2): the samples consist of varying mixtures of seawater and hydrothermal fluid (20–100% hydrothermal fluid). The chondrite-normalized REE + Y distributions vary strongly between individual fluid samples: whereas some samples display a smooth decrease from LREE to HREE ($\text{Pr}_{\text{CN}}/\text{Yb}_{\text{CN}} > 1$, $\text{Gd}_{\text{CN}}/\text{Yb}_{\text{CN}} > 1$) and positive Eu anomalies (max. $\text{Eu}/\text{Eu}^* = 3.55$) – defined as type I, others display a depletion of the lightest REE compared to the middle REE (MREE) with $\text{Ce}_{\text{CN}}/\text{Nd}_{\text{CN}} \leq 1$, higher $\text{Gd}_{\text{CN}}/\text{Yb}_{\text{CN}}$ ratios and very small positive or even negative Eu anomalies (minimum: $\text{Eu}/\text{Eu}^* = 0.81$; Fig. 1A and B) – defined as type II. All samples display an anomalous abundance of La, as indicated by positive La anomalies $\text{La}/\text{La}^* > 1$. The molar Y–Ho ratios are close to the chondritic value (46–60), suggesting that REE + Y scavenging by Fe(III) oxides did not significantly impact REE + Y distribution or concentration (Bau and Dulski, 1999).

We observe a significant co-variation of the relative fractionation of the REE and the size of the Eu anomaly with calculated endmember concentrations in the discrete samples, with higher concentrations in type II fluids. Calculated REE endmember concentrations for an individual sampling campaign display a strong variability, with $\text{REE}_{\text{TOTAL}} = 16.3 - 28.7 \text{ nM}$ (2006) and $15.7 - 81.7 \text{ nM}$ (2008). In contrast, the absolute Eu concentration is similar in all individual fluid samples and varies only between 700 and 1100 pM (2005–2008). It should be noted that the

variable endmember composition is independent of the amount of seawater intermixed with the hydrothermal fluid. Worth mentioning is the significant seawater proportion of 57% in the sample with the highest REE concentration (46 ROV-7). The maximum stable emanation temperature is about 400–410 °C for the 2006 and 2008 sampling campaigns.

As normalization to chondrite may obliterate the real fractionation of REE relative to the host rock (N-type mid-ocean ridge basalt is depleted in LREE in chondrite-normalized REE patterns), we additionally normalized the 5°S fluid to fresh, glassy N-type MOR basalt from 5°S. The pattern are similar to chondrite-normalized plots, except for a relative enrichment of LREE with $\text{Ce}_{\text{CN}}/\text{Nd}_{\text{CN}} > 1$ and $\text{Pr}_{\text{CN}}/\text{Nd}_{\text{CN}} > 1$ in both fluid types.

The Sisters Peak chimney at Comfortless Cove was first sampled in 2006 with two samples (M68/1) and re-sampled in 2008 with four samples (Ata-2). During both sampling campaigns, the fluids were successively recovered during the same ROV dive within 20–40 min. The chondrite-normalized REE distributions of individual fluid samples display a smooth decrease from the MREE to HREE ($\text{Gd}_{\text{CN}}/\text{Yb}_{\text{CN}} > 1$) and a depletion of the lightest REE ($\text{Ce}_{\text{CN}}/\text{Nd}_{\text{CN}} < 1$) (Fig. 2A and B). The size of fractionation between the LREE varies and is correlated with the size of the positive Eu anomaly (2008: $\text{Eu}/\text{Eu}^* = 1.41 - 9.43$). The calculated endmember concentrations differ strongly between individual fluid samples, with $\text{REE}_{\text{TOTAL}} = 97.5 - 363 \text{ nM}$ (2006) and $19.2 - 113 \text{ nM}$ (2008); higher concentrations are correlated with decreased Eu anomaly, smaller $\text{Ce}_{\text{CN}}/\text{Nd}_{\text{CN}}$ ratio and larger $\text{Gd}_{\text{CN}}/\text{Yb}_{\text{CN}}$ ratio. The absolute Eu concentrations are similar for samples of one sampling campaign (2008: $2.48 - 3.23 \text{ nM}$). The Y/Ho ratio is close to the chondritic value for all samples (44–57). Although the most REE-enriched fluid sample (20 ROV-5) is strongly influenced by seawater, with only 25% hydrothermal fluid, there is no clear correlation of REE distribution and seawater admixture. Temperature measurements recorded during the individual fluid sampling stations vary between 350 °C and 378 °C (2006), and 367 °C (2008).

In addition to the REE distribution in filtered fluid samples, we determined the REE content in eight non-filtered fluid aliquots. For most samples, the calculated endmember REE concentrations and chondrite-normalized REE patterns are very similar, with deviations of less than 10% for most REE (Table 3). The non-filtered hydrothermal fluid aliquots commonly contain sulfide particles formed prior, during, or after sampling due to cooling and/or seawater mixing. This leads to strongly decreased transition metal concentrations like Cu, Co, and Zn (and partly Fe) in filtered aliquots relative to the original fluid. As demonstrated by the similar REE concentrations in filtered and non-filtered aliquots of most Two Boats and Sisters Peak vent fluids, sulfide precipitates do not incorporate significant amounts of REE, which proves the conservative behavior of REE in these hydrothermal fluids during sulfide particle formation caused by cooling and/or mixing with seawater.

In summary, each fluid sample set from both vent sites (Two Boats and Sisters Peak), taken independently during different sampling campaigns, in different years, with

Table 2

Measured REE + Y composition of individual vent fluid samples at 5°S; F refers to filtered aliquots, NF refers to non-filtered aliquots.

	Sisters Peak 2006 (cruise M68/1)			2008 (cruise Ata-2)					
	20 ROV-5		20 ROV-6	42 ROV-3		42 ROV-4	42 ROV-5	42 ROV-7	
	F	NF	F	F	NF	F	F	F	NF
La	6250	6970	7010	1240	1010	969	1070	3570	3400
Ce	20,400	22,100	21,000	3200	2930	2950	2900	14,600	14,400
Pr	3740	3910	3700	529	516	513	489	3110	3090
Nd	20,200	21,800	18,700	2950	2760	2790	2660	20,100	20,200
Sm	5340	5500	4650	736	685	674	635	5930	6050
Eu	1880	2000	3460	1870	1800	1960	1930	2820	2770
Gd	4780	4790	3960	709	679	658	652	6400	6450
Tb	600	618	516	90.9	87.4	87.5	83.8	795	804
Dy	2890	2950	2380	460	453	459	430	3910	4040
Y	23,200	21,200	16,000	4070	4280	3990	3920	35,200	35,000
Ho	442	427	364	77.7	80.9	69.5	70.4	631	642
Er	889	886	781	176	179	176	159	1280	1310
Tm	—	—	—	—	—	—	—	—	—
Yb	345	330	343	96	131	103	97.3	516	535
Lu	40.1	32.4	25.4	13.6	15.5	15.4	14.3	55.5	75.2
Y/Ho	52	50	44	52	53	57	56	56	55
sw% ^a	75	67	15	29.6	29.0	21.0	21.7	12.6	13.0
Fluid% ^a	25	33	85	70.4	71.0	79.0	78.3	87.4	87.0
Yield ^b	100	102	107	97.6	90.3	90.4	94.4	97.3	98.9

	Two Boats		2005 (cruise M64/1)				2006 (cruise M68/1)				2008 (cruise Ata-2)			
	141 ROV		12 ROV-8		12 ROV-5	3 ROV-10	35 ROV-8		46 ROV-7		57 ROV-5	57 ROV-4		
	F	NF	F	NF	F	F	F	NF	F	NF	F	F	NF	
La	2530	3630	2700	3370	1560	2400	2650	2920	2770	4730	948	1350	2420	
Ce	4970	4980	5340	6580	3220	4620	5930	6320	6140	12,200	1900	2700	4180	
Pr	675	635	696	809	395	665	856	911	922	1900	256	359	393	
Nd	3310	3200	3030	3420	1780	3390	4680	4920	5070	10,800	1230	1670	1850	
Sm	851	811	734	806	460	922	1400	1470	1570	3400	332	443	486	
Eu	401	398	792	810	547	702	1100	1120	447	677	345	552	578	
Gd	988	955	740	823	511	1160	1750	1820	2100	4540	399	510	553	
Tb	130	126	102	119	77	171	259	254	291	628	64	81.5	91.3	
Dy	695	694	614	682	407	899	1320	1330	1440	3250	354	440	496	
Y	6990	11,100	4770	5350	3610	8830	11,500	13,900	14,300	30,100	3240	4120	4710	
Ho	124	117	104	117	73.1	146	227	212	247	520	60.4	79.1	84.3	
Er	272	269	254	271	168	345	439	429	489	1070	142	177	190	
Tm	—	—	—	—	—	—	—	—	—	—	—	—	—	
Yb	146	162	135	156	96.6	178	200	188	195	445	80.1	101	122	
Lu	19.8	21.6	15.8	17	10.9	19.4	28.8	20.8	20.5	51.1	9.18	14.8	14.7	
Y/Ho	56	95	46	46	49	60	51	66	58	58	54	52	56	
sw% ^a	51	53	5	4	22	15	0.3	0.1	56.1	57.5	58.8	21.4	21.4	
fluid% ^a	49	47	95	96	78	85	99.7	99.9	43.9	42.5	41.2	78.6	78.6	
Yield ^b	70 [*]	96	95	106	95	100	106.0	88.4	91.4	96.4	99.9	103.7	95.0	

	Mephisto 2008 (cruise Ata-2)						TAG-sw	5°S sw	NASS-5	SLRS-4 (n = 2)	SLRS-4 % RSD
	67 ROV-3	67 ROV-4	67 ROV-5	67 ROV-6	67 ROV-7	67 ROV-8					
	F	F	F	F	F	F	F	F			
La	553	414	493	414	234	527	29	23.9	94.7	1920	0.16
Ce	986	644	633	586	327	685	5.5	12	37.4	2620	1.34
Pr	135	83.1	79.4	73.2	41.3	87.7	4.4	4.57	13.7	482	1.68
Nd	603	385	346	322	195	372	21.4	19.4	60	1860	1.25
Sm	172	110	93.4	97.8	51.6	106	4.1	3.29	31	370	1.57
Eu	266	285	328	288	114	309	1.1	1.21	2.07	51.4	2.62

Continued on next page

Table 2 (*continued*)

	Mephisto 2008 (cruise Ata-2)						TAG-sw F	5°S sw F	NASS-5	SLRS-4 (<i>n</i> = 2)	SLRS-4 % RSD
	67 ROV-3 F	67 ROV-4 F	67 ROV-5 F	67 ROV-6 F	67 ROV-7 F	67 ROV-8 F					
Gd	227	141	124	123	52.4	135	6.3	5.05	11.1	215	0.43
Tb	32.3	21.9	18.6	18.5	10	21.8	0.919	0.773	1.5	27.7	0.14
Dy	181	121	110	107	57	122	6.4	5.67	11.7	145	1.19
Y	1790	1180	1310	1610	699	1340	170	163	236	1530	4.06
Ho	30.9	22.6	21.7	20.9	9.77	19.8	1.7	1.51	2.66	27.4	1.10
Er	74.7	52.9	50.6	54.6	28.6	54.4	5.49	5.11	8.63	78.1	1.08
Tm	–	–	–	–	–	–	–	–	–	–	–
Yb	45.4	n.d.	33.9	35.8	21.3	37.8	5.41	5.06	7.17	66.5	0.48
Lu	5.08	4.39	4.79	4.44	2.93	4.15	0.88	0.926	1.09	10.2	0.09
Y/Ho	58	52	60	77	72	68	100	108	89	56	
sw% ^a	35	21	3	20	66	6					
Fluid% ^a	65	79	97	80	34	94					
Yield ^b	103	103	100	103	102	105					

^a Calculated from measured Mg concentration.

^b Yield refers to Tm recovery in %.

different sampling devices, displays the same systematic in REE composition: higher REE_{TOTAL} concentrations mean lower Ce_{CN}/Nd_{CN} ratios and a smaller positive or even negative Eu anomaly (Fig. 3). The REE vent fluid composition (REE_{TOTAL} and Eu/Eu*) of the single vents displays a strong variability within minutes, hours, and days. The exact sequence of sampling and further details are described in detail in the [Electronic annex EA-1](#) and in [Table 1](#). The strongest variation occurred after re-positioning the sampling device, i.e., between samples obtained at different days or after changing of the sampling device from KIPS to Ti-Major. In most cases, the vent orifice had been (re)opened prior to sampling. As derived from EA-1, the emanation of fluid samples with unusual REE + Y distribution seems to be correlated to this opening/widening of vent orifices.

4.2. REE distribution in the filtered and the original aliquot of sample 46 ROV-7

We emphasize here the distribution of REE in one sample from Two Boats (46 ROV-7), with a nearly doubled REE concentration and a larger negative Eu anomaly in the non-filtered aliquot (46 ROV-7 NF, Eu/Eu* = 0.56, Fig. 1B) relative to the filtered aliquot, accompanied by enhanced concentrations of sulfide-forming elements. This sample represents the most REE-enriched fluid at Two Boats displaying a negative Eu anomaly. Particles obtained by filtration from sample 46 ROV-7 are characterized by significant amounts of anhydrite, besides Cu–Fe–Zn sulfide particles. This suggests that the anhydrite particles may control the REE + Y inventory of the non-filtered aliquot of sample 46 ROV-7.

4.3. Comparison of REE distribution and major and minor element composition at Turtle Pits and Comfortless Cove

As discussed by [Koschinsky et al. \(2008\)](#), the chemical composition of the phase-separated hydrothermal fluids

from Turtle Pits and Comfortless Cove did not change significantly between 2005 and 2006. New samples obtained in 2008 confirm this stability, with less than 5% deviation in the calculated endmember concentration of major elements compared to the former sampling campaigns. The concentrations of the major elements Na, Cl, K, Si and the minor elements Li, Fe, and Mn in individual samples of the 2008 campaign define single mixing lines between seawater and endmember hydrothermal fluid; endmember data for individual samples, as given in [Table 3](#), differ by less than 10% (in most cases by less than 5%). The major element Ca, however, varies by several mM, both at Two Boats and Sisters Peak ([Table 3](#)). At Two Boats, the Ca endmember concentration of filtered aliquots varies between 8.4 and 9.5 mM in 2006 (= 12%) and 8.9–11.7 mM in 2008 (= 24%), respectively. At Sisters Peak, the endmember Ca concentrations of filtered aliquots vary between 11.1 and 16.4 mM in 2005 (= 32%) and 10.7–12.5 mM in 2008 (15%). In contrast to the concentrations of Na, Cl, K, Li, and Mn, the endmember Ca concentration of individual fluid samples is positively correlated with total REE + Y concentration (Fig. 4); the size of the Eu anomaly is negatively correlated with Ca concentration. Furthermore, the Ca concentration in 46 ROV-7 NF is strongly increased relative to the filtered aliquot (by about 40%, despite similar concentrations of K, Na, Li).

The calculated endmember compositions of Cu, Co, and Zn, determined in non-filtered aliquots, are highly variable between individual fluid samples from Two Boats and Sisters Peak. At Two Boats, the endmember Cu concentration ranges between 9 μM and 76 μM (2006) and between 50 μM and 229 μM (2008). At Sisters Peak, the Cu endmember concentration ranges between 120 μM and 280 μM (2006) and between 27 μM and 118 μM (2008). We particularly emphasize the similar trend of endmember concentrations of Cu and Co with REE and Ca. Strontium co-varies with Ca in individual fluid samples. Significant correlation of

Table 3

Calculated endmember composition of individual vent fluid samples, major and minor element data for 2005 and 2006 are calculated from data given in Koschinsky et al. (2008); F and NF refer to filtered and non-filtered aliquots, respectively.

		Sisters Peak 2006 (cruise M68/1)			2008 (cruise Ata-2)					
		20 ROV-5		20 ROV-6	42 ROV-3		42 ROV-4	42 ROV-5	42 ROV-7	
		F	NF	F	F	NF	F	F	F	NF
pH	25 °C		4.9	3.1		4.33	3.8	4.28		3.36
T	°C		350	380		367	367	367		—
Cl	mM	244	—	235	265	—	243	255	253	—
Na	mM	220	227	202	206	206	205	205	199	208
K	mM	7.4	7.4	7.2	7.7	7.6	7.7	7.7	7.4	7.7
Ca	mM	16.4	17.4	11.1	10.7	10.6	10.8	10.9	12.5	12.8
Si	mM	13.4	13.5	13.9	15.3	14.8	15.5	15.3	14.9	15.2
Li	μM	303	326	320	349	347	352	349	339	349
Fe	mM	1.51	3.1	3.22	2.84	2.95	2.94	2.89	2.74	3.11
Mn	μM	663	657	700	708	723	722	707	691	739
Cu	μM	—	309	120 ^c	—	31	27 ^c	28 ^c	—	118
Zn	μM	—	138	49 ^c	—	100	91.7 ^c	92.8 ^c	—	84.4
Sr	μM	44.2	52	33.1	33.9	34.9	34.2	34.1	38.8	41.5
La	pM	24,900	27,800	8240	1740	1410	1220	1360	4080	3900
Ce	pM	81,600	88,300	24,700	4540	4130	3730	3700	16,800	16,600
Pr	pM	14,900	15,600	4350	750	725	648	623	3560	3550
Nd	pM	80,600	87,000	22,000	4180	3890	3530	3400	22,900	23,200
Sm	pM	21,300	22,000	5470	1040	964	852	810	6790	6960
Eu	pM	7520	8000	4070	2660	2540	2480	2470	3230	3180
Gd	pM	19,100	19,100	4650	1000	954	832	830	7320	7410
Tb	pM	2400	2470	606	129	123	111	107	910	924
Dy	pM	11,500	11,800	2800	651	635	579	547	4480	4640
Y	pM	92,300	84,400	18,800	5710	5950	5010	4960	40,200	40,200
Ho	pM	1760	1700	428	110	113	87.6	89.4	722	738
Er	pM	3540	3530	918	248	249	221	201	1460	1510
Yb	pM	1360	1300	402	134	183	129	123	590	614
Lu	pM	158	127	29.7	19	21.4	19.3	18	63.4	86.2
Sum REE		363,000	373,000	97,500	22,900	21,900	19,400	19,200	113,000	113,000
Eu _{CN} /Eu _{CN} ^a		1.13	1.16	2.39	7.98	8.29	9.05	9.43	1.47	1.41
Ce _{CN} /Nd _{CN}		0.74	0.74	0.82	0.79	0.77	0.77	0.79	0.53	0.52
Gd _{CN} /Yb _{CN}		10.5	11	8.69	5.63	3.93	4.85	5.09	9.32	9.07

Continued on next page

Rare earth element distribution in >400 °C hot hydrothermal fluids from 5°S, MAR

Table 3 (continued)

	Two Boats														Mephisto														
	2005		2006 (cruise M68/1)				2008 (cruise Ata-2)								2008 (cruise Ata-2)														
	(cruise M64/1)		141 ROV-12		12 ROV-B5		12 ROV-B2		3 ROV-10		35 ROV-8		46 ROV-7		57 ROV-4		57 ROV-5		67 ROV-3		67 ROV-4		67 ROV-5		67 ROV-6		67 ROV-7		67 ROV-8
	F	NF	F	NF	F		F		F	NF	F	NF	F	NF	F	NF	F	NF	F	F	F	F	F	F	F	F	F	F	F
pH	25 °C	5.19			3.1	3.4			3.2		2.92		3.47		2.85	4.51			3.51		4.01		2.85		3.62		5.06		3.22
T	°C	–			407	405			395		429– 451 ^a		412 ^b		–	–			363		363		363		363		363		363
Cl	mM	235	–		278	–		275	277		283	–	298	–	–	–	294		547		541		532		528		565		542
Na	mM	218	223		240	236		227	241		240	247	227	248	224	250	241		423 (448) ^c		444		455		450		454		443
K	mM	7.8	8.1		8.8	8.7		8.4	8.9		9.0	9.2	9.1	9.7	8.5	9.3	9.6		18.5 (19.2) ^c		19.4		19.4		19.6		20.3		19.2
Ca	mM	8.9	9.1		8.6	8.7		8.4	9.5		10.0	10.1	11.7	16.3	8.9	9.5	10.8		15.4 (16.2) ^c		16.0		16.0		16.1		16.2		15.6
Si	mM	10	–		11.7	11.6		11.5	11.9		12.0	12.0	11.9	12.6	11.2	11.4	12.2		17.3		18.1		18.3		18.4		18.4		18.0
Li	μM	383	389		419	431		405	425		434	438	428	451	411	447	440		1046		1102		1110		1115		1111		1093
Fe	μM	3.54	4.33		4.01	3.85		3.83	3.96		3.86	4.1	2.6	7.59	3.45	4.09	3.3		0.35 (1.89) ^c		0.62		0.63		0.70		0.18		0.76
Mn	μM	467	466		489	469		474	494		490	505	483	518	455	510	486		615 (664) ^c		650		664		659		657		650
Cu	μM	–	112		–	9		18 ^a	76 ^a		–	50	–	229	–	65	71 ^c		209 ^c		–		–		–		–		3.9 ^c
Zn	μM	–	55.2		–	27		65 ^a	28.1 ^a		–	38.3	–	92.9	–	26.2	32.3 ^c		257 ^c		79 ^c		86 ^c		93 ^c		80 ^c		63 ^c
Sr	μM	21.8	26.7		24.8	25.2		23.8	27		29.7	30.7	32.4	46.9	26.9	30.2	33.8		51 (55) ^c		54		55		55		53		54
La	pM	5140	7700		2840	3510		1970	2820		2650	2930	6270	11,100	1680	3070	2260		838		516		506		509		626		559
Ce	pM	10,100	10,600		5620	6850		4120	5430		5930	6320	14,000	28,700	3380	5320	4610		1520		814		651		730		940		728
Pr	pM	1370	1350		732	842		502	781		856	912	2090	4460	447	499	615		207		104		81.5		90.3		112		92.9
Nd	pM	6730	6780		3180	3560		2260	3990		4680	4930	11,500	25,400	2080	2350	2950		920		481		355		396		527		394
Sm	pM	1730	1720		772	840		585	1080		1400	1470	3560	8000	552	617	799		263		139		95.8		121		142		112
Eu	pM	816	845		834	843		700	826		1100	1120	1020	1590	689	735	835		411		361		337		359		330		329
Gd	pM	2010	2020		779	857		648	1360		1750	1820	4760	10,700	636	702	959		347		177		127		152		140		143
Tb	pM	265	268		108	124		97.8	201		259	254	661	1480	102	116	154		49.4		27.5		19.1		22.8		27.5		23.2
Dy	pM	1410	1470		646	710		515	1060		1320	1330	3280	7640	549	629	850		276		151		113		133		153		129
Y	pM	14,100	23,500		5010	5570		4450	10,400		11,500	13,900	32,500	70,500	5110	5940	7630		2670		1450		1350		1970		1710		1410
Ho	pM	252	247		110	122		91.9	171		227	212	560	1220	98.5	107	144		46.7		28.2		22.3		25.6		25.2		21
Er	pM	550	565		267	282		209	405		439	429	1110	2520	220	240	337		112		65.5		51.9		66.7		72.8		57.5
Yb	pM	292	339		142	163		118	209		200	188	438	1040	125	154	187		67.1		34.7		43.4		51.6		39.8		
Lu	pM	39.5	45		16.6	17.7		13	22.6		28.8	20.8	45.5	119	18.3	18.4	21		7.36		5.32		4.9		5.33		6.83		4.35
Sum REY		44,800	57,400		21,100	24,300		16,300	28,700		32,300	35,800	81,800	174,000	15,700	20,500	22,400		7730		4310		3740		4630		4860		4040
Eu _{CN} /Eu _{CN} ^a		1.41	1.46		3.3	3.03		3.49	2.16		2.23	2.21	0.81	0.56	3.55	2.93	2.93		4.42		7.25		9.79		8.4		6.52		8.06
Ce _{CN} /Nd _{CN}		1.09	1.14		1.28	1.39		1.33	0.99		0.92	0.93	0.88	0.82	1.18	1.65	1.13		1.2		1.23		1.34		1.34		1.3		1.35
Gd _{CN} /Yb _{CN}		5.16	4.5		4.12	3.96		4.12	4.92		6.58	7.29	8.16	7.74	3.82	3.43	3.86		3.89		2.76		2.63		2.04		2.7		

^a Measured with KIPS, sampled with Ti-Major.^b Maximum temperature.^c Measured in non-filtered aliquot.

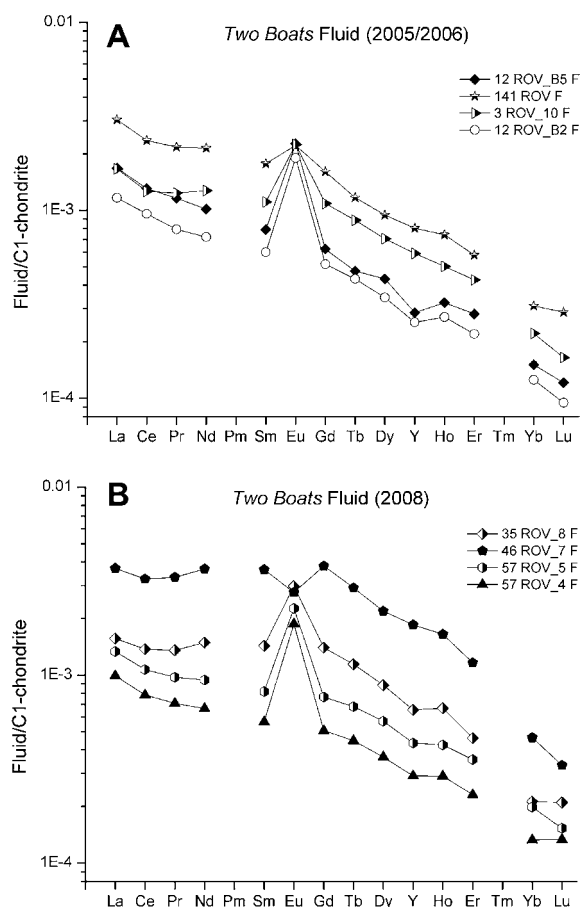


Fig. 1. Chondrite-normalized distribution of REE + Y (endmember values) of individual hydrothermal fluid samples (filtered) from Two Boats (TB); (A) sampling campaigns 2005 + 2006; (B) sampling campaign 2008, includes the non-filtered aliquot of sample 46 ROV-7, Normalization data from [Anders and Grevesse \(1989\)](#).

absolute Sr concentrations (2006: 33.1–44.2 μM ; 2008: 33.9–38.8 μM) with $\text{REE}_{\text{TOTAL}}$ exists at Sisters Peak.

4.4. REE and Y in the Red Lion field

Six fluid samples were taken during the sampling campaign in 2008 from one single orifice of the Mephisto chimney in the Red Lion vent field. Except for the first sample, the measured REE distributions in these fluids are quite homogenous and similar to other MOR vent fluids, with a smooth decrease from Ce to Lu ($\text{Ce}_{\text{CN}}/\text{Yb}_{\text{CN}} = 3.7\text{--}4.1$), positive Eu anomalies ($\text{Eu}/\text{Eu}^* = 6.5\text{--}9.8$) and positive La anomalies ($\text{La}/\text{La}^* = 1.6\text{--}1.9$) (Fig. 5). Total REE concentrations range between 3.7 and 4.9 nM. The slight variation is correlated with a variation in the size of the positive Eu anomaly, with the highest anomaly in the least REE-enriched sample, which is the same trend as observed in Turtle Pits and Comfortless Cove fluids. The first sample taken after widening the vent orifice is characterized by significant seawater mixing (35% seawater), almost doubled REE concentrations ($\text{REE}_{\text{TOTAL}} = 7.7$ nM), a reduced Eu anomaly

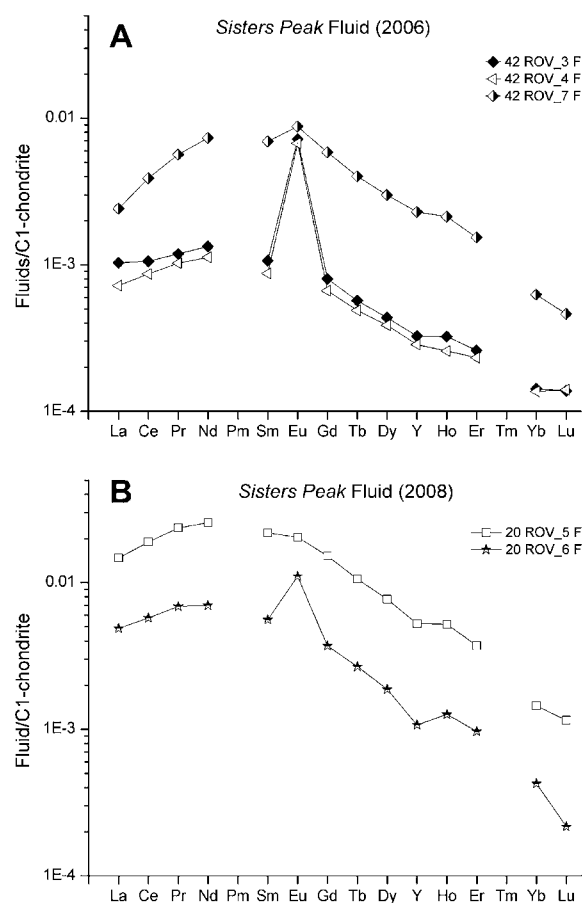


Fig. 2. Chondrite-normalized distribution of REE + Y (endmember values) of individual hydrothermal fluid samples (filtered) from Sisters Peak (SP); (A) sampling campaign 2006; (B) sampling campaign 2008, Normalization data from [Anders and Grevesse \(1989\)](#).

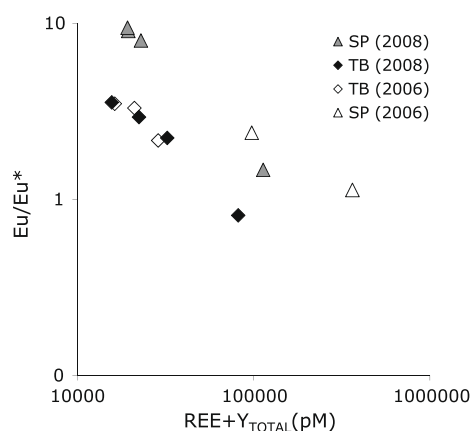


Fig. 3. Size of Eu anomaly (Eu/Eu^*) as function of total REE + Y concentration for Two Boats (TB) and Sisters Peak (SP).

of $\text{Eu}/\text{Eu}^* = 4.4$, and a stronger fractionation between LREE and HREE ($\text{Ce}_{\text{CN}}/\text{Yb}_{\text{CN}} = 4.9$) compared to the other, more uniform samples. Furthermore, the non-filtered

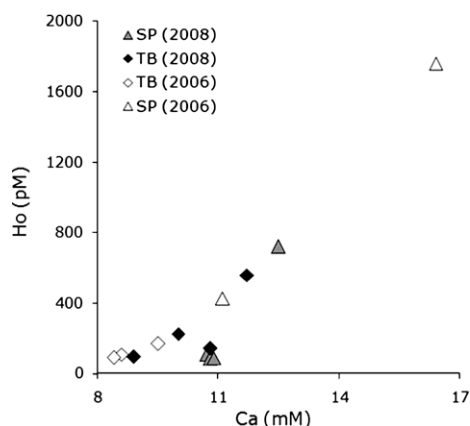


Fig. 4. Holmium concentration (representative for all REE) as function of Ca concentration for individual fluid samples from Two Boats (TB) and Sisters Peak (SP) chimneys.

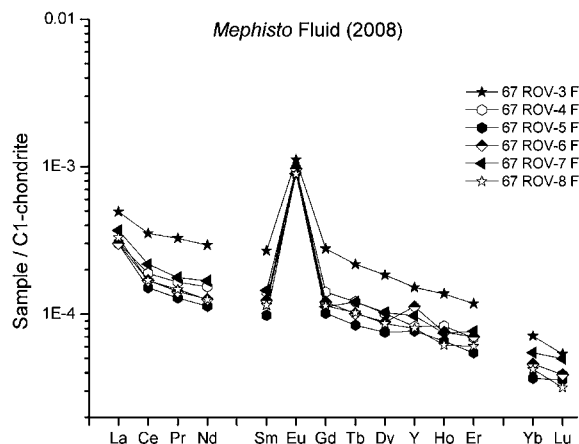


Fig. 5. Chondrite-normalized REE + Y pattern of individual hydrothermal fluids (filtered) from Mephisto, Red Lion field (2008), Normalization data from [Anders and Grevesse \(1989\)](#).

aliquot of this sample contains strongly enhanced concentrations of Fe, Cu, and Co indicating an incorporation of sulfide particles.

4.5. REE and Y in hydrothermal anhydrites from Turtle Pits and Comfortless Cove

We analyzed anhydrite samples of both active and inactive chimney pieces from the Turtle Pits vent field ([Table 4](#)). This hydrothermal anhydrite is often associated with Cu and Fe sulfides; the interior of zoned chimney pieces commonly consists of chalcopyrite and anhydrite. In some cases, the conduit is lined with anhydrite, partially intergrown with fine-grained sulfide, indicating formation in the hottest part of the fluid. The total REE concentrations vary between 3 mg/kg and 9 mg/kg, which is in the lower range of hydrothermal anhydrites from the TAG mound (3–21 mg/kg, [Humphris, 1998](#)). The chondrite-normalized REE display relatively flat LREE to MREE patterns, a negative Eu anomaly and a relative depletion of the HREE

Table 4

REE + Y composition of anhydrite samples from Two Boats chimney pieces.

	123 ROV-4 (mg/kg)	139-415-c (mg/kg)	139-415-9 (mg/kg)
La	1.385	0.534	0.107
Ce	2.781	1.262	0.222
Pr	0.401	0.208	0.036
Nd	2.046	1.172	0.195
Sm	0.586	0.354	0.058
Eu	0.128	0.105	0.065
Gd	0.695	0.414	0.071
Tb	0.098	0.053	0.009
Dy	0.529	0.263	0.047
Y	2.806	1.170	0.246
Ho	0.088	0.040	0.008
Er	0.185	0.073	0.015
Tm	0.019	0.007	0.002
Yb	0.092	0.029	0.009
Lu	0.010	0.003	0.001

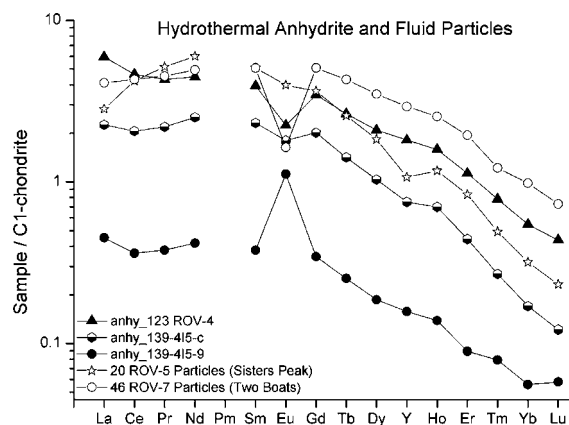


Fig. 6. Chondrite-normalized REE + Y pattern of hydrothermal anhydrite from the active chimney Two Boats and of filtered particles 46 ROV-7P (Two Boats) and 20 ROV-5P (Sisters Peak) dominantly consisting of anhydrite, Normalization data from [Anders and Grevesse \(1989\)](#).

([Fig. 6](#)). The Ce_{CN}/Nd_{CN} ratio is ≤ 1 . The size of the Eu anomaly is inversely related to the total REE concentration. Lanthanum displays a small positive anomaly ($La/La^* > 1$). Anhydrite particles filtered from fluid samples 20 ROV-5 (named as 20 ROV-5P) and 46 ROV-7 (named as 46 ROV-7P) display a depletion in the lightest REE and in HREE and a pronounced negative (46 ROV-7P) or slightly negative Eu anomaly (20 ROV-5P) in chondrite-normalized patterns ([Fig. 6](#)).

5. DISCUSSION

The extremely hot vapor-phase fluids emanating from two vent fields at 5°S on the MAR display a unique REE distribution compared to formerly investigated fields along mid-ocean ridges ([Fig. 7](#)). Formerly reported data on the REE composition of high-temperature ($>250^\circ\text{C}$) vent

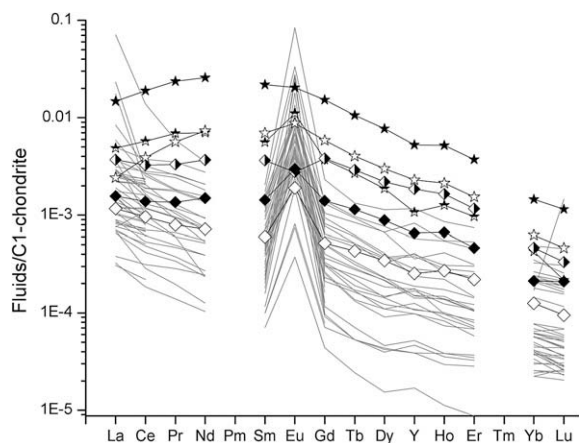


Fig. 7. Chondrite-normalized distribution of REE + Y (endmember values) of mid-ocean ridge hydrothermal fluids (gray lines: compiled data from Douville et al., 1999; Mitra et al., 1994; Bau and Dulski, 1999; James et al., 1995), for comparison, selected fluid data from this study (black stars: 20 ROV-5; half-filled stars: 20 ROV-6; white stars: 42 ROV-7; black diamonds: 35 ROV-8; half-filled diamonds: 46 ROV-7; white diamonds: 12 ROV-B2); Normalization data from Anders and Grevesse (1989).

fluids from mid-ocean ridge hydrothermal systems cover a large range in total REE concentration (between ~ 1 and 50 nM), but display generally uniform chondrite-normalized distribution patterns with a smooth decrease from Ce to Lu ($Ce_{CN}/Yb_{CN} = 9\text{--}48$) and positive Eu anomalies ranging between $Eu/Eu^* = 5\text{--}46$. Positive La anomalies are reported for some of these systems. In contrast, fluids emanating at 5°S at the vent sites Two Boats and Sisters Peak are different in, (1) the behavior of Eu with respect to the other REE, (2) the fractionation between light, middle and heavy REE including the Ce/Nd ratio, (3) total REE concentrations and in (4) their strong (temporal) variability of REE concentration and distribution within minutes, hours, and days despite similar major element concentrations. Fig. 8 emphasizes the uniqueness of most of 5°S vent fluids with respect to their relative REE distribution and the positive correlation between Ce_{CN}/Nd_{CN} and Eu/Eu^* in comparison to other MOR fluids.

In contrast to the phase-separated Turtle Pits and Comfortless Cove vent fields, the adjacent Red Lion vent field about 2 km north of Turtle Pits emanates ~ 350 °C hot fluid with seawater salinity, and shows a REE composition rather typical for MOR hydrothermal systems. Here, the fluid composition is stable on time scales of minutes to years. This points towards special conditions governing the hydrothermal system at Turtle Pits and Comfortless Cove, with active phase separation at conditions above the CP_{SW} . The REE distribution in the emanating vent fluids seem to be related to a very young, recently recharged and highly dynamic circulation system.

5.1. Hydrothermal anhydrite and the variable REE fluid composition at 5°S

The two generally different REE signatures in Two Boats and Sisters Peak fluids cannot be related to different

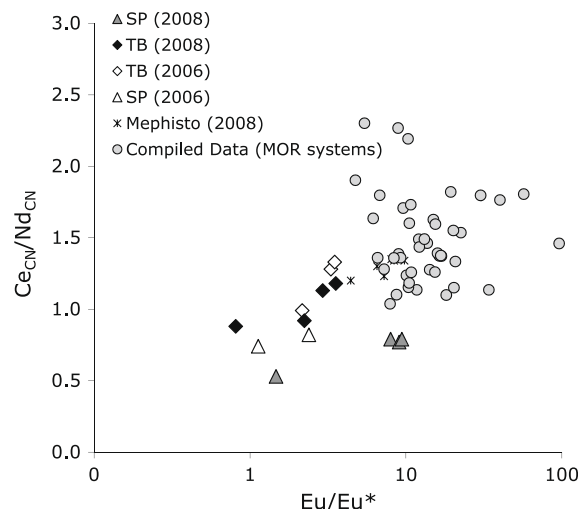


Fig. 8. Size of Eu anomaly (Eu/Eu^*) as function of LREE fractionation (Ce_{CN}/Nd_{CN}) for mid-ocean ridge hydrothermal fluids (gray circles, references see Fig. 9), for comparison, data from this study, visualizing the special REE signature at Two Boats (TB) and Sisters Peak (SP) (white diamonds: Two Boats-2006; black triangles: Two Boats-2006; gray triangles: Sisters Peak-2008; white triangles: Sisters Peak-2006; black stars: Mephisto-2008), note the positive correlation of both parameters for each sampling campaign.

fluid types generated at depth, as this should be reflected in further differences in the concentrations of elements determined by p - T dependent fluid-mineral equilibria (Si, K, Fe) and the intensity of water/rock interaction (Li), which has not been observed. Based on the significant inter-correlation of REE_{TOTAL} , Eu/Eu^* , Ce_{CN}/Nd_{CN} with Ca and Sr in filtered endmember vent fluids from Turtle Pits and Sisters Peak, it seems likely that the formation of the calcium sulfate mineral anhydrite plays a major role in controlling the variable fluid composition in these hydrothermal systems, modifying a single fluid type.

A direct evidence for the control of anhydrite on the fluid chemistry at 5°S comes from the non-filtered aliquot of 46 ROV-7 (Two Boats). Compared to the filtered aliquot, the concentrations of REE_{TOTAL} , Ca and Sr are significantly increased, and inversely correlated with Eu/Eu^* and Ce_{CN}/Nd_{CN} . The REE + Y pattern of this fluid sample closely reflects the pattern of the anhydrite-dominated particles filtered from the original fluid. In the non-filtered aliquot, the digestion of these particles during the sample pretreatment must have led to a strongly enhanced REE + Y concentration, accompanied by increased endmember Ca concentrations (16.3 mM in contrast to 11.7 mM in the filtered aliquot) and endmember Sr concentration (46.9 μ M compared to 32.4 μ M in filtered aliquot). The REE + Y signature of the particle samples display a concave-downward distribution with a maximum for the MREE and an even more pronounced negative Eu anomaly of $Eu/Eu^* = 0.34$ and a smaller Ce_{CN}/Nd_{CN} ratio compared to the non-filtered aliquot. A mass balance calculation for the fluid sample 46 ROV-7 demonstrates that the increase in REE_{TOTAL} , Ca, and Sr and the size of the neg-

active Eu anomaly in the non-filtered aliquot can be explained by the dissolution of about 0.06 g anhydrite in 100 ml fluid, i.e., the acidification of about 100 ml non-filtered hydrothermal solution (with subsequent dissolution of 0.06 g of anhydrite particles) would change the concentrations and relative distribution of REE, Ca, Sr and the Eu/Eu* ratio in the way observed between the 46 ROV-7 filtered and non-filtered fluid sample aliquots (see *Electronic annex Figure EA-2-1*).

5.1.1. Constraints on the formation of anhydrite in submarine hydrothermal systems

Anhydrite is a calcium sulfate mineral commonly occurring in hydrothermal systems. At Turtle Pits, anhydrite is a common mineral in active chimneys and it has also been observed in white blocks littered around the sulfide mound. Due to its retrograde solubility (Blouinot and Dickson, 1969; Freyer and Voigt, 2004) anhydrite becomes saturated in seawater at temperatures $>150\text{ }^{\circ}\text{C}$ (Bischoff and Seyfried, 1978; Monnin et al., 2003). Anhydrite formation requires the presence of free sulfate, and may form in the entire convection system during heating of seawater in recharge zones, during mixing of hot hydrothermal fluid with sulfate-containing seawater in discharge zones, or at the emanation sites. Hydrothermal anhydrites are characterized by strong enrichments of REE compared to hydrothermal fluids. A link between REE fluid patterns and anhydrite precipitation/dissolution has been suggested for several hydrothermal fields: Mills and Elderfield (1995) argued that precipitation of anhydrite in the TAG hydrothermal mound represents a major sink of REEs from solution in hydrothermal systems. Enhanced positive Eu anomalies in diffuse fluids from the Endeavour Segment are attributed to anhydrite precipitation in the subseafloor (Bao et al., 2008).

The rare earth elements and Y composition of hydrothermal anhydrites has been described from the active TAG and PacManus hydrothermal fields (Mills and Elderfield, 1995; Humphris, 1998; Bach et al., 2003; Humphris and Bach, 2005) and ancient massive sulfide ore deposits from Kuroko (Ogawa et al., 2007), with formation temperatures up to $390\text{ }^{\circ}\text{C}$ and highly variable formation conditions (Humphris and Bach, 2005 and references therein). Chondrite-normalized REE distributions range from LREE enriched to LREE depleted patterns (relative to MREE) with variably positive, or negative, Eu anomalies.

The incorporation of REE into anhydrite may be controlled by three different parameters: crystal chemistry, solution complexation, and non-selective incorporation. (1) Kagi et al. (1993) experimentally investigated the partitioning of REE between anhydrite and a CaSO_4 solution at temperatures up to $70\text{ }^{\circ}\text{C}$, proposing a crystallographic control on the partitioning of REE in anhydrite. In 8-fold coordination, the ionic radius of Nd^{3+} resembles most closely that of Ca^{2+} , the difference becoming bigger with decreasing and increasing masses. The calculated partition coefficients describe a hyperbolic curve, with the highest values for Ce, Nd, and Sm. (2) In addition to crystal chemistry constraints, REE + Y solution complexation may play an important role in determining the REE incorporation into hydrothermal anhydrites (Pavlenko et al., 1959; Mineyev,

1963; Bach et al., 2003; Humphris and Bach, 2005). At high mixing temperatures of hydrothermal fluid and heated seawater $>300\text{ }^{\circ}\text{C}$, the REE are strongly complexed with Cl (Wood, 2003). Light REE–chloride and Eu^{2+} –chloride solution complexes are more stable than other trivalent REE–chloride complexes (e.g., Mayanovic et al., 2008) and are supposed to be discriminated against the other REE during incorporation into anhydrite (Humphris and Bach, 2005). In addition, the ionic radius of Eu^{2+} is larger than Eu^{3+} and the other trivalent REE and, thus, Eu does not fit into the crystal lattice of anhydrite as well as the other REE. Anhydrite formed at such conditions displays a relative depletion in the lightest REE relative to the middle REE and a smaller Eu anomaly relative to the source fluid, as observed in some anhydrite samples from the TAG mound. At lower fluid temperatures, REE–chloride complexes are less important and thus cannot control the incorporation of REE into anhydrite. Humphris and Bach (2005) attributed different REE patterns in TAG anhydrites to various mixing ratios between hot hydrothermal fluid and cool or heated seawater influencing the concentration and speciation of REE in the solution. (3) Some anhydrite minerals from the Kuroko ore deposit show similar depletions in the light REE as some TAG anhydrites and even negative Eu anomalies in chondrite-normalized plots, which has been interpreted by Ogawa et al. (2007) as secondary signature caused by recrystallization processes, with a preferential mobilization of LREE and Eu from primary anhydrite with an inherited REY fluid signature typical for MOR black smoker fluids. A non-selective incorporation of REE into anhydrite however, is unlikely for 5°S , as then anhydrite participation would not change the fluid chemistry between individual samples in the observed way. Furthermore, secondary recrystallization recesses are unlikely to play a dominant role in recent mineral precipitates in the 5°S vent fields.

The chimney anhydrite from Turtle Pits with relatively flat LREE and $\text{Pr}_{\text{CN}}/\text{Yb}_{\text{CN}} > 1$ display variable Eu anomalies correlating with the total REE concentration: these systematics and trends are similar to other anhydrite precipitates from TAG and seem to mirror the variable fluid REE distribution at Two Boats and Sisters Peak. The negative anomaly in the sample with the highest REE content indicate a relative discrimination of Eu relative to its REE neighbors; possible formation conditions will be discussed further below.

Fig. 9 illustrates the normalization of the most REE-enriched to the least REE-enriched fluid samples (for one sampling campaign) for Two Boats and Sisters Peak. The pattern shows the strongest enrichment for MREE, with decreasing enrichments for Er to Lu and La to Nd. In contrast, the relative ratio for Eu is close to one, attributed to the narrow range of Eu concentrations for fluid samples collected from the same vent. These patterns closely reflect those of black smoker-normalized anhydrites from TAG, which were likely be formed at formation temperatures of $190\text{--}390\text{ }^{\circ}\text{C}$ (Humphris and Bach, 2005, and references therein). Anhydrite grains from chimney material at Two Boats display a very similar, fluid-normalized (type I) REE distribution. Assuming that anhydrite with a

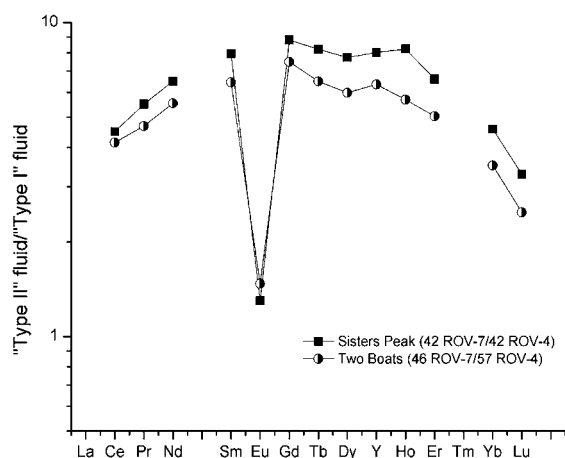


Fig. 9. Normalization of the most REE-enriched to the least REE-enriched hydrothermal fluid samples from Sisters Peak (black squares) and Two Boats (b/w circles): 42 ROV-7 normalized to 42 ROV-4; 46 ROV-7 normalized to 57 ROV-4.

fractionated distribution of REE + Y relative to its source fluid controls the variability of REE fluid composition at 5°S, two scenarios may explain the transformation of one fluid type to the other: (1) incorporation of anhydrite previously being formed in a fluid with a REE distribution typical for mid-ocean ridge hydrothermal systems, or (2) precipitation of anhydrite and removal from a fluid highly enriched in REE, but relatively depleted in Eu and the lightest REE relative to their REE neighbors in chondrite-normalized plots. As mentioned above, solution complexation is likely a critical parameter controlling the fractionation between individual REE + Y elements during incorporation into anhydrite and will thus briefly discussed in the very hot 5°S fluids.

5.2. REE + Y fluid speciation at 5°S

The complexation of elements in solution is controlled by the concentrations of ligands and the physico-chemical conditions of the fluid (dielectric constant, temperature, pressure, pH, redox potential). Chloride complex formation constants strongly increase with increasing temperature and decreasing fluid density (Ding and Seyfried, 1992). Under given p - T conditions at 5°S, the REE-speciation in the vent fluids is probably dominated by strong neutral or lower charged Cl-complexes that are more stable for LREE than for HREE (Gammons et al., 2002; Mayanovic et al., 2007b, 2008; Migdisov and Williams-Jones, 2008). Mayanovic et al. (2008) explored the importance of hydrated REE-chloride complexes forming more than 70% of all Cl-complexes at 500 °C. Vapor-phase fluids formed by phase separation at p - T conditions above the CP_{SW} are able to dissolve large amounts of metals, controlled by the hydration of metal species (Williams-Jones et al., 2002; Pokrovski et al., 2005). Shmulovich et al. (2002) suggested the dominance of neutral REE-oxy-chloro-complexes in high- T vapor phases. The potential influence of fluoride complexation on the mobility of REE in 5°S vent fluids

can be excluded, as this would fractionate Y from Ho (Bau and Dulski, 1995) which has not been observed. Theoretically, REE + Y-sulfate complexes could also become of importance in the presence of sulfate in solution. The stability of REE sulfate complexes increases with temperature (Schijf and Byrne, 2004); accompanied by an enhanced difference in the stability constants between LREE and HREE with an increase from La to Sm, and then a smooth decrease to Yb at 100 °C; the stability of Eu^{2+} -sulfate and Y-sulfate complexes is lower compared to their trivalent REE neighbors. However, a significant role of REE-sulfate complexation at 5°S is unlikely, as the extremely low solubility of $CaSO_4$ (see above) at high temperatures should inhibit the availability of free SO_4^{2-} in the solution required for the formation of REE-sulfate complexes (although no experimental data are available regarding the solubility of REE sulfate minerals relative to other sulfate minerals like anhydrite and barite). Also, chondritic Y/Ho ratios in investigated hydrothermal fluids argue against a significant REE-sulfate complexation in solution.

Although strongly increased chloride complex stabilities close to the CP_{SW} might explain the enhanced REE concentrations in some 5°S vent fluids, a significant change in the relative REE-stabilities at these p - T conditions is not supported by presently available data. Phase separation close to the critical point is probably not sufficient to cause the observed features in REE concentration and distribution in REE enriched 5°S vent fluids: the fractionation of Cl-complexed elements relative to Cl during phase separation (and thus inter-element fractionation of REE) is minor near the critical curve of the NaCl-H₂O system, which has been demonstrated by field data for Brandon vent fluids at 21°S EPR and experimentally derived data (Pokrovski et al., 2005; Von Damm et al., 2003; Foustoukos and Seyfried, 2007a).

5.3. Model 1: anhydrite precipitation from typical MOR fluid and subsequent re-dissolution

In this model, the 5°S vent sites emanate a fluid with a rather typical REE distribution (for MOR hydrothermal systems), most closely represented by the samples 57 ROV-4 (Two Boats, 2008) and 42 ROV-3 (Sisters Peak, 2008). Anhydrite is formed in the fluid prior to sampling, caused by incipient mixing of the hydrothermal fluid with seawater. This may happen either during fluid ascent – recently, Coumou et al. (2009) have shown in mathematical fluid flow simulations that hydrothermal systems affected by phase separation above the CP_{SW} continuously mix with heated seawater at shallower sub-seafloor levels, causing the onset of anhydrite precipitation – or during exit of the fluid at the seafloor. The samples with the most REE-enriched fluid signature are characterized by strong seawater admixture, which favors the formation of anhydrite. This is documented in the occurrence of anhydrite-rich particles filtered from these samples. Alternatively, previously formed anhydrite (and sulfide) particles from the surrounding mineralized material could be incorporated into the ascending fluid. Since anhydrite displays a retrograde solubility, in either case cooling of the fluid sample after recov-

ery will initiate the dissolution of entrained anhydrite. The REE content of the dissolved anhydrite will overprint the primary signature in the fluid, accompanied by a shift in the Ca and Sr concentration. The variable REE concentrations in the individual fluids would result from various amounts of dissolved anhydrite overprinting the original fluid signature.

We conducted mass balance calculations for the mixture of a fluid with typical REE distribution with different types and amounts of anhydrite for Two Boats and Sisters Peak (chimney anhydrites, anhydrite particles directly filtered from the fluids) to check whether the concentration differences of REE_{TOTAL}, Ca, and Sr and the REE distribution differences in 5°S fluids can be explained by the dissolution of anhydrite. The Ca concentration in hydrothermal fluids from Two Boats (2008) increases by about 2.9 mM between the samples with lowest and highest concentrations, which, assuming anhydrite dissolution, would correspond to about 0.4 g CaSO₄ incorporated into 1 kg of fluid. At Sisters Peak, about 0.3 g anhydrite per kg fluid is required. We can conclude that chimney anhydrites similar to those sampled at Turtle Pits (123 ROV-4; 139-4I5-c) cannot control the REE inventory in hydrothermal fluids from the Two Boats and Sisters Peak sites, as the relative fractionation between LREE and MREE, the Eu and REE_{TOTAL} concentrations in the chimney anhydrite are not sufficient to cause the differences in fluid patterns. However, these chimney anhydrites need not to resemble the hypothetical anhydrite overprinting the original fluid signature, which could have formed at different conditions. More likely is the incorporation of anhydrites with a REE distribution similar to particulate anhydrite filtered from the fluids themselves (20 ROV-5P; 46 ROV-7P; see [Figures EA-2-2 and EA-2-3](#)). These particles could represent remnants of the incorporated and dissolved anhydrite proposed in this model. This model is able to explain the differences in REE concentration, REE distribution, Ca and Sr concentration between individual fluid samples. The co-variation with total Cu and Co concentration in non-filtered aliquots may be explained by the formation/incorporation of isocubanite or chalcopyrite prior to sampling. In contrast to anhydrite, these sulfide particles remain un-dissolved in the samples until acidification.

The strong involvement of anhydrite at Two Boats and Sisters Peak relative to other vent sites like Red Lion may be explained by the special *p*–*T* conditions and the type of convection at these vent sites. During mixing of hydrothermal fluid with heated seawater during recharge, anhydrite may form in the fluid and partly precipitate in the marginal zones of the central upflow channel due to reduced velocities at the walls. Turbulent flow, possibly initiated by the opening of a new vent orifice might remove this anhydrite from the channel walls. Unfortunately, no experimental data for anhydrite solubility in the *p*–*T* regime of 5°S are available. It is known that anhydrite solubility also depends upon pressure, with increasing solubility with increasing pressure ([Newton and Manning, 2005](#)). It could be speculated that a pressure increase in the fluids due to clogging of feeding channels and a pressure drop caused by the opening of vent orifices may initiate anhydrite disso-

lution/precipitation leading to variable REE fluid composition. Relative to other hydrothermal systems, the solubility of anhydrite may be even more decreased at the very high fluid temperatures at Two Boats and Sisters Peak.

The variable concentration and distributions of REE in anhydrite samples from the active and inactive smoker chimneys either indicates different formation conditions in the chimney walls – different mixing conditions in the porous chimney walls may result in different fluid REE complexation and redox conditions, controlling the incorporation of REE in addition to ionic radii constraints – or a temporal evolution – REE could become increasingly fractionated with time during anhydrite growth under stable conditions: a non-selective incorporation of REE into anhydrite in similar proportions as in the source fluid may be favored by rapid precipitation relative to an equilibrium fractionation and has been discussed by [Kagi et al. \(1993\)](#) in a 2-stage model, with a non-selective incorporation during the first, fast-growing stage, followed by an equilibrium fractionation according to distribution coefficient thermodynamics.

5.4. Model 2: the formation of an early-stage reaction zone fluid and its modification by anhydrite precipitation and removal

In contrast to model 1, the hydrothermal fluid samples of type II may represent a primary fluid signature that is variably modified by the formation of anhydrite resulting in fluids with a more typical REE distribution.

In general, the REE content in hydrothermal solutions is determined from the fraction that is initially available (leachable) from the host rock, the transport capacity of the water (solution complexation), and by ion exchange with rock-forming minerals and surface coatings (e.g., [Bach and Irber, 1998; Douville et al., 1999](#)). Leaching experiments have shown that, independent of temperature, w/r ratio, and pH, the LREE are more easily leached from basaltic or andesitic rocks relative to the MREE and HREE, most likely due to a preferred alteration of late-stage interstitial material and clinopyroxene, as well as desorption from grain boundaries ([Giese and Bau, 1994; Bach and Irber, 1998; Bau et al., 1998; Allen and Seyfried, 2005; Shibata et al., 2006](#)). In the absence of chloride in the alteration fluid, all leaching solutions are, both in low-temperature and in high-temperature experiments, characterized by negative rock-normalized Eu anomalies ([Giese and Bau, 1994; Bach and Irber, 1998; Bau et al., 1998; Allen and Seyfried, 2005; Shibata et al., 2006](#)). In contrast to low-temperature conditions, the oxidation state of Eu in hot (>~200 °C), acidic, hydrothermal solutions is Eu²⁺ ([Sverjensky, 1984; Bilal, 1991](#)), which is decoupled from the trivalent REE by solution complexation and sorption. This is demonstrated in high-temperature experiments by [Allen and Seyfried \(2005\)](#) that produced leaching solutions with strong positive Eu anomalies normalized to the host rock in the presence of Cl, emphasizing the influence of solution complexation on the REE distribution and fractionation in alteration fluids. Furthermore, sorption onto alteration mineral surfaces has been shown to be more pronounced

for HREE than LREE and weakest for divalent Eu (e.g., (Bau, 1991; Tertre et al., 2008). The incorporation of REE into alteration mineral lattices depends on the mineral itself, with chlorite and smectite discriminating against LREE and Eu^{2+} (c.f., Allen and Seyfried, 2005). Thus, migration of a Cl-containing reaction fluid with continuous sorption and incorporation of REE into alteration minerals is probably an important factor determining the REE distribution in mid-ocean ridge hydrothermal fluids. The “enriched” fluid type II with high REE concentrations, small but significant enrichments of LREE over MREE relative to the source rock (except sample 42 ROV-7, see Electronic annex EA-3) and negative to small positive Eu anomalies, sampled at Two Boats and Sisters Peak, could thus represent an early-stage reaction fluid which is not completely modified by secondary processes like solution complexation, adsorption/desorption and incorporation into secondary minerals, similar to the hypothetical reaction zone fluid postulated by Bach and Irber (1998). We exclude the presence of Eu^{3+} in the 400 °C hot, strongly reducing (high Fe, high H_2) fluids of Two Boats and Sisters Peak: the variable Eu anomalies relative to MORB indicate a fractionation of Eu and its trivalent REE neighbors. Furthermore, a discrimination against Eu during anhydrite formation is only possible in the presence of Eu^{2+} . More likely, fluid migration was not sufficient to fractionate and enrich Eu^{2+} relative to its trivalent neighbors and to further enrich LREE relative to MREE.

However, the existence of the hypothesized primary fluids being strongly enriched in REE (and Ca) must be critically viewed with respect to the general fluid chemistry and experimental data: the constant concentrations of Na, K, Si, Li, Fe, Mn and other elements since 2005 prove stable reaction zone conditions in the seafloor for at least 3 years at temperatures >400 °C. The Ca concentration in hydrothermal fluids is strongly temperature-dependent, with Ca fixation in hydrous Ca-bearing silicates like clinozoisite at temperatures >350 °C (Seyfried, 1987; Berndt et al., 1988, 1989). Thus, the enriched Ca signature in type II fluids (relative to seawater, up to 16 mM) as a primary signal can only be explained when assuming Ca gain during water/rock interaction <350 °C prior to further heating of the fluid, or assuming high water/rock ratios in the high-temperature reaction zone. Furthermore, experimental data by Allen and Seyfried (2005) show significant positive Eu anomalies in the presence of Cl after a reaction time of less than 30 days, related to the effect of solution complexation and to the formation of secondary alteration minerals, which also argues against the prevalence of neutral to negative Eu anomalies relative to the precursor rock over a period of 3 years.

A significant contribution of vapor-phase fluids formed near the vapor–halite phase boundary to the REE budget at 5°S can be excluded. Although enhanced Br/Cl ratios at Two Boats and Sisters Peak may suggest the formation of such a vapor phase (Foustoukos and Seyfried, 2007a; Koschinsky et al., 2008), which could have been mixed during ascent with a hot single-phase liquid fluid resulting in a fluid with moderately decreased salinity (see fluid flow simulations of Coumou et al., 2008a; Coumou et al., 2009), the

REE transport capacity in these vapors with strongly reduced chlorinity (5–10 mM Cl corresponding to 300–350 bars, 475–520 °C) would be minimized (Douville et al., 1999; Allen and Seyfried, 2005). Furthermore, there is no reasonable explanation for the required extreme Ca and Sr enrichments in such vapors.

5.4.1. Precipitation and removal of anhydrite from the early stage-reaction zone fluid resulting in a “common” MOR fluid type

Assuming an early-stage reaction zone fluid as primary fluid type, the variability of 5°S vent fluids originates from the formation of anhydrite during mixing with variable proportions of heated, sulfate-bearing seawater in the seafloor (Humphris and Bach, 2005). Assuming a fractionated incorporation of REE + Y, subsequent removal of anhydrite from the solution would result in a hydrothermal fluid depleted in all REE, but enriched in LREE and Eu relative to the HREE. Eventually, a fluid with REE pattern similar to a typical black smoker fluid will evolve. The variation with Cu and Co could be explained by the formation and removal of a high-temperature Cu solid solution (isocubanite) in the seafloor due to cooling and/or mixing with seawater. Anhydrite particles filtered from 46 ROV-7 fluid may represent precipitated, but not yet sequestered anhydrite formed in the seafloor or within the chimney.

5.5. Compositional REE variability in 5°S vent fluids and other MOR black smoker fluids on a temporal scale

Only few data on the time scale of years are available on the temporal evolution of REE composition and distribution in other hydrothermal vent fluids (Douville et al., 1999, 2002; Schmidt et al., 2007). Stable REE composition has been reported for the Logatchev field (1996–2007; Douville, 1999; Schmidt et al., 2007); for TAG (1993; Mitra et al., 1994), and Snake Pit (1986–1990; Mitra et al., 1994). Reported changes in REE distribution and concentrations in individual vent fields, as for the Snake Pit vent field (1990–1995) and the Lucky Strike vent field, are related to variations in fluid temperature and duration of water–rock interaction and are accompanied by variations in major element composition (Douville et al., 1999). To our knowledge, this is the first study investigating the temporal evolution of the REE composition at a single vent site on time scales from minutes to years. Due to these sampling intervals, we were able to resolve a strong temporal variability in REE composition, which is likely related to the highly dynamic fluid emanation at the vent sites.

6. CONCLUSIONS

This study has demonstrated that the REE + Y content and distribution in submarine hydrothermal vent fluids at mid-ocean ridges is not as uniform as previously thought. Investigations of phase-separated vapor-phase fluids from the Turtle Pits and Comfortless Cove vent fields with venting temperatures above 400 °C (at >300 bars, i.e., phase separation above the CP_{SW}) resolved a strong temporal var-

iability over several orders of magnitude on different time scales of minutes to years, despite a constant bulk composition of the fluid. Some of these fluids obtained between 2005 and 2008 at Two Boats and Sisters Peak display a rather normal distribution pattern with strong positive Eu anomalies and $Ce_{CN}/Nd_{CN} > 1$ (type I). Others are strongly enriched in all REY but Eu, relative to formerly investigated hydrothermal systems. This enriched fluid type (type II) displays a unique REE + Y_{CN} distribution with a smooth decrease from the middle to the heavy REE, a relative depletion in light REE with $Ce_{CN}/Nd_{CN} < 1$, and weakly positive or even negative Eu anomalies. The behavior of the LREE and Eu is especially different compared to other MOR systems. In addition, mixtures of both end-member fluid types were obtained. Based on inter-correlations of Ca, Sr, REE, Eu/Eu^* , and Ce_{CN}/Yb_{CN} , and on constraints on REE incorporation into anhydrite we conclude that the transformation between both fluid types at Two Boats and Sisters Peak is controlled by anhydrite formation/dissolution. Two different models have been discussed to explain the unique and highly variable REE signature of 5°S vent fluids. The first model involves the entrainment of particulate (or colloidal) anhydrite into a fluid with an REE + Y signature typical for other mid-ocean ridge systems during ascent. Anhydrite may be formed due to mixing of an evolved fluid with a common REE distribution (type I) with heated seawater, thereby retaining a REE signature enriched in MREE, but relatively depleted in Eu. A fluid accumulating this anhydrite will inherit its signature (i.e., the concave-downward REE distribution), as soon as a temperature decrease causes dissolution, as the REE + Y concentrations of the anhydrite by far exceed those in the fluid. In the second scenario, we discussed the discharge of a primary reaction zone fluid (fluid type II) from the high-temperature reaction zone, partially mixing with heated seawater entraining the hydrothermal circulation system at relatively shallow depths. The mixing causes anhydrite formation and subsequent precipitation, leading to a variable fluid modification with relative enrichments in LREE and Eu in the remaining fluid (type I). We may be observing an early stage of a hydrothermal system, with the seafloor emanation of a primary reaction zone fluid favored in young, hot hydrothermal systems like at 5°S with shallow reaction zones (implying short migration ways). This activity state might be common at hydrothermal sites of high magmatic activity, but the primary fluid REE signature will later be completely modified by anhydrite precipitation, in addition to the effects of solution complexation and sorption/incorporation onto/into alteration minerals. Other scenarios involving changing thermodynamic states of the fluid over small temperature-pressure shifts close to the CP_{SW} as well as phase separation above the CP_{SW} , which might explain the REY systematics in the “supercritical” vapor-phase fluids are too speculative at the present state of knowledge and are not supported by available experimental data.

Although both models could explain the REE + Y systematics and the co-variation of REE with Ca and Sr, the model of a primary reaction zone fluid emanating at 5°S is not straightforward, because some experimental results

such as Ca mobility during high-temperature basalt alteration argue against this interpretation. Based on the existing data, there is more conclusive evidence for the modification of an evolved fluid type. It cannot be excluded, however, that two processes – (1) the emanation of a fluid with primary REE signature and its modification by anhydrite precipitation and (2) the incorporation of anhydrite into the ascending/emanating fluid could shape the REE + Y pattern of hydrothermal fluids at 5°S.

The strong compositional variability with respect to elements affected by sulfate/sulfide precipitation as resolved for Two Boats and Sisters Peak, as well as the variation in fluid temperature are supposed to be related to the young, post-eruptive stage of hydrothermal venting and may be a common effect in other hydrothermal systems in similar geological settings. Further investigations in other hydrothermal systems venting under similar p – T conditions including the determination of stable isotope signatures of Ca, Sr, H, and Cl and experimental studies are necessary to definitely constrain the origin of the REE-enriched fluid type II and broaden the knowledge of REE + Y geochemistry in marine hydrothermal systems.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the on-line version, at [doi:10.1016/j.gca.2010.04.007](https://doi.org/10.1016/j.gca.2010.04.007).

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Chapter 5

Fluid elemental and stable isotope composition of the Nibelungen hydrothermal field (8°18'S, Mid-Atlantic Ridge): constraints on fluid–rock interaction in heterogeneous lithosphere



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Fluid elemental and stable isotope composition of the Nibelungen hydrothermal field (8°18'S, Mid-Atlantic Ridge): Constraints on fluid–rock interaction in heterogeneous lithosphere

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ABSTRACT

Depending on the geological setting, the interaction of submarine hydrothermal fluids with the host rock leads to distinct energy and mass transfers between the lithosphere and the hydrosphere. The Nibelungen hydrothermal field is located at 8°18'S, about 9 km off-axis of the Mid-Atlantic Ridge (MAR). At 3000 m water depth, 372 °C hot, acidic fluids emanate directly from the bottom, without visible sulfide chimney formation. Hydrothermal fluids obtained in 2009 are characterized by low H₂S concentrations (1.1 mM), a depletion of B (192 μM) relative to seawater, lower Si (13.7 mM) and Li (391 μM) concentrations relative to basaltic-hosted hydrothermal systems and a large positive Eu anomaly, and display a distinct stable isotope signature of hydrogen ($\Delta^2\text{H}_{\text{H}_2\text{O}} = 7.6\text{--}8.7\text{‰}$) and of oxygen ($\Delta^{18}\text{O}_{\text{H}_2\text{O}} = 2.2\text{--}2.4\text{‰}$).

The heavy hydrogen isotopic signature of the Nibelungen fluids is a specific feature of ultramafic-hosted hydrothermal systems and is mainly controlled by the formation of OH-bearing alteration minerals like serpentine, brucite, and tremolite during pervasive serpentinization. New isotopic data obtained for the ultramafic-hosted Logatchev I field at 14°45'N, MAR ($\Delta^2\text{H}_{\text{H}_2\text{O}} = 3.8\text{--}4.2\text{‰}$) display a similar trend, being clearly distinguished from other, mafic-hosted hydrothermal systems at the MAR.

The fluid geochemistry at Nibelungen kept stable since the first sampling campaign in 2006 and is evident for a hybrid alteration of mafic and ultramafic rocks in the subseafloor. Whereas the ultramafic-fingerprint parameters Si, Li, B, Eu anomaly and $\Delta^2\text{H}_{\text{H}_2\text{O}}$ distinguish the Nibelungen field from other hydrothermal systems venting in basaltic settings at similar physico-chemical conditions and are related to the interaction with mantle rocks, the relatively high concentrations of trace alkali elements, Pb, and Tl can only be attributed to the alteration of melt-derived gabbroic rocks. The elemental and isotopic composition of the fluid suggest a multi-step alteration sequence: (1) low- to medium-temperature alteration of gabbroic rocks, (2) pervasive serpentinization at moderate to high temperatures, and (3) limited high-temperature interaction with basaltic rocks during final ascent of the fluid. The integrated water/rock ratio for the Nibelungen hydrothermal system is about 0.5.

The fluid compositional fingerprint at Nibelungen is similar to the ultramafic-hosted Logatchev I fluids with respect to key parameters. Some compositional differences can be ascribed to different alteration temperatures and other fluid pathways involving a variety of source rocks, higher water/rock ratios, and sulfide precipitation in the sub-seafloor at Logatchev I.

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1. Introduction

The slow-spreading Mid-Atlantic Ridge (MAR) is characterized by an irregular lithosphere without a continuous layered crust,

with frequent exposures of mantle rock lithologies and melt-derived gabbroic rocks (Früh-Green et al., 2004). This is caused by a discontinuous magma supply associated with tectonic stretching of the lithosphere (Searle and Escartin, 2004), in contrast to fast-spreading ridges like the East-Pacific Rise (EPR) with a continuous magmatic crust formed by intrusion and extrusion of magma along the ridge. In ultramafic rock settings, high-temperature hydrothermal systems exchanging material and heat between the lithosphere and the hydrosphere are affected by specific water-rock mineral

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reactions (serpentinization). Depending on the physico-chemical conditions, geochemical gradients associated with serpentinization reactions lead to characteristic elemental and isotopic fluxes when compared to black smoker systems in mafic host rocks (Wetzel and Shock, 2000; Douville et al., 2002; Allen and Seyfried, 2003; Kelley et al., 2005; Ludwig et al., 2006; Proskurowski et al., 2006; Bach and Klein, 2009). The understanding and quantification of geochemical processes in such systems is crucial for the discussion of modern and also ancient elemental budgets of the ocean, however, the consequences of serpentinization for global lithosphere-hydrosphere exchange budgets are presently poorly known (Alt et al., 2009).

Within the past 15 years, 6 actively venting hydrothermal systems in ultramafic substrate rocks have been discovered along, or off-axis to the MAR, venting two types of hydrothermal fluids: (1) Lost City located off-axis in the Atlantis Massif, emanating fluids with temperatures <200 °C and alkaline pH, low Si activity, high dissolved H₂ and CH₄ concentrations, and very low transition metal concentrations (Kelley et al., 2001), and (2) Logatchev I and II at 15°N, MAR (Charlou et al., 2002, 2007; Douville et al., 2002), Ashadze I and II at 13°N (Charlou et al., 2007) and Rainbow at 36°N, MAR (Douville et al., 2002; Seyfried et al., 2004), emanating fluids with temperatures >300 °C, and acidic pH, moderate Si activity, high dissolved H₂ and CH₄ concentrations and high transition metal concentrations. Based on the frequency of ultramafic rock outcrops at the seafloor along the MAR and other slow-spreading ridges (see (Früh-Green et al., 2004) and references therein), ultramafic-hosted hydrothermal systems can be expected to be common. Recently, a new high-temperature hydrothermal system – Nibelungen – has been discovered at 8°18'S on the southern MAR (cruise M68/1 in 2006; (Koschinsky et al., 2006). Extremely high dissolved hydrogen and methane concentrations in these vent fluid indicate seawater-peridotite interaction (serpentinization) in the subseafloor (Melchert et al., 2008). Further evidence that active serpentinization of mantle peridotites is a widespread phenomenon along the MAR comes from hydrothermal plume data with methane and/or hydrogen anomalies (Charlou and Donval, 1993), the Gakkel Ridge (Edmonds et al., 2003), and Kolbeinsey Ridge (Botz et al., 1999). Several other hydrothermal systems located in ultramafic rocks along the MAR are known, but are either inactive (Lena Trough, (Snow et al., 2001) or emanate presently only diffuse fluids (Saldanha field, (Dias and Barriga, 2006). The Kairei field located at the intermediate spreading Central Indian Ridge north of the Rodrigues Triple Junction is likely being influenced by the alteration of troctolite, a rare type of ultramafic rocks (Kumagai et al., 2008; Nakamura et al., 2009).

During seawater–mantle rock interaction, peridotite is hydrated in a multi-step reaction of olivine to brucite, followed by the breakdown of brucite and the formation of serpentine and magnetite, which is accompanied by the formation of large amounts of hydrogen (e.g., (Bach et al., 2006). At temperatures above 300 °C, the alteration of mantle rocks is dominated by the hydration of orthopyroxenes, with the formation of alteration minerals like tremolite and talc (Allen and Seyfried, 2003). The low pH of high-temperature fluids is controlled by the alteration assemblage tremolite-talc-serpentine and has as strong impact on metal solubility (Allen and Seyfried, 2003). The heat source of ultramafic-hosted hydrothermal systems is most likely gabbroic intrusions or the lithospheric mantle (German and Lin, 2004), as exothermic serpentinization reactions are not sufficient to produce enough heat to drive a high-temperature hydrothermal circulation (Allen and Seyfried, 2004). Often, the chemical composition of high-temperature hydrothermal fluids in ultramafic environments indicates a hybrid alteration of both ultramafic and mafic rocks (e.g., Logatchev, Douville et al., 2002).

Only few studies investigated the vent fluid geochemistry of hydrothermal systems affected by serpentinization reactions and qualitatively inferred geochemical processes in the subsurface.

The occurrence of hydrothermal activity associated with mantle rock alteration is often linked to off-axis tectonic fault zones (Lost City, Logatchev I, Nibelungen – (Kelley et al., 2001; Melchert et al., 2008; Petersen et al., 2009), which provide fluid pathways and may promote access to, and penetration of, mantle lithologies. At the MAR, axial-parallel normal faults and detachment faults accommodating plate separation may extend 10–30 km off-axis (Gràcia et al., 2000; Escartin et al., 2008). Further, the setting in older lithosphere provides more complex fluid–rock interaction possibilities compared to fresh MORB settings, with pelagic sediment, altered and seafloor-weathered mafic crust, gabbro and peridotite as potential host rocks. It is likely that high-temperature venting in off-axis settings is more common than represented by the few fields discovered so far.

Only few studies investigated the vent fluid geochemistry of hydrothermal systems affected by serpentinization reactions and qualitatively inferred geochemical processes in the subsurface (Douville et al., 2002; Charlou et al., 2007; Schmidt et al., 2007). This paper reports the first fluid compositional data for Nibelungen including stable isotope data for oxygen and hydrogen, and discusses constraints on the geochemical processes during fluid circulation. The Nibelungen data will be compared to new elemental and isotopic data obtained for the Logatchev I field. We will show that Nibelungen fluid composition is controlled by a hybrid alteration of ultramafic and mafic rocks resulting in a characteristic geochemical fingerprint.

2. Geological setting

The Nibelungen hydrothermal field is situated on the Southern MAR 8°18'S at a water depth of 3000 m, located on an east-facing fault scarp and about 9 km east of the presently active ridge axis (Koschinsky et al., 2006; Melchert et al., 2008). All active and extinct vents follow the fault geometry in the subseafloor. There is a prominent fault west of the field providing fluid pathways and efficient heat extraction. The area surrounding the Nibelungen hydrothermal vent field is characterized by a sedimented seafloor with common outcrops of strongly altered (weathered) pillow lava and lava flows (Seifert et al., 2009). Talus blocks of basalt and serpentinites have been recovered directly at the crater rim. The only active vent in the Nibelungen field consists of one 4–5 m wide circular depression (“smoking crater”) and a single orifice with vigorous emanation of enormous volumes of black smoke. This led to its name *Drachenschlund* (*Dragon Throat*). So far, such a depression-like morphology of vent sites is only known from the ultramafic-hosted vent fields Logatchev I and Ashadze at 13°N (Charlou et al., 2007) where several “smoking craters” exist. In addition, several extinct sulfide chimneys occur aligned along the N–S trending fault in the near vicinity of this crater. Dissolved gas fluid chemistry indicates the interaction of seawater and peridotite in the subseafloor (Melchert et al., 2008). The unusually low ³He flux (Keir et al., 2008) suggests a deeply stored, old and degassed heat source, such as lower gabbroic cumulates, rather than active magmatic activity.

The Logatchev I hydrothermal field is located at 14°45'N, MAR at 3000 m water depth, situated on a plateau on the eastern flank of the rift valley about 7 km away from the neovolcanic zone (Batuev et al., 1994; Petersen et al., 2009). In this region uplift of upper mantle sequences occurs along large detachment faults and results in core complex formation (Smith et al., 2008). According to McCaig (2008) and Petersen et al. (2009) the Logatchev I field is, in analogy to the Rainbow field at 36°14'N, located at the ultramafic footwall of a detachment fault, allowing for extensive penetration of seawater into the footwall. A detailed description of the vent field complex with its vent site morphologies and surrounding host rocks is given in Petersen et al. (2009). Hydrothermal fluids were first sampled in 1996 by the French–Russian Microsmoke cruise (Douville et al., 2002), and subsequently in 2004, 2005, 2007, constantly venting at ~350 °C

(Douville et al., 2002; Charlou et al., 2007; Schmidt et al., 2007); this study).

3. Fluid sampling and analytical methods

Due to the Drachenschlund vent position within a narrow gully or depression it could not be closely approached with the ROV'S. During the first sampling 2006 with ROV *Quest* (Marum Bremen, cruise M68/1 R/V Meteor) fluids could only be sampled approx. 1 m above the vent. However, sampling of undiluted fluids directly from the orifice was successful in 2009 with ROV *Kiel6000* (IFM-Geomar, Kiel, cruise M78/2 R/V Meteor). During both cruises the inert KIPS (Kiel pumping system) flow-through pumping system was used, which is mounted on the ROV (Garbe-Schönberg et al., 2006), but in 2009 with a 2 m long extension of the nozzle/temperature probe assembly. With KIPS, the fluid is pumped through a titanium nozzle and further through PFA tubing and a multiport valve into PFA bottles mounted on the ROV (further details on KIPS are given in cruise report M78/2 (Seifert et al., 2009). Hydrothermal fluids from the Logatchev I hydrothermal field were obtained during a research cruise in January 2007 (MSM04/3, R/V Merian); fluid sampling was utilized with titanium syringes (Ti-Majors) mounted on the ROV *Jason II*, Woods Hole Oceanographic Institution.

Fluid samples from both locations have been treated as follows: Immediately after arrival of the samples on board, pH, Eh and the dissolved gases H_2S , H_2 , and CH_4 were determined (for a detailed description of on-board analytical methods see (Schmidt et al., 2007). Dissolved concentrations of H_2S were measured with a spectrophotometer, based on the light absorption of methylene blue (Cline, 1969). After homogenization due to shaking, further aliquots were taken for subsequent analyses at the University of Kiel and at Jacobs University Bremen: (1) filtered, acidified to pH 2 with HNO_3 (dissolved major and trace elements), (2) non-filtered, acidified (total concentration of major, minor, and trace elements), (3) non-filtered, non-acidified (determination of halides). For the determination of oxygen and hydrogen isotopes, separate aliquots of 2 ml were collected in gas-tight glass vials without headspace.

The elements Cl, Na, Br, B, Ca, K, Si, Li, Sr, Fe, Mn, Cu, and Zn were measured utilizing Inductively Coupled Plasma Optic Emission Spectrometry (ICP-OES) (Spectro CIROS SOP) at Jacobs University Bremen, whereas Rb, Cs, Co, Pb, Mo, Ti, W, Sn, Cd, and U were analyzed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Agilent 7500cs) at Christian-Albrechts-Universität Kiel. A complete dissolution of particles in non-filtered aliquots was achieved by centrifuging the fluid samples, followed by a pressure-digestion of the particles in PTFE Teflon™ beakers with HCl, HNO_3 , and HF at 160 °C.

To ensure the accuracy and reproducibility of the analytical results, we used the seawater salinity reference standard IAPSO with certified major element composition, the seawater standard NASS-5 for certified trace element composition, artificial hydrothermal fluid, and an in-house hydrothermal fluid reference standard. The external long-term reproducibility of the same sample – IAPSO used for the elements Br, Ca, Cl, K, Mg, Na; hydrothermal fluid reference standard used for minor and trace elements – is <1% RSD for B, Br, and Cl, <2% RSD for Cs, Pb, Rb, Ti, W, <3% RSD Ca, Cd, Co, Fe, K, Li, Mg, Mo, Na <5% RSD for Mn, Sn, U, and Zn, and 11% RSD for Si. The analytical accuracy, defined as deviation from a reference standard mean (average of all measurements) from the recommended data (Br, Ca, Cl, K, Mg, Na, and Sr: IAPSO; Rb, Mo, and U: NASS-5) is <1% for Br, Ca, K, Na, Mo, U, <4% for Cl, Rb, Sr, and 5% for Mg. No certified reference values are available for the trace elements Cu, Zn, Co, Sn, Cd, Pb, and W in seawater. For these elements, the accuracy has been monitored using artificial hydrothermal fluid samples with known concentrations, with deviations of <5%. The determination of rare earth elements (REE) followed the method presented in Schmidt et al. (2010) utilizing an

immobilized mixture of bis-2-ethylhexyl-hydrogen- and ethylhexyl-dihydrogenphosphate for matrix separation.

Hydrogen isotopes ($\delta^2\text{H}$) were measured at Westfälische-Wilhelms-Universität Münster using a fully automated chromium reduction system at 800 °C (H/Device, ThermoFinnigan) directly coupled to the dual inlet system of a Thermo Finnigan Delta XP isotope ratio mass spectrometer. The $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ was measured using an automated equilibration unit (Gasbench 2, ThermoFinnigan) in continuous flow mode. All samples were measured at least in duplicate and results are principally given in the standard delta notation in permil (‰) vs. VSMOW according to $\delta [‰] = (R_{\text{sample}}/R_{\text{reference}} - 1) \times 1000$. External reproducibility – defined as standard deviation of a control standard during all runs – was better than 0.7‰ and 0.10‰ for $\delta^2\text{H}$ and $\delta^{18}\text{O}$, respectively.

Assuming that Mg is quantitatively removed in hot hydrothermal fluids (Mottl and Holland, 1978), the endmember composition of hydrothermal fluids was calculated using a least-squares regression of the individual components versus Mg with extrapolation to Mg zero and including the respective seawater values. Due to extensive seawater mixing during sampling at Nibelungen in 2006, large extrapolations are needed to obtain endmember concentrations. We applied a Monte-Carlo-simulation to determine the combined effect of measurement uncertainties (i.e., run precision, see above) and the standard deviation based on the regression line. In none of the fluid samples, the run precision has an influence on the regression uncertainty. The uncertainty of regression is given as error of Y intercept at 95% confidence in Table 1. Endmember values for hydrogen and oxygen isotopic composition are reported as Δ values, with $\Delta^{18}\text{O}$ and $\Delta^2\text{H}$ taking into account the isotopic composition of ambient bottom water ($\delta^{18}\text{O} = 0.3$, $\delta^2\text{H} = 0.45$).

4. Results

4.1. Major and trace element composition of the Nibelungen vent fluids sampled in 2006 and 2009

The measured composition of individual fluid samples from the “smoking crater” Drachenschlund and calculated endmember values of filtered and non-filtered aliquots for both sampling campaigns are given in Tables 1 and 2, respectively. Due to the inaccessibility of the orifice the minimum Mg concentration in the samples collected in 2006 is 43.6 mM, thus the relative percentage of hydrothermal fluid in the samples is as low as 22%. The compositional trends, however, are straightforward for extrapolation. The maximum temperature during sampling was 192 °C, but venting style and fluid chemistry constraints have been used to estimate a more realistic venting temperature of 350–400 °C (Melchert et al., 2008). The recent measurements at Drachenschlund during cruise in 2009 confirmed this first estimate now recording a stable emanation temperature of 372 °C. An extension of the KIPS nozzle allowed to obtain more undiluted hydrothermal fluid with less than 4–11% admixed seawater (except for one sample).

Fluid samples taken in 2006 are strongly enriched in H_2 and CH_4 (endmember concentrations of 11.4 mM and 1.4 mM, respectively). Na (473 mM) and Cl (551 mM) concentrations are nearly identical to seawater values, while concentrations of K (19.4 mM), Ca (29.6 mM), and Si (12.7 mM) are enriched over seawater. The trace alkali elements Li (364 μM), Rb (17.5 μM) and Cs (231 nM) are elevated, whereas B is depleted compared to seawater. Strontium is slightly depleted relative to seawater. The fluids display a strong enrichment in transition metals in the non-filtered aliquots, with calculated endmember concentrations of Fe = 4870 μM , Mn = 877 μM , Cu = 202 μM , and Zn = 101 μM . The Cu content is among the highest reported for mid-ocean ridge hydrothermal systems, which is also expressed in very low Fe/Cu ratios of ~20. Further endmember

Table 1
Measured fluid composition at Nibelungen (filtered and non-filtered aliquots).

Cruise number	Sample	Add Info.	Vent Site	T (°C) max	pH	H2S μM	Mg mM	Na mM	Cl mM	K mM	Ca mM	Si mM	Li μM	Rb μM	Sr μM	Cs nM	Ba μM	Br μM	B μM	Fe μM	Mn μM	Zn μM	Cu μM	Co μM	Pb nM	U nM	Tl nM	W nM	Sn nM	Cd nM	Mo nM
M68/1	62 ROV-4	NF	Drachenschlund		6.37	n.d.	51.8	476	554	10.7	10.9	0.38	34	1.67	85	8.40	n.d.	851	413	132	23	2.8	4.6	0.05	8.07	13.4	0.44	0.71	6.17	3.65	110
M68/1	62 ROV-5	NF			7.11	n.d.	52.3	477	550	10.7	10.9	0.30	32	1.58	87	6.70	n.d.	830	420	114	17	4.0	8.6	0.06	8.49	14.3	0.46	1.4	6.64	4.21	119
M68/1	62 ROV-9	NF		>190	6.37	0.007	43.6	468	551	11.8	13.9	2.34	87	4.2	85	43.2	n.d.	856	382	906	158	19.2	40.8	0.3	63.9	12.6	2.36	2.97	37.7	20.4	113
M68/1	62 ROV-10	NF			6.43	0.006	44.1	470	551	11.9	13.7	2.28	85	4.16	84	43.0	n.d.	840	381	873	155	17.7	34.1	0.26	53.6	12.2	2.11	2.7	35.7	20.3	98
M68/1	69 ROV-4	NF			7.45	n.d.	51.5	478	n.d.	10.6	10.8	0.23	30	1.59	85	5.70	n.d.	n.d.	419	n.d.	13	1.7	<3	0.03	4.41	12.9	0.33	0.56	4.16	2.34	113
		SW EM R ²				0 0.03 −1.00	54.0 473 −	464 551 −	546 551 −	9.8 19.4 −0.96	10.2 29.6 −1.00	0.04 12.7 −0.99	26 364 −0.99	1.3 17.5 −0.99	87 75.8 0.72	2.30 231 −0.99		838 840 −	430 179 0.99	0.0045 4869 −1.00	0.0013 877 −0.99	0.0280 101 −0.99	0.0033 202 −0.99	0 1.52 −0.99	0.013 329 −0.99	14.3 5.04 0.85	0.05 12.0 −0.99	0.27 13.5 −0.95	0.5 200 −0.99	0.7 109 −0.99	119 54.0 0.68
		Uncertainty of regression																													
M78-2	314 ROV-1	NF	Drachenschlund	372	n.d.	477	29	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
M78-2	314 ROV-2	NF		372	3.1	1003	4.69	448	567	17.9	29.4	12.6	313	17.7	84.8	237	23	886	215	4750	878	n.d.	47	0.84	216	0.981	7.17	11.8	59.8	79.5	18.8
M78-2	314 ROV-3	NF		372	2.9	1147	2.96	453	568	18.1	30.1	13.1	326	18.8	85.9	247	31.2	896	207	4950	917	91	36	0.57	178	0.795	7.32	13.3	70	82.5	6.78
M78-2	314 ROV-4	NF		372	3.2	612	6.23	450	565	17.7	28.6	11.9	305	15.3	85.9	199	23.1	892	218	4660	857	71	129	0.58	150	1.34	5.22	9.58	107	71.4	10.8
M78-2	314 ROV-5	NF		372	3.1	945	5.11	443	564	17.6	28.9	12.6	311	17.1	84.6	225	26.4	890	213	4770	866	96	196	0.77	205	1.14	6.21	10.4	136	86.1	10.6
M78-2	314 ROV-6	NF		372	3.3	1106	5.52	445	567	17.6	28.5	12.3	306	17.4	84	226	22.6	883	214	4760	864	66	158	0.8	151	1.17	6.29	10.3	98.2	59.3	11.4
M78-2	314 ROV-7	NF		372	5.3	7	47.7 [#]	470	575	11.6	14.5	2.28	78	3.92	89.2	36.9	3.5	849	392	894	159	15	27	0.23	34.4	9.77	1.62	2.42	25.5	12.8	95.8
		SW EM R ²				0 1066 −0.95	54 449 −	464 567 −	546 567 −	9.8 18.6 −1.00	10.2 30.9 −1.00	0.036 13.7 −1.00	26 340 −1.00	1.3 18.9 −0.99	87 84.8 0.81	2.3 249 −0.99		838 894 −0.96	430 192 1.00	0.005 5245 −1.00	0.001 962 −1.00	0.028 n.d. −0.97	0.003 n.d. −0.63	0.010 n.d. −0.93	0.013 n.d. −0.96	14.3 −0.18 0.99	0.05 7.09 −0.98	0.27 12.2 −0.98	0.5 n.d. −0.84	0.2 83.5 −0.97	119 1.1 1.00
		Uncertainty of regression																													
M78-2	314 ROV-3	F					2.99	454	560	18.2	30.7	13	330	n.d.	86.2	n.d.	30.9	924	n.d.	4830	898	<3	<3	0.5	7.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
M78-2	314 ROV-4	F	Drachenschlund				6.31	455	569	17.8	29.5	12.3	310	n.d.	84.9	n.d.	10.5	920	n.d.	4610	857	<3	<3	0.44	15.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
M78-2	314 ROV-5	F					5.12	455	561	17.7	29.5	12.3	313	n.d.	84	n.d.	15.5	913	n.d.	4630	857	<3	<3	0.47	5.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
M78-2	314 ROV-7	F					46.6	461	564	11.4	14.2	2.23	76.4	n.d.	87.1	n.d.	n.d.	842	n.d.	838	156	17.7	18.7	0.32	31.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		SW EM R ²					54 455	464 563	546 563	9.8 18.7	10.2 31.8	0.036 13.75	26 346		87 85			838 927		0.005 5145	0.001 955										
		Uncertainty of regression																													
MSM04/3	271 ROV-11	NF	I2 Main Structure	300	4.6	0.62	1.35	445	543	23.4	30.7	7.58	225	27.4	129	350	43.7	844	336	2510	354	31.4	40.0	0.12	102	0.35	14.4	6.36	33.3	25.6	29.6
MSM04/3	244 ROV-7	NF	I2 Mikrosmoker	340	4.01	0.68	0.39	447	531	23.8	30.6	8.26	228	25.9	134	339	68.8	826	326	2530	359	38.2	35.7	0.86	522	0.14					n.d.
MSM04/3	253 ROV-10	NF	I2 Mikrosmoker		3.78	0.37	2.00	454	545	23.0	29.8	8.05	221	26.6	128	344	42.6	849	343	2420	348	34.3	30.9	1.01	131	0.43	14.0	10.9	18.8	25.4	5.76
MSM04/3	253 ROV-9	NF	I2 Mikrosmoker		4.02	0.61	1.06	450	534	23.2	30.4	8.19	224	27.0	129	352	43.2	820	332	2460	349	38.5	36.8	0.93	156	0.24					n.d.
MSM04/3	255 ROV-3	NF	Site B	343	4.17	0.81	1.17	446	524	23.3	30.0	8.30	225	27.1	129	347	48.2	830	335	2450	348	32.8	36.1	0.90	140	0.66	13.9	4.79	24.5	26.0	8.92
MSM04/3	255 ROV-12	NF	Irina I	n.d.	5.19	0.03	26.4	462	541	14.5	17.4	3.48	108	13.9	93	173	6.4	820	386	1060	152	18.0	24.4	0.62	74	4.57	10.1	4.12	21.8	15.9	55.2
MSM04/3	255 ROV-13	NF	Irina I		5.3	0.0078	23.1	n.d.	n.d.	16.9	20.7	4.52	134	16.5	105	210	11.9	n.d.	376	1380	197	20.7	25.5	0.64	59	4.06					n.d.
MSM04/3	255	NF	Candelabra	335	4.22	0.65	1.09	451	549	23.2	30.4	8.44	224	26.2	130	355	54.8	856	342	2390	347	37.7	35.2	0.86	361	0.19	17.0	6.88	26.8	41.5	5.33

Table 1 (continued)

Cruise number	Sample	Add Info.	Vent Site	T (°C) max	pH	H2S μM	Mg mM	Na mM	Cl mM	K mM	Ca mM	Si mM	Li μM	Rb μM	Sr μM	Cs nM	Ba μM	Br μM	B μM	Fe μM	Mn μM	Zn μM	Cu μM	Co μM	Pb nM	U nM	Tl nM	W nM	Sn nM	Cd nM	Mo nM	
MSM04/3	ROV-17 275	NF	Anna Louise	349	4.8	0.31	12.7	450	544	19.7	24.8	6.40	174	20.9	115	266	25.6	835	353	1740	264	27.9	34.2	0.77	90	2.59	13.0	8.75	27.5	20.8	25.0	
MSM04/3	ROV-8 275	NF	Anna Louise		4.19	0.76	1.32	438	521	23.4	30.3	8.68	223	27.4	128	352	48.7	797	328	2230	343	41.7	34.4	0.85	95	0.23	15.0	6.17	28.8	27.0	4.3	
MSM04/3	ROV-7 259	NF	Quest	347	3.52	0.67	0.31	450	542	23.5	30.4	8.25	225	26.3	128	344	43.8	845	336	2460	354	28.6	29.4	0.92	69	0.21	11.4	6.34	22.8	20.5	2.01	
	ROV-25																															
		SW				0	54.0	464	546	9.8	10.2	0.04	26	1.3	87	2		838	430	0.0045	0.0013	0.0280	0.0033	0	0.013	14.3	0.05	0.27	0.5	0.2	119	
		EM				0.62		450	542	23.5	30.5	8.4	227	27.2	129	354	51.0	835	333	2462	356	36.1	36.4	0.94	n.d.	−0.19	n.d.	n.d.	n.d.	n.d.	5.62	
		R2				−0.85		-	-	−0.99	−0.99	−0.99	−1.00	−1.00	−0.95	−1.00	−0.92	-	0.99	−0.99	−1.00	−0.95	−0.93	−0.97	−0.48	0.98	−0.93	−0.74	−0.84	−0.85	0.97	
		Uncertainty of regression						-	-	0.6	0.8	0.3	6	0.5	4	6	6.3		4	76	8	2.8	3.0	0.06		0.60					8.39	
MSM04/3	275	NF	Site A	330	4.41	0.79	0.37	444	533	23.1	31.5	10.67	223	27.0	129	0.352	56.2	840	331	1184	311	20.6	29.5	0.35	122	0.30	11.5	5.66	28.0	22.6	2.7	
	ROV-5																															
		SW				0	54.0	464	546	9.8	10.2	0.04	26	1.3	87	0.0023		838	430	0.0045	0.0013	0.0280	0.0033	0.0000	0.013	14.3	0.1	0.27	0.5	0.7	119	
		EM				0.80		444		23.2	31.7	10.7	224	27.2	129	0.354		840	330	1192	313	21	30	0.35	123	0.20	11.6	5.7	28	23	1.9	
MSM04/3	271	F	I2 Main Structure			n.d.	1.31	n.d.	n.d.	23.2	29.0	7.54	222	n.d.	128	n.d.	43.2	n.d.	n.d.	2320	339	<3	<3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	ROV-11																															
MSM04/3	244	F	I2 Main Structure			n.d.	19.6	n.d.	n.d.	18.7	22.3	5.05	156	n.d.	111	n.d.	10.6	n.d.	n.d.	1320	227	<3	<3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	ROV-3																															
MSM04/3	244	F	I2 Mikrosmoker			n.d.	0.35	n.d.	n.d.	23.2	29.0	8.18	226	n.d.	130	n.d.	67.0	n.d.	n.d.	2390	344	<3	<3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	ROV-7																															
MSM04/3	253	F	I2 Mikrosmoker			n.d.	1.96	n.d.	n.d.	23.0	28.5	7.98	223	n.d.	128	n.d.	42.5	n.d.	n.d.	2340	338	23.7	<3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	ROV-10																															
MSM04/3	253	F	I2 Mikrosmoker			n.d.	1.02	n.d.	n.d.	23.1	29.3	8.13	226	n.d.	128	n.d.	43.3	n.d.	n.d.	2370	343	<3	<3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	ROV-9																															
MSM04/3	255	F	Site B			n.d.	0.89	n.d.	n.d.	23.8	29.6	8.46	232	n.d.	130	n.d.	44.3	n.d.	n.d.	2410	349	4.1	<3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	ROV-4																															
MSM04/3	255	F	Site B			n.d.	1.15	n.d.	n.d.	23.5	28.8	8.29	228	n.d.	129	n.d.	48.9	n.d.	n.d.	2370	340	3.2	<3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	ROV-3																															
MSM04/3	255	F	Irina I			n.d.	28.6	n.d.	n.d.	16.5	19.3	4.08	122	n.d.	103	n.d.	3.1	n.d.	n.d.	1090	234	<3	<3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	ROV-12																															
MSM04/3	255	F	Candelabra			n.d.	1.10	n.d.	n.d.	23.6	29.3	8.50	229	n.d.	132	n.d.	55.7	n.d.	n.d.	2360	345	3.5	<3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	ROV-17																															
MSM04/3	275	F	Anna Louise			n.d.	1.27	n.d.	n.d.	22.9	27.7	8.37	222	n.d.	127	n.d.	46.7	n.d.	n.d.	2220	374	4.7	<3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	ROV-7																															
MSM04/3	259	F	Quest			n.d.	0.28	n.d.	n.d.	23.8	29.2	8.30	229	n.d.	131	n.d.	44.4	n.d.	n.d.	2420	349	3.5	<3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	ROV-25																															
		SW					54.0			9.8	10.2	0.04	26		87					0.0045	0.0013											
		EM								23.6	29.3	8.3	230		130		50.1			2390	355											
		R2								−1.00	−1.00	−1.00	−1.00		−0.99		−0.92			−1.00	−0.98											
		Uncertainty of regression								0.2	0.4	0.2	2.1		1.5		5.9			59	15											
MSM04/3	275	F	Site A				0.34			23.2	30.1	10.55	225	n.d.	128	n.d.	56.2	820	n.d.	1141	304	<3	<3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	ROV-5																															
		SW					54.0			9.8	10.2	0.04	26		87					0.0045	0.0013											
		EM								23.3	30.3	10.6	226		128					1148	306											

NOTE: T°C (max): maximum stable temperature measured in the same orifice; F: filtered aliquot; NF: nonfiltered aliquot; EM: endmember; n.d.: not determined; I2 Irina II, IAPSO: natural seawater reference standard; seawater data were taken from Douville et al., 2002, except for Br (Charlou et al., 2002), B, W, Sn, Tl, Cd, Mo (this study, Atlantic bottom water, 5°S, MAR); endmember concentrations were calculated using a least-square regression versus Mg, including the seawater values; Uncertainty of regression given as error of Y intercept at 95% confidence; R2: correlation coefficient; n.d. not detected,

^a Metals Zn, Cu, Co, Cd, Pb, Sn, W, Mo, U were determined in sample 314 ROV-8 with a Mg concentration of 44.9 mM.

Table 2
Calculated endmember data for hydrothermal fluids from Logatchev I and Nibelungen, data for the ultramafic-hosted Rainbow field and for Snakepit as basaltic-hosted system are given for comparison.

		Logatchev I (1996) ¹	Logatchev I (2005) ²	Logatchev I (Jan. 2007) [#]	Nibelungen (2006) ^{3,5}	Nibelungen (2009) [#]	Rainbow (1996) ¹	Snake Pit (1996) ¹
T	°C	353	350	349	>192	372	365	341
pH (25 °C)		3.3	3.9	3.5	n.d.	2.9	2.8	3.7
CH ₄	[mM]	2.1	3.5	1.5	1.4	2.5	–	–
H ₂	[mM]	12	19	5.8	11.4	16	–	–
H ₂ S	[mM]	0.8	2.5	0.5–0.8	0.035	1.1	1.0	6.0
Cl	[mM]	515	551	542	551	567	750	550
Na	[mM]	438	455	450	473	449	553	515
Br	[μM]	–	837	835	840	894	–	–
Si	[mM]	8.2	8.6	8.6	12.7	13.7	6.9	20
B	[μM]	–	335	333	179	192	–	518*
K	[mM]	22	24	23.5	19.4	18.6	20	23
Ca	[mM]	28	29	30.5	29.6	30.9	67	11
Li	[μM]	245	252	227	364	391	340	835
Rb	[μM]	28	27	27	17.5	18.9	37	12
Sr	[μM]	138	127	129	75.8	84.8	200	54
Cs	[nM]	385	343	354	231	250	333	170
Fe	[μM]	2500	2410	2460	4870	5240	24000	2400
Mn	[μM]	330	338	356	877	962	2250	400
Cu	[μM]	27	44	(43)	202	(162)	140	35
Zn	[μM]	29	36	(37.8)	101	(90)	160	53
Pb	[nM]	86	138	(140)	329	(206)	148	256
Tl	[nM]	7	–	(15.5)	12	(9.5)	9	25
Sn	[nM]	–	–	(36)	200	(151)	–	–
W	[nM]	–	–	(11)	13.5	(13)	–	–
Cd	[nM]	63	32	(40)	109	(76)	130	440
Mo	[nM]	1	4	1.8	54	1	2	3
Co	[μM]	<2	0.75	(0.94)	1.52	(1.3)	13	–

Notes: ¹Douville et al. (2002), Charlou et al. (2002), ²Schmidt et al. (2007), ³data for H₂ and CH₄ from Melchert et al. (2008), ⁴Von Damm (1990), [#] endmember values for Cu, Zn, Co, Pb, Tl, Sn, W, Cd given as best estimate value based on Mg regression with diluted samples (see text for discussion), ⁵ high seawater content (endmember values to be used with caution).

concentrations were determined for Pb, Cd, Tl, Sn, W and Co using the two samples with lowest Mg and relatively similar trace metal concentrations.

The REY composition has been determined in non-filtered aliquots; data are given in Table 3. Chondrite-normalized REY pattern display an enrichment of light rare earth elements over heavy rare earth elements ($Ce_{CN}/Yb_{CN} = 4.8$) and a pronounced positive Eu anomaly ($Eu/Eu^* = 46$). The anomalous behavior of Eu is quantified as Eu/Eu^* using normalized data, where Eu is the normalized measured concentration and Eu^* is the predicted concentration based on interpolation of neighboring REY; the anomaly is defined as $Eu/Eu^* = Eu/(0.675Sm + .33Tb)$ following the method of Bau and Dulski (1996).

In 2009, the Drachenschlund vent was sampled again. As in 2006, black smoke was vigorously venting from the bottom of the crater. The measured pH is 2.9 at 25 °C in the most undiluted sample. The calculated fluid endmember composition is very similar to data

obtained from the 2006 samples for Na, Cl, Br, Si, K, Ca, Li, Rb, Cs, B, Fe, and Mn (Tables 1 and 2). Samples with similarly high fluid content (90–95%) show generally high, but strongly variable concentrations: Cu = 30–286 μM, and Zn = 70–125 μM, Pb = 151–216 nM, Cd = 59–86 nM, Tl = 5.3–7.3 nM, Sn = 60–126 nM, W = 10.3–13.3 nM and Co = 0.88–1.51 μM. These elements do not form a single mixing line (i.e., no correlation with Mg content), which is evident for a non-conservative behavior during mixing with seawater and cooling of the samples, which is typical for sulfide-forming elements (Metz and Trefry, 2000). This strong variability is related to particle formation and likely an inhomogeneous particle distribution and does therefore not allow determining definite endmember values for these elements. An estimation of the dissolved concentrations in the undiluted hydrothermal fluid can be obtained by extrapolating the concentration in the diluted sample to zero Mg (supplementary data, Plate 1). The measured concentrations of Cu, Zn, Co, Pb in the filtered aliquot of the most diluted sample are similar to those of the non-filtered aliquot, which shows that this sample was not much affected by sulfide precipitation after sampling (Table 1). Thus it seems valid to use the non-filtered aliquot to construct the endmember concentrations. As this sample may have lost some of its metal load by sulfide precipitation before sampling (although dilution might have been faster than precipitation), these values (Table 2) should be considered as lower limits.

4.2. Major and trace element composition of fluids from the Logatchev I hydrothermal field obtained in January 2007

The Logatchev I hydrothermal field was sampled in Jan. 2007, with the objective to further characterize this fluid type with respect to trace metal and stable isotope composition.

Hydrothermal fluids were sampled at all high-temperature sites within the Logatchev I field (from NW to SE: Quest, Irina II, Site B, Irina I, Candelabra, Anna Louise, Site A). Measured fluid composition of individual samples and calculated endmember data are given in Tables 1 and 2, respectively. The maximum emanation temperatures

Table 3
Endmember fluid oxygen and hydrogen isotopic composition from the Logatchev I and Nibelungen vent fields.

Sample ID	Vent field	Vent site	Δ ¹⁸ O endm.	ΔD endm.
MSM04/3				
253 ROV-10	Logatchev	I Irina II Microsmoker	1.42	3.82
255 ROV-3		Site B	1.23	4.07
255 ROV-17		Candelabra	1.31	4.07
259 ROV-25		Quest	1.45	4.52
271 ROV-11		Irina II Main Structure	1.32	4.19
275 ROV-5		Site A	1.36	3.92
275 ROV-7		Anna Louise	1.42	3.88
MSM 10/3				
314 ROV-2	Nibelungen	Drachenschlund	2.39	8.70
314 ROV-3		Drachenschlund	2.24	7.59
314 ROV-4		Drachenschlund	2.20	6.90
314 ROV-5		Drachenschlund	2.16	7.77
314 ROV-6		Drachenschlund	2.24	8.05

vary between 300 °C (beehive-like chimney at *Irina II*) and 349 °C (*Anna Louise*). Despite very different emanation site architectures (massive chimneys and beehive at *Irina II*, “smoking craters”) and varying fluid temperatures the measured composition of individual high-quality samples from the different vent sites (>95% hydrothermal fluid) is very homogenous with respect to major and minor elements throughout the Logatchev field except for *Site A*, so all samples have been treated as a single group for the endmember calculation. The endmember composition for *Site A* has been calculated separately because of deviations in composition compared to other vents (see below). The pH of the undiluted fluids, measured at 25 °C, ranges from 3.5 to 4.6, with the higher pH value measured at the massive chimney complex of *Irina II*. The calculated endmember composition for the major elements Na, Ca, K, Si and the trace elements Li, Sr, Rb, Cs, B, Fe, Mn is very similar to the fluid composition observed in 2005, together with strong enrichments of dissolved H_2 and CH_4 (max. 6 mM and 1 mM, respectively) and low H_2S concentrations of max. 0.8 mM. The use of non-gastight fluid samplers did not allow the determination of reliable maximum concentrations of dissolved gases. Thus, endmember concentrations of H_2 , CH_4 , and H_2S represent only lower limits, but the degassing of H_2S is expected to be less than that of H_2 and CH_4 , due to Henry's law. The chlorinity (median value: 542 mM) is similar to local seawater (551 mM).

The distribution of rare earth elements plus yttrium (REY) has been determined in samples from all high-temperatures sites except for *Irina I*. The measured concentrations of individual fluid samples are given in [supplementary data Table 1](#). Chondrite-normalized REY patterns display an enrichment of light rare earth elements compared to heavy rare earth elements ($Ce_{CN}/Yb_{CN} = 11–16$), chondritic Y/Ho ratios and a pronounced positive Eu anomaly ($Eu/Eu^* = 33–51$).

Concentrations of the trace elements Cu, Zn, Co, Pb, Ti, W, Sn, Cd, Mo, and U are partly variable between individual high-quality, non-filtered fluid samples (>98% hydrothermal fluid). This non-conservative behavior is likely related to the formation of sulfides during sampling and cooling, and endmember concentrations based on all samples were only calculated for Mo (5.6 nM) and U (~0 nM). The concentrations of the other trace metals in the individual high-quality fluid samples range between 28.6–41.7 μM (Zn), 29.4–40 μM (Cu), 0.85–1.01 μM (Co), 90 nM–156 nM (Pb, excluding 2 outliers with much higher concentrations), 11–17 nM (Ti), 5–11 nM (W), 19–33 nM (Sn), and 20–41 nM (Cd). In [Table 2](#), endmember values of these elements for the Logatchev field are given as best estimate values, based on a regression involving more diluted samples, from which it becomes obvious that some of the undiluted samples lost part of their metal content prior or during fluid sampling due to sulfide formation and precipitation ([supplementary data, Plate II](#)). This is especially evident for the Quest site, with the lowest trace metal content (except for Co) in the Logatchev field.

Site A at the south-eastern end of the Logatchev field ($T = 330$ °C) displays a different fluid composition compared to the other vent sites: Si is more enriched and the transition metals Fe, Mn, Zn and Co are depleted relative to the other vent sites. The calculated endmember concentrations for H_2S and other major and minor elements including Cl are similar to the other vent sites.

4.3. Stable isotopic composition of Nibelungen hydrothermal fluids

Calculated stable oxygen and hydrogen isotopic values for hot hydrothermal fluids from the Nibelungen field emanating at the Drachenschlund crater, collected in 2009, range from 2.2 to 2.4‰ ($\Delta^{18}O$) and from 7.6 to 8.7‰ (Δ^2H), respectively ([Table 3](#)). The hydrogen isotopic composition is the highest reported so far for high-temperature mid-ocean ridge hydrothermal systems.

4.4. Stable isotopic composition of Logatchev hydrothermal fluids

The oxygen and hydrogen isotopic composition were determined for hot hydrothermal fluids from the Logatchev field collected in 2007 ([Table 3](#)). Calculated individual endmember values group in a small field and range from 1.2 to 1.5‰ ($\Delta^{18}O$) and from 3.8 to 4.2‰ (Δ^2H), respectively. Similar to the elemental composition, the isotopic composition reflects a single endmember fluid venting at Logatchev from several vent sites.

5. Discussion

The Nibelungen hydrothermal field at 8°18'S represents the southernmost hot vent field at the Mid-Atlantic Ridge discovered so far and its fluid chemistry gives new insights into the hydrothermal activity at slow-spreading ridge axes. The special location of this vent field (relative to most of the vent fields described so far) venting about 9 km east of the active ridge axis makes it especially interesting, as such systems may play a significant role in heat and mass transfer from the lithosphere to the hydrosphere.

The Nibelungen fluids are characterized by strong enrichments of dissolved H_2 and CH_4 , seawater-like chlorinity, low H_2S concentration, intermediate Si concentration, low Li concentrations, depletion in B compared to seawater, and strong enrichments in Fe, Cu, Zn, Pb, Sn, and Cs. Based on the geological constraints, different rock types like unaltered MORB and peridotite as well as altered MORB, serpentinized peridotite and also lower crustal gabbroic rocks and pelagic sediment have to be considered as potential sources (and sinks) during fluid circulation. This is in contrast to the source rocks of hydrothermal systems located within the neovolcanic zone of mid-ocean ridge axes (e.g., Snake Pit, Broken Spur, Lucky Strike at the MAR), which are relatively uniform and consist of basaltic pillow lava and sheeted dikes.

5.1. Dissolved H_2 and CH_4

The Nibelungen field is characterized by strong enrichment of the dissolved gases H_2 and CH_4 , with endmember concentrations of

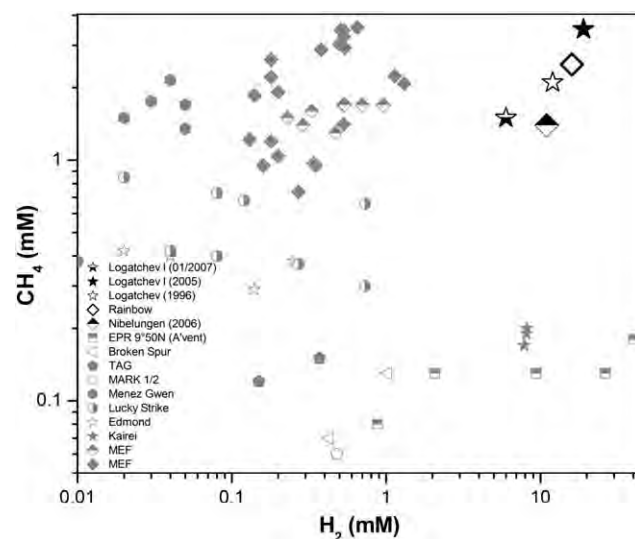


Fig. 1. Concentration of dissolved H_2 and CH_4 in hydrothermal vent fluids; data sources for mafic-hosted systems: MAR: Lucky Strike, Menez Gwen, TAG, Broken Spur, MARK 1/2 ([Charlou et al. \(2002\)](#) and references therein); EPR 9°46'N (A vent) ([Lilley et al., 2003](#)); Southwest Indian Ridge (SWIR) Kairei field, Edmond field ([Gallant and Von Damm, 2006](#)); Juan de Fuca Ridge (JFR) – Main Endeavour field (MEF) ([Lilley et al., 2003](#); [Seewald et al., 2003](#)); data sources for ultramafic-hosted systems: Rainbow ([Charlou et al., 2002](#)); Logatchev 1996: ([Charlou et al., 2002](#)); 2005: ([Schmidt et al., 2007](#)); Jan 2007: this study; Nibelungen 2006: endmember values calculated from data provided in [Melchert et al. \(2008\)](#).

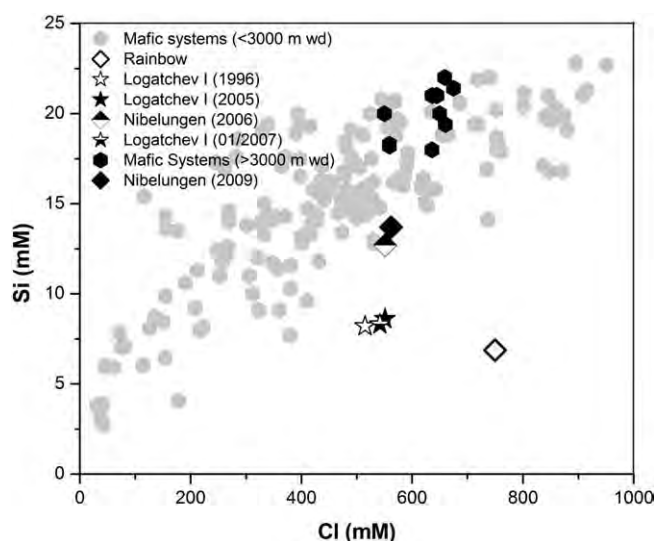


Fig. 2. Silica concentration vs chloride concentration for mid-ocean ridge hydrothermal fluids; data sources for mafic-hosted systems: EPR: 9°17'N; 9°33.5'N, 9°39'N, 9°46.3'N, 9°46.5'N, 9°50.3'N, 9°50.7'N, 9–10°N (Von Damm, 2000, 2004; Shanks, 2001), 9°16N EPR (Von Damm, 2000, 2004; Shanks, 2001), EPR 17°24' to 17°27'S, 17°35' to 17°44'S (Shanks, 2001), 17°25'S, 18°10'S (Charlou et al., 1996b), 18°23' to 18°26'S (Shanks, 2001), 18°26'S (Charlou et al., 1996b), 21°24' to 21°27'S, 21°33' to 21°34'S (Shanks, 2001), 13°N, 21°N, 11°N (Charlou et al., 1996a); SWIR: Kairei (Gamo et al., 2001); JFR: ASHES (Butterfield et al., 1990), Southern JFR (Von Damm and Bischoff, 1987), Northern Cleft Segment (Butterfield and Massoth, 1994), MEF (Butterfield et al., 1994; Seyfried et al., 2003), MAR: Snakepit (Von Damm, 1990; Douville et al., 2002); TAG (Edmonds et al., 1996; Gamo et al., 1996; Douville et al., 2002), Lucky Strike (Von Damm et al., 1998; Charlou et al., 2000), Menez Gwen (Charlou et al., 2000); data sources for ultramafic-hosted systems: Rainbow (Charlou et al., 2002); Logatchev 1996: (Charlou et al., 2002); 2005: (Schmidt et al., 2007); Jan 2007: this study; Nibelungen 2006 and 2009: this study; wd: water depth.

11.4 mM H₂ and 1.4 mM CH₄. Whilst either H₂ or CH₄ may also be enriched in basaltic-hosted hydrothermal systems in sediment-free settings under certain conditions (Von Damm et al., 1995; Welhan and Lupton, 1987; Butterfield et al., 2003; Lilley et al., 2003), only serpentinization of mantle rocks produces the characteristic coupled and constant enrichment of both gases observed in ultramafic-hosted

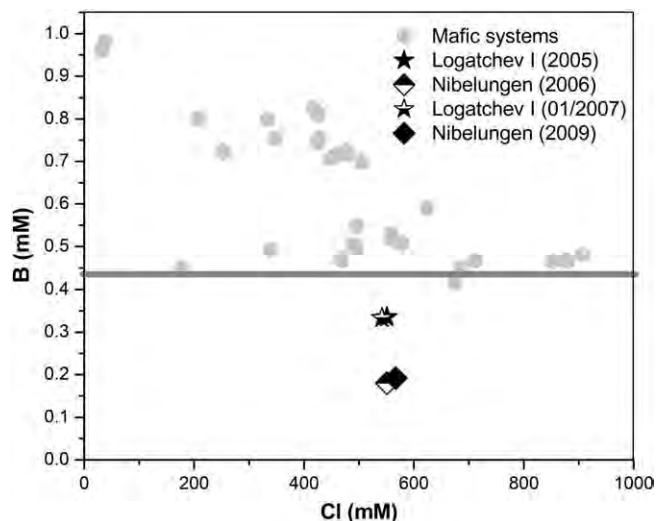


Fig. 3. Boron concentration vs chloride concentration for mid-ocean ridge hydrothermal fluids; data sources for mafic systems: EPR: 13°N, 21°N, 11°N (Von Damm, 1990); JFR: ASHES (Butterfield et al., 1990), Southern JdFR (Von Damm and Bischoff, 1987), Northern Cleft Segment (Butterfield and Massoth, 1994), MEF (Butterfield et al., 1994; Seyfried et al., 2003), MAR: Broken Spur (James et al., 1995), Snakepit (Von Damm, 1990), TAG (Gamo et al., 1996); data source for ultramafic-hosted systems: Logatchev 1996: (Charlou et al., 2002); 2005: (Schmidt et al., 2007); Jan 2007: this study; Nibelungen 2006 and 2009: this study; grey bar marks seawater concentration.

hydrothermal systems (Fig. 1; Douville et al., 2002; Schmidt et al., 2007; Melchert et al., 2008) which groups the Nibelungen field together with the Logatchev I and Rainbow vent fields. Dissolved H₂ is produced in a two-step process by oxidation of ferrous Fe-bearing silicate minerals (olivine and pyroxenes) to magnetite, via the formation of serpentine and Fe-bearing brucite (Allen and Seyfried, 2003; McCollom and Bach, 2008; Klein et al., 2009). High CH₄ concentrations in ultramafic-hosted hydrothermal systems result from the reduction of CO₂ under strongly reducing conditions and is likely catalyzed by Ni–Fe alloys and/or oxides (Fischer–Tropsch–Type synthesis – Foustoukos and Seyfried (2004)).

Also, the serpentinization of rocks constituting the lower oceanic crust (e.g., troctolite, olivine gabbro) can produce strong enrichments of H₂ (up to 8.2 mM in the Kairei field at the Central Indian Ridge, however, the absence of Ni–Fe alloys in such rocks probably leads to a drastic suppression of CH₄ formation (Kumagai et al., 2008; Nakamura et al., 2009), which distinguishes this field from the ultramafic-hosted fields at the MAR.

5.2. Silica

The Nibelungen fluids are characterized by a low Si content, relative to other hydrothermal systems with similar salinity (Fig. 2). In mafic-hosted systems, the Si concentration is controlled by the pressure–temperature dependent solubility of amorphous silica (Fournier, 1983; Von Damm et al., 1991; Foustoukos and Seyfried, 2007; Fontaine et al., 2009), resulting in Si concentration of more than 18 mM in fields located at water depths of 3000 m and more. Compared to this the Nibelungen fluid emanating at about 3000 m water depth either is clearly depleted in silica. Only the ultramafic-hosted field Logatchev I and Rainbow have lower Si concentrations (Douville et al., 2002).

Defined by the specific geochemical gradients during the alteration of ultramafic rocks, the Si content in fluids interacting

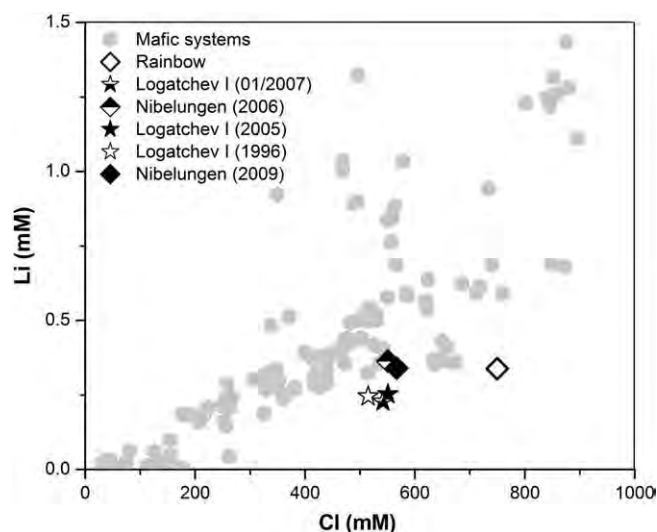


Fig. 4. Lithium vs chloride concentration for mid-ocean ridge hydrothermal fluids; data sources for mafic systems: EPR: 9°17'N; 9°33.5'N, 9°39'N, 9°46.3'N, 9°46.5'N (Von Damm, 2000), 9°50.3'N (Von Damm, 2004), 9°50.7'N, 9–10°N (Von Damm, 2000), 9°16N (Von Damm, 2004), 17°25'S, 18°10'S (Charlou et al., 1996b), 18°26'S (Charlou et al., 1996b), 13°N, 21°N, 11°N (Von Damm, 1990); JFR: ASHES (Butterfield et al., 1990), Southern JdFR (Von Damm and Bischoff, 1987), Northern Cleft Segment (Butterfield and Massoth, 1994), MEF (Butterfield et al., 1994; Seyfried et al., 2003), MAR: Snakepit (Von Damm, 1990; Douville et al., 2002); TAG (Edmonds et al., 1996; Gamo et al., 1996; Douville et al., 2002), Lucky Strike (Von Damm et al., 1998; Charlou et al., 2000), Menez Gwen (Charlou et al., 2000), Broken Spur (James et al., 1995); data sources for ultramafic-hosted systems: Rainbow (Charlou et al., 2002); Logatchev 1996: (Charlou et al., 2002); 2005: (Schmidt et al., 2007); Jan 2007: this study; Nibelungen 2006 and 2009: this study.

with ultramafic rocks is very low. At high fluid temperatures (400 °C), higher Si activities (up to about 2 mM) can be buffered, according to thermodynamic reaction path modeling by Bach and Klein (2009) and Klein et al. (2009) and experimental work conducted by Allen and Seyfried (2003). However, the resulting Si contents in the modeling calculations as well as in experiments are well below those measured at Nibelungen. Thus, an external Si source like the additional alteration of mafic rocks is suggested in order to explain the measured Si concentrations at Nibelungen. These may either be rocks of the lower oceanic crust or the basaltic rocks hosting the Nibelungen field.

5.3. Trace elements

5.3.1. Li, Rb, Cs, B, and Tl

The fluid-mobile alkali metals Li, Rb and Cs and also B are good indicators of source rock composition and seafloor alteration processes in hydrothermal systems. The elements are highly incompatible during magmatic processes and strongly depleted in mantle rocks (Salters and Stracke, 2004) relative to N-type MOR basalts (compare supplementary data Table 2). During high-temperature fluid–rock interaction, they are easily mobilized and the concentrations in the fluid are thought to primarily depend on the initial concentration in the host rock and the effective water–rock ratio (Seyfried et al., 1984).

Whereas Rb and Cs concentrations at Nibelungen are broadly similar to other MOR hydrothermal systems with similar salinity, Li and B are strongly depleted (Figs. 3 and 4). In seawater, the B concentration is relatively high. At Nibelungen, B is depleted relative to seawater concentration. This is in contrast to mafic-hosted hydrothermal systems where B loss from entraining seawater during the formation of low-temperature alteration minerals is followed by mobilization of B in the high-temperature reaction zone (Seyfried et al., 1984) commonly leading to slight B enrichments in high-temperature hydrothermal fluids. Hydrothermal systems at the MAR are generally characterized by somewhat lower B concentrations relative to systems from the fast-spreading EPR, attributed to more intense water–rock interaction at slow-spreading ridges resulting in enhanced B removal during fluid circulation (James et al., 1995). A distinct depletion of B relative to seawater, however, is a characteristic fingerprint of ultramafic-hosted hydrothermal systems (Schmidt et al., 2007; Foustoukos et al., 2008), since especially B has a strong affinity to serpentine minerals (substitution for Si) and brucite (adsorption) (Page, 1968; Thompson and Melson, 1970; Bonatti et al., 1984; Spivack and Edmond, 1987; Mevel, 2003; Früh-Green et al., 2004; Boschi et al., 2008; Vils et al., 2008). Serpentinized peridotites are characterized by strong enrichments of B. The uptake of B during serpentinization is favored at moderate temperature (200–300 °C), high integrated w/r ratios and neutral to alkaline pH (Janecky and Seyfried, 1986; Früh-Green et al., 2004; Boschi et al., 2008; Foustoukos et al., 2008; Vils et al., 2008). Due to the extremely low B content fresh peridotite, high-temperature alteration of these rocks does not mobilize significant amounts of B. However, some B may be gained during mafic–rock alteration. The low B content at Nibelungen indicates serpentinization of ultramafic rocks at low w/r ratios.

The absolute concentrations of Rb, Cs, and Li in the fluid are strongly elevated relative to fresh peridotite rock. Unless assuming unrealistically low w/r ratios, this requires the alteration of a rock significantly more enriched than relatively unaltered residual peridotites (compare values in supplementary data Table 2), in addition to the alteration of mantle rocks. These are either gabbroic rocks, leached with an effective w/r ratio close to 1 – or low-temperature alteration products of basalts being enriched in fluid-mobile elements (Jochum and Verma, 1996). Such rocks host the Nibelungen field. The alteration of seafloor-weathered peridotite, being enriched in fluid-mobile elements, cannot be excluded, although the similarity in Rb

and Cs fluid concentrations between Nibelungen and mafic-hosted hydrothermal systems rather suggests a mafic rock source. The net release of Li into the high-T fluid at Nibelungen is lower than in fresh basaltic-hosted hydrothermal systems, as also observed in other ultramafic-hosted hydrothermal systems (Schmidt et al., 2007). The relative depletion of Li compared to Rb and Cs is likely related to differences during mobilization of alkali elements from the host rock, especially at low fluid temperatures and low w/r ratios – e.g., a net release of Li into the fluid requires fluid temperatures >250 °C (Seyfried et al., 1984; Berger et al., 1988; James et al., 2003); or to different affinities to serpentine minerals during the moderate to high-temperature alteration of ultramafic rocks. Lithium enrichment in abyssal serpentinites is common and its uptake is favored at low temperatures (Decitre et al., 2002; Niu, 2004; Agranier et al., 2007; Morishita et al., 2009). Serpentinized rocks formed at higher temperatures and low w/r ratios are not significantly enriched in Li (Decitre et al., 2002; Vils et al., 2008). A similar decoupling of trace alkali elements has been observed elsewhere in mafic-hosted hydrothermal systems (e.g., Lucky Strike) and has also been attributed to the different mobility of Rb, Cs, and Li during alteration (Charlou et al., 2000). The lower mobility of Li at Nibelungen might be further enhanced by Li removal into serpentine minerals.

Thallium, whose geochemical behavior in hydrothermal systems is, despite the chalcophile character, closely associated with Rb and Cs (Jochum and Verma, 1996; Metz and Trefry, 2000) is highly mobile at high temperatures (Nielsen et al., 2006). Similar to the other fluid-mobile elements, the calculated endmember fluid concentration of Tl (8–12 nM) at Nibelungen proves a mafic rock source. Compared to other MOR hydrothermal systems, the Tl concentration at Nibelungen is somewhat lower, similar to the Rainbow field (Douville et al., 2002; Nielsen et al., 2006), which is likely related to the chalcophile character of Tl: Tl is affected by sulfide precipitation at the emanation site of the fluids, as evident from the variable concentrations in fluid samples with similar fluid percentage.

5.3.2. Fe, Cu, Zn, Co, W, Mo, Cd, Pb, and Sn

The transition metals Fe, Cu, Zn, Co, Cd as well as Pb and Sn easily form sulfide minerals or are incorporated into sulfide minerals in hydrothermal environments. Critical for the final concentration of these elements in the fluid are the specific physico-chemical conditions in the reaction zone defining phase equilibria (p, T, pH, redox state), the transport capacity of the fluid during ascent (e.g., available ligands, total Cl content, pH, T, sulfur activity), and sulfide/sulfate precipitation during ascent below and at the seafloor, rather than the total bulk rock concentration (Seewald and Seyfried, 1990; Hemley et al., 1992; Seyfried and Ding, 1995). Previous studies of ultramafic-hosted hydrothermal systems (Logatchev I and Rainbow) concluded that there is no consistent difference in the concentrations of these trace metals relative to basaltic-hosted hydrothermal systems (Douville et al., 2002; Seyfried et al., 2004).

At Nibelungen, the metal to H₂S ratio is extremely high (>5), which has important implications for the solubility of metals in the high-temperature fluid and probably also for the input of metals into the open ocean. Hydrogen sulfide in ultramafic-hosted hydrothermal systems is buffered by Fe–Ni sulfide mineral equilibria (see discussion in Klein et al., 2009) and the low H₂S activity is known to enhance the solubility of Fe, Cu, Zn (Hemley et al., 1992).

Due to sulfide mineral formation and inhomogeneous particle distribution during sampling absolute endmember values cannot be given except for Fe (~5.2 mM). The minimum endmember values, as given in Table 2, however, indicate high dissolved concentrations especially of Cu (~160 μM), Co (1.3 μM), Zn (~90 μM), and Sn (~150 nM) in the Nibelungen fluid, relative to other hydrothermal systems with comparable chlorinity. This is in agreement with the high fluid temperatures and low H₂S activity. Formation constants of metal–chloride complexes increase with increasing temperature and

decreasing water density (Ding and Seyfried, 1992), and at p-T conditions around the critical point of seawater the relative stability of metal–chloride complexes is strongly enhanced. Especially Cu and Co are highly sensitive to temperature. At fluid temperatures below ~350 °C, the mobility of Cu sharply decreases, related to the saturation of chalcopyrite/isocubanite (Metz and Trefry, 2000). The high Fe mobility is further favored at high a_{H_2} and indicative for strongly reducing conditions typical for high-temperature ultramafic-hosted hydrothermal systems (Seyfried et al., 2004). In addition, the solubility of Fe and Zn is controlled by pH, increasing at low fluid pH (Seewald and Seyfried, 1990; Metz and Trefry, 2000). At Nibelungen, the high fluid temperature (370 °C), the low fluid pH of 2.9 (at 25 °C) and the low a_{H_2S} likely promote high dissolved transition metal concentrations.

At Nibelungen, Sn co-varies with the Cu concentration. The geochemical behavior of Sn in submarine hydrothermal systems seems to closely follow that of Cu. Tin in the form of Sn(IV) in stannite forms solid solutions in chalcopyrite (e.g., Okinawa Trough: Kase, 1987; Gena et al., 2005). Similar associations have been observed in massive sulfide samples from the Logatchev I field (S. Petersen, unpublished data). Unfortunately, due to the absence of published fluid data for Sn from mafic-hosted MOR hydrothermal systems it remains speculative that the mobility of Sn is enhanced in ultramafic-hosted hydrothermal systems. Considering unpublished data from the basaltic-hosted Red Lion vent field at 5°S, MAR, Nibelungen is strongly enriched in Sn (about 2 orders of magnitude).

The estimated endmember Pb concentration is significantly higher than the Pb content in depleted mantle rocks, which indicates the mobilization of Pb from a mafic rock source. Relative to other MOR hydrothermal systems, Pb is depleted in the Nibelungen hydrothermal fluids. Lead and also Cd are fluid-mobile elements and are enriched in serpentinized abyssal peridotites (Niu, 2004; Paulick et al., 2006; Agranier et al., 2007), which might explain the somewhat higher Zn/Pb and Zn/Cd ratios at Nibelungen relative to basaltic-hosted hydrothermal systems.

Tungsten is clearly enriched in the Nibelungen fluid (12–14 nM), relative to seawater W. Tungsten concentration data for other submarine hydrothermal fluids are scarce (see Gallant and Von

Damm, 2001; Kishida et al., 2004). The Nibelungen fluid has similar W concentrations as other MOR fluids implying that there is no direct influence of the host-rock in these environments. The range of W concentration at Nibelungen in samples with more than 90% hydrothermal fluid remains relatively stable, as W is not so much affected by sulfide precipitation. Molybdenum, characterized by a contrasting geochemical behavior relative to W in reduced aqueous systems, is highly immobile under these conditions and precipitates in the presence of sulfide in high-temperature hydrothermal systems (e.g., Metz and Trefry, 2000). At Nibelungen, Mo is quantitatively removed from the fluid, which suggests the incorporation of Mo in secondary sulfide minerals in the reaction zone, independent from chalcopyrite/isocubanite precipitation at the seafloor.

5.3.3. Europium anomaly

The distribution/fractionation of REE in hydrothermal fluids can be used to reconstruct geochemical processes and temperature- and redox conditions in the reaction zone (e.g., Mitra et al., 1994; Douville et al., 1999; Bau et al., submitted for publication).

In the Nibelungen fluids, the size of the Eu anomaly ($Eu/Eu^* = 46$) is significantly enhanced relative to most other MOR hydrothermal systems (majority ranging between values of 5 and 20, Fig. 5) (Douville et al., 1999).

Europium is redox sensitive and its geochemical behavior during fluid–rock interaction and fluid transport is decoupled from its REE neighbors in acidic, high-temperature (>200 °C) solution, where its dominant redox state is Eu^{2+} (Sverjensky, 1984; Haas et al., 1995; Douville et al., 1999; Allen and Seyfried, 2005). As discussed above and below, the Nibelungen hydrothermal system is characterized by an intense water–rock interaction resulting in small effective w/r ratios (i.e., long fluid pathways). As the decoupling of Eu^{2+} and REE^{3+} is mainly related to the fractionated partitioning into Fe–Mg-bearing secondary minerals (and partially anhydrite) along the fluid pathway (Douville et al., 1999; Allen and Seyfried, 2005), the enhanced Eu anomaly at Nibelungen may likely be attributed to the massive formation of serpentine and tremolite in pervasively serpentinized peridotite leading to a continuous relative enrichment of dissolved Eu in the fluid. This implies that although the relative distribution of light REE to heavy REE and the absolute REE concentrations are

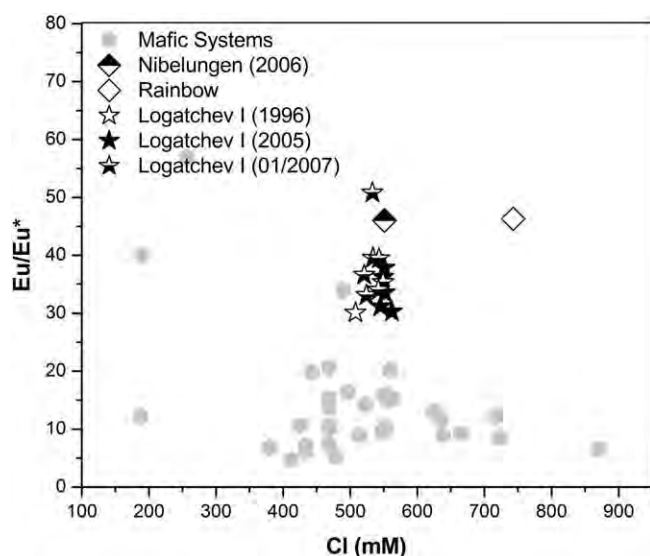


Fig. 5. The Eu anomaly (expressed as Eu/Eu^* of chondrite-normalized concentrations) vs chlorinity, data sources for mafic systems: EPR: 13°N, 17–19°S (Douville et al., 1999), 21°N (James et al., 1995); JFR: ASHES (James et al., 1995); MAR: TAG, Menez Gwen, Lucky Strike (Douville et al., 1999), Broken Spur (James et al., 1995; Bau and Dulski, 1999), MARK (James et al., 1995), 23°N (Michard, 1989); data sources for ultramafic-hosted systems: Logatchev 1996: (Douville, 1999; Douville et al., 1999); 2005: (Schmidt et al., 2007), (Jan 2007: this study); Rainbow (Douville et al., 1999), Nibelungen (2006: this study).

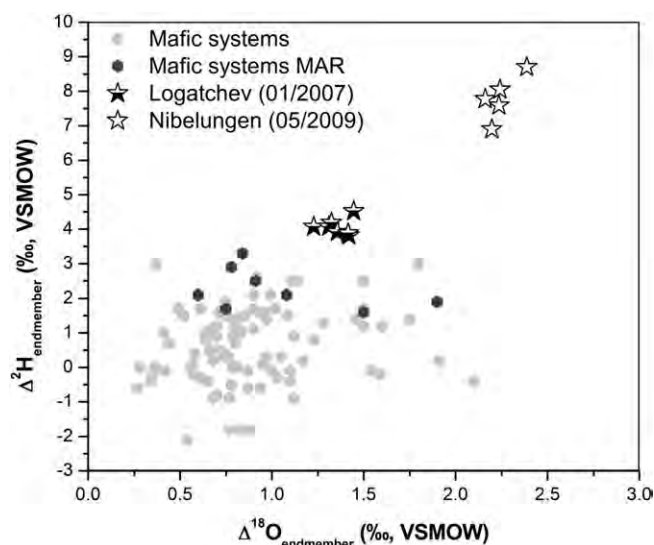


Fig. 6. Stable isotopic composition of hydrogen and oxygen of mid-ocean ridge hydrothermal fluids. Data source for mafic systems: (Shanks, 2001) and references therein: EPR: 9°17'N; 9°33.5'N, 9°39'N, 9°46.3'N, 9°46.5'N, 9°50.3'N, 9°50.7'N, 11°N, 13°N, 21°N, 17°24'–17°27'S, 17°35'–17°44'S, 18°24'–18°26'S, 21°24'–21°27'S, 21°33'–21°34'S; JFR: ASHES, Southern JdFR, MEF; MAR: Snakepit, MARK 1/2, TAG, Lucky Strike; Logatchev Jan 2007: this study; Nibelungen 2006 and 2009: this study.

independent of the source rock composition (Allen and Seyfried, 2005), the characteristic, large size of the Eu anomaly is indicative of ultramafic rock alteration.

The two ultramafic-hosted vent fields Logatchev I and Rainbow are characterized by similarly strong enrichments of Eu in hydrothermal fluids (Douville et al., 2002; Schmidt et al., 2007; this study), which has been attributed to the strongly reducing conditions in these fluids (Douville et al., 2002). Here we propose, however, that the size of the Eu anomaly is rather controlled by the intensity of w/r interaction and the type and amount of alteration minerals in ultramafic host rocks.

5.4. Hydrogen and oxygen isotopic compositions of Nibelungen hydrothermal fluids

5.4.1. Fractionation processes

The isotopic signature of light stable isotopes in hydrothermal fluids can provide insights into the conditions and the type of seafloor alteration processes and can be used to quantitatively constrain water–rock interaction in hydrothermal systems. At Nibelungen, the isotopic compositions of hydrogen and oxygen in the vent fluids can be discriminated from those of fluids venting in bare-ridge basaltic settings, with a significantly heavier $\Delta^2\text{H}_{\text{H}_2\text{O}}$ signature (up to 8.7‰) and a $\Delta^{18}\text{O}_{\text{H}_2\text{O}}$ signature of up to 2.4‰ (Fig. 6).

The isotopic composition of oxygen and hydrogen of hydrothermal fluids emanating at the seafloor is determined by the T–p-dependent isotope exchange between rock–water and the formation of hydrous alteration minerals (Shanks et al., 1995; Taylor, 1997; Shanks, 2001; Horita et al., 2002). A major difference in the importance of these two processes for oxygen and hydrogen isotope fractionation arises from the very small amount of hydrogen in mafic and ultramafic rocks being the host rocks for the circulating seawater: whilst the oxygen isotopic composition in vent fluids is dominated by the temperature-dependent isotopic exchange between the rock minerals and the fluid and strictly depends on the cumulative water–rock ratio, the major fractionation mechanism for hydrogen is the formation of OH-bearing secondary minerals, with deuterium being concentrated in the remaining fluid relative to the hydroxyl group in the secondary silicates. The degree of fractionation is dependent on the composition and the hydroxyl content of these minerals and on the fluid temperature, with increasingly heavier $\delta^2\text{H}$ values in the water at higher OH contents of the rock (Satake and Matsuda, 1979; Shanks et al., 1995; Taylor, 1997). In strongly reducing environments, the formation of molecular H_2 and CH_4 (most effective fractionation mechanisms of hydrogen isotopes in water, enriching the heavier deuterium in the reacting water) may also modify the fluid hydrogen isotopic composition (Mevel, 2003).

In general, vent fluids from the slow-spreading MAR are more enriched in ^2H (Fig. 7) compared to fluids from fast-spreading ridges. Similar as to B, this has been ascribed to longer reaction paths accompanied by more intense water–rock interaction as the isotopic fractionation increases with decreasing w/r ratios (Shanks et al., 1995; Bach and Humphris, 1999; Shanks, 2001).

Given the obvious alteration of mantle rocks below Nibelungen it seems reasonable to relate the enhanced $\delta^2\text{H}$ values to the high amount of water incorporated into altered ultramafic rocks during serpentinization. Serpentine minerals contain about 12% water, bound in the mineral structure, completely serpentinized rocks at the seafloor may contain as much as 15% water (Mevel, 2003). This is in contrast to altered mafic rocks bearing smaller amounts of hydrous minerals and having typically less than 5% total water content.

5.4.2. Quantitative evaluation of water–rock interaction based on hydrogen isotopic data – reaction path modeling

The dominating hydrous alteration minerals in abyssal peridotite are serpentine, tremolite, and brucite. A single, systematic trend of the D–H serpentine–water fractionation is defined by the empirical

equilibrium D–H fractionation curve of (Wenner and Taylor, 1973), and the experimentally deduced fractionation curve of (Saccocia et al., 2009). Here, the D–H serpentine–water fractionation factors decrease with increasing temperature with $\sim\!-\!45\%$ at 100 °C to $\sim\!-\!20\%$ at 400 °C (Saccocia et al., 2009). Similar fractionation factors are reported for tremolite ($\sim\!-\!22\%$ at $T > 350$ °C; (Graham et al., 1984), talc ($\sim\!-\!33\%$ at 350 °C; Saccocia et al., 2009) and brucite ($\sim\!-\!20$ to $\sim\!-\!30\%$ at 350 °C, depending on pressure (Horita et al., 2002). Both, brucite and serpentine, display increasing fractionation factors with decreasing temperature and pressure, whereas talc is only weakly temperature-dependent.

At 370 °C, the transformation of 15% water into crystal water (crystolite) would result in a shift in $\delta^2\text{H}$ in the water by about 3.2‰, applying an isotopic fractionation of $\delta^2\text{H}_{\text{H}_2\text{O}-\text{crystolite}}$ of $\sim\!-\!21\%$. As the water content of fresh peridotite is close to zero and the maximum water content of completely altered peridotite is 12–15%, this shift in $\delta^2\text{H}$ would correspond to an effective water–rock ratio close to 1.

As mentioned before, the oxygen isotopic composition of vent fluids is only little affected by the amount of water incorporated during alteration (due to small alteration factors of $<2\%$) and the isotopic signal represents the temperature and the w/r ratio at the last point of fluid–rock equilibrium. As the fluid temperature in the reaction zone is between 370 °C and 400 °C (as phase separation is not evident, the reaction zone temperature should be below the critical temperature at the respective depth), the fluid signature provide a direct indication of w/r ratio. The relatively heavy $\Delta^{18}\text{O}_{\text{H}_2\text{O}}$ signature relative to other MOR systems mainly reflects the high fluid temperatures of >370 °C and smaller w/r ratios less than one.

To assess the changes in the hydrogen and oxygen isotopic compositions of intergranular fluids during serpentinization of mantle peridotites, we conducted reaction path modeling using the geochemical software package Geochemist's Workbench (Bethke, 1996). A modified thermodynamic database has been used, containing log K values for a constant pressure of 1 kbar and temperatures from 0 to 600 °C. The equilibrium constants were calculated with the SUPCRT92 code and database (Johnson et al., 1992); modifications to the database are detailed in McCollom and Bach (2008) and Klein et al. (2009). The isotope data base contains regression coefficients for the calculation of equilibrium fractionation of stable isotopes as a function of temperature (Bethke, 1996). It has been extended by data for chrysotile (Saccocia et al., 2009), brucite (Satake and Matsuo, 1984; Saccocia et al., 1998), tremolite (Graham et al., 1984; Zheng, 1993), and talc (Saccocia et al., 2009).

In our calculations, a model harzburgite with a modal and mineral composition of 78% Ol (Fo90.5), 20% Opx (En91), 2% Cpx (Di90) has been defined as starting material. This composition corresponds to a depleted harzburgite typically for the Mid-Atlantic Ridge (e.g., Paulick et al., 2006). To allow for the formation of metastable chrysotile during harzburgite alteration, antigorite formation has been suppressed. The chemical composition of seawater is taken from Klein et al. (2009), for the isotopic composition we included the values determined for ambient bottom seawater at Nibelungen ($\delta^2\text{H} = 0.45\%$ and $\delta^{18}\text{O} = 0.3\%$). Oxygen isotope values for the mantle minerals olivine (5.2‰), orthopyroxene and clinopyroxene (both 5.6‰) were taken from Sharp (2007). The oxygen isotopic composition of plagioclase in model 3 has been set the same as the average MORB value of 5.5‰ (Eiler et al., 2000).

5.4.2.1. Model 1a: Temperature controlling stable isotope fractionation

Hydrothermal systems are non-static, with changing w/r ratios and changing reaction temperatures along the fluid pathway. To demonstrate the effect of temperature on the fractionation of hydrogen and oxygen isotopes, 1 kg of seawater has first been speciated at 25 °C and then reacted with 1 kg of harzburgite. In a second reaction path, the entire water–rock system was heated up to 400 °C to model the equilibrium fractionation of hydrogen and oxygen as a function of

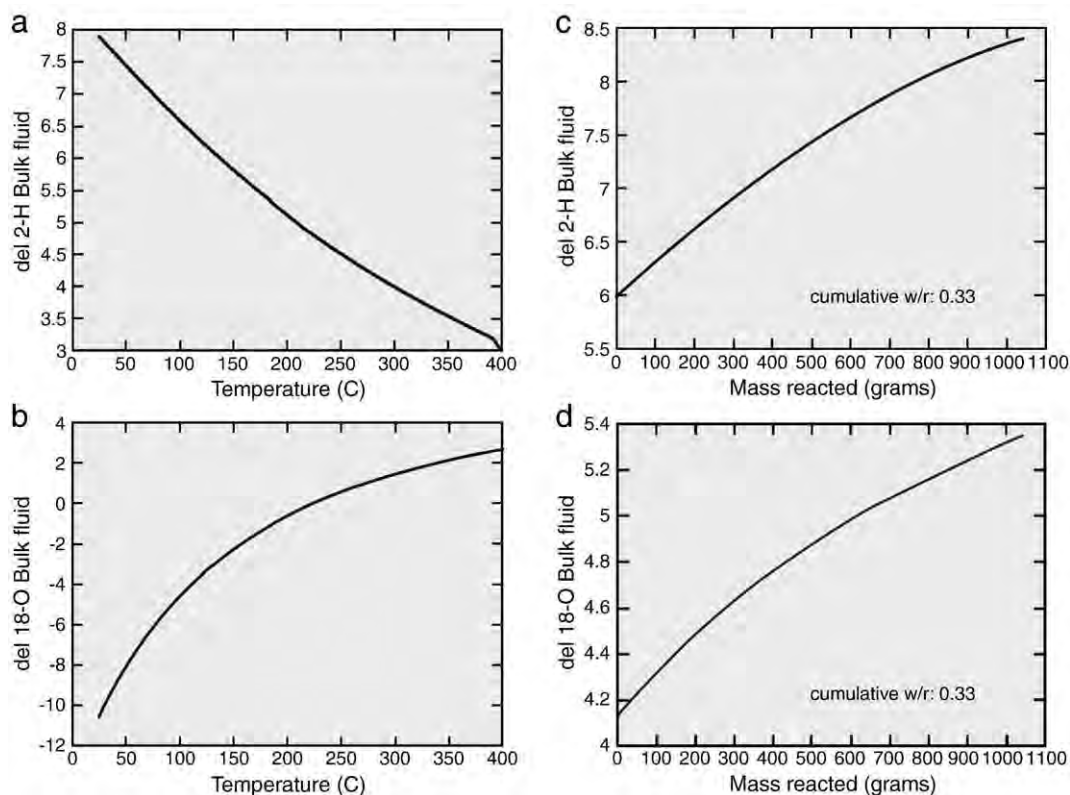


Fig. 7. Isotopic composition of hydrogen and oxygen in a hydrothermal fluid reacted with fresh harzburgite (78% Ol + 20% Opx + 2% Cpx) as function of temperature (panels a and b, at constant $w/r = 1$) and as a function of w/r ratio (panels c and d, at constant temperature of 370 °C, shown is last step with w/r ratio decreasing from 0.6 to 0.33), respectively, initial $\Delta^2\text{H}$ and $\Delta^{18}\text{O}$ of the starting seawater have been set to zero, see text for discussion.

temperature. The results are illustrated in Fig. 7a and b. $\Delta^2\text{H}$ is constantly decreasing with increasing temperature, and at 370 °C the fluid has a signature of about 3.2‰. The hydrogen isotopic composition of the fluid is determined by the alteration mineral assemblage, which is sensitive to temperature. The equilibrium alteration mineralogy at the different temperatures is in general agreement with modeling results of other studies (at 370 °C: serpentine, olivine, magnetite) and will not be further discussed here. In contrast to $\delta^2\text{H}$, $\delta^{18}\text{O}$ is positively correlated with reaction temperature.

5.4.2.2. Model 1b: Water–rock ratio controlling stable isotope fractionation

In another set of calculations the effect of changing w/r ratio on the isotopic signature of hydrogen and oxygen in hydrothermal fluids interacting with fresh mantle rocks was examined (Fig. 7c and d). In these model runs the temperature was kept constant at 370 °C while the w/r ratio along the reaction path decreases down to ~0.33. To simulate open system behavior (i.e., suppress the effect of isotope exchange of the fluid with already formed alteration minerals), the fluid was reacted with fresh harzburgite in each step. (i.e., the fluid has been removed from the system after equilibrating with harzburgite at $w/r = 100$, at $w/r = 1$, at $w/r = 0.5$ and finally at $w/r = 0.33$ and subsequently reacted with fresh rock). With decreasing w/r ratio, $\delta^2\text{H}$ and $\delta^{18}\text{O}$ are increasing. At a very low w/r ratio of 0.33, $\delta^2\text{H}$ has been increased to about 8.4‰, whereas $\delta^{18}\text{O}$ is about 5.3‰.

It becomes obvious from the results above, that serpentinization at very high fluid temperatures of 370 °C is not sufficient to explain the high $\delta^2\text{H}$ values in the Nibelungen fluid. Only at small w/r ratios < 1 , fluid hydrogen would become as heavy as the Nibelungen fluid, but this would force the $\delta^{18}\text{O}$ signature to values $> 5\text{‰}$, which is far more heavy than measured at Nibelungen.

5.4.2.3. Model 2: Serpentinization along a reaction path with increasing temperature (25–370 °C) and decreasing integrated w/r ratio (5 to 0.5)

This reaction path model simulates the entrainment of 1 kg seawater into fresh harzburgite starting at low temperature (25 °C) and high w/r ratio (5), with subsequent heating and water–rock interaction at progressively lower w/r ratios. The final, integrated w/r ratio at a reaction temperature of 370 °C is 0.5. To allow the reacted fluid to entrain fresh harzburgite, the fluid has been picked up at 100 °C, 200 °C, 300 °C and titrated with fresh amounts of model harzburgite. This is in agreement with the common assumption of expanding reaction zones with fluids continuously penetrating unaltered crust at least in the high-temperature reaction zone (Lister, 1974; Saccoccia et al., 1994). The resulting isotopic composition, the alteration mineralogy, and the change in water mass are illustrated in Fig. 8 for the final step of the model calculation from 300 °C to 370 °C. The serpentinization model results with respect to alteration mineralogy (equilibrium mineral assemblage at 370 °C consists of serpentine, olivine, magnetite, clinopyroxene) and fluid composition (pH = 5.6, Si = 0.02 mM, Ca = 110 mM) is in general agreement with other theoretical studies conducted by Mc Collom and Bach, 2009 and Bach and Klein, 2009 and will not be further discussed here. The resulting isotopic composition with $\delta^2\text{H} = 8.8\text{‰}$ and $\delta^{18}\text{O} = 2.5\text{‰}$ is very close to that observed at Nibelungen suggesting that progressive alteration of fresh peridotite at increasing temperatures could explain this observed trend at Nibelungen.

5.4.2.4. Model 3: Hybrid alteration: gabbro alteration with subsequent harzburgite alteration

In this model, we simulate the reaction of seawater with gabbro (50%An, 50%Di) at 200 °C and at a constant w/r ratio of 1, followed by the reaction of the resulting fluid with fresh harzburgite between 200 °C and 370 °C at a w/r ratio decreasing to 0.5. The model accounts for the presumed moderate-temperature fluid–gabbro/basalt interaction inferred from the fluid–mobile element signature. Fig. 9 shows

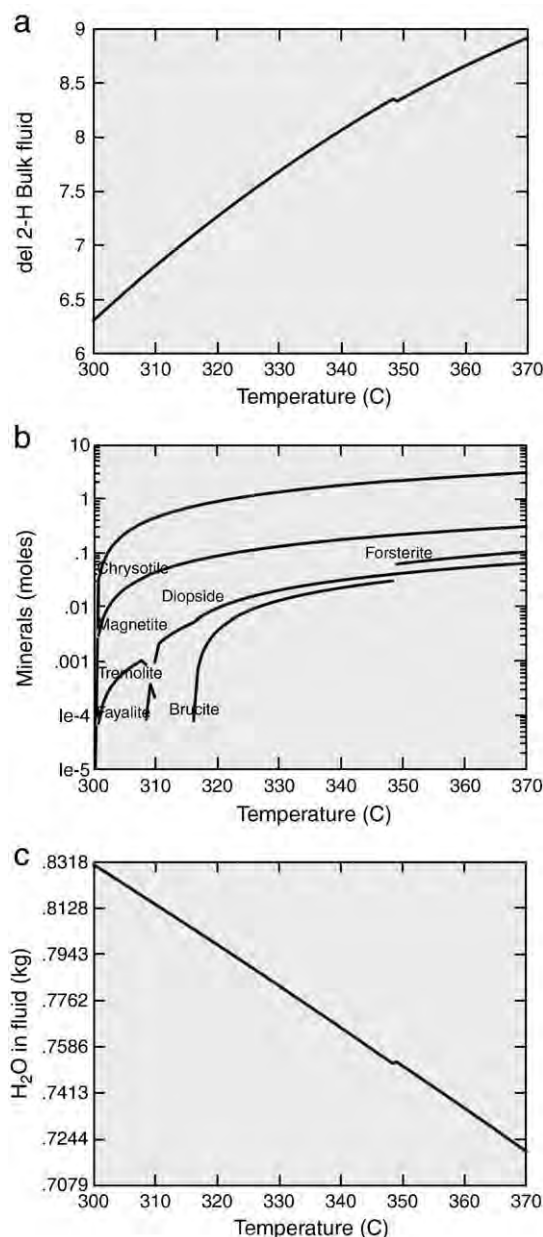


Fig. 8. Predicted isotopic composition of the alteration fluid (a), alteration mineralogy (b) and water mass (c) for the final step of model 2: 1 kg of seawater heated up from 25 °C to 370 °C, while stepwise reacting with increments of fresh harzburgite (78% Ol + 20% Opx + 2% Cpx) at decreasing w/r ratios (25–100 °C: w/r = 5, 100–200 °C: w/r = 3, 200–300 °C: w/r = 1.6, 300–370 °C: w/r = 1.25), with an integrated w/r ratio at the end of the reaction path of 0.5, see text for discussion.

the predicted stable isotope composition and the alteration mineralogy for the final step of this reaction path model. Similar to model 2, this model could explain the isotopic signature of hydrogen and oxygen in the fluid at Nibelungen.

The Nibelungen fluid contains about 12.7 mM dissolved Si. According to experimental results and thermodynamic modeling, only up to 2 mM Si are buffered in a serpentinization fluid temperatures >350 °C (see discussion in Allen and Seyfried, 2003; Mc Collom and Bach, 2009 and Bach and Klein, 2009). In our model calculations dissolved silica from the reaction of a fluid with mafic rocks is immediately consumed during fluid-peridotite alteration. This implies that the relatively high Si concentrations in the Nibelungen fluid are either buffered by a metastable mineral assemblage or, more likely, that high-temperature serpentinization

is followed by limited mafic-rock alteration leading to elevated Si in the fluid. We conducted model calculations to evaluate the effect of such an alteration sequence on dissolved Si in the fluid. Extensive fluid-mafic rock alteration at high fluid temperatures is highly unlikely, as any geochemical signal of serpentinization would be overprinted (i.e., trace alkali elements, Si, B). Thus, only small amounts of gabbro were titrated into the serpentinization fluid. Fig. 10 shows the predicted development of Si concentration at 370 °C, while adding 30 g gabbro to 1 kg of alteration fluid. The resulting Si concentration of 16 mM is still well below the equilibrium concentration determined by quartz solubility (about 25 mM at 1 kbar pressure). This model could simulate a fluid penetrating a basaltic or gabbroic layer just before emanating at the seafloor.

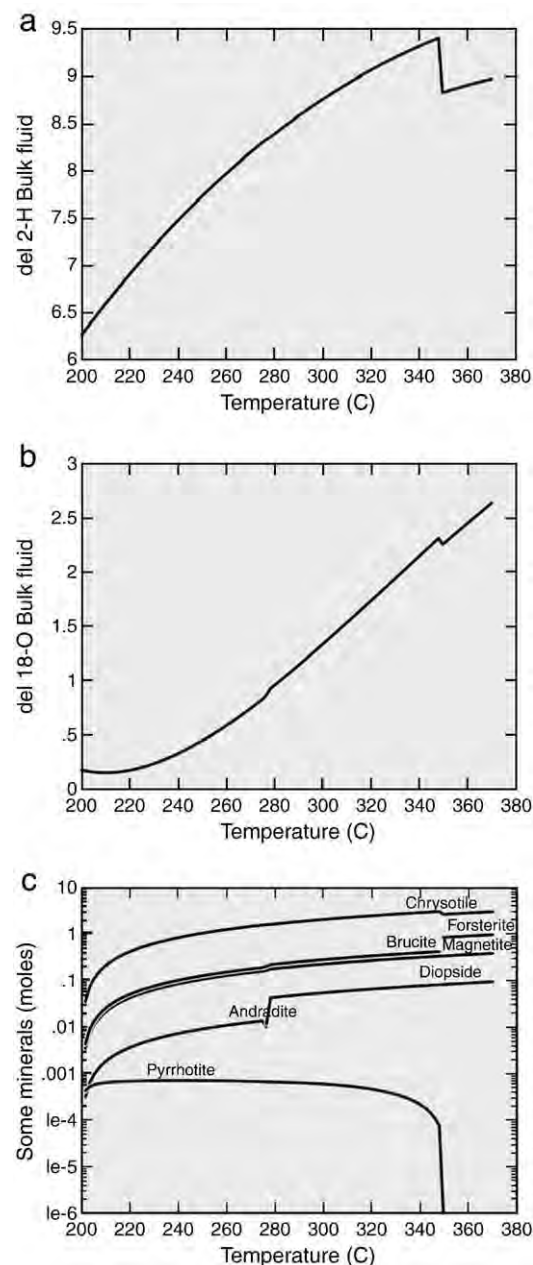


Fig. 9. Predicted isotopic composition (a, b), and alteration mineralogy (c) for the final step of reaction path model 3: seawater has been equilibrated with gabbro (50% An, 50% Cpx) at 200 °C, w/r = 1, followed by a stepwise titration of fresh harzburgite (78% Ol + 20% Opx + 2% Cpx) at 200 °C (w/r = 1) and 200–370 °C (w/r = 1) into the altered seawater, simulating the entrainment of gabbro-altered seawater into mantle rocks, see text for discussion.

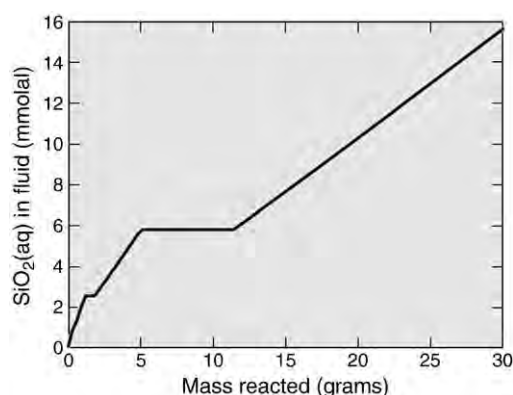


Fig. 10. Predicted evolution of dissolved Si concentration in a hydrothermal fluid at 370 °C, while titrating 30 g of gabbroic rock into 1 kg of fluid, which previously reacted with harzburgite (e.g., as derived from calculation model 3, see text for explanation).

It should be noted, that the reaction path modelling does not account for any kinetic effects or metastable equilibria, and that it ignores isotope exchange with already formed alteration minerals.

Besides the massive formation of hydrous alteration minerals, the alteration of ultramafic rocks also supports another possible hydrogen fractionation mechanism: the formation of molecular H₂ and of CH₄ in a strongly reducing environment. The temperature-dependent fractionation factors lead to a depletion of ²H in the dissolved gases (e.g., Bottinga, 1969; Horibe and Craig, 1995; Shanks et al., 1995). Both gases are strongly enriched in ultramafic-hosted systems. At 350 °C, an increase of 1‰ in δ²H_{H₂O} would require the equilibrium production of >100 mM H₂ from 1 L H₂O (with average isotopic fractionation between H₂O and H₂ of about –370‰ (Proskurowski et al., 2006)), significantly more than observed in the sampled vent fluid (11.4 mM). As the isotopic fractionation between H₂O and CH₄ is smaller than between H₂O and H₂ (about –110‰, (Proskurowski et al., 2006)), a significant shift in δ²H in the water due to the formation of CH₄ cannot be expected. Considering these calculations it seems unlikely, that the formation of molecular H₂ and CH₄ at Nibelungen causes significant isotopic shifts in the alteration fluid, despite strong enrichments of both gases. Only when significantly more H₂ is produced this could be an important process. Experimental and theoretical studies have shown that the production of hydrogen during fluid–mantle rock alteration strongly depends on the temperature and w/r ratio (c.f., Klein et al., 2009). Modeling results by Klein et al. (2009) and experimental results of serpentinization suggest the formation of >150 mM H₂ at temperatures of about 200 °C. However, with Geochemist's Workbench, the net effect of H₂–H₂O fractionation on the fluid isotope composition of hydrogen presently cannot be satisfactory modeled.

5.4.3. Implications for chloride concentration in the fluid

The Cl content of hydrothermal fluids from Nibelungen is very close to, or slightly higher than seawater (with mean values of 551 mM for 2006 and 568 mM for 2009). Assuming that 15% of water is transformed into crystal water during serpentinization, a conservative behavior of Cl would lead to an enrichment of Cl by about 85 mM over seawater in the emanating fluids at a w/r ratio of one. However, serpentinized peridotites represent a sink for oceanic Cl (Mevel, 2003), where Cl can substitute for (OH)[–] in phyllosilicates like serpentine (Anselmi et al., 2000) or occurs as water-soluble salt (Barnes and Sharp, 2006). The chloride concentration at Nibelungen can thus likely be explained by the incorporation of Cl into serpentine minerals accompanying the loss of water. If we assume pervasive serpentinization of fresh peridotite in the Nibelungen reaction zone, a

decrease of Cl by about 85 mM in the fluid along with the loss of water would correspond to 2900 ppm Cl being incorporated into the serpentinized rock, which is slightly higher than the average bulk Cl concentrations in oceanic serpentinites (up to 2600 ppm – (Barnes and Sharp, 2006); c.f., (Mevel, 2003).

The enhanced ratio of Br/Cl of ~1.57 (μM/mM) reflects the enrichment of Br relative to Cl in 2009 samples, relative to the seawater with a ratio of 1.53. Bromine may not fit as good as Cl into the serpentine or soluble salts, leading to somewhat enhanced Br/Cl ratios in the venting fluids.

5.5. Model of hydrothermal circulation at the active Nibelungen vent field

Based on the fluid geochemistry discussed above, the following constraints can be made for hydrothermal circulation below the presently active Nibelungen vent field:

1. High-temperature alteration of fresh basaltic or gabbroic rocks at low water/rock ratios can be excluded (should result in a similar mobility of Rb, Cs, Li, and B enrichment). The alteration sequence is determined as follows: Moderate-temperature (>150–250 °C) alteration of mafic rocks prior to serpentinization of fresh peridotite at medium to high temperatures, at small integrated w/r ratios less than unity. Limited wall rock alteration during ascent results in an increase of Si.
2. The combination of very high fluid temperatures, low H₂S concentrations, and limited mixing of hot fluid with cold seawater below the emanation site (c.f., Petersen et al., 2009) likely prevent any significant sulfide mineral precipitation in the upflow zone, which leads to the generally high transition metal concentrations.
3. The absence of active chimney structures at the vent orifice is likely related to combined influences of fluid composition (lower Si and H₂S concentrations), limited admixture of sulfate-containing seawater to the hot upflow zone (see point 2), and fast mixing of hot fluid and cold seawater at the emanation site with subsequent strong cooling and dilution. As a consequence, saturation with respect to both anhydrite with its retrograde solubility and amorphous silica as matrix minerals is not reached and initial chimney structures do not form.

The elemental and isotopic composition of fluids from the Drachenschlund vent is indicative for a heterogeneous subseafloor lithology with a hybrid alteration pattern. This environment leads to chemical gradients resulting in an intermediate fluid composition with signatures of both fluid–basalt and fluid–peridotite interaction. The lithosphere below the Nibelungen hydrothermal field probably consists of a thin layer of extrusive basalts (as evident from altered pillow lava hosting the vent field) overlying peridotite rocks with gabbro intrusions, as described as typical feature of segment ends at slow-spreading axes (Searle and Escartin, 2004). Fluid flow is likely channeled along a deep-rooted fault, possibly a detachment fault.

5.6. Comparison of hydrothermal alteration underneath Nibelungen and Logatchev I

The newly obtained fluid chemical data for the Nibelungen hydrothermal field situated at the southern MAR resemble that of vent fluids emanating in the Logatchev I hydrothermal field at the northern MAR (Douve et al., 2002; Schmidt et al., 2007; this study) with respect to key parameters. Characteristic fingerprints of this ultramafic signature are the strong enrichment in dissolved H₂ and CH₄, depletion of B compared to seawater, and lower concentrations of Si and Li relative to basaltic-hosted hydrothermal systems. Further similarities like the crater-like structure of the vent site, the association of the vent field with faults and missing sulfide chimneys at the crater bottom are

obvious and strongly indicate similar geological conditions and processes in the seafloor. In contrast to Rainbow, the other well-characterized high-temperature field located in ultramafic host rocks (Douville et al., 2002) emanating a phase-separated brine, both Logatchev I and Nibelungen are not significantly influenced by phase separation. Although the Logatchev I fluid is slightly depleted in Cl (maximum 10%, see Table 3), possibly indicating phase separation close to, or above the critical point of seawater (407 °C, 298 bars), the venting temperature of about 350 °C requires in this case either conductive cooling within a few tens of meters below the seafloor or, more likely, mixing with large proportions of cooler fluid or seawater. An alternative explanation for the Cl depletion is given by the massive formation of hydrous minerals, with the incorporation of Cl as discussed for the Nibelungen field.

Despite the similarities in chemical trends and geological conditions significant compositional differences discriminate the Nibelungen fluids from those at Logatchev I (Table 2): (i) higher concentrations of Si, (ii) stronger depletion of B, (iii) higher concentration of Li, (iv) relative depletion of Rb, Cs, Tl, (v) stronger enrichments of sulfide-forming elements Cu, Co, Zn, Cd, Pb, Sn, W, and (vi) heavier $\delta^2\text{H}_{\text{H}_2\text{O}}$. The significantly enhanced mobility of the fluid-mobile elements Rb and Cs at Logatchev I when compared to Nibelungen and mafic-hosted hydrothermal systems probably reflects leaching of Rb and Cs from low-temperature alteration products of mafic rocks or from pelagic sediments (which are strongly enriched in fluid-mobile elements) at temperatures not allowing Li mobilization (i.e., below ~250 °C), followed by moderate to high temperature interaction with both gabbroic and ultramafic rocks (see also discussion in Butterfield et al., 1994; Charlou et al., 2000).

At Nibelungen, the concentrations of the sulfide-forming elements Cu, Zn, Cd, Co, as well as Pb and Sn are distinctively higher than at Logatchev I (Table 2, supplementary data, Plates I and II). The relative depletion at Logatchev I is likely linked to an elevated precipitation of sulfides in the seafloor underneath the Logatchev vent field. This is in agreement with Seyfried et al. (2004), who concluded that in the ultramafic-hosted Rainbow and Logatchev I fields a large proportion of initially mobilized Cu likely accumulates in stockwork deposits and chimneys.

The oxygen isotopic signature at Logatchev I of about 1.2–1.5 per mille reflects the lower fluid temperature of 350 °C and is indicative for a w/r ratio of above 1. Although the hydrogen isotopic signature is distinctively enriched relative to basaltic-hosted hydrothermal systems, the lower values relative to the Nibelungen fluid might be related to less low- to moderate-temperature serpentinization or less fresh mantle rock alteration. In contrast to the Nibelungen field, the Logatchev I area is characterized by talus material of pervasively serpentinized rocks directly at the seafloor (90–95%; Augustin et al. (2008)). Serpentinization at 350 °C and a cumulative w/r ratio close to one could explain the hydrogen isotopic signature at Logatchev I.

6. Summary and conclusion

The Nibelungen hydrothermal system is characterized by a stable fluid composition between 2006 and 2009, with strong enrichments of the dissolved gases H_2 and CH_4 , a relative depletion in H_2S , Si, Li and B, an enhanced Eu anomaly and the stronger enrichment of deuterium in the fluid. Furthermore, the trace metals Cu, Zn, Co, (Sn) are significantly enriched. This composition is markedly different to that of fluids from mafic-hosted hydrothermal systems along the MAR and EPR. The geochemical signature of the Nibelungen hydrothermal fluids strongly suggests a hybrid alteration pattern in the sub-seafloor involving both significant seawater-peridotite interaction (corroborating the interpretation of Melchert et al. (2008)), but also seawater-gabbro (or basalt) alteration: the fluid mobile elements Li, Cs, and Rb as well as Pb and Tl are mainly derived from mafic rocks. The

concentrations of dissolved gases H_2 , CH_4 and H_2S are controlled by serpentinization reactions, and the reduced mobility of B and Li relative to mafic-hosted hydrothermal systems can be directly linked to the alteration of mantle rocks. Especially B strongly partitions into alteration minerals during serpentinization at low and probably also high temperatures. In addition, the concentration of Li and B in residual peridotite is very low and leaching at high alteration temperatures cannot compensate the removal. The different mobility of the alkali elements Rb, Cs, and Li at Nibelungen is linked to differences in binding sites affecting mobilization during medium-temperature mafic rock alteration and incorporation into alteration minerals during serpentinization.

For the first time, the stable isotope composition of hydrogen in ultramafic-hosted hydrothermal systems has been determined. The signature of the Nibelungen fluids being strongly enriched in deuterium ($\Delta^2\text{H}_{\text{H}_2\text{O}} = 8.7\text{‰}$) is clearly different from mafic-hosted systems. The isotopic shift of $\delta^2\text{H}$ in the alteration fluid requires a complete serpentinization of the protolith at small cumulative w/r ratios. In a possible scenario derived from the fluid elemental signature and reaction path modeling, serpentinization takes place at medium to high temperatures with ongoing alteration of fresh rocks, following low-to medium-temperature alteration of gabbroic rocks. During ascent, limited high-temperature interaction of the ascending fluid with mafic (basaltic) rocks takes place, which is in agreement with the geological conditions at Nibelungen. As the dissolved Cl of the vent fluids is not distinctly elevated above seawater despite significant loss of water during alteration/serpentinization, Cl must also be incorporated into the alteration minerals. There is no evidence for phase separation at Nibelungen. The enhanced concentrations of sulfide-forming elements at Nibelungen (Fe, Cu, Co, Zn, Sn) are likely related to the combined effects of high fluid temperatures close to the critical point of seawater enhancing the stability of chloride complexes, a low *in situ* fluid pH, strongly reducing conditions, a low H_2S activity. Obviously, this high dissolved metal content is not significantly modified by sulfide precipitation in the subseafloor. The concentrations of Pb, Cd and Tl, being both chalcophile and fluid-mobile, depend more on the host rock composition and their incorporation into serpentine minerals.

The fluid chemistry at the Nibelungen field shows similar geochemical trends compared to the Logatchev I field with respect to dissolved gases, Si, trace alkali elements, B, and $\Delta^2\text{H}_{\text{H}_2\text{O}}$, but also indicates differences in the absolute concentrations attributed to differences in cumulative w/r ratios, the amount of fresh rock alteration, alteration temperatures of mafic and ultramafic rock types and the amount of sulfide precipitation in the subseafloor. Overall, the compositional key parameters (dissolved gases, Si, trace alkali elements, B, and $\Delta^2\text{H}_{\text{H}_2\text{O}}$) of Nibelungen and Logatchev I as well as those reported from the Rainbow vent field collectively define a unique geochemical fingerprint that might be typical for hot fluids emanating in heterogeneous ultramafic–mafic lithosphere environments at slow-spreading ridge axes. The results of this study further contribute to the understanding of the geochemical processes and mechanisms controlling the elemental and isotopic composition of hydrothermal fluids in heterogeneous, mafic–ultramafic lithosphere settings. With our new geochemical data for the Nibelungen and Logatchev fields, we extend the data record in both space and time for hydrothermal systems influenced by mantle rock alteration, with emphasis on trace metals, and stable isotopes ($\delta^2\text{H}$, $\delta^{18}\text{O}$) in the hydrothermal fluid.

It is likely that there exist a larger number of similar hydrothermal systems characterized by the alteration of ultramafic rocks in off-axis, fault-controlled settings on slow-spreading ridges. These parts of the spreading ridges are still under-explored, and the distinct fluxes of elements and isotopes in such systems may have important implications for the budgets of specific elements in the ocean.

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Appendix A. Supplementary Data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemgeo.2010.07.008.

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**Manganese and Fe-Mn mineralization in the Logatchev-1
hydrothermal field, Mid-Atlantic Ridge: temporal and spatial
variability and implications for hydrothermal fluxes**

6.1 Introduction

In hydrothermal environments, Fe and Mn oxides occur as primary and secondary precipitates, forming Fe oxide chimneys, Mn oxide crusts, Fe-Mn-SiO₂ deposits, Fe-Mn coatings on rock substrate or massive Fe oxide crusts, and stratabound Mn-oxide layers and lenses (Hannington and Jonasson, 1992 and references therein). The oxidic precipitates either form as oxidation products of massive sulfides, as plume fallout or as primary precipitates from low-temperature hydrothermal fluids, each group being characterized with distinct mineralogical and geochemical compositions. Whereas large accumulations of Fe oxyhydroxides occurring for example in the TAG hydrothermal field are often associated with massive sulfides (Tivey et al., 1995; Petersen, 2000), pure Mn deposits are mainly reported from island arc and backarc settings in the Pacific, away from high-temperature emanation sites (Cronan et al., 1982; Moorby et al., 1984; Rodgers et al., 2001; Eckhardt et al., 1997; Usui and Someya, 1997; Usui and Glasby, 1998; Hein et al., 1997; Hein et al., 2008; Glasby et al., 2006; Hein et al., 1996), Hein et al., 1999; Kuhn et al., 2003) and are considered to be low-temperature, distal hydrothermal deposits formed near the sediment-seawater interface. Similar Mn oxide deposits were also found in the MAR rift valley (Mills et al., 2001), on the flank of the Juan de Fuca Ridge (Fitzgerald and Gillis, 2006), on the flank of the East Pacific Rise (Benjamin and Haymon, 2006), and in the Galapagos Rift (Migdisov et al., 1983) and are likely related to fluid flow along faults. These deposits are often stratified, a few cm thick and characterized by high Mn/Fe ratios, generally low concentrations of Cu, Co, Ni, Zn, Pb, and REE, common enrichments of Mo and Li and fast growth rates (cm/ka), which, when considered together, clearly separates these deposits from hydrogeneous ferromanganese crusts.

Detailed studies on the formation and compositional variability of ferromanganese deposits in close proximity (within a few hundred meters) to active, high-temperature venting sites at mid-ocean ridges are rare and have previously mainly focused on massive Fe oxyhydroxide deposits (e.g., Petersen, 2000). The only study particularly considering Mn precipitates at high-temperature vent sites is for the Ashadze-1 vent field (Davydov et al., 2007). Bodganov et al. (2004) reported first geochemical data for Fe oxyhydroxides and mixed Fe-Mn rock coatings in the Logatchev-1 area, and Davydov et al. (2007, 2009) presented a few data for cm-thick Mn crusts from Logatchev-2. In contrast to distal low-temperature Mn deposits described before, these data show occasional strong enrichments of metals like Cu, Zn, Ni, and Co, which is indicative of proximal sulfide precipitation. Occasional enrichments of specific elements in Mn crusts in island arc settings are often used to obtain information about the type of leached source rock (Hein et al., 2008) and seafloor processes like massive sulfide formation (Hein et al., 2008).

High-temperature hydrothermal fluids venting in the Logatchev-1 field are characterized by geochemical fingerprints indicative for hybrid alteration of mafic and ultramafic rocks: The fluids are characterized by high metal/H₂S ratios ≥ 1 , high Co concentrations and moderate Cu and Zn concentrations. However, as has been shown in Schmidt et al. (in press), the fluid content of metals like Cu, Co, Zn, Pb, Sn, W is rather determined by sulfide formation processes below and at the seafloor and temperature-controlled solubility than by the host rock composition, which may complicate the tracing of a clear ultramafic fingerprint in low-temperature hydrothermal deposits. Bogdanov et al. (2004) and Davydov et al. (2009) proposed that MAR ferromanganese deposits reflect the type of basement rocks that were leached, based on observations that low-temperature deposits from the Rainbow and Logatchev fields are enriched in Co and Ni, whereas deposits from basaltic-hosted hydrothermal fields at the MAR are not. However, no data for proximal ferromanganese deposits from basalt-hosted hydrothermal systems are available (or only available in Russian).

Manganese and iron(oxyhydr)oxide particles formed in hydrothermal environments may gain their adsorbed metal content from (low-temperature) hydrothermal fluids percolating through the subseafloor and emanating at the seabed and also due to scavenging from seawater. The understanding of enrichment processes and element sources is important for the interpretation of the observed geochemical signatures of ferromanganese deposits. Commonly used tracers of hydrothermal input are the isotopic signatures of Os, Nd, (Hf), and the REE distribution (Eu anomaly, Ce anomaly and the normalized Nd/Yb ratio - Mills et al., 2001; Frank et al. 2006; Ravizza et al., 1996; Hein et al., 2008, Davydov et al., 2007, 2009). The relative contribution of a hydrothermal source is different for different elements and will depend on the respective concentrations and the speciation in the endmember source fluids, distribution coefficients between fluid and mineral, and the geochemical behavior during sorption (i.e., formation of surface complexes and surface precipitates). The investigation of hydrothermal tracers in the different types of Fe-Mn oxide deposits in the Logatchev-1 field will provide important information about (1) the mode of crust formation and (2) the geochemical cycling of elements at high-temperature hydrothermal vent sites.

The mineralogy of the hydrothermal Mn oxides is commonly characterized by 7Å and 10Å manganates as well as vernadite (Hein et al., 2008). The 7Å and 10Å manganates can accommodate high concentrations of metal cations, either being incorporated as exchangeable hydrated cations into the interlayer or tunnel sites (e.g., Li, Mg), chemically sorbed via inner-sphere surface complexes (e.g., Zn, Cu, REE), structurally incorporated on Mn vacancy sites (Co³⁺), isomorphic substitution for Mn⁴⁺ (e.g., Co³⁺, Ni) or via the formation of surface hydroxide complexes (e.g., Ti). The sorption capacity of manganates depends on the crystallinity and the relative enrichment of metals is dependent on the concentration and speciation in the source fluid, the physico-chemical conditions (pH, Eh, T) of mineralizing

fluids and at the mineral-water interface, and the sorption mechanism. Elements like Ce and Co are adsorbed via surface oxidation and their concentration in Mn oxides is directly dependent on the growth rate. Microbial activity in controlling the uptake of trace metals in oxide minerals has recently received enhanced attention (e.g., REE - Tanaka et al., 2009). Considering these, changes in the chemical composition of stratified Mn crust profiles, which are commonly referred to as direct precipitates from low-temperature hydrothermal fluids, reflect changes in the local growth environment, which may be used to trace changes in the hydrothermal circulation system over time. However, local fluctuations at low-temperature emanation sites are not necessarily related to large-scale changes in the hydrothermal circulation patterns or different evolutionary stages of a hydrothermal system.

This chapter describes the mineralogy and the elemental and isotopic composition of the diverse oxide deposits within and around the active Logatchev-1 hydrothermal field, occurring as semi-consolidated Fe-oxyhydroxides, Fe-Mn coatings on serpentinites and as cm-thick, pure Mn oxides. The aim is to characterize proximal Fe-, Fe-Mn-, and pure Mn deposits and to determine the controls on trace metal accumulation (including REE and HFSE) in the different depositional types of oxide deposits in high-temperature hydrothermal vent fields. Stratified Mn oxide crusts, composed of individual layers with distinct elemental and isotopic compositions, might potentially be used as an archive of hydrothermal activity over time.

6.2 Samples and methods

Ferromanganese deposits from the Logatchev I hydrothermal field were recovered during two research cruises within the SPP 1144 in January/February 2005 (cruise M60/3) and May 2005 (cruise M64/2) (Fig. 1). Several ROV dives and TV-grab stations recovered Fe-Mn-oxyhydroxides, Fe oxides and Mn-oxides, among hydrothermal sediment, sulfide-rich precipitates and wall rocks (Table 1). The sample locations are either close to the high-temperature vent sites (78 GTV, 225 GTV and 32 GTV, 33 GTV) or in the near vicinity of the Logatchev field in distances of not more than 300m (222 GTV, 230 GTV, 239 GTV). Pure Mn oxides (**78 GTV and 225 GTV-3**) were obtained from two locations west of the *Quest* site, in close association with Fe-Mn coatings on peridotite. Massive Fe oxyhydroxide accumulations (**32GTV, 33 GTV**) are associated with massive sulfide talus and sulfide-bearing mud and were sampled close to the smoking crater walls in the southeastern part of the field.

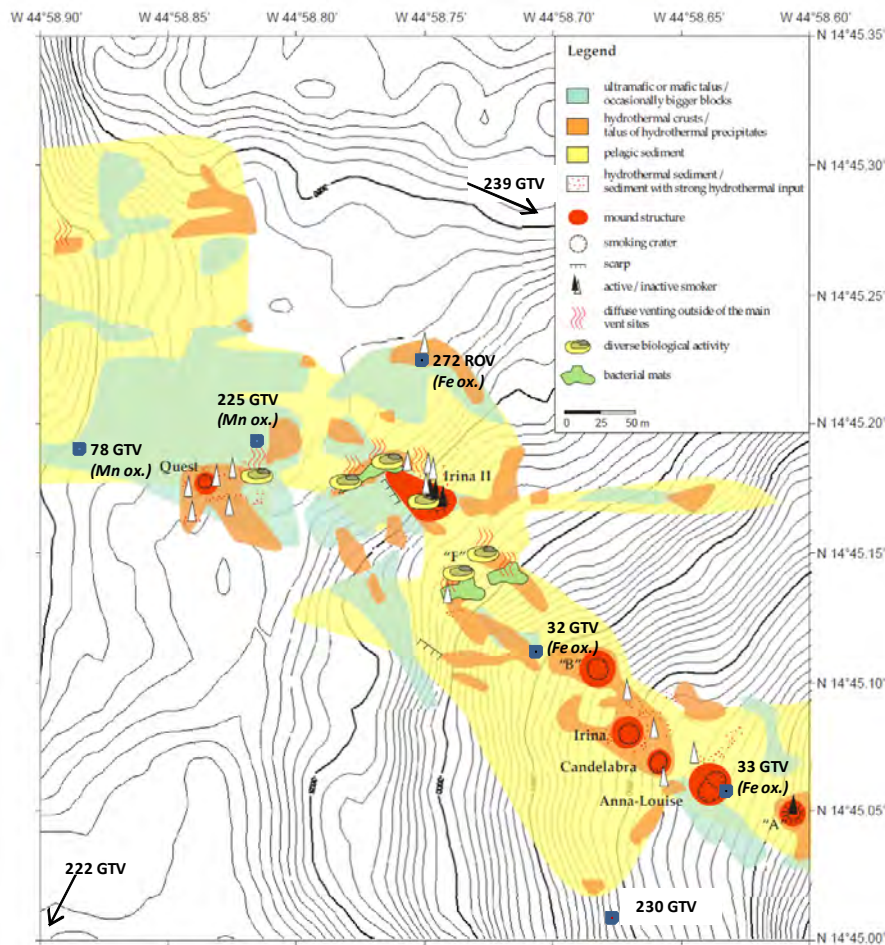


Fig. 1: Generalized geological map of the Logatchev-1 hydrothermal field, based on ROV operations. ROV and TVG stations of cruises M60/3, M64/2 and MSM04/3 are marked with blue squares, modified from Petersen et al., 2009

Manganese oxide and ferromanganese oxide samples were soaked in seawater and stored in airtight boxes immediately after recovery. After a macroscopic description, the samples were prepared for mineralogical and geochemical analysis. In order to determine the mineralogical structure and microscopic textures of the different (Fe)-Mn deposits in the Logatchev field, detailed studies by X-ray diffraction (XRD, with Cu K α radiation), microscopy, and scanning electron microscopy (SEM) were performed.

For geochemical crust profiles, three pieces of pure manganese crusts (78 GTV-1) and one piece of thick Mn-coating on peridotite (225 GTV-1F-1) were mechanically separated into individual layers. All other samples were prepared for bulk analyses. For chemical analysis the samples were dried at 105°C, ground to a fine powder in an agate mortar and re-dried prior to analysis. Sample decompositions were performed in 30 ml PTFE vessels using a Picotrace DAS acid digestion system (Bovenden, Germany). Typically, 100mg of sample were digested at 180°C for 12h, using a mixture of 1ml of 40% HF, 3 ml of 30% HCl and 1ml of 65% HNO₃. After cooling, samples were evaporated at 120°C for approximately 2h to near dryness, redissolved with 3ml 20% HCl and heated again at 120°C to incipient dryness. The

residues were taken up again in 3ml 20% HCl and heated at 120°C to incipient dryness. Finally, the residues were made up to 50ml in a matrix of 0.5M HNO₃/0.5%HCl. A smaller sub-set of samples was digested with 30% HCl at 90°C without additional HF and HNO₃. This digestion should completely dissolve the oxide mineral phases but not most detrital minerals like silicates. The digestion efficiency for the individual elements can thus be used to obtain information on the relative mineral associations. The following elements were measured with Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) at the Jacobs University Bremen (JUB): REE, Y, Rb, Sr, Sc, Ti, Zr, Nb, Cs, Ba, Hf, Ta, W, Th, U, whereas Mg, Na, K, Fe, Mn, Al, Cu, Co, Ni, Zn, Pb, Mo, Li were determined with Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). ICP-MS analyses were performed at JUB with a PerkinElmer DRC-e quadrupole instrument. For details on instrumental performance the reader is referred to Alexander (2008). ICP-OES analyses were performed at the JUB Geochemistry Lab using a Spectro Ciros SOP instrument. Accuracy and precision of the analytical methods have been checked using certified Fe-Mn crust (GSMC-1) and Fe-Mn nodule (JMn-1, Nod-P1, Nod-A1, GSPN-3) reference materials (CRM). The precision is given as method precision of control standards, i.e., the precision of multiple sample decompositions and multiple analyses as % relative standard deviation (%RSD). Control standards have been measured several times during one run, to monitor the accuracy of the measurement over time. The Appendix Table 1 and Table 2 list the average concentrations of the different CRMs in comparison to the recommended values, determined by ICP-OES and ICP-MS, over a period of four years.

ICP-OES: The *precision* of the JMn-1 standard, which has been used most extensively in the four years, is better than 4% for all elements except for P and Cu (<8%). Precisions of better than 3% have been achieved for the nodules Nod-P1 and Nod-A1 as well as the crust CRM GSMC-1, except for P and Cu in Nod-P1 (<9%), Li, S, and V in Nod-P1 (<5%) and Ca, Cu, Fe, Mn, Na, and P with <4% in GSMC-1, and for Ni, Cu, Fe, Al, Mg, Mn <5% for Nod-A1. The *accuracy* of the measurements is generally very good, with less than 3% deviation from the average of published reference values except for <5% for V, Zn, Cu, Mo, Ni, P in JMn-1, for Cu, Fe, Mn, Na in GSMC-1, and Li, Mn, Ni in Nod-P1. Sulfur concentrations are always too high up to about 30%, whereas Mo, V, and P are partly too low. Published values of reference values often display relatively high ranges especially for the minor elements V, Mo, P, and Sr, which complicates a clear statement on the accuracy of the method for these elements.

ICP-MS: The *precision* of the ICP-MS data is generally very good, with 1-5% RSD for most elements, except for Sc, Sr, Cs, Ce, and Ta with better than 10% RSD in JMn-1 and Hf, Ta, Sr better 10% RSD in Nod-P1. Best precisions have been achieved for the rare earth elements. The measured concentrations of CRMs are in very good agreement with published data, proving the *accuracy* of the analytical measurements. Data for Nb and Ta in Fe-Mn oxide

CRMs are rare. This study reports the first Ta data for the GSPN-3 and GSMC-1 standards. Measured Nb concentrations are in excellent agreement with published data for GSPN-3 (Wang et al., 1998) and Nod-P1 (Axellson et al., 2002). Measured Ta concentrations are in agreement with those reported for JMn-1 (Imai et al., 1999) and Nod-P1 (Axellson et al., 2002), but somewhat higher for Nod-A1 (Axellson et al., 2002). The Nb/Ta ratios are in excellent agreement for Nod-P1 but about 9% lower for Nod-A1. Reference determinations for high-field strength elements Zr, Hf, Nb, and Ta in the JMn-1 and other Fe-Mn crust samples have been conducted at the University of Münster (Appendix Table 3), applying the matrix separation method of Münker et al. (2001). While the absolute concentrations obtained by this method are lower by about 20% for JMn-1, the ratios of Nb/Ta and Zr/Hf are in excellent agreement between both laboratories and approve the accuracy of the HFSE concentrations determined at JUB. Furthermore, Ta concentrations determined independently are in very good agreement in Mn crust samples with very low concentrations (Appendix Table 3).

Osmium isotope analyses were done by Michael Brauns (at present: Curt-Engelhorn-Zentrum Archäometrie gGmbH), Nd isotope analyses were performed at LIG/Stockholm by Hans Schönberg, and Hf isotope analyses were carried out in cooperation with Carsten Münker at the Westfälische Wilhelms-Universität in Münster (now: Universität Köln).

Table 1: Sample list of oxidic Fe-Mn deposits in the Logatchev-I hydrothermal field

Cruise Nr.	Station Nr.	Station description	Sample ID	Sample Description
M64/2	230 GTV	Mn-coated (max. 1cm) pyroxenites	230 GTV-1 (D3)	FeMn coating, mm in diameter
M64/2	239 GTV	light brown clay, in the middle grouse of Mn-crusts, atacamite grouse and talc, hematite-impregnated serpentinites	230 GTV-1-F 239 GTV-5A	FeMn coating, mm in diameter Porous Mn crust, brownish, green particles (atacamite), irregular shape, cavities with soft Fe oxide deposition
M64/2	225 GTV	no hydrothermal sediments or crusts found, no sulfides, weakly serpentinized pyroxenites, some Mn-crusts	225 GTV-1F 225 GTV-1F-1 225 GTV-3 (B1) 225 GTV-3 (D2)	Fe-Mn coated, weakly serpentinized pyroxenites (<1mm) Up to 1.5 cm in diameter Mn coating on weakly serpentinized pyroxenite (same piece as 225 GTV-1F), subdivided into 4 individual layers Mn crust, 2 cm in diameter, dark-brownish, weak layering Granular Mn crust, up to 5 cm in diameter, rough surface, needles, irregular shape
M64/2	222 GTV	serpentinized peridotites and pyroxenites, partly Mn-coated, some atacamite	222 GTV-4B	FeMn-coated, serpentinized peridotites
M64/2	272 ROV	nonactive chimney north of Irina II	272 ROV-8	Fe oxide, piece of non-active Fe-oxide chimney
M60/3	78 GTV	Upper part of grab consists of abundant Mn oxides, rest is peridotitic rock	78 GTV-1 78 GTV-5A 78 GTV-Mn on Per.	Stratified Mn crust, subdivided into 6-9 individual layers Brown Fe-Mn coating on pyroxenite, mm Brown Fe-Mn coating on serpentinite, granular, no internal structure
M60/3	33 GTV	Massive Fe oxyhydroxides with abundant atacamite, semi-consolidated, overlying altered wallrock, abundant massive sulfides and sulfide-bearing mud	33 GTV-1	
	32 GTV 79 GTV	See above Pelagic sediment, semi-lithified pieces encrusted in Mn oxides, abundant red-brown to orange Fe-rich sediment	32 GTV-1	
	82 GTV	Are of T anomaly north of Logatchev-1, Fe-Mn oxide crusts of irregular shape		
MSM04/3	249 ROV		Mn on Per.	mm in diameter Mn crust on Peridotite

6.3 Results:

6.3.1 Macroscopic textures:

At different locations within the Logatchev I hydrothermal field, oxidic precipitates were recovered (Plate I). Five different types of Fe-Mn deposits can be distinguished:

- o **Group 1.** Black, slab-like crusts up to 3cm thick, with prominent internal layering,
- o **Group 2.** Porous, massive Mn crusts, up to 2 cm thick, dark-brownish, partly soft sediment on top, rarely weak layering indicated, irregular shape,
- o **Group 3.** Friable, brownish to black mm-thick coatings on peridotite,

- o **Group 4.** semi-consolidated, orange-colored Fe-Mn precipitates, dm thick, thin, black beds intercalated, massive and of irregular shape, often show internal structures like slumping folds and concentric forms, probably alteration products of massive sulfides, often containing green particles (atacamite, nontronite or smectite),
- o **Group 5.** Orange-colored, hollow Fe oxide tubes, recovered from ancient chimney structure.

Crust Morphology of stratified Mn crusts:

The pure manganese crust samples occur as flat slabs up to 3 cm thick and have a black color. They are composed of layers, which can be classified into three morphological types (Fig. 2):

1. Friable black layer or layers with a alternating acicular and grainy, porous texture, up to 1.5 cm thick, with detrital sand particles being dispersed at the surface,
2. Velvety, massive dense layers with fine, submillimetre laminations, black to grey, submetallic lustre; columnar growth structures are seen in some samples, surface is slightly undulating, layer is very water-rich and disintegrates into small bits upon drying,
3. Small, closely packed botryoids, ranging in size from submillimetre to 5 mm size; in places they are coalesced to form a layer of material similar to layer 2; detrital material between the botryoids.

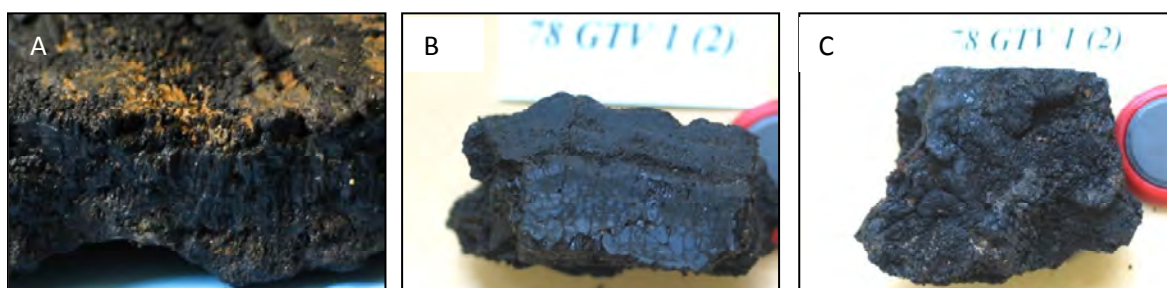


Figure 2: Stratified Mn crusts group I: A: from top to bottom: botryoids with dispersed sediment, dense, shiny black layer, granular/acicular layer, B: alternating massive and acicular, porous laminae in the upper half, grey, shiny layer in the lower part with transition to botryoidal layer, C: bottom side of B, with botryoids of different sizes

6.3.2 Microscopic textures

SEM-analyses were performed at USGS by Jim Hein. One stratified crust sample was broken into 3 layers (botryoidal layer, velvety black layer and a layer composed of alternating acicular and massive laminae as defined by macroscopic texture), carbon coated and imaged using backscatter and secondary electrons (Plate II). Semiquantitative chemical analyses were done using an energy dispersion X-ray analyser (EDX).

- 1) The botryoids of layer 1 are made up of individual layers. Outer casings surround several of these botryoids. At the bottom side (which is in contact with the velvety layer 2), nucleation centers can be seen. Elements measured are: Mn, Na, Cl, Si, K, Ca, Mg, C, Cu, Ni. Copper and Ni are variable between the individual layers of botryoids, and the Cu content increases from the lower part to the upper part of each layer that makes up botryoids. The highest Cu was measured in the outer casings. The underside of the botryoidal layer in contact to layer 2 shows nucleation centers.
- 2) The velvety layer, which was very water-rich, is highly fractured as the result of dewatering. A close-up shows small globules making up this layer.
- 3) This layer is composed of alternating acicular and massive laminae. Acicular layers show branching textures and partly hollow acicular tubes. Massive laminae are highly porous, and characterized by a mix of granular and botryoidal textures. Grains seem to concentrate around channel ways, whereas small botryoids formed in void space. The layer rarely contains ribbon-like forms, which are composed of carbon and oxygen (bacteria?).

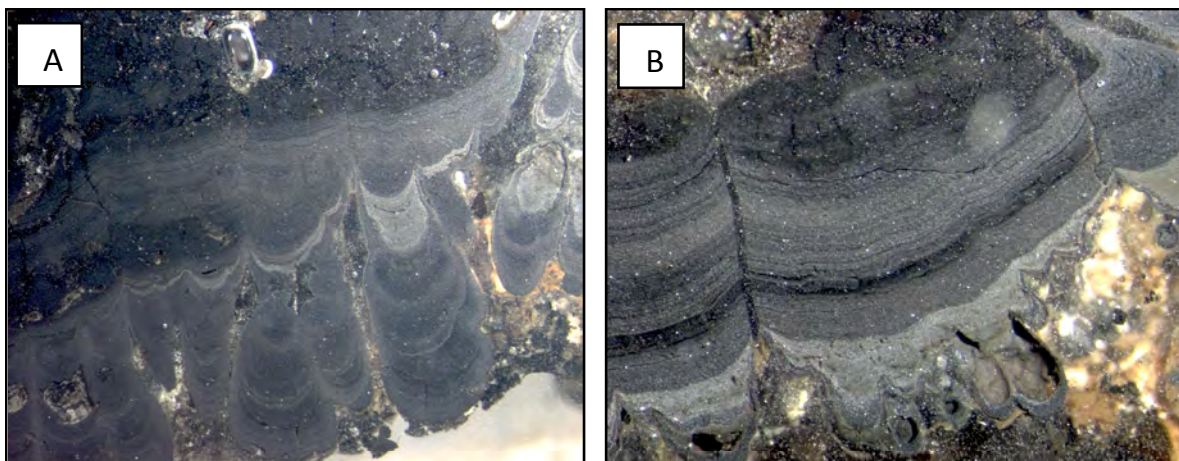


Figure 3: Microscopy images A: Botryoidal layer, columnar growth structures, in contact to massive, grainy layer, at the contact laminated zone, width of the pictures: 6mm (right) and 4 mm (left), B: close-up of laminated zone, note the different brightness of individual laminae, which indicate different crystallinity, columnar growth structures clearly indicate a direction of growth towards the bottom

The individual layers of single botryoids differ slightly in their brightness, resulting from differences in the mean atomic mass, and may indicate variable water contents (Hein et al., 2008).

Microscopic investigations with reflected light show columnar growth structures in the botryoidal layer with the individual botryoids composed of alternating laminae, indicating the direction of growth towards the bottom (Fig. 3). The different brightness of the single layers indicate differences in crystallinity along with a different water content (pers. comm. J. Hein) and probably correspond to the layering observed with SEM images. The velvety layer 2 displays narrow, submillimeter lamination of layers with different brightness. The individual

Plate I

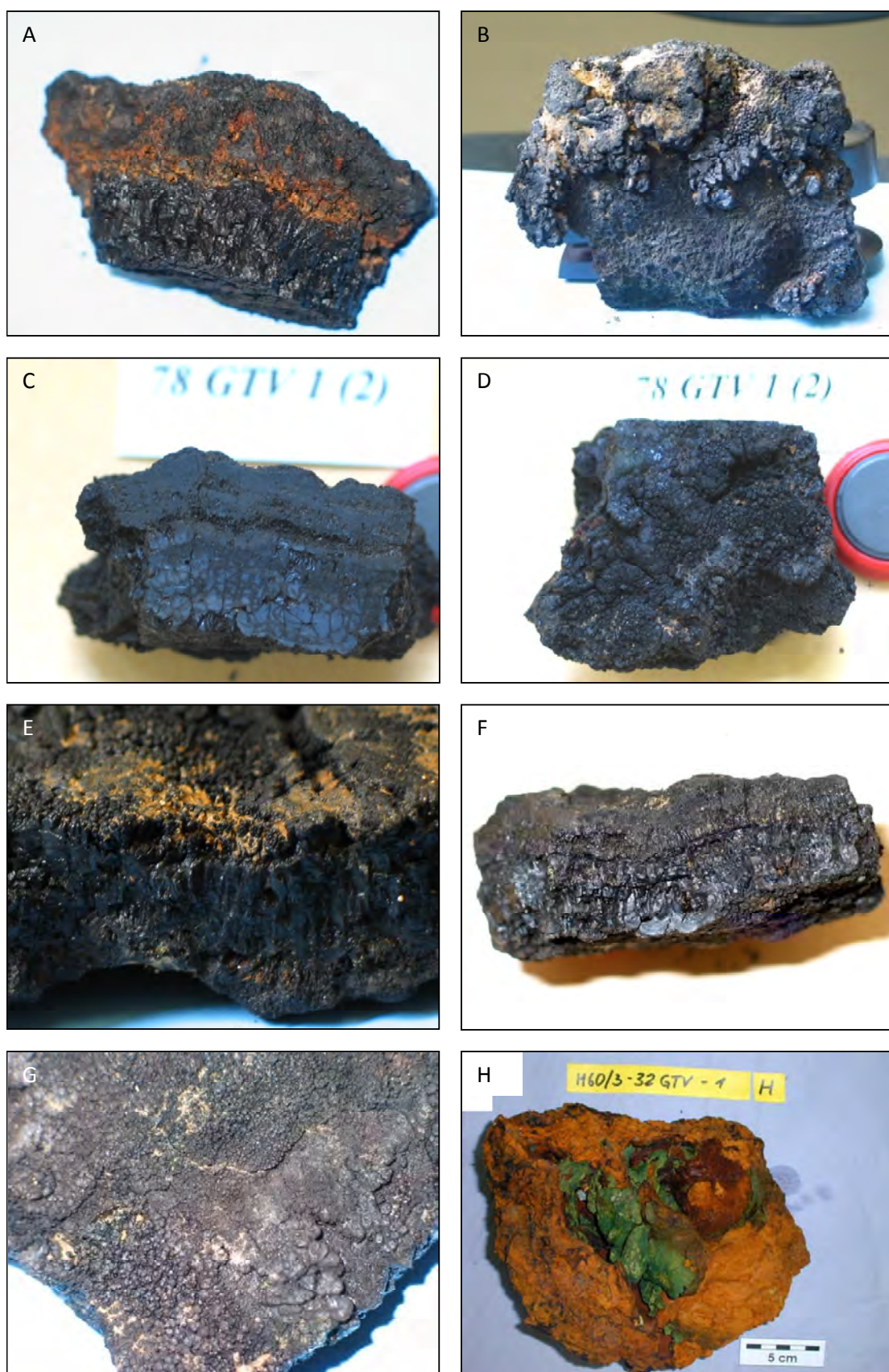




Plate I: Textures of different oxide deposits from the Logatchev I hydrothermal field, A: Stratified Mn crust with grainy layer 1 (upper part) and dense, velvety layer 2 (lower part), length about 5 cm, height: 3 cm, B: botryoidal layer 3, view from bottom, with intercalated pelagic sediment, in the lower half the botryoids are gone, C: cross section of stratified Mn crust, note the alternating acicular and massive laminae on the upper half of the crust (layer 1), width is about 6 cm, D: bottom view of C with differently-sized botryoids, E: stratified Mn crust, bottom is top, with grainy/acicular layer 1 in the lower part, followed by dense layer 2 and a sharp transition to botryoidal layer 3, F: cross section of stratified Mn crust, length of the crust is about 7 cm, G: close-up of the botryoidal layer, picture width: 3 cm, H: massive Fe-oxyhydroxides with atacamite mineralization, station 32 GTV-1, I: brownish Fe-Mn oxide coating on serpentinized peridotite, 78 GTV-5B, K: black Fe-Mn oxide coating on peridotite, 78 GTV, L+M: massive Fe-oxyhydroxide deposits 32 GTV, width of the picture: 13 cm

Plate II

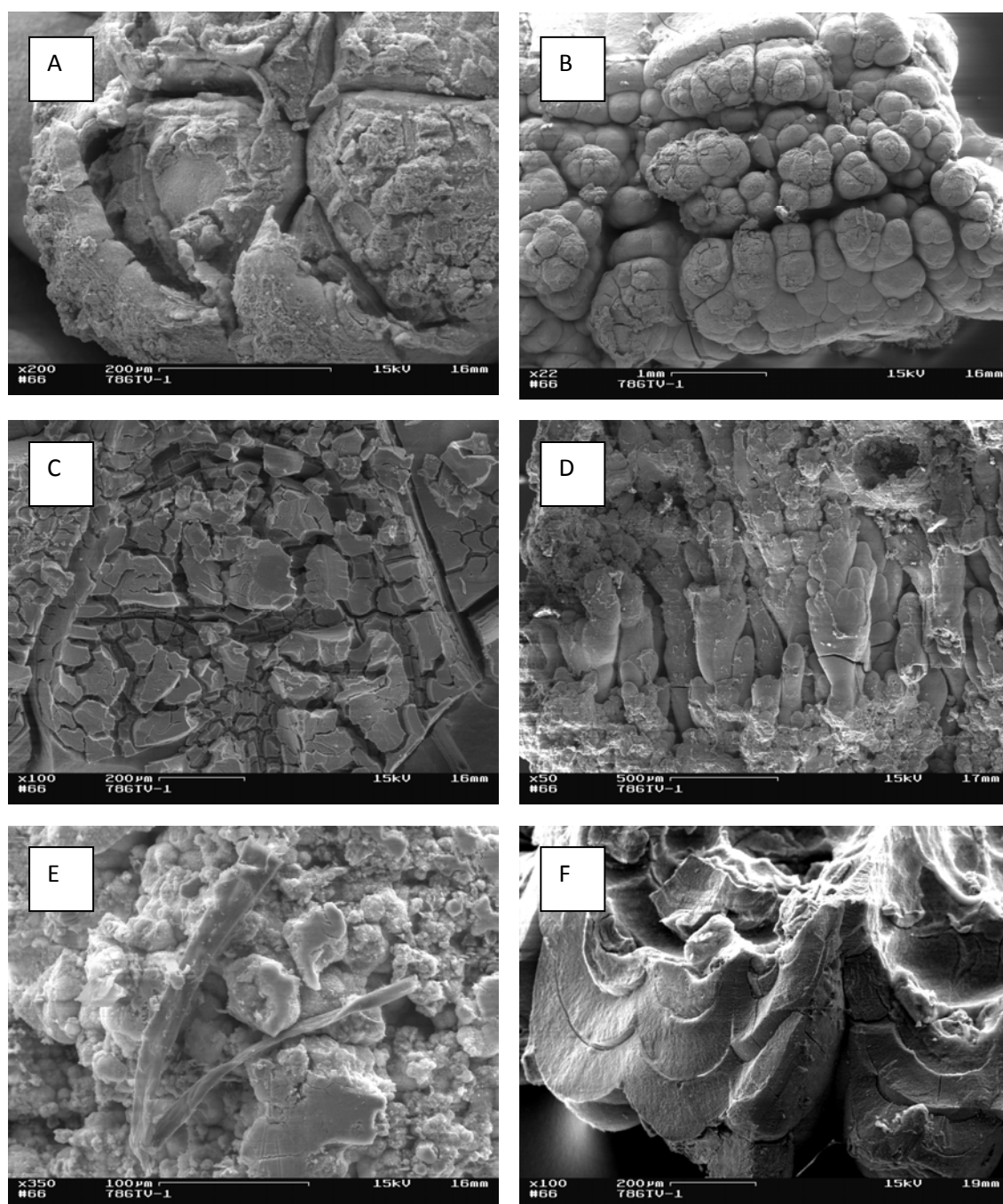


Plate 2: SEM images of stratified Mn crust group I **A:** broken botryoid, outer casing has the highest Cu contents. **B:** General view of botryoidal surface **C:** General view of velvety layer, highly fractured as the result of dewatering- desiccation. **D:** Close-up of branching acicular layer (top is at the top) **E:** Ribbon-like form (rare; bacteria?) composed of carbon and oxygen; in massive layer, small areas with enhanced Fe, together with Si, Al, O, K, Na, Mg – volcanic glass?, clay? **F:** Side-view (X-section) of botryoids showing layering. The Cu content of each layer is higher toward the surface than the base of each layer.

laminae probably represent layers of different crystallinity. The border of both sublayers is marked by a very bright mineralization zone.

6.3.3 Mineralogy

The mineralogy of the Fe-Mn and Mn-crusts was investigated using X-ray diffraction analyses. The 2 cm thick, pure manganese crusts were subdivided into layer 1 (78 GTV-10.L.; friable upper layer) and layer 2 (78 GTV-1; dense, botryoids and laminae) and analysed in wet as well as under air-dried conditions to ascertain structural stability during dehydration. Furthermore, thin, brown to black coatings on serpentinized peridotites (78 GTV-5A), granular, dark-brown crusts (225 GTV-3) and massive, orange to yellow-brown Fe oxides were investigated for mineralogy; the X-ray diffractograms are presented in Figures 4A-4D.

[1] The Mn crust consists mainly of pure Mn-oxides, only in layer 1 few other minerals like quartz, clay minerals and calcite occur. Measured under wet conditions, the Mn-oxide XRD patterns are similar to synthetic buserite with peaks at 10.1 / 5.0 / 2.47 / 1.42Å. After drying for 24 hours at 105°C, the lower, botryoidal/laminar layers of slab-like Mn crusts completely transformed to 7Å birnessite, with the typical reflections at 7.12 / 3.61 / 2.45 / (2.33) / 2.04 / 1.42Å and a major reflection at 1.78Å (Fig. 4A-4C). As the phyllomanganates 10Å buserite, 7Å birnessite and vernadite are structurally the same (Manceau et al., 2007), they are here called in the descriptive form 10Å manganate, 7Å manganate, and vernadite, to be consistent with recent work on hydrothermal Mn crusts (e.g., by Hein et al., 2008). The shift of the 10Å reflection to 7Å is caused by the removal of one water layer from a 2-water layer phyllomanganate resulting in a 1-water layer phyllomanganate, changing the interlayer d-spacing from 10Å to 7Å. Unstable 10Å manganate transforming to 7Å manganate is known to occur in marine ferromanganese crusts (Ostwald & Dubrawski, 1987), in marine Mn nodules in the Pacific and Atlantic oceans (Ito et al., 1998) and in hydrothermal Mn crusts (e.g., Hein et al., 2008).

[2] The upper, granular layer of the same Mn crust shows a similar transformation of 10Å manganate to 7Å manganate, but in contrast to the lower layer, a small fraction of the 10Å manganate remained stable after drying. The peak at 1.78Å, observed upon drying of layer 1, is not present. The stability of 10Å manganate upon drying has been reported from other hydrothermal Mn precipitates (e.g., Hein et al., 2008) and may result from stabilization of the mineral structure due to high concentrations of cations like Ni, Ca, Mg, Co (Giovanoli et al., 1975) or, as proposed by Mellin and Lei (1993) may reflect higher mineralization temperatures.

[3] The somewhat higher intensity of the peaks in the botryoidal/laminae Mn layer may reflect a higher crystallinity compared to the friable Mn layer. The crystallinity is reflected in peak height and peak width (broad low intensity to sharp high intensity) and generally

increases during transformation from 10Å to 7Å due to dehydration by loss of absorbed and structural water. In the Logatchev-1 Mn crusts, this is only evident from the lower part of the pure Mn crust, where the sharpness of the peaks slightly increases.

[4] The granular, dark-brown crusts of group II mainly consist of 10Å manganate, in some samples with minor amounts of calcite and clay minerals.

[5] The friable Fe-Mn coatings (78 GTV-5A) show identical XRD patterns as the pure Mn crusts, plus variable amounts of goethite, calcite and quartz. Upon drying, the 10Å mineral completely transformed to the 7Å mineral, including the peaks at 1.78Å and 2.04Å. The reduced noise relative to pure Mn crusts may be related to higher crystallinity. Although the Fe-Mn oxide precipitates contain between 5 and 20% Fe (see below), peaks typical of crystalline Fe minerals could not always be identified. It is assumed that in those samples, the Fe-phase is X-ray amorphous, which is also often described in natural hydrothermal Fe-oxyhydroxide precipitates (Thomson et al., 1985). Furthermore, marine Fe-bearing vernadite ($\delta\text{-MnO}_2$) cannot easily be identified in the presence of 10Å and 7Å marine Mn minerals as the peaks (1.4Å and 2.4Å) completely overlap. As the relative intensities do not differ between the different precipitates, the presence of vernadite in the coatings remains speculative.

[6] The relative intensities of the reflections in the Logatchev Mn crust are different compared to synthetic 7Å manganate and to 7Å manganate described in other hydrothermal environments: The peak at 2.04Å is the 100 intensity peak upon drying, positioned at a hump-like high in the diffractogram. Besides the atypical occurrence of the 2.04Å peak, an additional, prominent peak at 1.78Å appears in the lower part of the crust. As both the peak at 2.04Å and at 1.78Å only occur after the transformation of the 10Å manganate, both peaks have to be attributed to 7Å manganate. Both reflections were not previously reported from hydrothermal manganese deposits, but are known from land-based birnessite (J. Hein, pers. comm.) The major reflection at 2.04Å and variable reflections at 1.78Å only occur upon drying. Having these two peaks indicates that the Mn oxide has better crystallinity than many marine Mn oxide deposits. Peak positions, peak broadness and peak intensities are a function of crystallinity as well as crystallography. The characteristics of birnessite XRD patterns depend not only on the layer stacking but also on the presence of vacant layer sites, and on the type, location and local environment and the amount of sorbed cations (e.g., Lanson et al., 2002; Drits et al., 2007). As will be shown later, the Mn oxides found at the Logatchev-1 field are strongly enriched in trace metals like Cu, Ni, and Co in contrast to previously described hydrothermal Mn deposits, which may have an influence on the XRD pattern of the oxides upon drying. Although the exact reason is not clear, it can be assumed that the crystallography and crystallinity of the Logatchev-1 samples are appropriate for the 2.04Å and 1.78Å reflections to be the major intensity peaks.

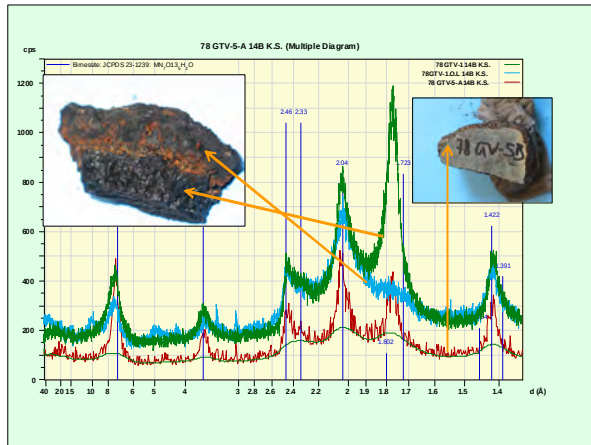


Figure 4A: X-ray reflection pattern of a massive Mn crust (78 GTV-1 upper, sandy layer and lower, botryoidal layer) and Fe-Mn cover a rock fragment (78 GTV-5A) from Logatchev I, measured after drying at 105°C, note the reflections at 2.04Å and 1.78Å in the Fe-Mn coating (78 GTV-5A) and in the lower, botryoidal layer of the Mn crust.

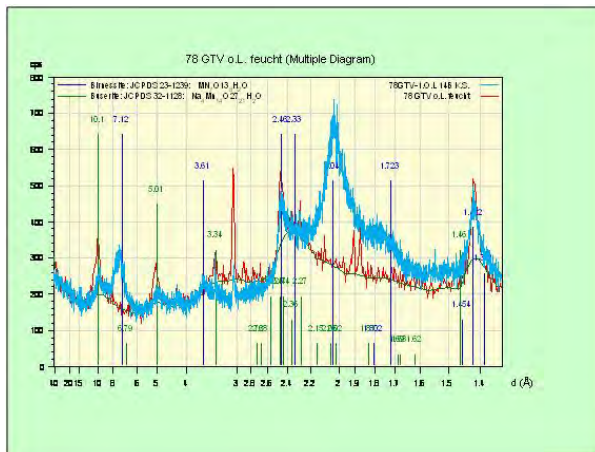


Figure 4B: X-ray reflection pattern of crust 78 GTV-1 (sandy layer), measured at wet conditions (red line) and dry conditions (blue line), showing the transformation of 10Å manganate to 7Å manganate and the additional presence of stable 10Å manganate, note the major reflection at 3.03Å (calcite) and 3.34Å (quartz).

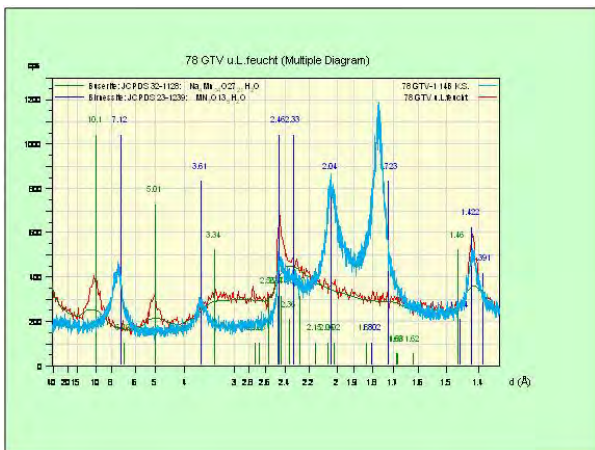


Figure 4C: X-ray reflection pattern of crust 78 GTV-1 (botryoidal layer and laminae), measured at wet conditions (red line) and dry conditions (blue line), showing the transformation of 10Å manganate to 7Å manganate, note the absence of any additional mineral peaks.

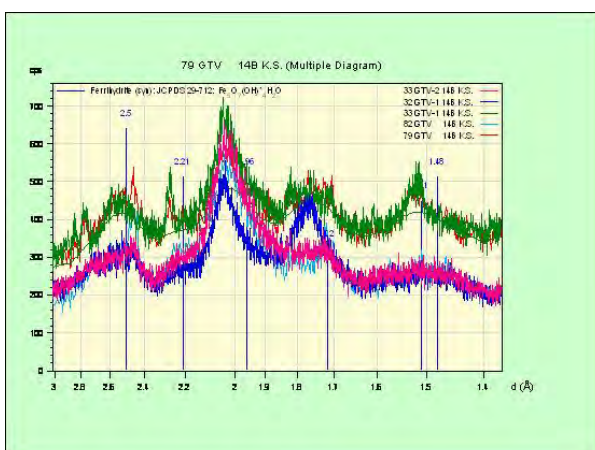


Figure 4D: X-ray reflection pattern of different orange, Fe-rich crusts, measured at dry conditions.

[7] The XRD pattern of Fe-rich crusts, which are characterized by high background noise, are characterized by a dominant broad peak at 2.04Å, partly accompanied by a peak at 1.78Å (Fig. 4D). This observation complicates the discussion of those peaks in dried, pure Mn crusts and needs further investigation. Other than that, the mineralogy the Fe oxyhydroxides consists of goethite. The pure Fe crust chimney consists of goethite with reflections at 4.18Å and 2.45Å.

6.3.4 Geochemistry

Based on texture and mineralogy the oxidic precipitates in the Logatchev area can be divided into five groups (see chapter 3.1). Here, the elemental composition and selected isotope signatures (Os, Nd, Hf) will be presented for *group I* (stratified, pure Mn crust), *group II* (massive, pure Mn crusts and pure Mn encrustations on rocks), and *group III* (porous Fe-Mn encrustations on hard rock substrate). *Group I* Mn crusts were further subdivided into individual layers to obtain geochemical profiles from bottom (botryoidal layer) to top (friable layer). Chemical data for *group IV* (massive, semi-consolidated, orange-colored Fe-Mn precipitates) and *group V* precipitates (orange-colored, hollow Fe oxide tubes) are provided and will briefly be presented at the end of this chapter. Concentration data for major, minor, and trace elements are given in Tables 2 and 3.

6.3.4.1 Major elements

Group I and group II samples are both composed of pure Mn oxide, with about 40% Mn and less than 1.5% Fe. Aluminium concentrations, which can be used as index for the presence of aluminosilicates, are generally below 1%; and the concentrations of Ca, Mg, K and Na sum to about 6%. Whereas Al does not correlate with Fe in stratified group I Mn oxides, Al and Fe co-vary in group II Mn oxides. The observation of small amounts of detrital material in the top layer of group I is in agreement with generally increasing Al concentrations towards the top over.

In contrast to the pure Mn oxides, the mm-thick brownish to black covers on serpentinite and pyroxenite (group III) show variable Fe/Mn ratios, with Fe concentrations between 6% and 25%. The Al content ranges between 1.7% and 2.5%, positively correlated with the total Fe concentration. Considerable Ca concentrations of up to 9.6% indicate a significant “dilution” of some of these precipitates with detritus (mainly carbonates). Silica concentrations could not be obtained from these precipitates. [

6.3.4.2 The rare earth element and yttrium (REY) distribution

To distinguish the REY distribution of the different groups, one can use specific normalized elemental ratios (e.g., Pr/Gd for cross-group fractionation) and single element anomalies, as

Ce/Ce* (Ce anomaly) and Eu/Eu* (Eu anomaly). The Ce anomaly is defined as $Ce_{PN}/2 \cdot Pr_{PN} - Nd_{PN}$; (Bolhar et al., 2004) where PN refers to PAAS (Anders and Grevesse, 1989)-normalized values. The Eu anomaly is quantified as $Eu_{PN}/(0.67Sm_{PN} + 0.33Tb_{PN})$; Bau and Dulski, 1996). All analyzed ferromanganese and pure Mn deposits from the Logatchev field show a depletion of the heavy REE relative to the middle REE, negative Y anomalies, and a depletion of the light REE, a pattern that is often referred to as hydrogenetic (Bau et al., 1996). Normalized to seawater, all types show a strong positive Ce anomaly, a negative La anomaly and a smooth decrease from the light to the heavy REE (Fig. 5).

A common feature of all of group I samples is the small, but significant Eu anomaly in PAAS-normalized plots ($Eu/Eu^* = 1.52-1.75$), the positive Ce anomaly, and the generally low total REE concentrations (Fig. 6). In contrast, massive Mn crusts of group II are characterized by neutral to negative Ce anomalies, which is accompanied by generally smaller Pr/Gd ratios (i.e., stronger depletion of light REE to the middle REE), but higher total REE concentrations relative to the stratified Mn crusts of group I (Fig. 7). Small positive Gd anomalies are also restricted to group II Mn oxides. Ferromanganese encrustations of group III are generally strongly enriched in total REE and characterized by neutral to positive Ce anomalies (Fig. 8). Both, concentration and size of the Ce anomaly vary systematically with Mn content: Mn-rich samples have much smaller Ce anomalies and have less REY relative to Fe-rich samples, similar to top layer group I. Group 2 samples display a very small positive Eu anomaly (1.31-1.62, for comparison: hydrogenetic ferromanganese crusts are characterized by $Eu/Eu^* = 1.20-1.23$), whereas the Fe-Mn-coatings of group I mainly do not display a Eu anomaly (1.19-1.34).

REE distribution profiles within the pure Mn crusts show systematic variations with depth: The absolute REY concentration generally increases from the bottom, botryoidal layer to the granular layer at the top, negatively correlating with the size of the Ce anomaly. This means, that the layer displaying the lowest REE content (layer 3, velvety layer) is characterized by the highest Ce anomaly. Furthermore, the Ce anomaly is coupled to the Pr/Gd ratio, with the least Pr/Gd fractionation in the layer with smallest Ce anomaly (topmost, granular layer). The three different crust profiles show a weak positive correlation of Ce anomaly and Eu anomaly, which may indicate that the REE distribution in these crusts resemble a primary layering reflecting variable compositions of the source water and/or different physico-chemical conditions during the formation of the crust.

The difference in the Ce anomaly between the groups is generally correlated with the relative depletion of LREE, with the lowest Pr/Gd ratios in granular group II Mn crusts, which are characterized by negative Ce anomalies. With respect to REE distribution, the top-layer of stratabound Mn deposits and the compact, granular Mn deposit of sample 225 GTV-3 (B1) are most closely related. However, both patterns can still be distinguished with respect to

Table 2: Major, minor and trace element composition of Fe-Mn oxide deposits Logatchev-1

Cruise-Nr.	Sample ID	Sample name	Ca	Mg	Na	Fe	Mn	Al	Cu	Co	Ni	Zn	Mo	Li	Pb	Zr	Th	U	V	Ti	P	Os	S	Ba	Cs	Sc	W	Mn/Fe	U/Th	Growth rate (Manheim & Lane- Bostwick, 1988)
			%	%	%	%	%	%	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppt	ppm	ppm	ppm	ppm	ppm			
Group I: stratified, pure Mn Crusts																														
M60/3	M01	78 GTV-1 (1) bottom layer	1.84	1.93	2.95	1.43	41.9		1.46	3470	817	173	1910	1140	8.53	13.6	1.07	0.877	409			240		334	0.382			29.3	0.82	3.1
	M02	78 GTV-1 (2)	1.86	1.77	2.95	1.37	39.4	0.378	1.65	3450	457	142	1890	863	6.32	8.16	0.553	0.66	394	205	0.276			307	0.216			28.7	1.19	2.9
	M03	78 GTV-1 (3)	2.06	1.74	3.28	1.32	40.5	0.122	2.17	3310	326	65.1	1670	609	5.62	3.82	0.106	0.631	527	50	0.0921			299	0.042			30.6	5.96	3.2
	M04	78 GTV-1 (4)	1.76	2.13	2.81	0.899	41	0.449	1.39	2340	1550	129	1970	881	5.05	9.54	0.545	0.591	451	229	0.499	407		318	0.205			45.6	1.08	5.7
	M05	78 GTV-1 (5)	1.54	2.33	2.78	1.31	39	0.975	1.19	1730	3140	445	1890	1100	7.51	17.1	1.07	0.663	393	414	0.744			286	0.439			29.7	0.62	8.9
	M06	78 GTV-1 (6)	1.52	2.3	2.67	1.22	38.9	0.935	1.25	1810	2730	671	2560	1150	7.33	16.3	1.09	0.664	336	439	0.765			277	0.425			31.9	0.61	8.2
	M07	78 GTV-1 (7) upper layer	1.76	2.06	2.98	1.19	39	1.01	2.08	1680	3830	1380	3030	993	12	18.4	1.3	0.855	328	523		175		274	0.423			32.7	0.66	9.3
M60/3	M32	78 GTV-1 (1) bottom layer	1.61	1.77	2.75	1.23	39	0.679	1.15	2850	932	130	1680	1250	8.23	17.7	1.15	0.805	308	401				355	0.447			31.6	0.70	3.9
	M33	78 GTV-1 (2)	1.62	1.75	2.82	1.75	38	0.796	1.26	3160	975	108		1180	9.07	20	1.29	0.798	355	457				362	0.518			21.7	0.62	3.2
	M34	78 GTV-1 (3)	1.83	1.75	3.3	1.35	39.1	0.366	1.71	3260	1040				6.58	8.54	0.532	0.645						303	0.201			29.0	1.21	3.1
	M35	78 GTV-1 (4)	1.74	1.81	3.3	1.39	39.1	0.582	1.56	3110	1940				7.3	12.3	0.86	0.682						291	0.337			28.1	0.79	3.4
	M36	78 GTV-1 (5)	1.7	2	2.94	1.09	39.3	0.546	1.38	2830	1430	108		1040	5.96	14.2	0.731	0.622	373	254				320	0.299			36.2	0.85	3.9
	M37	78 GTV-1 (6)	1.61	2	2.83	0.73	38.9	0.494	1.11	2320	1520				5.93	10	0.642	0.656						333	0.252			53.3	1.02	5.3
	M38	78 GTV-1 (7)	1.43	2.37	2.4	0.727	39.5	0.739	0.895	1950	2340	349	1720	1160	5.85	15.4	0.871	0.641	301	335				357	0.34			54.3	0.74	7.3
	M39	78 GTV-1 (8)	1.4	2.19	2.6	0.871	37.1	0.946	1.18	1860	3760	682		1120	6.75	18.2	1.1	0.683	271	377				293	0.427			42.6	0.62	7.1
	M40	78 GTV-1 (9) upper layer	1.61	2.13	2.77	0.949	36.8	1.15	1.92	1590	4490	1240	2010	965	10.9	22.1	1.33	0.904	275	501				282	0.471			38.7	0.68	9.2
	M60/3		78 GTV-1 (1) bottom layer	1.74	1.78	3.84	0.657	44	0.358	1.58	2060	2610	203	1900	1280		6.3	0.526	0.546	439	181	295			289	0.258	0.319	19.1	67.0	1.04
		78 GTV-1 (2)	1.72	1.84	3.78	0.916	44.2	0.465	1.49	2570	2200	173	1720	1270		8.18	0.769	0.54	454	257	298			306	0.303	0.658	17.2	48.2	0.70	5.5
		78 GTV-1 (3)	1.72	1.84	3.69	0.664	45	0.285	1.34	2620	1200	128	1800	1320		5.13	0.462	0.52	448	152	323			323	0.181	0.138	17	67.8	1.12	5.5
		78 GTV-1 (4)	1.72	2.09	3.5	1.53	42.7	0.661	1.28	2920	1210	141	1670	1090		11.3	1.06	0.848	489	369	398			360	0.421	1.15	14.7	28.0	0.80	4.3
		78 GTV-1 (5)	2.06	2.5	3.22	1.52	42	0.963	1.11	2220	891	138	1700	974		11	0.731	0.708	484	321	404			353	0.305	2.56	19.4	27.7	0.97	6.7
		78 GTV-1 (6) upper layer	1.8	2.27	3.38	1.45	42	1.1	1.66	1910	2480	844	2190	1130		18.2	1.32	0.876	438	499	493			321	0.505	1.72	18.9	29.0	0.66	8.6
Group II: massive, granular Mn Crusts + 1cm thick Mn coating																														
M64/2	M01	225 GTV-3 (B1) porous	2.92	2.22	2.24	1.5	37.4	0.613	0.49	67	1530	807	2920	1200	32	21	2.4	0.8	203		142			591	0.282	1.64	7.59	24.9	0.33	1909
	M02	225 GTV-3 (B1) bottom	1.98	2.36	2.48	2.01	37	0.709	1.29	147	2710	1700	2310	893	38	29	2.8	1.2	245		372			636	0.255	1.8	12.1	18.4	0.43	517
	M05	225 GTV-3 (D2) cavity	1.99	2.62	2.65	1.73	37.5	0.864	0.37	57	3870	1380	2730	1390	26	24	2	0.7	381		163			424	0.253			21.7	0.35	2537
	M06	225 GTV-3 (D2) bottom	1.53	2.44	2.69	0.47	40	0.432	0.42		3220	1830	1400	835	10	10	0.9	0.2	328		13			589	0.169			85.1	0.22	
	M08	225 GTV-1-F	1.72	2.62	2.08	0.16	42.6	0.174	0.11	20	2180	484	4120	1140	3.16	3.49	0.25	0.17	303				729	0.0673			266.0	0.68		
	M33	225 GTV-1-F1(1)	1.84	2.38	3.21	0.721	41.9	0.396	0.294	43	4140	1440	2830	1350	14	12.6	0.882	0.442	798		240			512	0.155			58.2	0.50	4673
	M34	225 GTV-1-F1(2)	1.61	2.23	2.91	0.496	41.3	0.331	0.225	28	3470	996	2950	1470	10.5	8.95	0.725	0.383	701		161			474	0.159			83.2	0.53	9232
	M26	225 GTV-1-F1(3)	1.51	2.44	2.95	0.316	43.3		0.184	20	2810	755	2760	1570	3.49	7.49	0.472	0.321	665				483	0.143			137.0	0.68		
M28	225 GTV-1-F1(4)	1.5	2.68	2.67	0.68	43	0.358	0.318	44	2320	887	2450	1410	10.2	9.96	0.688	0.449	646		166			455	0.14			63.3	0.65	4685	

Table 2, continued

Cruise-Nr.	Sample ID	Sample name	Ca	Mg	Na	Fe	Mn	Al	Cu	Co	Ni	Zn	Mo	Li	Pb	Zr	Th	U	V	Ti	P	Os	S	Ba	Cs	Sc	W	Mn/Fe	U/Th	Growth rate (Manheim & Lane- Bostwick, 1988)	
			%	%	%	%	%	%	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppt	ppm	ppm	ppm	ppm	ppm				
Group III: Fe-Mn coatings on serpentinite																															
M60/3	M08	78 GTV-5A	7.04	1.46	1.01	24.8	11.3	1.67	1.13	1560	575	655	230	9	318	345	35.4	10.3	1180	5030				973	0.297			0.5	0.29	8.8	
	M09	78 GTV Mn on Per.	7.83	1.43	0.62	20	9.2	2.09	0.23	1430	580	430	203	9.7	342	370	32.9	8.37	980	4870				823	0.799			0.5	0.25	7.1	
	M18	78 GTV-5A	2.17	1.9	1.94	9.1	32.1	0.726	0.56	2150	2790	492	2220	912	138	173	14.7	4.3	773	1850		796		542	0.199		3.5	0.29	6.4		
	M19	78 GTV Mn on Per.	8.36	2.45	0.54	16.8	7.21	2.54	0.31	1320	764	354	153	20	330	317	27.3	6.86	784	4320		1530		598	0.82	16.5	27.9	0.4	0.25	5.9	
	M26	78 GTV-5A	1.61	1.99	2.2	6	34.4		0.65	2190	2070	200	1670	941	73	100	8	3.7	484					652	0.497			5.7	0.46	6.0	
	M27	78 GTV Mn on Per.				21	10		0.5		700	500			57	330	370	30	7	1000					683	0.88			0.5	0.23	
M64/2		78 GTV_5A	6.68	1.45	1.24	24.9	11.7		1.17	1550	593	728	133			307	34.5	11.7	1110	4520				1020	0.311	9.39	29.9	0.5	0.34	9.1	
	M30	225 GTV-1-F1	6	2.23	0.0014	22	0.0095		0.0838	1510	4170	469	131	25	284	259	23	7.59	1020		5540			787	0.291	12	19.8		0.33	4.1	
	M07	239 GTV-5A	2.91	2.07	2.68	12.5	15.5		7.42	1840	1170	1680	94	8	66	33.1		4.27	245									1.2		4.4	
	M09	230 GTV-1 (D3)	6.47	1.42	1.62	20.5	6.11		0.38	1290	58	408	164	17	644	278	12.3	5.9	796					614	0.546			0.3	0.48	7.2	
	M29	222 GTV-4B	3.59	2.49	1.71	25.5	8.18		0.05	1120	274	530	100		243	228	16.5	7.99	1230		6660			741	0.172	17.5	18.5	0.3	0.48	13.6	
	M37	230 GTV-1F	6.44	1.39	1.7	23.3	6.87	1.72	0.32	1420	246	500	96		254	254	13.4	6.57	1040		5770			671	0.462			0.3	0.49	7.6	
		230 GTV_1_D3	9.78	1.59	1.61	23.3	6.66		0.41	1450	164	459	56.3			292	12.9	6.85	1060					739	0.662	10.1	19.6	0.3	0.53	7.3	
	230 GTV_1_F	9.59	1.48	1.64	23.9	6.91		3.37	1430	205	494	63.8			260	12.3	6.26	1060					665	0.462	8.25	20.4	0.3	0.51	7.8		
MSM04/3	10	Mn on Per.	3.79	2.36	1.73	24.8	10.5	2.09	0.41	2770	495	600	155		628	341	28.3	8.13		4990	6260			803	0.548	15	29	0.4	0.29	3.2	
Group V: Fe crust chimney																															
M64/2	M03	272 GTV	0.51	0.44	0.73	42.9	0.15		0.15	27		1390			237	1.76	0.08	22.6	174		4400										
	M04	272 GTV	0.55	0.41	0.76	45.6	0.16		0.18	175		930	142	6	491	11.6	0.11	25.2	447		6130										
Group IV: Semi-consolidated, massive Fe-Mn deposits																															
M60/3	M10	79 GTV Mn cov.	2.33	3.52	1.12	20.3	1.23		0.606	745	57.5	480		15.9	225	114	4.06	2.55	507												
	M11	79 GTV unt. MnLage	1.95	2.28	1.44	13.6	15.8		8.19	386	1950	562	111	11.1	196	72.2	1.44	9.39	789												
	M12	79 GTV bulk	1.23	2.63	1.03	29.7	1.11		2.25	21	127	550		10.7	157	18.1	0.421	4.96	1030			881									
	M13	82 GTV bulk	1.21	1.27	1.3	36.4	7.45		0.112	164	877	406		92	30	122	3.2	5.9	1330			189									
	M14	32 GTV u.L.	0.48	0.85	1.28	27.6	8		0.107	22.5		119	211	2.4	10	4	0.15	0.2	102		3590		0.109								
	M15	32 GTV o.L.	1.44	1.18	1.89	26.8	12.8		0.88	162	307	681							743												
	M16/2	32 GTV-1 bulk				36	2		0.6	300	26	600		4.6	144	200	3.3	5.9	1500												
		M17	32 GTV-Mn				31	10		0.9	230	280	780		52	17.8	21	0.9	2.6	780											
		M20	82 GTV	1.05	0.87	0.89	40.4	3.21		0.0704	55.1	308	176	115	16					711											
		M21	32 GTV-1	1.08	0.99	1.38	39.5	1.77		0.135	77.9	99.6	149		16	6	18	0.4	4.3	553											
		M22	33 GTV-1	0.41	0.57	1.17	27.6	0.68		4.53	59.2		1470		4					780		3630		0.097							
		M23	33 GTV-2	0.89	0.93	1.22	38.6	1.09		0.0874	54.5	82.4	192							752											
		M24	79 GTV	1.16	2.2	0.93	27.8	2.15		4.91	119	141	592		6					887		4340		0.176							
		M28	32 GTV (R)				38	2		0.09		50	200		0.5	4.5	3.8	0.1	0.4	320											
		M29	79 GTV-Mn-1	2.59	3.02	1.42	13.2	9.94		4.67	352	1580	606		11	200	80	1.4	5.6	696											
M30		79 GTV Fe-1	1.55	2.82	1.16	22	2.14		2.48	58.3	318	518		8	250	37	0.6	4.7	1020												
M31		79 GTV-Mn-2	1.54	3.05	1.12	25.8	1.25		1.81	16	156	596		13	180		18	0.3	4	910											
		82 GTV_bulk	1.12	0.981	1.24	45.4	3.67		0.1	7.5	365	239	144				35.8	0.896	7.15	725											
		32 GTV_1	2.01	1.49	1.34	40.8	1.51		0.66	358	41.3	744	22.5				180	3.08	6.17	1570											

Table 3: Trace element composition of Fe-Mn oxide deposits Logatchev-1

	Group I Mn oxides																							
	78 GTV-1	78 GTV-1	78 GTV-1	78 GTV-1	78 GTV-1	78 GTV-1	78 GTV-1	78 GTV-1	78 GTV-1	78 GTV-1	78 GTV-1	78 GTV-1	78 GTV-1	78 GTV-1	78 GTV-1	78 GTV-1	78 GTV-1	78 GTV-1	78 GTV-1	78 GTV-1	78 GTV-1	78 GTV-1	78 GTV-1	
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(1)	(2)	(3)	(4)	(5)	(6)		
	M01	M02	M03	M04	M05	M06	M07	M32	M33	M34	M35	M36	M37	M38	M39	M40								
Rb	8.87	6.07	3.02	6.67	9.70	9.74	9.16	9.55	9.74	5.44	7.14	7.26	6.95	9.71	9.17	9.55								
Sr	509	554	622	533	440	438	491	395	391	422	394	413	388	363	338	364								
Y	8.11	6.94	6.01	7.57	10.7	10.1	11.7	8.14	8.73	6.52	8.06	7.59	7.36	9.17	9.97	11.8	7.37	8.62	6.87	9.30	7.72	9.78		
Zr	13.6	8.16	3.82	9.54	17.1	16.3	18.4	17.7	20.0	8.54	12.3	14.2	10.0	15.4	18.2	22.1	6.30	8.18	5.13	11.3	11.0	18.2		
Cs	0.38	0.22	0.04	0.21	0.44	0.43	0.42	0.45	0.52	0.20	0.34	0.30	0.25	0.34	0.43	0.47								
Ba	334	307	299	318	286	277	274	355	362	303	291	320	333	357	293	282								
La	9.44	7.15	4.89	7.42	10.9	10.2	12.2	9.35	9.65	6.26	8.16	7.90	7.32	9.64	10.2	12.4	6.78	7.43	6.24	8.87	7.20	9.61		
Ce	38.1	34.5	36.5	31.2	29.4	29.5	33.4	32.7	35.2	33.4	34.6	33.6	29.6	27.1	27.7	28.7	24.4	25.9	24.2	39.2	32.6	35.5		
Pr	2.78	2.24	1.76	2.17	2.85	2.65	3.28	2.74	2.74	2.02	2.41	2.36	2.18	2.61	2.71	3.23	2.08	2.24	1.95	2.52	2.23	2.67		
Nd	11.6	9.56	8.28	9.57	12.5	11.5	13.9	11.5	11.5	9.01	10.4	10.3	9.55	11.2	11.9	14.0	9.28	9.81	8.68	11.2	9.71	11.5		
Sm	2.46	2.09	1.74	2.03	2.54	2.47	3.13	2.48	2.48	1.90	2.21	2.16	2.01	2.27	2.46	3.00	1.98	2.03	1.79	2.30	2.02	2.38		
Eu	0.74	0.65	0.58	0.62	0.76	0.77	0.95	0.77	0.78	0.60	0.68	0.70	0.62	0.75	0.79	0.93	0.62	0.65	0.58	0.73	0.64	0.74		
Gd	2.41	1.98	1.60	1.91	2.62	2.50	3.10	2.38	2.33	1.74	2.09	1.99	1.90	2.32	2.56	3.16	1.95	2.07	1.80	2.28	1.92	2.37		
Tb	0.34	0.27	0.22	0.27	0.37	0.36	0.46	0.36	0.35	0.25	0.30	0.28	0.27	0.34	0.37	0.45	0.29	0.29	0.27	0.32	0.28	0.34		
Dy	2.00	1.61	1.25	1.61	2.22	2.12	2.69	1.99	1.94	1.38	1.64	1.60	1.52	1.89	2.08	2.56	1.65	1.71	1.51	1.82	1.59	2.01		
Ho	0.41	0.30	0.24	0.31	0.45	0.42	0.54	0.40	0.40	0.28	0.35	0.33	0.32	0.41	0.45	0.55	0.32	0.34	0.30	0.36	0.32	0.40		
Er	1.05	0.82	0.67	0.97	1.22	1.16	1.43	1.11	1.08	0.79	0.97	0.91	0.90	1.13	1.24	1.51	0.89	0.94	0.84	1.02	0.84	1.09		
Tm	0.14	0.11	0.09	0.11	0.16	0.17	0.19	0.15	0.15	0.10	0.12	0.12	0.11	0.15	0.17	0.20	0.11	0.12	0.10	0.12	0.10	0.14		
Yb	0.87	0.64	0.50	0.68	1.04	0.98	1.21	0.90	0.88	0.60	0.74	0.72	0.67	0.89	0.99	1.21	0.67	0.74	0.66	0.78	0.66	0.89		
Lu	0.12	0.09	0.07	0.10	0.15	0.14	0.18	0.14	0.14	0.08	0.11	0.11	0.10	0.14	0.16	0.19	0.10	0.10	0.09	0.11	0.10	0.13		
Hf	0.29	0.14	< 0.05	0.18	0.34	0.36	0.41	0.24	0.39	<0.25	0.29	0.20	<0.25	0.24	0.31	0.43	0.12	0.17	0.11	0.25	0.21	0.36		
Pb	8.53	6.32	5.62	5.05	7.51	7.33	12.0	8.23	9.07	6.58	7.30	5.96	5.93	5.85	6.75	10.9								
Th	1.07	0.55	0.11	0.54	1.07	1.09	1.30	1.15	1.29	0.53	0.86	0.73	0.64	0.87	1.10	1.33	0.53	0.77	0.46	1.06	0.73	1.32		
U	0.88	0.66	0.63	0.59	0.66	0.66	0.85	0.81	0.80	0.65	0.68	0.62	0.66	0.64	0.68	0.90	0.55	0.54	0.52	0.85	0.71	0.88		
Nb	1.53	0.80	0.14	0.80	1.66	1.80	2.38	1.48	1.93	0.63			0.85			2.03	0.81	1.09	0.66	1.55	1.03	2.11		
Ta	0.064			0.033	0.063	0.062	0.071	0.078	0.109	0.035			0.046			0.093	0.046	0.059	0.041	0.085	0.057	0.116		
Zr/Hf	47	57		53	51	46	45	73	52		43	70		63	58	52	50	47	49	45	52	50		
Nb/Ta	24			24	26	29	33	19	18	18			18			22	18	18	16	18	18	18		
Ce/Ce*	1.66	1.92	2.99	1.86	1.33	1.41	1.25	1.47	1.57	2.19	1.82	1.82	1.75	1.30	1.33	1.13	1.56	1.48	1.63	2.04	1.88	1.69		
Eu/Eu*	0.61	0.60	0.58	0.60	0.58	0.56	0.56	0.61	0.62	0.61	0.61	0.63	0.61	0.59	0.56	0.54	0.56	0.57	0.57	0.58	0.61	0.59		
Pr/Gd	1.54	1.63	1.75	1.60	1.52	1.56	1.54	1.57	1.60	1.66	1.60	1.70	1.61	1.65	1.60	1.55	1.58	1.63	1.61	1.64	1.65	1.58		
Y/Ho	19.7	22.8	24.7	24.5	23.9	23.9	21.5	20.2	21.7	23.1	22.9	23.1	22.9	22.6	22.1	21.5	23.2	25.4	22.7	26.1	24.5	24.4		
REY	80.5	69.0	64.4	66.5	77.8	74.9	88.3	75.2	78.3	65.0	72.9	70.6	64.5	69.9	73.7	83.9	58.5	63.0	55.8	80.9	67.9	79.6		

Table 3 continued

	Group II Mn oxides								
	225 GTV-3 (B1)	225 GTV-3 (B1)	225 GTV-3 (D2)	225 GTV-3 (D2)	225 GTV-1F- 1	225 GTV-1F- 1 (1)	225 GTV-1F- 1 (2)	225 GTV-1F- 1 (3)	225 GTV-1F- 1 (4)
	M64-2 M01	M64-2 M02	M64-2 M05	M64-2 M06	M64-2 M08	M64-2 M33	M64-2 M34	M64-2 M26	M64-2 M28
Rb	8.82	8.50	7.60	7.31	6.44	6.25	6.36	6.28	6.74
Sr	561	552	527	465	489	560	506	465	457
Y	22.1	24.7	25.1	13.0	17.0	21.3	18.7	16.4	14.9
Zr	21.5	29.0	23.8	9.30	3.49	12.5	8.95	7.43	9.89
Cs	0.28	0.25	0.25	0.17	0.07	0.16	0.16	0.14	0.14
Ba	591	636	424	589	729	512	474	483	455
La	19.5	24.9	27.9	10.9	7.58	22.3	18.7	16.0	14.9
Ce	43.6	51.2	36.8	11.8	3.65	17.5	13.1	9.18	15.8
Pr	5.48	6.12	8.18	2.94	2.22	6.92	6.13	5.50	5.32
Nd	24.5	27.2	35.9	14.4	12.0	32.0	28.1	25.2	24.0
Sm	5.80	6.23	7.94	3.57	3.08	7.10	6.33	5.81	5.72
Eu	1.70	1.80	2.15	1.17	1.13	1.92	1.73	1.56	1.53
Gd	6.66	7.54	9.03	5.11	4.90	8.39	7.63	6.87	6.19
Tb	0.95	1.06	1.29	0.66	0.64	1.11	1.02	0.94	0.89
Dy	5.47	5.93	7.16	3.67	3.64	6.45	6.04	5.51	5.30
Ho	1.13	1.23	1.42	0.76	0.80	1.24	1.14	1.04	1.00
Er	2.99	3.24	3.69	1.97	2.04	3.29	3.04	2.82	2.70
Tm	0.39	0.42	0.47	0.24	0.24	0.42	0.40	0.36	0.37
Yb	2.29	2.53	2.87	1.46	1.36	2.47	2.31	2.18	2.18
Lu	0.33	0.38	0.42	0.22	0.21	0.35	0.33	0.30	0.30
Hf	0.44	0.57	0.54	<0.3	<0.3	0.26	0.16	0.20	0.22
Pb	32.3	37.7	26.2	10.7	3.16	13.9	10.5	3.47	10.1
Th	2.44	2.80	1.99	0.90	0.25	0.87	0.72	0.47	0.68
U	0.79	1.21	0.72	0.43	0.17	0.44	0.38	0.32	0.45
Nb	2.92	4.14	3.44	1.56	3.41	1.92	1.21	0.93	1.67
Ta		0.07	0.07	0.05	0.01	0.04	0.01	0.02	0.04
Zr/Hf	49	50	44			48	57	36	45
Nb/Ta		61	53	31	244	44	110	39	42
Ce/Ce*	1.05	1.10	0.58	0.62	0.31	0.35	0.29	0.23	0.40
Eu/Eu*	0.43	0.43	0.48	0.30	0.24	0.44	0.42	0.42	0.45
Pr/Gd	1.42	1.38	1.32	1.52	1.62	1.34	1.34	1.31	1.32
Y/Ho	19.7	20.0	17.7	17.2	21.3	17.1	16.4	15.8	14.9
REY	142.9	164.4	170.4	71.9	60.5	132.7	114.6	99.6	101.0

Table 3 continued

Group III Fe-Mn oxides											
	78 GTV-5A	78 GTV Mn on Per.	78 GTV-5A	78 GTV Mn on Per.	78 GTV-5A	78 GTV Mn on Per.	MSM_04_ 3_10	230 GTV-1 (D3)	222 GTV-4B	230 GTV-1F	225 GTV- 1F
	M60/3 M08	M60/3 M09	M60/3 M18	M60/3 M19	M60/3 M26	M60/3 M27		M64/2 M09	M64/2 M29	M64/2 M37	M64/2 M30
Rb	4.71	11.8	6.43	13.9	11.4	13.2	8.80	10.2	3.27	7.86	5.20
Sr	1132	1051	667	116	492	930	1045	1195	1111	1230	1188
Y	158	162	76.6	125	42.3	138	177	128	158	121	147
Zr	374	401	173	318	99.8	357	341	278	228	254	259
Cs	0.30	0.80	0.20	0.82	0.50	0.88	0.55	0.55	0.17	0.46	0.29
Ba	973	823	542	598	652	683	803	614	741	671	787
La	325	278	120	197	76.0	247	245	229	229	170	199
Ce	954	862	302	714	186	747	771	411	403	320	807
Pr	74.9	67.2	30.6	47.6	20.2	54.8	57.7	34.9	51.8	38.3	46.1
Nd	297	270	126	193	81.5	219	239	142	213	158	189
Sm	64.2	57.7	26.3	40.5	17.3	46.4	49.8	29.6	45.2	33.7	41.0
Eu	15.1	13.7	6.41	10.0	4.24	11.3	13.4	8.34	11.0	8.98	9.83
Gd	62.1	57.3	31.8	49.7	17.1	45.7	50.7	30.7	48.4	35.4	42.2
Tb	8.96	8.35	3.70	5.69	2.48	6.83	7.61	4.75	7.15	5.15	6.37
Dy	47.5	45.2	21.8	33.8	13.2	36.6	43.3	27.3	43.0	31.1	38.1
Ho	8.92	8.71	4.12	6.52	2.49	7.12	8.26	5.59	8.19	5.97	7.31
Er	23.3	23.1	10.9	17.6	6.63	19.1	22.5	15.3	22.8	16.9	20.2
Tm	3.14	3.13	1.47	2.38	0.87	2.58	2.89	2.06	3.05	2.32	2.75
Yb	18.9	19.2	8.96	14.5	5.38	15.8	18.6	12.8	18.6	14.1	16.8
Lu	2.83	2.91	1.33	2.17	0.82	2.31	2.87	1.88	2.65	2.00	2.40
Hf	10.1	9.75	3.80	7.68	2.00	8.02	7.13	5.89	6.32	7.23	7.24
Pb	309	326	139	330	72.9	329	628	644	243	254	284
Th	35.0	32.6	14.7	27.3	8.58	29.9	28.3	12.3	16.5	13.4	23.0
U	9.65	7.93	4.27	6.87	2.70	7.40	8.13	5.90	7.99	6.57	7.59
Nb	64.4	60.3	-	-	12.8	-	52.1	37.9	53	34.7	57.5
Ta	0.43	0.55	-	-	0.183	-	0.52	0.37	0.39	0.31	0.39
Zr/Hf	37	41	45	41	50	44	40	47	36	35	36
Nb/Ta	150	109			70		100	102	136	112	147
Ce/Ce*	1.46	1.49	1.18	1.77	1.08	1.58	1.61	1.38	0.93	1.00	2.08
Eu/Eu*	0.64	0.62	0.51	0.51	0.62	0.63	0.60	0.60	0.56	0.57	0.58
Pr/Gd	1.21	1.20	1.25	1.27	1.25	1.23	1.34	1.38	1.20	1.33	1.19
Y/Ho	17.7	18.6	18.6	19.2	17.0	19.3	21.4	23.0	19.4	20.3	20.1
REY	2063	1879	772	1459	477	1599	1711	1083	1265	962	1575

absolute REE (low versus high), the size of the Eu anomaly and the size of the Ce anomaly, and the LREE/MREE fractionation, indicating somewhat different growth conditions. This distinction is in agreement with huge differences in Co concentration, as will be discussed below.

6.3.4.3 Minor element distribution:

Stratified Mn crusts:

Geochemical profiles of stratified Mn crusts show strong compositional gradients (Figs. 9, 10), but are generally strongly enriched in metals such as Ni (817-3830 ppm), Co (1730-3470 ppm), Cu (1.19-2.17%), Mo (1675-3033 ppm), Li (609-1390 ppm), Zn (65-1679 ppm), V (328-527 ppm).

Nickel and Zn are enriched in the top, granular layer by a factor of about 5 and 10, respectively, relative to the bottom, botryoidal layer. Whereas other elements like Th, Ti, Zr, U do not show major differences but only slight enrichments towards the top, Co is depleted in the topmost layer; also Li is slightly depleted. Molybdenum is somewhat enriched towards the top and Cu is enriched only in the topmost layer. The concentrations of Th, Ti and Zr co-vary with Al concentration. Cobalt and the Ce/Ce* ratio are closely correlated, both decrease significantly towards the uppermost layer. Independent from the general trends, the velvety layer 3 is depleted in Zn, Ni, Li, Zr, Th, sumREY, but enriched in Cu, Co, Ce/Ce* and U/Th, accompanied by a small, but significant increase in Na and Ca relative to the adjacent layers. Vanadium follows the general trend of Co and Ce/Ce*, being enriched in layer 3 and depleted at the surface.

Similar distribution pattern for 1) Al, Ti, Zr, Th, REE, 2) Ni, Zn and 3) Co, Cu, V, Ce/Ce* ratio, U/Th ratio indicate similar geochemical behaviors within the 3 groups, determined by the geochemical behavior during crust accumulation. Copper seems to be decoupled in the topmost layer relative to Ce/Ce* and Co, which might be related to an additional parameter influencing the Cu content in this layer.

As evident from SEM analyses, the exceptionally high Cu concentrations in these crusts do not result from sulfide particle inclusions but are associated with the Mn minerals. Single layers making up the botryoids show variable elemental compositions, with Cu being higher towards the surface than the base of each layer. Highest Cu contents were observed in the outer casings surrounding several botryoids.

Massive, granular Mn crusts and massive Mn coatings:

This heterogeneous group, encompassing massive, granular Mn crusts and a pure, thick Mn coating on peridotite, is characterized by very low Co concentrations (28-147 ppm), which correlates with the low Ce/Ce* ratios in these deposits. Other than that, Ni (1525-4168 ppm), Zn (484-1829 ppm), Li (835-1572 ppm) and Mo (1402-4122 ppm) are strongly enriched, displaying a very similar geochemical signature as the top layers of stratified Mn crusts; Zn has a somewhat higher concentration. Copper is enriched as well (0.08-1.29%), but not as much as in group I samples. Nickel and V are closely coupled, which is not observed in the stratified Mn crusts of group I. The concentrations of Zr, Th, U, Pb closely correlate with Fe, in contrast to group I, where these elements vary independent of Fe concentration (Fig. 11). Also REY show a general correlation with Fe concentration. Similar to group I, Zr and Th also co-vary with the Al concentration. The about 1 cm thick Mn crust on a hard rock substrate shows a compositional trend with increasing concentrations of Ni and Zn towards the top layer. Also, Pb, Zr, and Th increase towards the top, probably related to the increasing Fe concentrations.

Fe-Mn coatings:

These thin Fe-Mn deposits on hard rock substrates are characterized by variable enrichments of metals, with a strong dependence on the relative Fe and Mn content: Whereas U, V, P are positively correlated with Fe, the Ni, Mo, Li, (and Co) contents are highest at high Mn concentrations. Copper and Zn concentrations are not correlated, whereas Pb as well as Al, Zr, Ti, Th are generally depleted in Mn-rich samples, but do not show a correlation with the relative amount of Fe. Despite the partly higher enrichment of detrital material, the geochemical composition of the Fe-rich samples of this ferromanganese deposit is generally similar to hydrogenetic ferromanganese crusts formed by adsorption of elements from seawater. Copper is significantly more enriched, with up to 1%, however, this might be related to the incorporation of sulfide particles or their alteration products, as evident from one Fe-Mn sample with 7% Cu (excluded in the data evaluation). Nickel and also Co are generally lower than mean values of hydrogenetic crusts. The Mn-rich coatings, on the other hand, are strongly enriched in Mo and Li relative to hydrogenetic Fe-Mn crusts.

A generally similar geochemical signature characterizes the Mn-rich Fe-Mn coatings of group III and massive Mn crusts of *group II*. Somewhat higher concentrations of Zr, Th and U and sumREY can be related to the higher amount of Fe in group III samples. The prominent exception is Co, which is strongly enriched in the Fe-Mn coatings. This is accompanied by the size of the Ce anomaly, being smaller in group II samples. On the other hand, the topmost layers of stratified Mn crusts of *group I* show similar Co and Ce/Ce* values as Mn-rich

coatings. Nickel, Mo and Zn are slightly depleted in the Mn rich coating, whereas Pb, Th, Ti, sumREY, and Zr significantly enriched.

In contrast to many other elements, Co and Ce are both enriched via surface oxidation. Logatchev-1 Fe-Mn deposits display a general trend, with increasing Ce/Ce* with increasing Co concentration (Fig. 12).

Although many elements correlate with either the Mn concentration or the Fe concentration, resulting in variable concentrations within the groups depending on Fe-Mn fractionation, their absolute concentrations are not controlled solely by the relative amount of Fe- and Mn minerals. Also, the concentrations of the sorbing element in the source fluid, the physico-chemical conditions (pH, T, Eh) and the rate of accumulation influence the final concentration in the oxide precipitate; the fractionation of Fe and Mn in the Logatchev I oxidic deposits itself expresses different formation conditions.

Figures 13-16 show the different geochemical trends and relations of the three individual groups, with overlaps for individual elements.

6.3.4.4 High field strength elements (Zr, Hf, Nb, Ta)

As a group, Zr, Hf, Nb, and Ta are most enriched in the Fe-rich Fe-Mn coatings of group III, with concentrations slightly less compared to hydrogenetic ferromanganese crusts (Zr: up to 340 ppm, Hf: up to 8.5 ppm, Nb: up to 62 ppm, Ta: up to 0.75 ppm). Stratified, pure Mn crusts have very low HFSE concentrations and are characterized by slightly higher to enhanced superchondritic Zr/Hf ratios (46-69) and chondritic to superchondritic Nb/Ta ratios (16-33). Iron-Mn coatings, however, display strongly superchondritic Nb/Ta ratios (69-153), whereas Zr/Hf ratios are almost chondritic to slightly superchondritic (35-49). The size of fractionation between Nb and Ta is generally correlated with the total amount of adsorbed Ta, i.e., with Fe. The ratios of Zr/Hf and Nb/Ta are negatively correlated, with the lowest Zr/Hf in Fe-rich Fe-Mn coatings having the highest Nb/Ta. Geochemical profiles in the stratified Mn crusts display higher HFSE enrichments in the upper, friable part of the crust relative to the lower, botryoidal part, accompanied by a decrease in Zr/Hf, but an increase in Nb/Ta. The massive Mn crusts of group II show intermediate Nb/Ta concentrations relative to the other groups (30-110), Zr/Hf does not differ significantly (36-57) and is not correlated with the relative HFSE enrichment. The different geochemical trends for Zr-Hf and Nb-Ta indicate either different geochemical behaviors/fractionation mechanisms or different sources. The HFS elements are among the most enriched elements in Fe-rich Fe-Mn coatings relative to pure Mn deposits, with Nb (60-100x), Hf (40-50x), Zr (20-30x) and Ta (about 20x), similar to Ti and Th, REE and Pb (enrichment factors of about 10-30), which can be related to the preferential scavenging of these elements by Fe oxyhydroxides.

6.3.4.5 Radiogenic isotopes (Nd, Os, Hf)

The radiogenic isotope composition of Nd, Hf and Os has been determined in selected samples of the three different groups (Table 5).

The $^{187}\text{Os}/^{188}\text{Os}$ ratios in the stratified Mn crusts range between 0.273 and 0.326, with the most unradiogenic value in the middle of the profile at the highest Os concentrations (408 ppt). In contrast, Fe-Mn coatings are characterized by isotopic values close to seawater (0.91-1.05; Levasseur et al., 1998), with the slightly less radiogenic value measured in a Mn-rich sample, correlating with a lower Os concentration (ranging from 795-1534 ppt). The low $^{187}\text{Os}/^{188}\text{Os}$ ratio in stratified Mn crusts indicates a significant input of unradiogenic Os from the hydrothermal alteration of oceanic lithosphere, whereas the Os signature of Fe-Mn coatings indicates incorporation of mostly seawater-derived Os.

The $\epsilon\text{Nd}(0)$ values of stratified Mn crusts range from -7.24 to -9.71, with the most radiogenic value in the middle part the crust (see Os), correlating with the lowest Nd concentration. Fe-Mn coatings are characterized by $\epsilon\text{Nd}(0)$ values of -11.53 to -11.76, which is close to seawater (NADW: -12.6, Jaendel, 1993). Similar to Os, the more Mn-rich sample is slightly more radiogenic than the others, correlated with lower Nd concentrations. The most unradiogenic $\epsilon\text{Nd}(0)$ has been determined in a massive, granular Mn crust sample, with -5.3.

Preliminary data for ϵHf show significant mantle contributions in stratified Mn crusts (3.8), relative to values more close to seawater in Fe-Mn coatings (2.1-2.3). For comparison, published ϵHf values for Atlantic seawater range between $+1 \pm 0.8$, Godfrey et al., 2008, and +1.3 to +4.4, Rickly et al., 2009, while published values of average ϵHf of hydrogenetic ferromanganese nodules and crust top layers in the Atlantic ocean, which should represent modern NADW range between -1 and +2.1; Albarede et al., 1998; van de Fliert et al., 2007; Piotrowski et al., 2000). Massive Mn crusts show values of 3.4-4.0, which is as unradiogenic as stratified Mn crusts. As already described for Nd and Hf, there is a general trend of decreasing mantle signature with increasing element concentration.

6.3.4.6 Geochemical signature of semi-consolidated Fe-Mn deposits and Fe crust chimney fragments

Massive, orange Fe oxyhydroxide deposits recovered close to the smoking crater vent sites are characterized by variable Fe/Mn ratios and very heterogeneous composition. Copper concentrations up to 7% result from the common association with the atacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$). Elements like Zr and Th are relatively depleted compared to Fe-Mn coatings, and Co concentrations are generally very low. The REY distributions range from HREE-depleted to HREE-enriched, with negative Ce anomalies, positive Eu anomalies on some samples and Y depletion to Y enrichment (the latter is associated with HREE enrichment).

The REY content is generally low but with more than one order of magnitude variation within this group. The isotopic compositions of Os and Nd indicate some mantle sourced Os and Nd and the deposits either represent oxidized sulfide material or direct precipitation from low-temperature hydrothermal fluids.

The pure Fe oxyhydroxides, sampled as fragments from a inactive chimney, have high U concentrations, but very low Cu, Co, Th, and Ni concentrations. Zinc is enriched, whereas Mo and Li are not. The REY distribution is characterized by a depletion of LREE to MREE and a significant positive Eu anomaly, which decrease with increasing REY content being accompanied by increasing Ce depletion, and Y and HREE enrichment. The Hf isotopic composition indicates that a significant amount of Hf is derived from the mantle, whereas Os isotopes are more like seawater.

6.3.5 Results of leaching efficiency test

In order to test the presence of detritus minerals in the different crust types, selected samples were digested solely with HCl at 90°C, which should completely leach all oxide phases but not most of the aluminosilicates or silicates. Whereas most elements including Fe, Mn, Cu, Zn, Co, Pb, Mo, Li, Ni, REY, P, and U were quantitatively dissolved during this digestion step, the elements Al, K, Ti, Cs, Rb, Sr and HFSE can be quantitatively determined only after pressure digestion with HF at 160°C. This indicates the presence of a detrital mineral phase, likely aluminosilicates. Differences in the leaching efficiency with hot HCl occur between the different groups as well as between the single elements: 90% of Al and Ti were leached in the Fe-Mn coatings containing high concentration of these elements. In contrast, only 65% of the Al and only 28-39% of the Ti is leached in the stratified Mn crusts, with increasing extraction efficiency of Ti at higher concentrations in the top layer. Interestingly, Th, which is often described as being associated with detritus in ferromanganese crusts, is almost completely leached during the HCl digestion in Fe-Mn coatings, but only to a degree of 72-84% in the stratified Mn crusts. Similar to Al, Cs shows a low leaching efficiency in pure Mn crusts (46-57%) and higher leaching efficiency in Fe-Mn coatings (83%). The extraction efficiency of Rb and Sr varies between 57 and 96%, with Sr being completely leached in the inner part of the Mn crust. The strongest effect is displayed by Zr and Hf, with Zr being extracted with the oxide phase by about 64-42% in the Mn crust and by only about 2% in the Fe-Mn coatings with high total HFSE concentrations. Similarly, Hf is most depleted in the Fe-Mn coatings (less than 2%), but also strongly depleted in the Mn crusts with 23% (bottom layer) and 9% in the top layer. As discussed below, the strong decrease in the leaching efficiency of HFSE in Fe-Mn oxide coatings is probably an artifact and does not represent the amount of detritus. The extraction efficiencies of elements from the Fe-Mn coatings is similar to results obtained for the CRM nodule JMn-1 (Table 5).

Table 4: Isotopic composition of Hf, Os, and Nd in oxide deposits from the Logatchev-1 hydrothermal field

Sample name	Sample ID	Hf (ppm)	$^{176}\text{Hf}/^{177}\text{Hf}$	eHf (rel. B.-T. 1997)	Os (ppt)	2s	$^{187}\text{Os}/^{186}\text{Os}$	2s	$^{187}\text{Os}/^{188}\text{Os}$	2s	Nd (ppm)	$^{143}\text{Nd}/^{144}\text{Nd}$	2s	eNd(0)	2s
78 GTV-1-1	M60/3M01				240	2.23	2.272559	0.00568	0.273500	0.000684	11.6	0.512197	0.000024	-8.60	0.47
78 GTV-1-4	M60/3M04				407	3.78	2.731990	0.00683	0.328792	0.000822	9.57	0.512267	0.000024	-7.24	0.47
78 GTV-1-7	M60/3M07				175	1.63	2.709498	0.00677	0.326085	0.000815	13.9	0.512140	0.000024	-9.71	0.47
	M60/3M07				168	1.56	2.783789	0.00696	0.335026	0.000838		-	-	-	-
79 GTV-bulk	M60/3M12				881	8.18	5.626705	0.0141	0.677168	0.00169		0.512214	0.000030	-8.27	0.59
82 GTV-bulk	M60/3M13	1.7	0.282838	2.3	189	1.75	2.179802	0.00545	0.262337	0.000656		-	-	-	-
78 GTV-5A	M60/3M18				796	7.39	7.618631	0.0190	0.916894	0.00229	126	0.512047	0.000030	-11.53	0.59
78 GTV-Mn on Per.	M60/3M19				1534	14.3	8.736700	0.0218	1.051461	0.00263	193	0.512035	0.000024	-11.76	0.47
	M60/3M19				1458	13.5	8.769177	0.0219	1.055361	0.00264					
272 GTV-8	M 64/2 M03	0.08	0.283002	8.1	187		7.627300		0.917900						
225 GTV-3 (D2)	M 64/2 06	0.17	0.282869	3.4 [#]							14.4	0.5123636	0.0000035	-5.35	0.07
225 GTV-1-F1(4)	M 64/2 28	0.20	0.282836	2.2 [#]											
78 GTV Mn on Per.	M 64/2 09	6.1	0.282830	2.1											
78 GTV 5A	M 60/3 26	1.83	0.282836	2.3											
32 GTV-1	M 60/3 21	0.26	0.282796	0.8											
78 GTV-1 (6)	M 60/3 37	0.16	0.282879	3.8											
78 GTV-1 (2)	M 60/3 33	0.30	0.282786	0.5 [#]											
225 GTV-3 (B1)	M 64/2 02	0.55	0.282885	4.0 [#]											
	JMn-1	5.64	0.282985	7.5											

Note: # some Lu in Hf cut, not yet corrected

Table 5: Leaching efficiency in % of bulk data

	M60/3-08 Fe-Mn coating	M60/3-02 Mn crust bottom	M60/3-07 Mn crust top	Nod-P1 leaching	hydroth. Mn crust leaching [#]
Ti				74.8	
Co				99.9	
Ni				100	
Rb	66.8	72.5	56.6	21.6	
Sr	76.9	96.4	85.1	95.2	
Y	96.0	108	95.8	95.9	
Zr	2.07	64.0	42.0	92.3	65-80
Nb				90.8	100
Mo				100	
Cs	83.4	61.9	45.8	21.2	75.0
Ba	101	123	108	96.5	
La	103	98.6	92.3	94.2	
Ce	105	108	96.6	95.7	
Pr	97.0	105	96.1	94.6	
Nd	96.5	109	101	94.9	
Sm	96.8	112	100	96.1	
Eu	98.4	118	99.2	96.6	
Gd	95.9	109	103	97.1	
Tb	98.4	112	101	97.5	
Dy	93.4	105	96.9	97.5	
Ho	93.9	103	100	97.4	
Er	96.7	108	101	97.2	
Tm	95.1	108	101	97.3	
Yb	95.1	101	95.5	96.9	
Lu	93.3	117	98.9	97.2	
Hf	<<2	23.4	9.07	86.8	90
Ta				18.6	80-90
W				98.9	
Pb	99.7	129	112	96.4	
Th	102	84.0	78.6	94.4	90.0
U	103	102	96.0	93.3	
Al	89.1	65.2	62.6	39.7	
Fe	101	107	96.9	82.5	40-80
Mn	99.8	108	104		
Ti	91.3	28.1	38.6	74.8	22-50
Cu	98.5	103	103	99.5	
Li			102		
P			100	89.6	
V			100		
Zn			101	97.9	98.0
Ni			102	100	
Ca			102	90.1	
Mg			100	87.8	
Na			102	86.0	
K	73.8		89.5	60.6	100

Note: #Koschinsky and Hein (2003)

Sequential leaching experiments on hydrothermal Mn crusts from the Fiji Basin (Koschinsky and Hein, 2003) have also shown significant quantities of Ti (50-78%), Fe (20-60%), Cs (25%), Zr (20-40%), and Ta (10-20%) being associated with the residual detritus phase. This is in contrast to hydrogenetic crusts investigated during the same study which do not show significant detritus influence for these elements and the other HFSE Nb and Hf (except for Cs). Leaching experiments with the polymetallic nodule Nod-P1 are generally similar to the results obtained from the digestion test with JMn-1 (A. Koschinsky, pers. comm.), with significant amounts of Al (60%), Ti (25%), Cs (80%), and Ta (82%) being retained in the residual phase. However, less than 10% of Zr, Hf, and Nb are retained in the residual phase, which is in contrast to the results of the digestion efficiency tests of this study. The reason for the discrepancy of HFSE-association with detrital minerals is likely related to the different ways to determine the residual fraction, but is not yet fully understood. The apparent association of Zr and Hf with the detritus phase in the Fe-Mn oxide coatings requires another explanation, as the concentrations are far too high to reflect a detrital component like clay minerals or volcanoclastic material and must instead result from scavenging on the oxide phase. This recalls another digestion-related process, like precipitation of insoluble phosphates or chlorides, precipitating out with HFSE without HF stabilization. Higher temperatures of HCl digestion (160°C) significantly enhance the digestion efficiency of Zr and Hf in JMn-1 (Zr: increase from 17% to 64%; Hf: 9% to 60%), but these values are still below those from leaching experiments. The phosphate content in the Fe-Mn oxide coatings as well as in the reference nodule JMn-1 is significantly higher than in the pure Mn oxides, correlating with a higher leaching efficiency in those precipitates. Thus, phosphate precipitation might explain the strong depletion of HFSE in HCl digestions.

SEM analyses of the topmost layer of the stratified Mn crust show rare particles possibly representing volcanoclastic fragments. As Fe is completely leached in the digested samples with hot HCl, the presence of such material is unlikely. However, small amounts of aluminosilicates may be present. The correlation of Al, Ti, and HFSE in the Mn crusts may reflect a genetic relationship. These elements are known to be commonly enriched in hydrogenetic ferromanganese crusts, with Ti and HFSE bound almost exclusively to the Fe oxide phase and not to Mn oxides. This general relationship is also evident in the Logatchev field, where Al, Ti, Th, HFSE are most enriched in the Fe-rich Fe-Mn coating of group III. However, the elements do not correlate with total Fe content in the Mn crusts, which might be related to Fe being present as Fe-vernadite, or the presence of aluminosilicates containing significant amounts of HFSE, Ti, and Cs.

Due to the generally very low contents on elements preferentially associated with the Fe-oxide phase in Mn crusts, small inclusions of detrital material will have a strong effect on the relative concentrations, whereas similar contributions in Fe-oxide rich deposits do not significantly affect the total concentrations. This is in agreement with digestion efficiency

tests showing that Al, Ti, and Cs have the highest relative detritus contributions in the pure Mn crusts but only minor contributions in the Fe-rich coatings. While this is in agreement with leaching studies done by Koschinsky and Hein (2003), comparing hydrothermal Mn crusts and hydrogenetic Fe-Mn crusts, the ferromanganese nodule standard Nod-P1 shows a somewhat different leaching behavior, with a significant amount of these elements retained in the residual phase. This might be related to the growth environment, as nodules are often influenced by diagenetic processes and authigenic minerals.

It can be concluded, that elements like Al, Ti, Cs, HFSE are of mixed origin in the Fe-Mn oxide deposits from Logatchev-1, being enriched due to detritus as well as due to scavenging from seawater.

6.4 Discussion

Mineralogical, textural, and geochemical data of oxidic deposits in the Logatchev-1 hydrothermal field display high variability reflecting different formation conditions. Taken together, textural characteristics and distinct geochemical compositions define five individual groups of Fe and Mn oxide precipitates, formed at different physico-chemical conditions. The focus of this chapter is on the cm-thick Mn crusts and Fe-Mn coatings on rock substrates, while massive Fe-rich deposits will be discussed briefly at the end of this section.

6.4.1 Mineralogy and textures

The mineralogy and texture of the oxidic mineral deposits in the Logatchev field provide information on the growth environments: Black and dark-brownish, cm thick crusts of groups I and II consist solely of 10Å manganates and possibly vernadite. The strong fractionation of Fe and Mn in pure Mn crusts is evidence for a hydrothermal origin, with the fractionation being related to the different redox chemistry (solubility) of Fe and Mn in the local growth environment and the slow oxidation rates of Mn. Pure Mn oxide deposits in proximal settings can be related to the circulation of low-temperature hydrothermal fluids, which are enriched in Mn and depleted in Fe. The formation of Mn oxide particles in the water column above the vent sites is not likely. Inorganic oxidation of Mn is extremely slow due to the large activation energy of oxidation (Stumm and Morgan, 1981), but is an autocatalytic process once a small amount of MnO₂ is formed. In hydrothermal plumes, Mn has a long residence time in contrast to Fe and is, as evident by constant TDM/3He ratios, a conservative tracer in the non-buoyant and dispersing buoyant plumes (e.g., German et al., 2010). Plume particles are dominated by Fe oxyhydroxide particles, eventually settling to the seafloor, except for Gyamas Basin, where Mn in plumes is immediately oxidized by microbial mediation (Dick et al., 2009). Plume fallout precipitates are expected to be dominated by Fe oxyhydroxide particles, with only

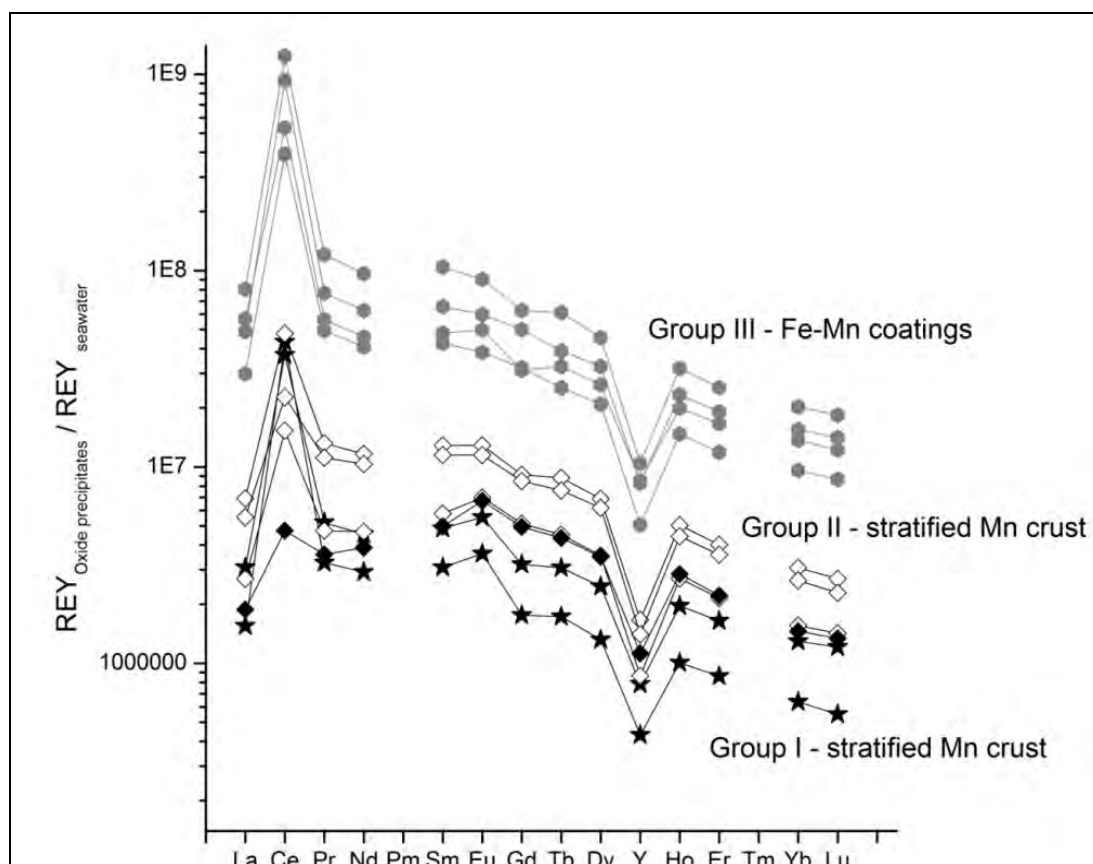


Figure 5: REY distribution of all oxide deposits from Logatchev I, normalized to seawater (Douville et al., 1999)

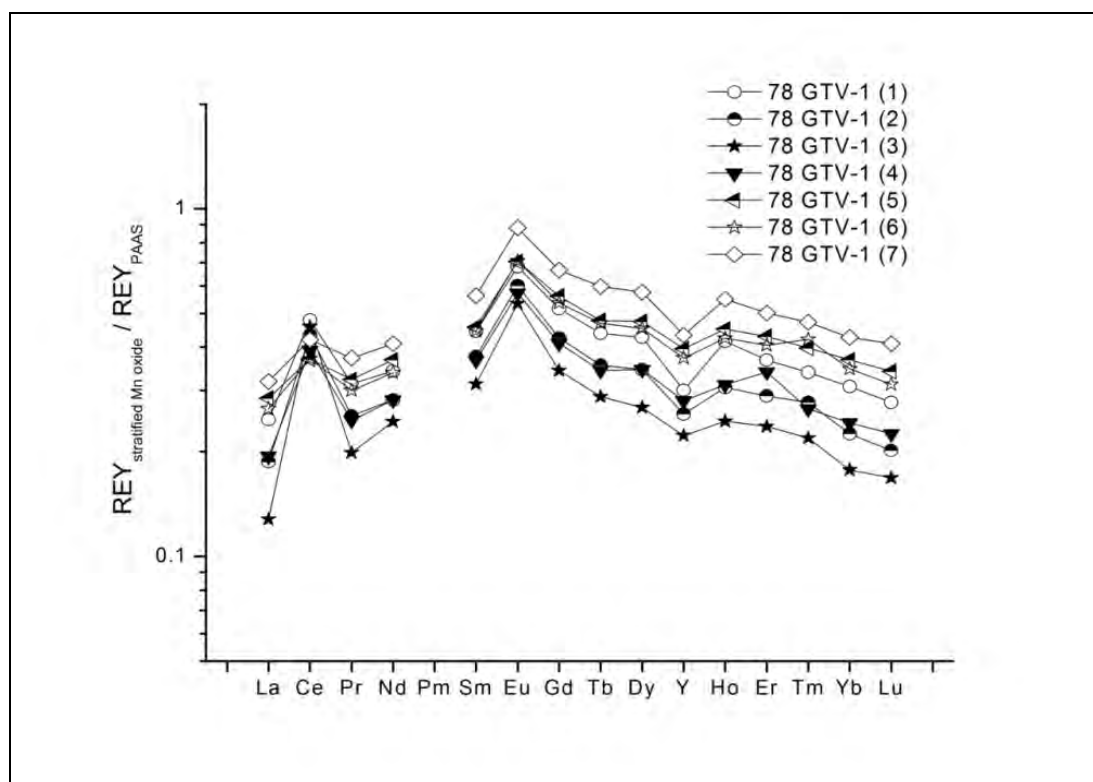


Figure 6: Shale-normalized REY distribution of Group I, stratified Mn oxides

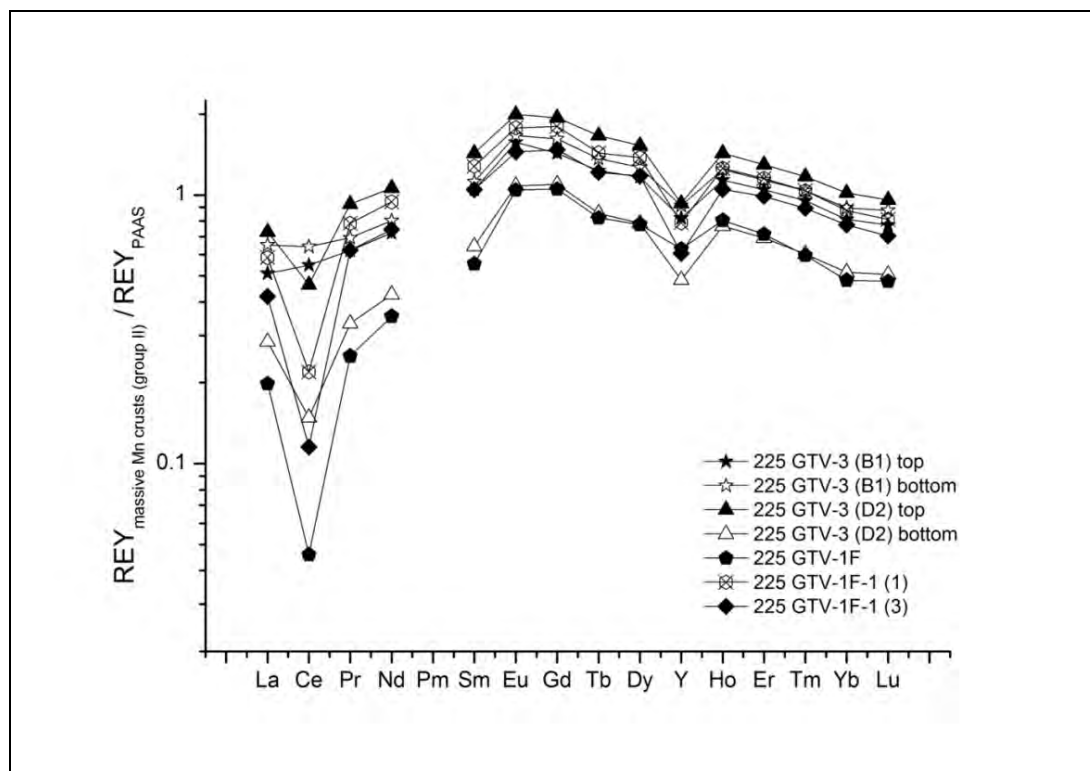


Figure 7: Shale-normalized REY distribution Group II, massive Mn oxides

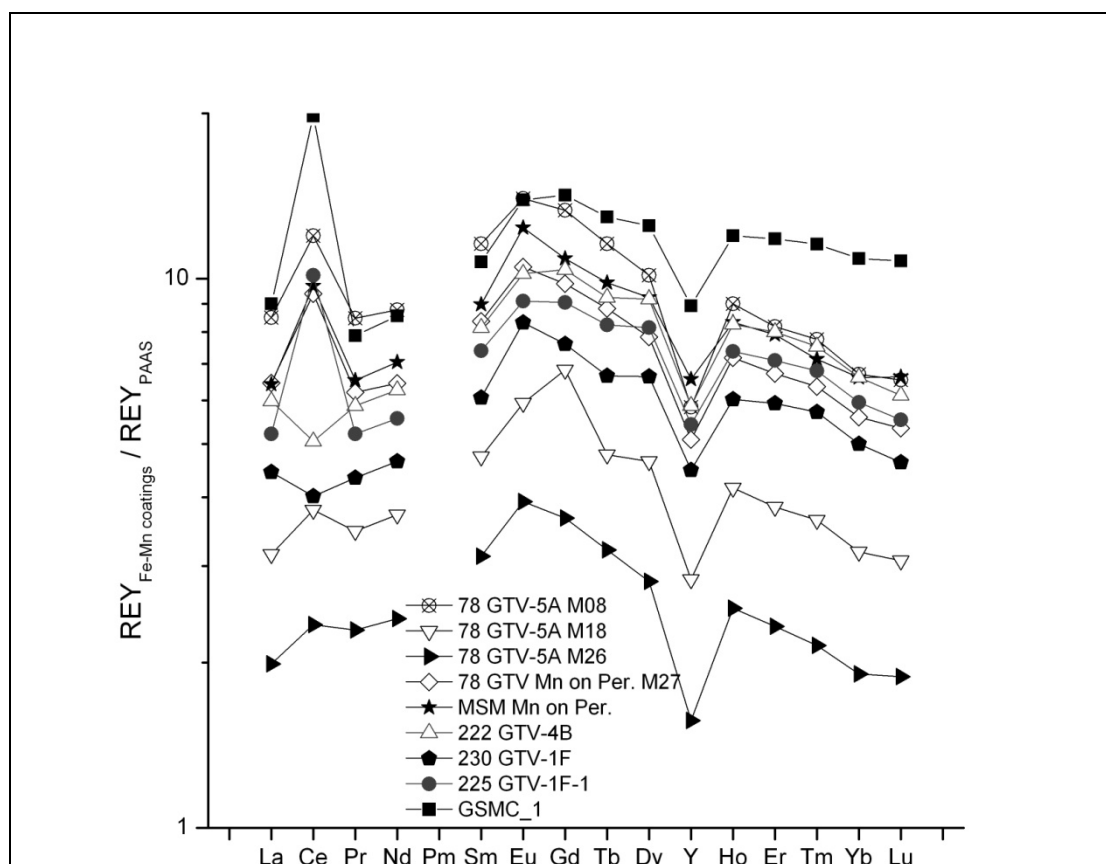


Figure 8: Shale-normalized REY distribution Group III, Fe-Mn oxide coatings, GSMC-1 is a ferromanganese crust georeference material

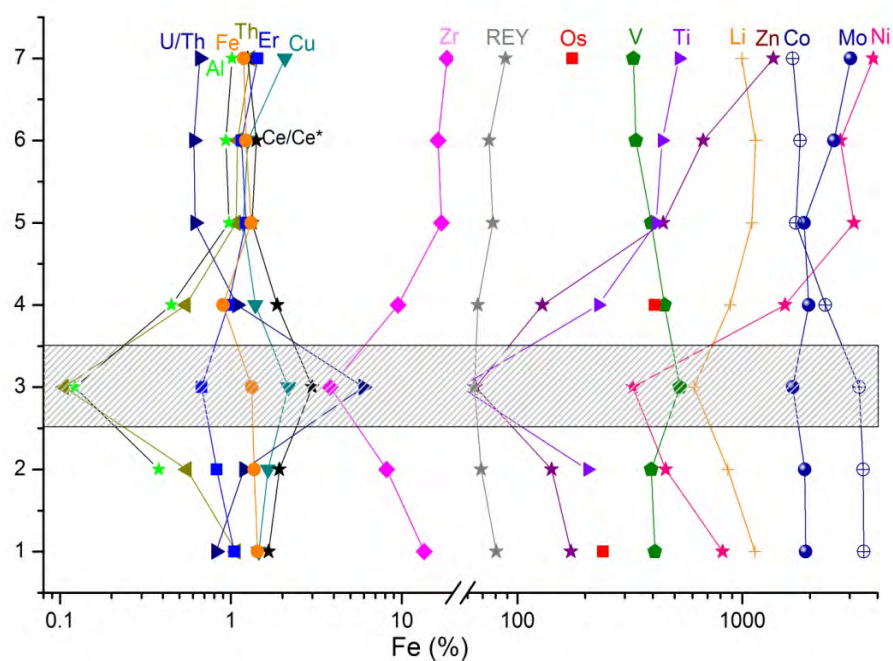


Figure 9: Geochemical profile of stratified Mn crust-1: not the correct scale, 7 is top, 1 is bottom, units are in ppm, except for Al and Fe (%) and Os (ppt), grey bar marks most depleted layer 3

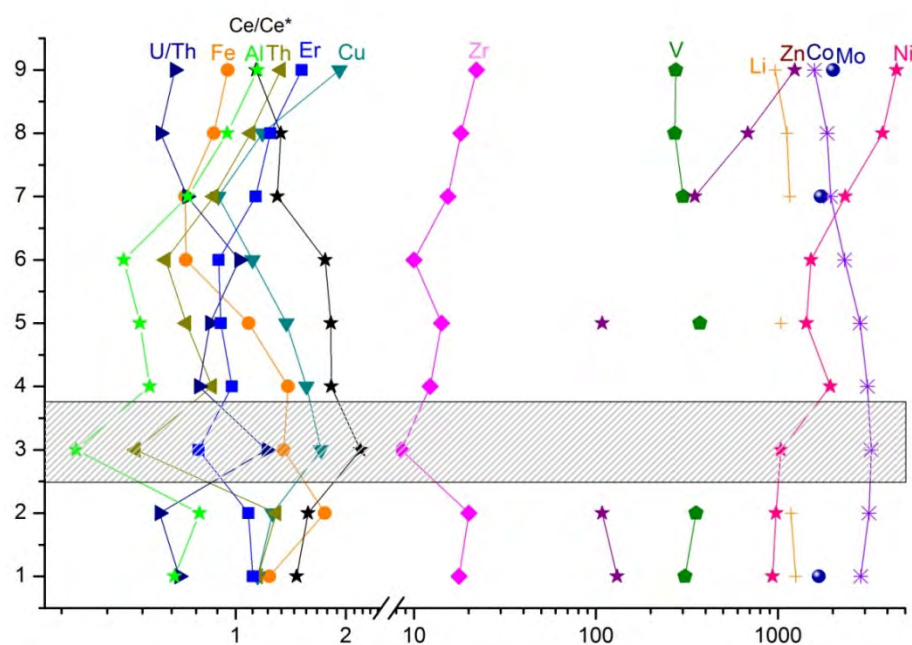


Figure 10: Geochemical profile stratified Mn crust-2: not the correct scale, 9 is top, 1 is bottom, units are in ppm, except for Al and Fe (%) and Os (ppt), grey bar marks most depleted layer 3

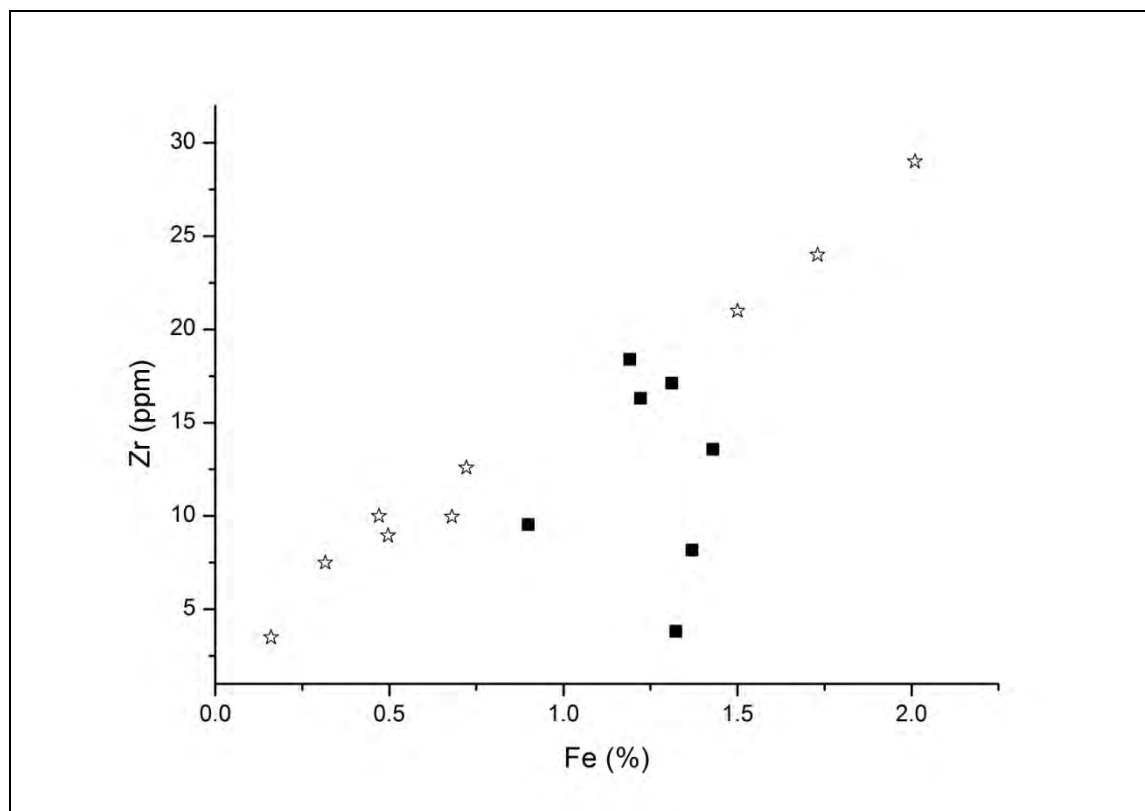


Figure 11: Relationship between Zr and Fe in group II Mn oxides (white stars) and group I Mn oxides, displaying contrasting trends

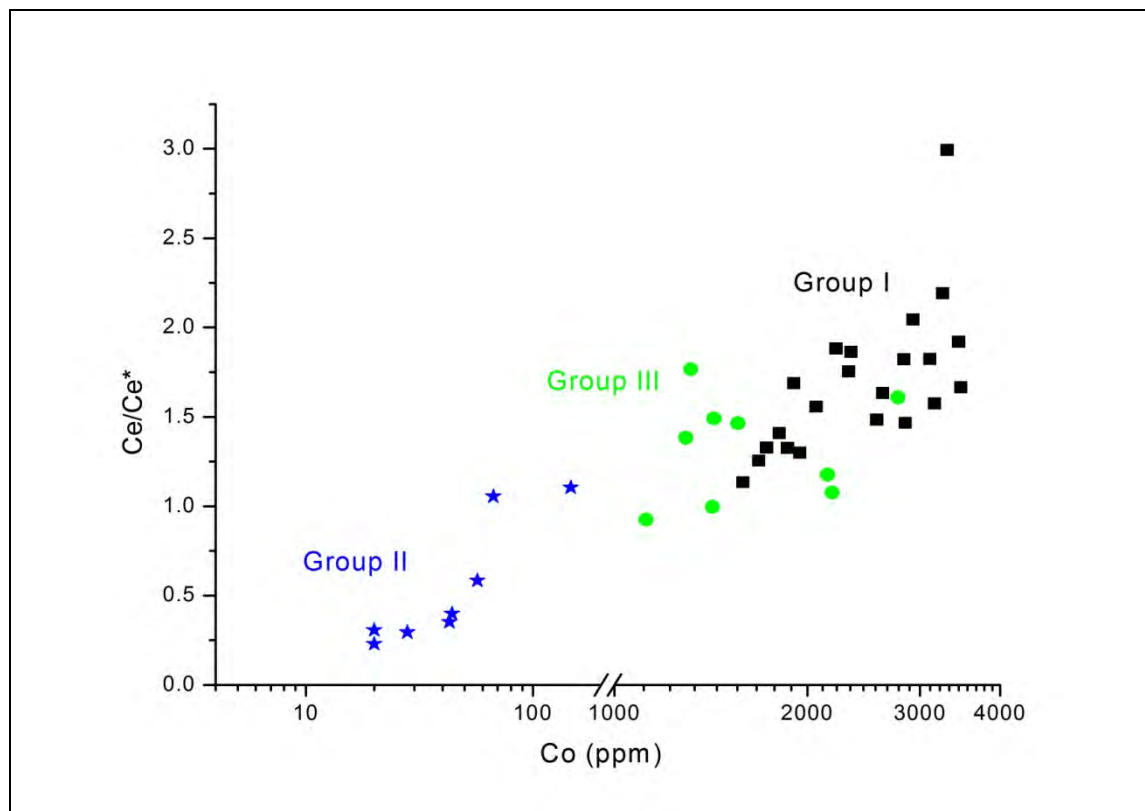


Figure 12: positive correlation of Co concentration and size of the Ce anomaly (Ce/Ce*) between and within the individual groups of oxide deposits

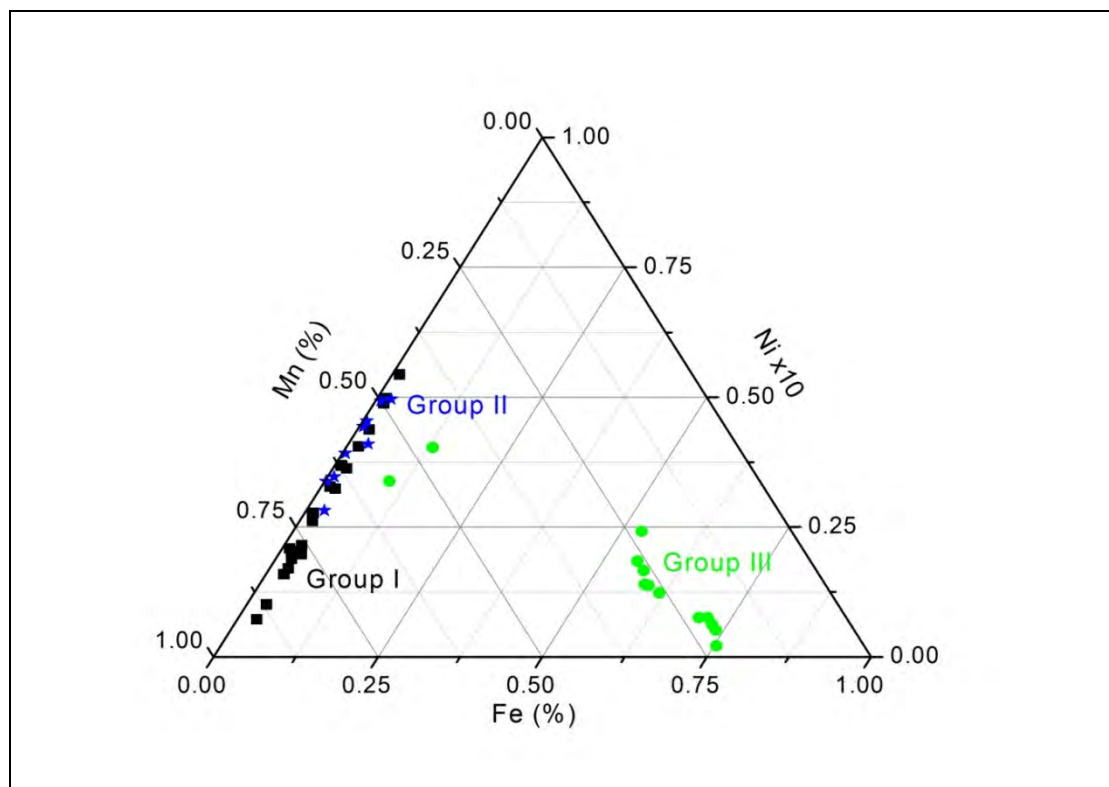


Figure 13: Ternary plot of relative Fe, Mn, and Zn concentrations separating the different groups of oxide deposits in the Logatchev I field, note the overlapping areas between group I and II

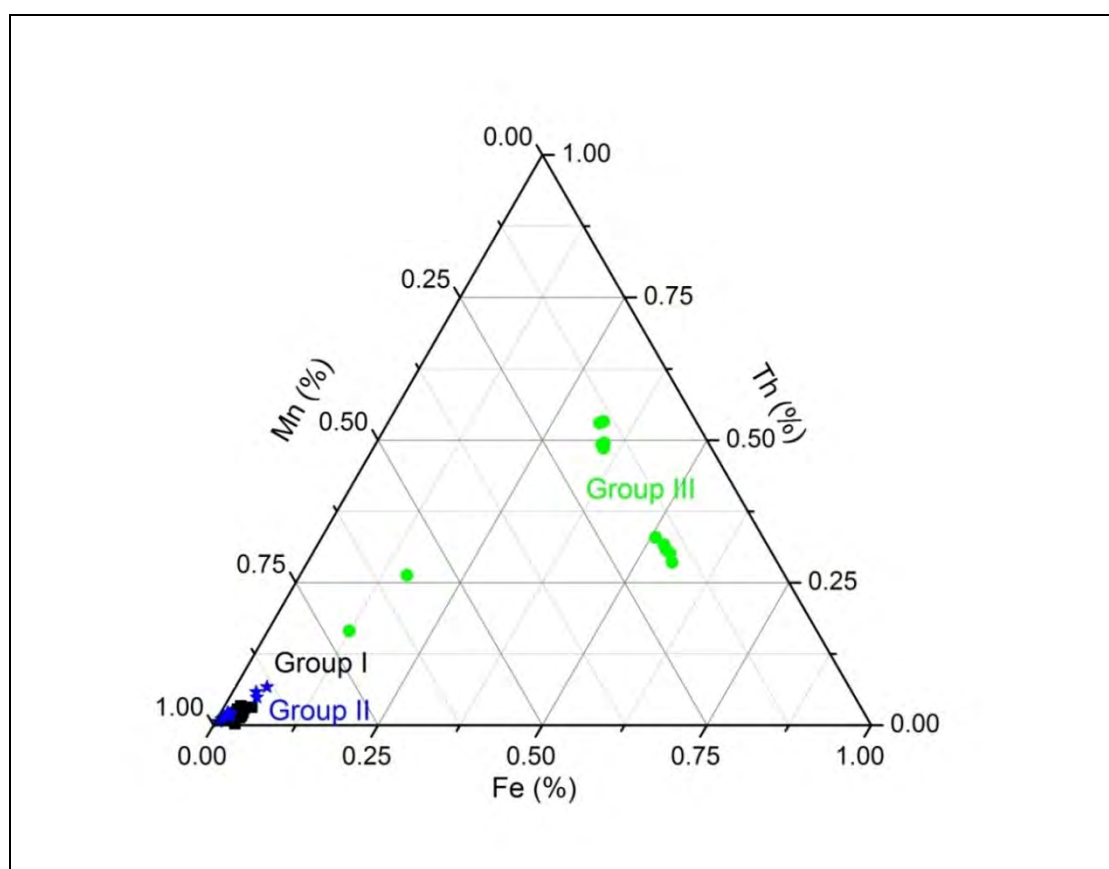


Figure 14: Ternary plot of relative Fe, Mn, and Th concentrations separating the different groups of oxide deposits in the Logatchev I field

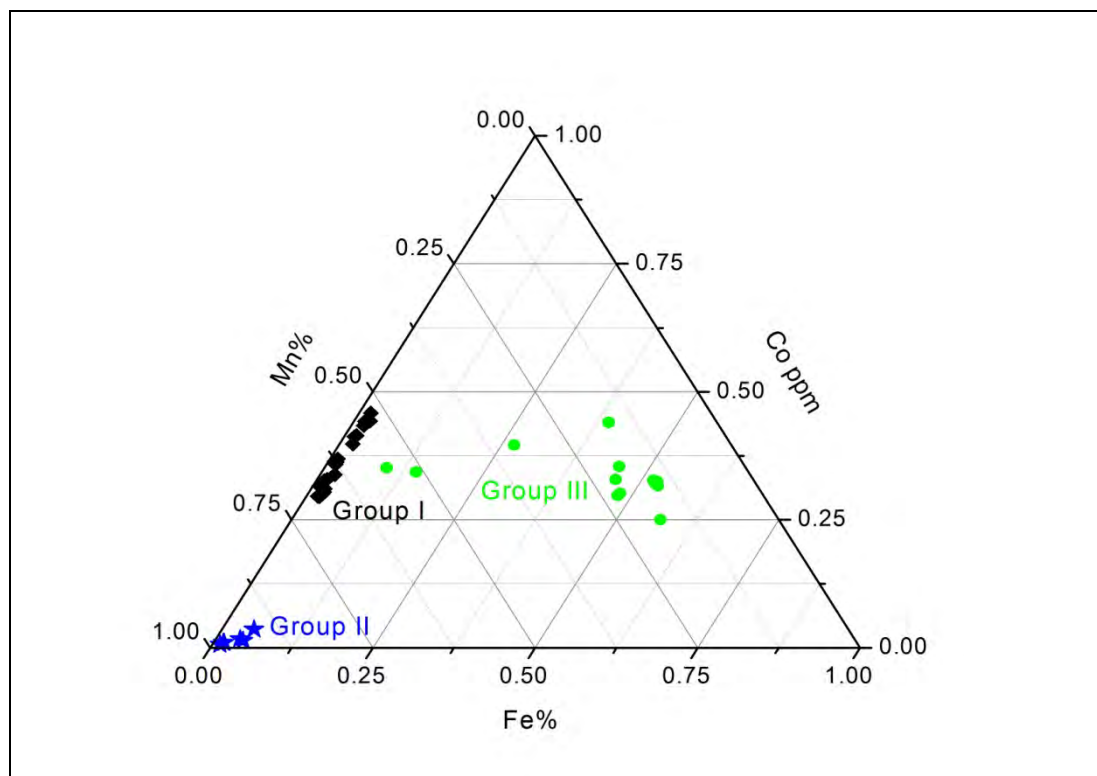


Figure 15: Ternary plot of relative Fe, Mn, and Co concentrations separating the different groups of oxide deposits in the Logatchev I field

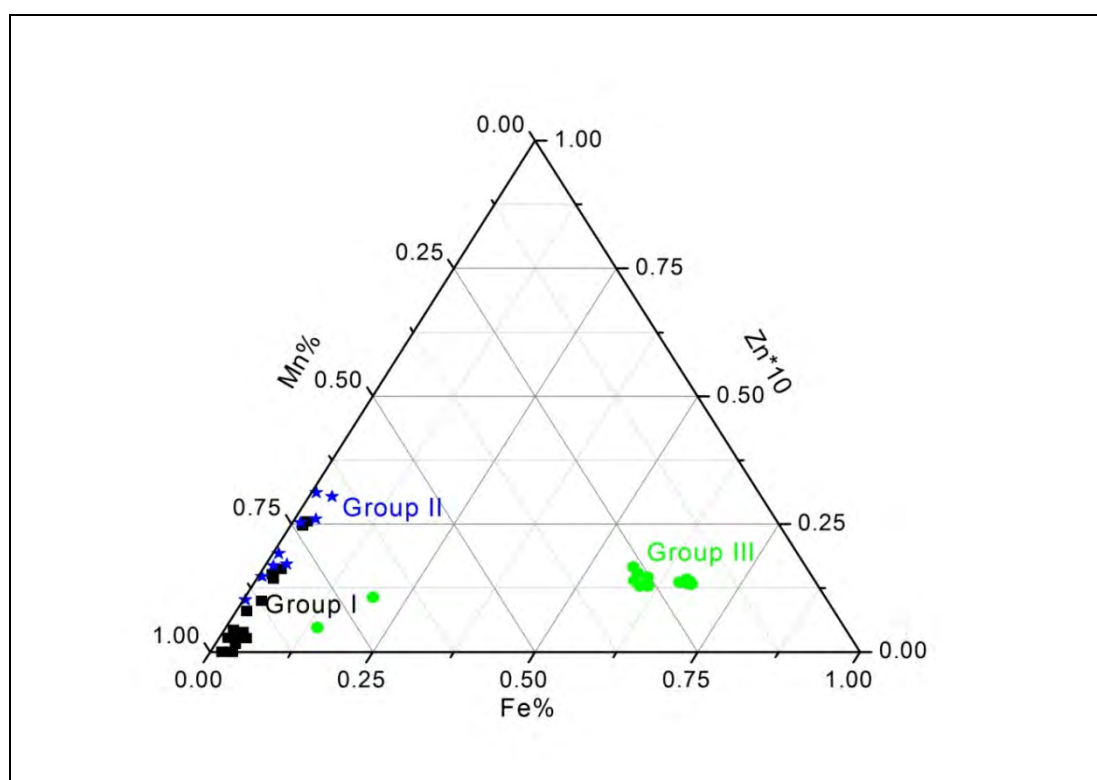


Figure 16: Ternary plot of relative Fe, Mn, and Zn concentrations with overlapping areas between the different groups of oxide deposits in the Logatchev I field

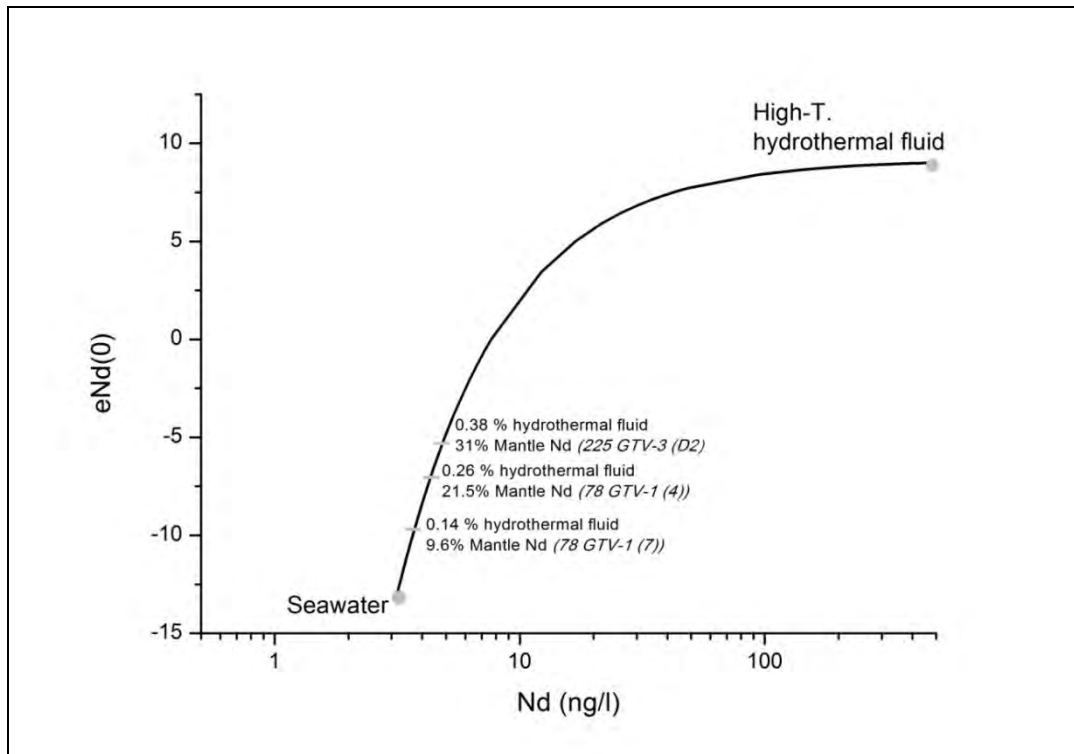


Figure 17: Conservative mixing line between seawater(ref) and endmember high-temperature hydrothermal fluid, showing that about 0.14% to 0.38% high-T hydrothermal fluid (Schmidt et al., 2010; Marques et al., 2006), mixing with ambient seawater (Douville et al, 1999; Piepgras and Wasserburg, 1988) would result in $eNd(0)$ signatures similar to those observed in hydrothermal Mn crusts from the Logatchev I hydrothermal field

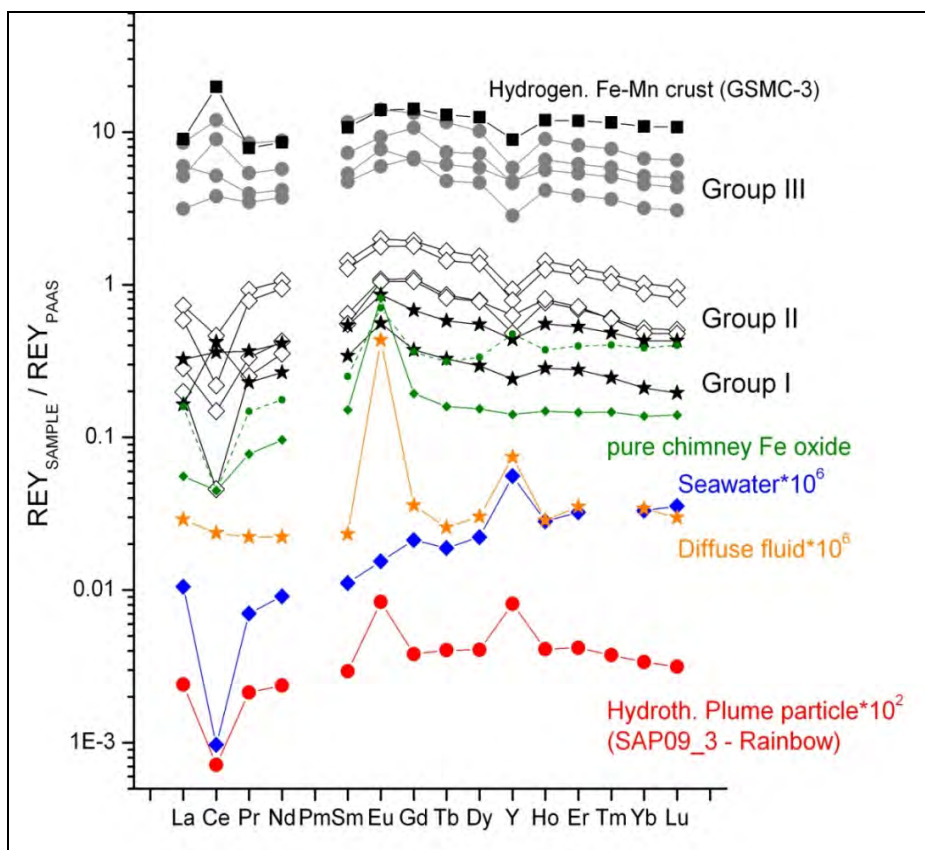


Figure 18: Shale-normalized REY distribution (PAAS: Anders and Grevesse, 1989) of various Fe-Mn oxide deposits in the Logatchev I field, for comparison, REYc distribution of seawater (Douville et al., 1999), diffuse

hydrothermal fluid (Logatchev I, Bau et al., 2010), and hydrothermal plume particles from Rainbow (Edmonds and German, 2004) are provided

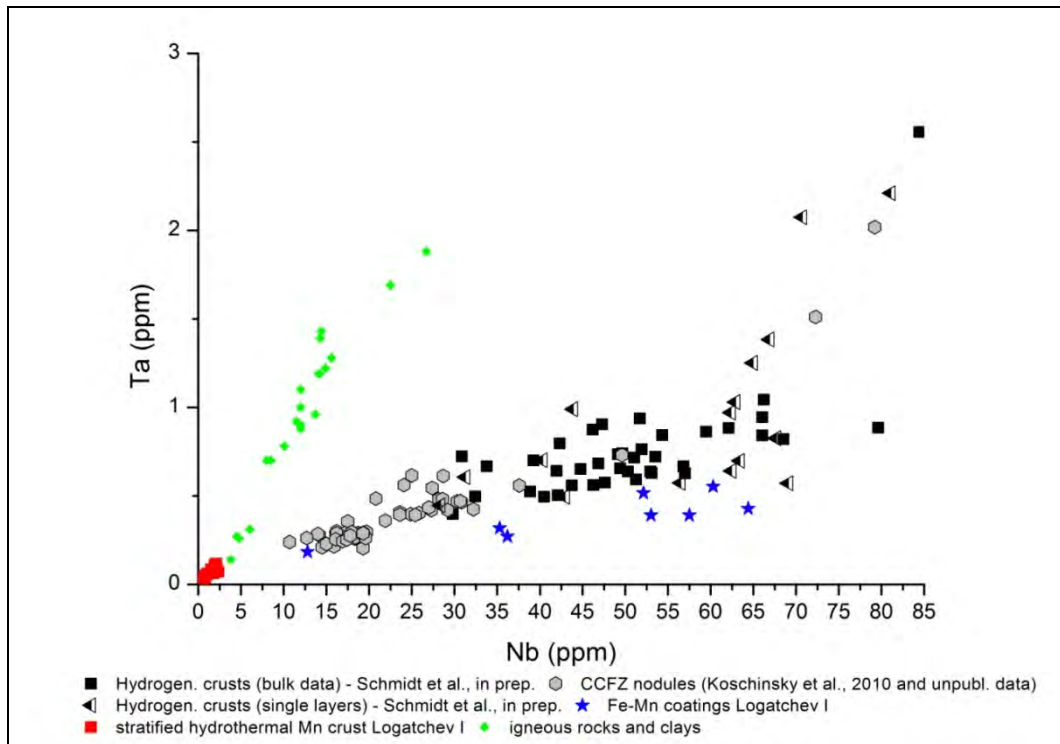


Figure 19: Niob and Ta concentrations in various marine ferromanganese deposits, including group I Mn oxide crusts and group III Fe-Mn oxide coatings, note the green dots representing the relative Nb an Ta concentrations in igneous rocks and clays and the relative enrichment of Nb in all ferromanganese oxide deposits

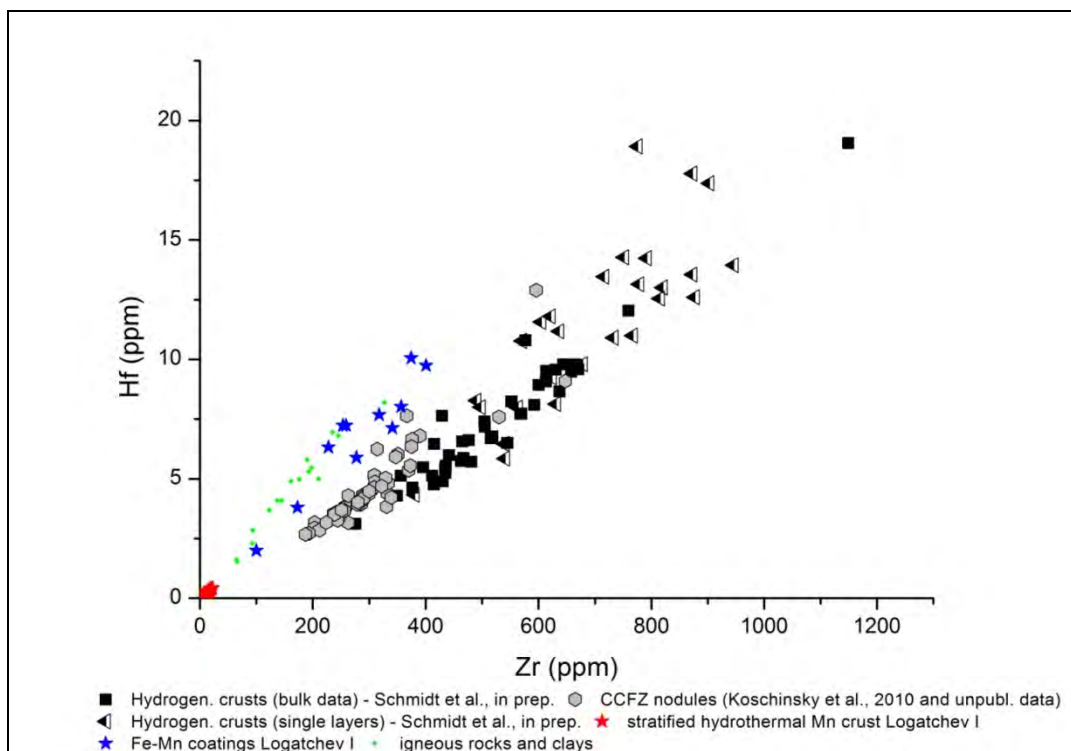


Figure 20: Zirconium and Hf concentrations in various marine ferromanganese deposits, including group I Mn oxide crusts and group III Fe-Mn oxide coatings, note the green dots representing the relative Zr an Hf concentrations in igneous rocks and clays

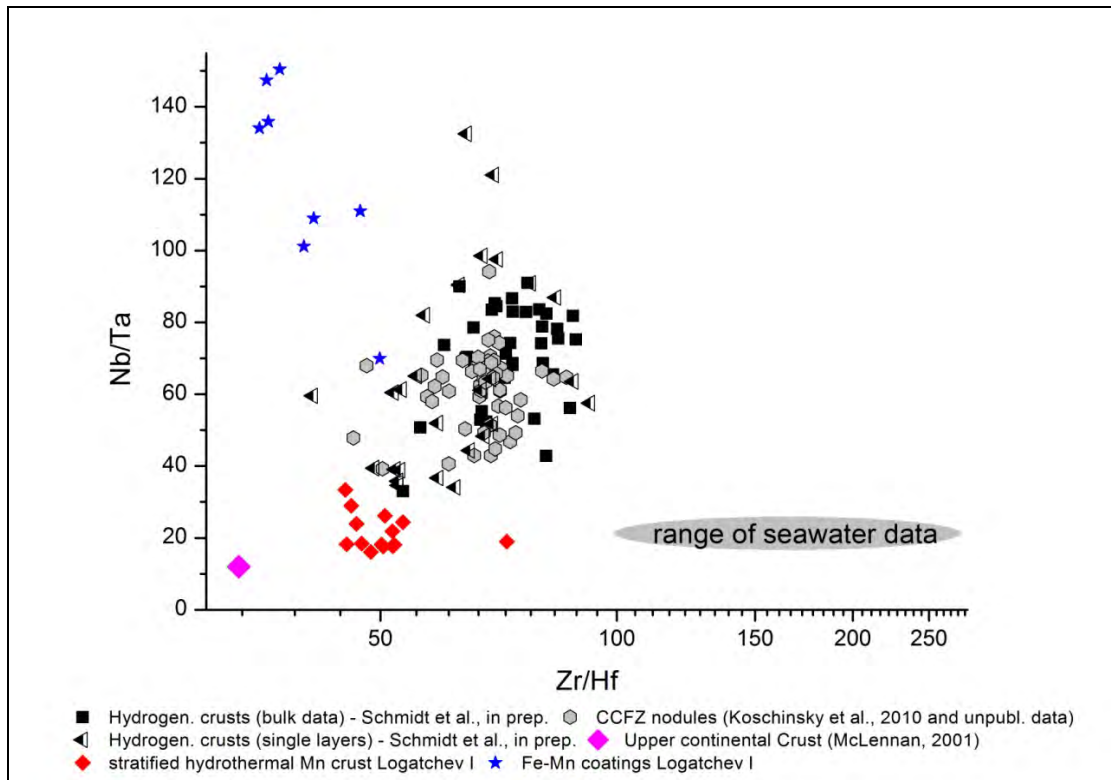


Figure 21: Nb/Ta ratio versus Zr/Hf ratios in different types of ferromanganese oxide deposits, the range of seawater data include published data by Firdaus et al. 2008 for the northwestern pacific and unpublished data by L. Firdaus for the southern Pacific and the southern Ocean for deep water (>2000m), (manuscript in prep.)

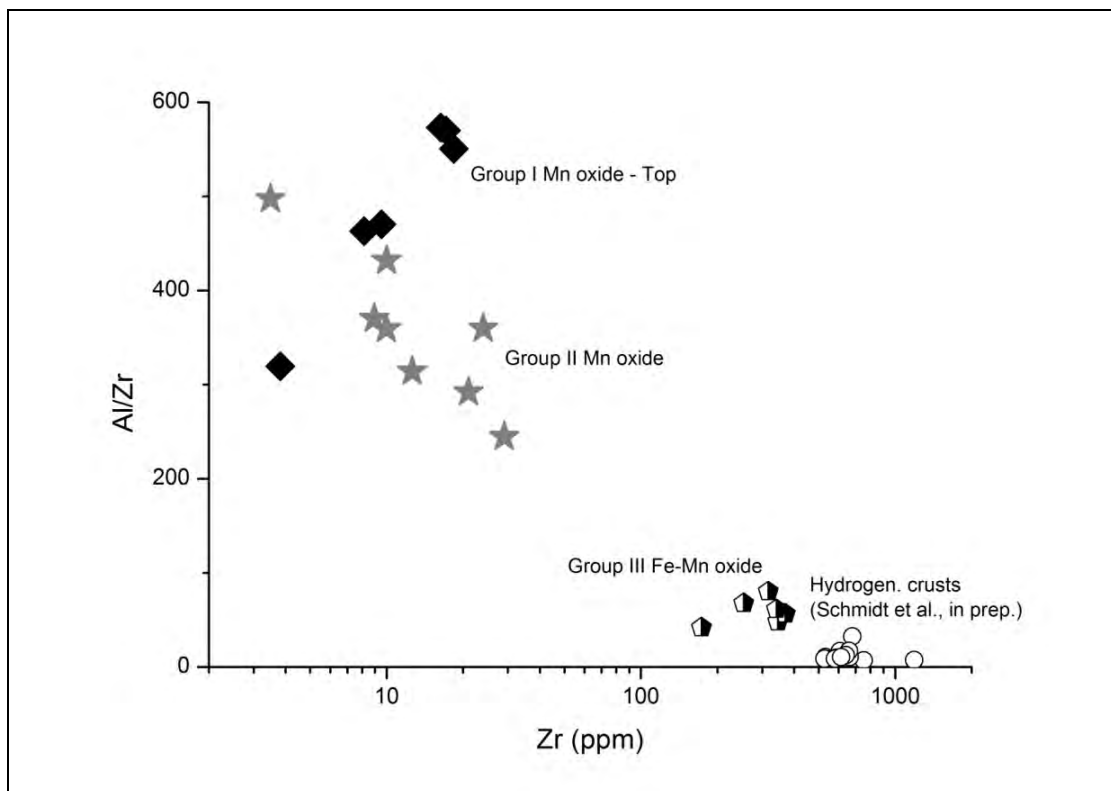


Figure 22: Al/Zr versus Zr concentration for different oxide deposits from Logatchev I, compared to hydrogenetic crusts, note that the Al/Zr ratio of Upper Continental Crust (UCC) is about 414, smaller ratios are thus evident for non-detrital Zr enrichment in the different oxide deposits

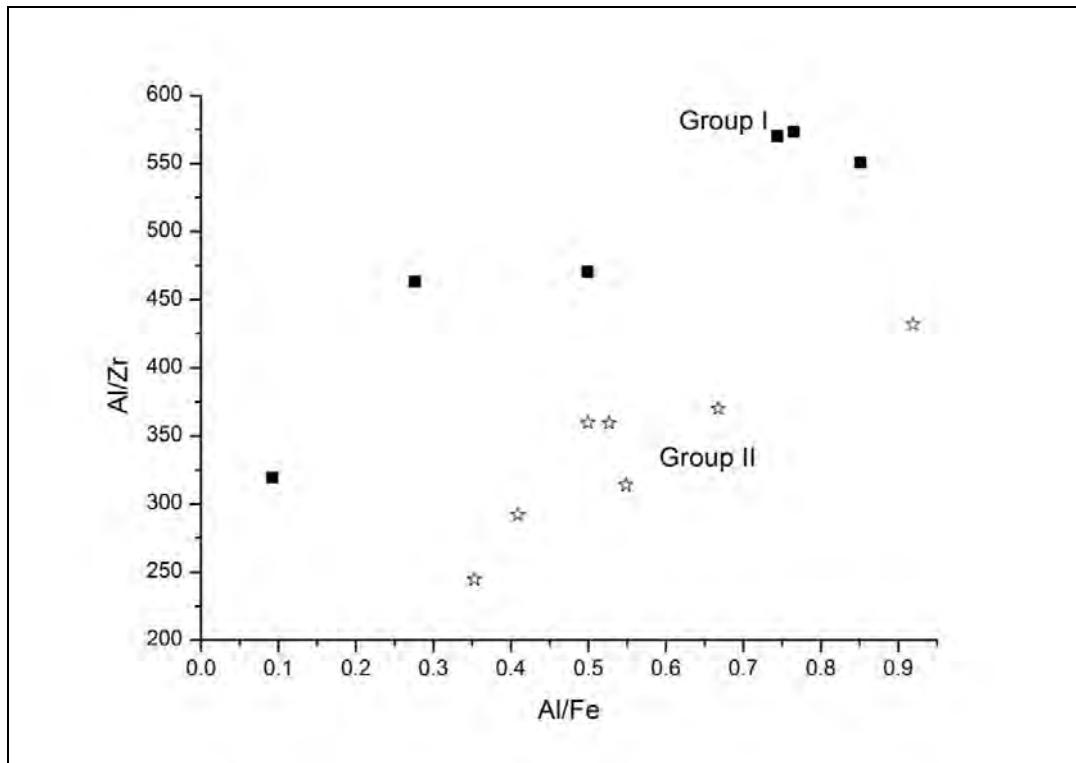


Figure 23: Trend of Al/Zr versus Al/Fe for group I and group II Mn oxides, Zr enrichment relative to Al is coupled to Fe enrichment in both groups, but controlled by different processes (see text for explanation)

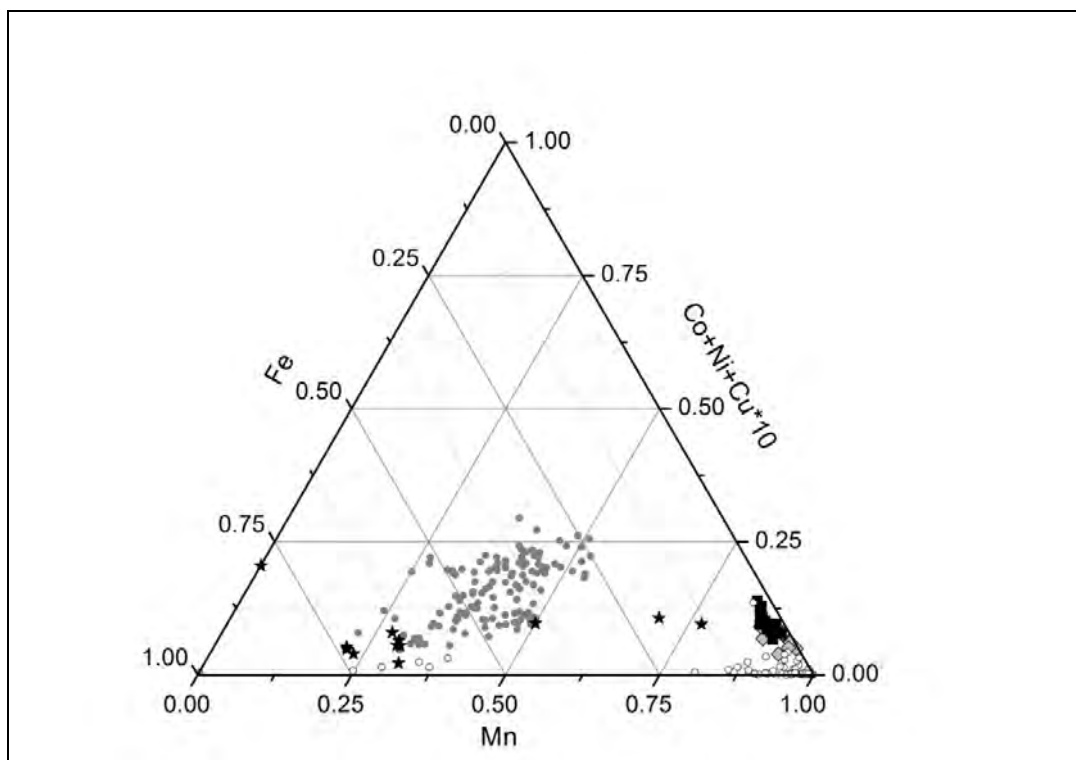


Figure 25: Ternary Fe-Mn-(Co+Ni+Cu)*10 diagram after Bonatti, xxx, grey filled circles are compiled data of hydrogenetic crusts from the Atlantic and Pacific, white circles are hydrothermal Mn crusts from the literature, black squares: Group I Mn oxides, grey diamonds: group II Mn oxides, black stars: group III Fe-Mn oxide coatings, not the general enrichment of Logatchev hydrothermal deposits in transition metals relative to previously reported Mn crusts from island arcs and in distal MAR locations, data for hydrogenetic crusts provided by J. Hein (USGS)

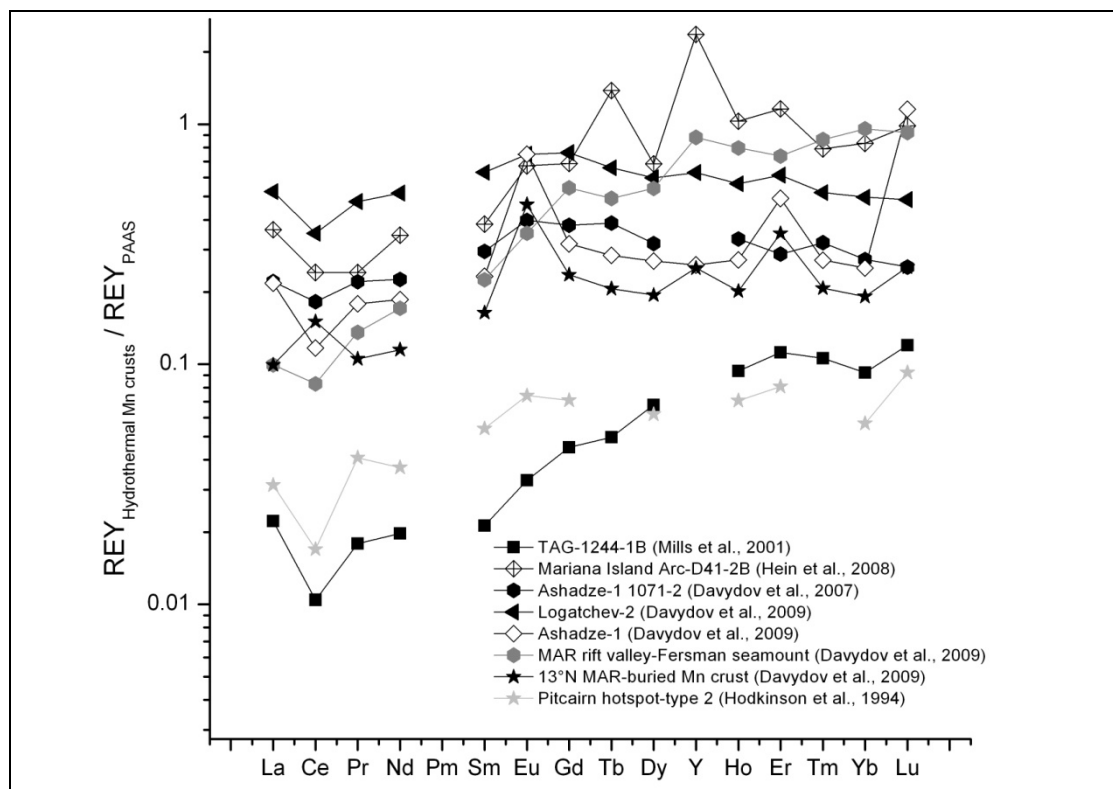


Figure 26: Shale-normalized REY distribution of hydrothermal Mn crusts, compiled from the literature, note the zic-zac pattern of some crusts, probably due to analytical issues

minor amounts of Mn oxide and will not consist of pure Mn oxide minerals. The ferromanganese coatings on rock substrates in the Logatchev field are composed of both 10Å manganates and goethite or X-ray amorphous FeOOH. For the above reason, Fe and Mn oxide particles forming these friable coatings are probably of mixed origin, with Fe oxide particles likely formed in the hydrothermal plume, whereas Mn oxide particles are related to local Mn enrichment in the bottom water due to the emanation of low-temperature hydrothermal fluids.

Further information regarding the mode of crust formation comes from the macroscopic and microscopic textures. Stratified Mn crusts from the Logatchev field are composed of texturally different layers (botryoidal, dense and laminated, massive granular or acicular), which indicate different formation conditions during crust growth. Textures of stratified Mn crusts are globally similar in active island arc settings, at hot-spot volcanoes, in back-arc basins and mid-ocean ridge spreading centers. Their formation is commonly related to Mn oxide initially precipitating within the very top of the surface sand layers (near the sediment-seawater interface) which prevents succeeding discharge of Mn-bearing hydrothermal solution to be dispersed in bottom waters. Subsequently, pure, dense Mn layers develop beneath the cemented surface hardpan (Usui & Nishimura, 1992). The orientation of columnar and botryoidal textures of stratified Mn crusts from the Logatchev I field suggest a downward growth, however, the morphological appearance should not be used as a sole argument for this hypothesis as pointed out by Glasby et al. (1997), and further geochemical investigations are needed to clarify the mode of crust formation. More critical than growth direction are the relative formation conditions including the question as to what is top and what is bottom. The individual, texturally different layers 1-3 of stratified Mn crusts are thought to have formed during distinct episodes of precipitation, reflecting different stages of hydrothermal activity or local changes in fluid dynamics. Different internal textures (granular, acicular, laminated, botryoidal) within these crusts result from differences in fluid flow dynamics, precipitation rates and the availability and connectivity of void space (porosity and permeability). Laminated, dense layers and botryoidal laminae are rather formed at relatively stable physico-chemical conditions, whereas massive, granular and acicular Mn oxides might be formed by precipitation from an open water column. Laminated, dense layers with submetallic luster likely form from rapid precipitation of nanoparticles in supersaturated solutions. The alternating acicular and massive textures in the layer 1 indicate different rates of accumulation: Acicular textures are formed at slower precipitation with growth of acicular crystallites, maybe at low hydrothermal activity, whereas massive laminae are formed by rapid precipitation. This would suggest that the massive granular layer precipitated under more dynamic mixing conditions between low-T hydrothermal fluid and seawater (top), whereas the laminated and botryoidal layers precipitated from a low-temperature fluid without major disturbance below the sediment-seawater boundary (bottom). This would be in agreement with common interpretations of Mn crusts from other localities (see Hodkinson et

al., 1994). The rapid oxidation and precipitation of Mn oxides is linked to mixing with oxygenated seawater and may be bacterially mediated. Bacteria-like structures were observed with SEM in the massive layer 1. Submillimetre laminations within the dense and botryoidal layers could result from small-scale changes in the Eh-pH conditions, a self-organization during precipitation or microbial activity.

Principle sources of elements accumulating in oxide deposits in hydrothermal environments are dilute hydrothermal fluids and seawater characterized by different chemical compositions. Further contributions could be expected by leaching of sulfide deposits and host rocks in the subseafloor. Detrital minerals like clay and volcanic glass may also contribute to the elemental composition of the crusts. Depending on where particles composing a Fe-Mn or Mn deposit form, they may scavenge elements from different sources. The relative enrichment of individual elements in the different groups in the Logatchev field depend on the particle reactivity (determined by geochemical behavior in solution and at mineral-solution interfaces), enrichment process, relative amounts of Fe and Mn minerals in the crusts, colloid surface charge, amount of surface area available (decreases with maturity of the crust), concentration in solution, availability of ligands in solution, and physico-chemical conditions.

The sorption capacity of Fe and Mn oxide and hydroxide minerals for metals in solution is generally high, but depends on the crystal structure and crystallinity. Iron and Mn oxide minerals attract dissolved metals in different ways: The basic building block of Mn oxides is the MnO_6 octahedra. Manganese oxides take on layer structures, i.e., stacks of sheets of edge-sharing MnO_6 octahedra, or tunnel structures with chains of edge-sharing MnO_6 octahedra. An important structural characteristic of these oxides is the presence of Mn(IV) cation vacancies. The arising charge deficit is typically compensated by metal cations or protons. Layer charges also arise from the common coexistence of heterovalent Mn cations. Depending on the coordination and size, metal cations either form inner-sphere surface complexes or enter the vacancy sites. The interlayer regions can further host water molecules or hydrated cations without the formation of chemical bonds with the oxide layer. Electrostatic attraction of ions is also related to the surface charge of Fe and Mn oxides in solution, which arises from the dissociation of acid and base surface hydroxyl groups, with the attraction of positively charged complexes on negatively charged Mn oxide surfaces with $\text{pH}_{\text{ZPC}}=2-3$ and neutral or negatively charged species on slightly positively charged Fe-oxyhydroxide surfaces. This process is often accompanied by the formation of specific chemical bonds with the hydroxide functional groups, which may be followed by surface precipitation of specific hydroxide compounds as solid solutions with the original solid (Farley et al., 1985) at high surface loadings. Further enrichment processes of metals in Fe and Mn oxide minerals include the isomorphic substitution of metals for Fe^{3+} , Mn^{3+} and Mn^{4+} , and surface oxidation processes.

In the literature, there is some controversial use of the term “hydrothermal” Mn or Fe-Mn deposit. Here, this term is used in the more general meaning considering the hydrothermal environment of formation and the origin of the mineral-forming Fe and Mn. The enrichment of other elements, however, is either referred to as *hydrogenetic* (i.e., oxide particles are exposed to seawater and dominantly scavenge elements from seawater) or *hydrothermal*, when the oxide particles precipitate from low-temperature fluids and the deposits are not exposed to open seawater during trace metal accumulation.

The chemical composition of individual layers provides information about the composition of the parental fluid (seawater, low-temperature fluid) and compositional differences may be related to local or “regional” changes in fluid compositions in the growth environment of the particles (e.g., less seawater mixing, more leaching of sulfides). However, the applied method to investigate the chemical composition of Mn crusts cannot resolve small-scale changes between neither individual laminae composing botryoids or dense layers nor the alternating massive and acicular laminae in layer 1, but represent an integrated signal over some time of crust growth.

Different trends for different elements were observed: (1) Nickel, Li, and Mo are associated with Mn and strongly enriched in group I, group II and Mn-rich coatings of group III, with concentrations being variable within stratified Mn crusts. (2) Rare earth elements, HFSE, Al, Ti, P, Th, U, V and Pb enriched in Fe-rich coatings, very low concentrations in all Mn crust samples, but generally somewhat higher in group II crusts, depending on the Fe concentration. (3) Cobalt is the element with the strongest differences in concentration, being very high in Mn crusts of group I and Mn-rich coating, but strongly depleted in massive Mn crusts of group II. Its close association with the size of the Ce anomaly suggests a primary control by the accumulation rate. (4) Cobalt, Ni and Zn are generally enriched in Mn oxides, but display different trends: Zn is most enriched in the top layers of stratified Mn crusts and in massive Mn crusts of group II, whereas its concentration in Fe-Mn coatings is relatively low, without a preferential enrichment in either the Fe or the Mn oxide phase. Copper is most enriched in the stratified Mn crusts and variably concentrated in the other genetic types, and (5) Vanadium is generally more highly concentrated in the Fe-rich samples, but has significant enrichments in the Mn crusts as well. Vanadium correlates with Co and Ce/Ce* in the stratified Mn crusts. These different compositional trends show that individual elements have different sources and their relative enrichment is controlled by different parameters. Their geochemical signature will be discussed in detail in the next section.

With respect to the chemical composition, Fe-Mn coatings on rock substrates most closely resemble those of hydrogenetic ferromanganese crusts (except for lower Ni and Co contents), whereas pure Mn crusts significantly differ with respect to the Mn/Fe ratio, the strong enrichment of Cu, Mo and Li, and partly Zn, and the depletion of elements mainly attracted

by Fe oxides (HFSE, REE, Ti, Th, U). This general observation has been confirmed by radiogenic isotopes of Nd, Os, and Hf, displaying seawater-like signals in Fe-oxyhydroxide-rich coatings, and variable mantle-influenced signatures in pure Mn crusts and Mn-rich coatings (see below for discussion). Comparing the Logatchev stratified Mn crusts to hydrothermal Mn crusts in distal settings from other localities; the most obvious difference is the common enrichment of Cu and Co at Logatchev, which can be attributed to the high-temperature venting and formation of massive sulfide in the Logatchev field.

Macroscopic and microscopic observations, in agreement with digestion efficiency studies, have shown that the different deposits contain variable amounts of detrital material. Aluminium is often used as an index of detritus material, although it is also enriched by scavenging from seawater. The Mn crusts of groups I and II contain up to 1.5% Al, which is at least partly related to the presence of aluminosilicates, likely clay minerals. The Al content increases towards the top in the stratified Mn crust, which is in agreement with the observation of dispersed sediment particles in the top layers. The association of elements with Fe concentration in group II Mn oxides (Fig. 11) indicates the presence of a separate Fe oxyhydroxide phase, hosting elements like Ti, Zr, Th, U. The brownish color of the massive Mn crusts of group II also suggests the presence of an Fe mineral phase. The co-variation of Al and Fe in group II can be explained by the parallel enrichment of aluminosilicates and Fe oxyhydroxide particles. Although some Al may also be scavenged by the Fe phase, this cannot explain the absolute Al concentration. As the association of Fe and other elements associated with Fe oxyhydroxides is not given in group I Mn oxides, it can be assumed that Fe is incorporated into the manganate minerals.

The following sections discuss the geochemistry of Fe-Mn oxide deposits and the resulting implications for crust formation conditions and hydrothermal fluxes.

6.4.2 Radiogenic isotopes (Nd, Os, Hf)

The isotopic compositions of Nd, Os and Hf in the different crust samples show variable deviations from pure seawater signals.

As first approximation, it can be assumed that the isotopic composition of Nd, Os and Hf in the samples is equal to those of the parental solution the elements are scavenged from. Of course it has to be kept in mind, that isotopic compositions (as do elemental compositions) obtained via sample digestion always represent an integrated value over time and space. In the case of the stratified Mn crust profiles of group I, one sample encompasses several mm of crust, which might have grown at different formation conditions. The geochemical signal, however, is averaged within this sample. On a second point, REE being complexed at the surface of Fe and Mn oxides are characterized by continuous sorption and desorption in order to keep an exchange equilibrium with REE in solution and even after the exchange

equilibrium has been reached (Bau and Koschinsky, 2008), as long as the mineral surface is exposed to the solution. This implies an isotopic re-equilibration of Nd in case of changing $\epsilon\text{Nd}(0)$ of the solution which could overprint the primary signals in a changing growth environment. Despite these shortcomings, it seems to be valid to approximate the relative contribution of mantle Nd, mantle Os, and mantle Hf to the total concentrations of Nd, Os and Hf in the different crust samples. This enables for a general discussion of the hydrothermal influence during formation of the different types of Fe-Mn deposits in the Logatchev field and the specific geochemical behavior of different elemental groups during mixing of hydrothermal fluid and seawater.

Based on the respective isotopic compositions of Nd, Os, Hf in the two principle sources presenting the mixing endmembers (hydrothermal fluid and seawater) one can calculate the relative contribution of mantle Nd, Os, Hf in the crust:

$$X_{\text{MANTLE}} \cdot I_{\text{MANTLE}} + X_{\text{SW}} \cdot I_{\text{SW}} = 100 \cdot I_{\text{SAMPLE}} \quad \text{Equation 1}$$

Where X is the proportion of mantle source in %, and I is the isotopic signature of the endmember reservoir.

Neodymium

Reported values for the Nd isotopic composition of North Atlantic deep seawater (NADW) range between -13.5 (Piepgras and Wasserburg, 1987) and -12.6 (Jeandel, 1993), while MORB has a composition of about +9, determined close to the Rainbow vent field (Marques et al., 2006). Applying these values, the relative contribution of mantle Nd in the Logatchev I oxide deposits is about 31-33% in the Mn crust with the most radiogenic isotopic signal (225 GTV-3 D2). In the stratified Mn crust, the relative contributions of mantle Nd range between 21.6-24.8% and 9.6-13.4% (on top), while the Fe-Mn coatings show the most seawater-like signals with less than 1-5% mantle Nd. The slightly lower isotopic value in the more Mn-rich coatings in contrast to the Fe-rich coatings, associated with lower Nd concentration, indicates the preferential adsorption of seawater Nd on the Fe mineral phases whereas the Mn oxide phase hosts relatively more mantle Nd. The isotopic signature of the Fe-Mn coatings is similar to other, Atlantic hydrogenetic ferromanganese crusts (e.g., Piepgras et al., 1979, Abouchami et al., 1999). More radiogenic isotopic signatures of hydrogenetic ferromanganese deposits were reported from the MAR western valley slope at 13°N (-11.44, Davydov et al., 2009), which either reflect a small hydrothermal component in these deposits, or a more radiogenic seawater composition in this part of the Atlantic, which would increase the calculated mantle Nd proportions in the Logatchev crusts. The measured $\epsilon\text{Nd}(0)$ values of hydrothermal Fe-Mn oxide deposits are in the range of those reported in Davidov et al. (2009) for hydrothermal Mn crusts from the Atlantic (-4.72 to -11.08).

With the assumption of conservative mixing of seawater and hydrothermal fluid and that the mantle component is solely delivered via the high-temperature hydrothermal fluid, it is possible to estimate the amount of hydrothermal contribution of the element in the Mn and mixed Fe-Mn mineralizations based on the isotopic composition of the two mixing endmembers (seawater and hydrothermal fluid) and the respective concentrations of the element of interest.

This approach has been used by others (Mills and Elderfield, 1995; Frank et al., 2006) and will be discussed below. The relative concentrations of Nd in seawater and in the Logatchev high-temperature hydrothermal fluid are known (about 3 ng/kg and 460 ng/kg, respectively). The calculation shows that conservative mixing of 0.4% hydrothermal fluid with 99.6% seawater would result in the mantle-derived Nd in the Mn crust with the most radiogenic isotopic signal (group II crust) (Fig. 17). In the stratified Mn crust of group I, the relative hydrothermal fluid contributions range between 0.25% and 0.15% (on top), whereas the Fe-Mn coatings of group III indicate seawater/hydrothermal fluid mixing ratios >1500. The relative amount of hydrothermal Nd in the pure Mn crusts is similar to those calculated for one crust from the east wall of the MAR axial rift valley close to the TAG field, which shows a contribution of about 0.29% hydrothermal Nd (Mills et al., 2001). However, the calculation of Mills et al. (2001) is based on the PAAS-normalized Nd/Yb ratio as conservative mixing tracer. However, this ratio is known to be fractionated during REE scavenging onto Fe-Mn crusts (e.g., Quinn et al., 2006) and should not be used. Although Nd is not strongly affected by sulfide precipitation during the initial mixing of hydrothermal fluid and seawater (as evident from straight mixing lines for Nd between hydrothermal fluid and seawater at the emanation sites, in contrast to other elements like Cu, Co, and Zn), it behaves non-conservative in the presence of oxidic mineral surfaces and in the presence of anhydrite. This makes the assumption of conservative mixing questionable and suggests an underestimation of the proportion of hydrothermal fluid in the proposed mixture solution (i.e., the diffuse fluid).

Osmium

The present-day $^{187}\text{Os}/^{188}\text{Os}$ ratio of seawater is about ~ 1.06 (Levasseur et al. 1998; Burton et al. 1999), with an Os concentration of about 11pg/kg. Almost completely serpentinized ultramafic rocks from the Logatchev-1 hydrothermal field have $^{187}\text{Os}/^{188}\text{Os}$ ratios that are typical for upper mantle rocks (0.13, Meisel et al., 1991). Applying these isotopic compositions of the two possible sources of Os in the crusts, the relative contribution of mantle Os range between 78.5%-84.5% in the stratified Mn crusts (with the lower value in the top layer), meaning that Os in these deposits is dominated by mantle-derived Os. In contrast to Nd, where the Nd isotopic signal in the stratified Mn crust is lowest in the middle part, correlating with lower Nd concentrations, the Os signature in this part of the crust is more seawater-influenced, correlating with higher Os concentrations relative to the other parts of

the crust. The Fe-Mn coatings contain as much as 15% mantle Os in Mn-rich samples and negligible mantle Os in the Fe-rich samples.

Similar to Nd, one can calculate the proportion of high-temperature hydrothermal fluid in the parental solutions from which the oxides were formed. The geochemical behavior of Os at hydrothermal vent sites has been investigated by Sharma et al. (2000) and Gannoun et al. (2007). Straight correlations between initial $^{187}\text{Os}/^{188}\text{Os}$ and $1/\text{Common Os}$ and the linear covariation in $^{187}\text{Os}/^{188}\text{Os}$ versus Mg/Os or Sr/Os at the seafloor high-temperature emanation sites reported by Gannoun et al. (2007) indicate conservative behavior during mixing of hydrothermal fluid and seawater. This is somewhat surprising, as PGE are often enriched in sulfide minerals like chalcopyrite (e.g., Pasava et al., 2007, Kuhn et al., 2005), but may depend on factors like T, Eh, pH, and mixing time (conservative behavior restricted to low-temperature fluids?). From the Logatchev field, no high-temperature hydrothermal fluid concentration data are available. Based on data from massive sulfides, Kuhn et al. (2005) assumed, that the hydrothermal fluids at Logatchev have Os isotopic ratios similar to peridotites and Os contents of ~ 100 pg/l, which is similar to calculations by Cave et al. (2003) for the Rainbow vent field (90 – 260 pg/l.). Rare literature data range between 2.8 and 38 pg/kg in high-temperature fluids from the Juan de Fuca Ridge (Sharma et al., 2000) or up to 1000 pg/kg for TAG (Gannoun et al., 2007). At the Juan de Fuca Ridge, low-temperature fluids are more enriched over seawater with up to 98 pg/kg (Sharma et al., 2000), indicating a significant amount of mantle Os delivered by low-temperature alteration of oceanic crust. Sulfide minerals at Logatchev partly have mantle-like isotopic values so it can be reasonably assumed, that the hydrothermal endmember Os isotopic composition is close to the mantle value of 0.13. Applying a range in Os endmember fluid concentrations between 100 and 1000 pg/kg in the high-temperature hydrothermal solution, a conservative mixing between seawater and hydrothermal fluid would imply hydrothermal fluid contributions of 40% and 6%, respectively, in the most hydrothermally influenced Mn crusts of group I and of 2% and 0.2%, respectively, in the Mn-rich Fe-Mn coatings of group III. As for Nd, the Mn oxides in the Fe-Mn coatings contain more mantle-like Os compared to the Fe-oxides. The isotopic composition is negatively correlated with Os concentration with highest Os and most seawater-like signature in Fe-rich Fe-Mn oxide coatings. This shows that Fe oxyhydroxides deliver mainly radiogenic Os. A high-temperature fluid contribution as high as 40% to the parental solution the oxides were formed from can be excluded, so either fluid Os concentration much higher than 100 ppt have to be assumed or, alternatively, the addition of mantle Os in the course of fluid mixing is required. The latter could be caused by the lower-temperature leaching of Os from the host rock (as suggested for the enrichment of Os in diffuse fluids from the Juan de Fuca Ridge, see above) or, being the most likely process, by leaching of Cu-sulfides containing significant amounts of mantle Os (Kuhn et al., 2005). It has been suggested that vent fluids in ultramafic-hosted hydrothermal systems are enriched in Os relative to mafic-hosted hydrothermal systems, resulting from the alteration of PGE-rich

mantle rocks (Cave et al., 2003; Kuhn et al., 2005; Pasava et al., 2007). The Os content in hydrothermal fluids from the Logatchev-I hydrothermal field is thought to be controlled by the reaction with peridotite, and secondary Cu sulfides are distinctively enriched in Os (30–300 ng/kg, Kuhn et al., 2005) relative to TAG sulfides (<1pg/kg) and Rainbow sulfides (3–10 ng/kg – Cave et al., 2003). In addition, seafloor weathering of abyssal peridotites also provides a significant source of mantle Os to the ocean (Snow and Reisberg, 1995). Thus the dominance of mantle Os in the Mn crusts is possibly caused by a combination of both high fluid Os concentrations and addition of mantle Os to a fluid mixture at lower temperatures due to sulfide leaching or low-temperature mantle rock alteration.

In hydrothermal plumes, the Os isotopic composition is indistinguishable to open seawater (Woodhouse et al., 1999), indicating that Os is non-conservative during mixing of high-temperature fluid and seawater, in close association with Cu (Cave et al., 2003). This is in agreement with the results of this study, with Fe oxyhydroxides having seawater-like Os signatures and it implies that high-T vent sites do not contribute to the marine Os budget. However, low-T vent sites in ultramafic-hosted settings may provide significant Os fluxes into the ocean.

The Os concentration in pure Mn crusts is significantly lower compared to Fe-rich oxide coatings, which have similar Os concentrations as hydrogenetic crusts. In open seawater, Os likely exists as Os(VIII) oxyanion (Byrne, 2002) and or organic complexes, preferentially accumulating on Fe oxyhydroxide mineral surfaces. However, the oxidation state of Os and its speciation may change under more reducing conditions, which could explain the relatively strong association with Mn oxide phase in hydrothermal crusts. Yamashita and coworkers (2007) suggested a reductive removal of Os in oxic sediments, where it is mainly bound as Os(IV) to ferromanganese oxides. Changing partition coefficients related to changing redox state has also been suggested for V in hydrothermal Mn crusts from the Logatchev field.

Osmium isotopic data from hydrothermal Mn crusts from the east wall of the axial rift valley 3 km east of the TAG field also show an unradiogenic Os input (30 ppt, $^{187}\text{Os}/^{186}\text{Os}=4.2\text{--}6.8$; Ravizza et al., 1996), which shows that supply of ocean mantle-derived Os to seawater is not strictly limited to high temperature hydrothermal vents making Os isotopes a sensitive tracer of low-temperature hydrothermal circulation on the seafloor. The source of Os on these precipitates is either low-temperature hydrothermal fluids channeled from the TAG field or oceanic crust leached by low-temperature fluids.

Chimney material consisting of pure Fe oxide (goethite) shows only a limited contribution of mantle Os of about 15%.

Hafnium

As for Nd and Os, the deviation of $\epsilon_{\text{Hf}}(0)$ of the Mn crusts from seawater clearly reflects a significant contribution from hydrothermal venting of Hf leached from igneous rocks. However, the background seawater isotopic signature at Logatchev-1 is ill constrained: Godfrey et al. (2009) reported values of $\text{NADW} = +1 \pm 0.8$, while ferromanganese crusts of the Atlantic reflecting modern seawater Hf range between -1 and +2.1 (Van de Fliert et al., 2007 and references therein). The calculations based on $\epsilon_{\text{Hf}}(0)$ of seawater = +2 and of mantle rocks = +8, the stratified Mn crusts contain about 28% mantle Hf, whereas the Fe-Mn-coatings contain less than 5% mantle Hf, with the most seawater-like signal in the Fe-rich parts of these coatings (as also observed for Nd, Os). The negative correlation of Hf concentration and $\epsilon_{\text{Hf}}(0)$ indicates that seawater-Hf is preferentially scavenged onto the Fe phase. This suggests that primary Fe oxyhydroxide particles formed at present-day hydrothermal emanation sites are not a major carrier of unradiogenic Hf into the ocean, contrasting to previous suggestions by Bau and Koschinsky (2006). This conclusion is in agreement with recent work by Van de Fliert et al. (2004, 2007) precluding a dominant hydrothermal contribution of dissolved or colloidal Hf to the seawater Hf budget. However, as mentioned above, lower ϵ_{Hf} isotopic values of dissolved seawater Hf may persist, and a calculation with these values would result in small but significant contributions of hydrothermal Hf in the ocean water column at Logatchev. Hydrothermal Mn crusts do show significant contributions of mantle Hf (this study, Godfrey et al., 1997), but the hydrothermal flux of Hf seem to be restricted to the high-temperature emanation sites. No data are available for non-buoyant hydrothermal plumes but is assumed, that the Fe oxyhydroxide particles in the Fe-Mn oxide coatings at Logatchev were at least partly formed in the hydrothermal plume. Further uncertainties on these calculations arise from the ill-constrained mantle isotopic signature in the MAR segment hosting the Logatchev hydrothermal field.

For Hf, is not possible to estimate the relative proportion of hydrothermal fluid as concentrations of Hf in hydrothermal fluids are unknown. During this project, a single hydrothermal fluid sample has been investigated for HFSE composition, with 114 pM Zr and 1.4 pM Hf, corresponding to a chondritic Zr/Hf ratio (which implies that high-temperature hydrothermal fluids are not a major source of HFSE but that they carry a chondritic Zr/Hf signal). Applying the above-mentioned concentration of Hf in a hydrothermal fluid, mixing with seawater containing about 1.4 pM Hf (Rickly et al., 2009), conservative mixing would indicate a hydrothermal fluid contribution of about 10% in the stratified Mn crusts. As this seems to be quite high for fluid-seawater mixtures, the Hf fluid concentration is either much higher than those measured or mantle Hf or is added to the fluid mixture. High field strength elements have been shown to be mobile during seafloor weathering of abyssal peridotites (Niu, 2004) and may be released to the circulating low-temperature hydrothermal fluids in ultramafic-hosted hydrothermal systems. As HFSE are not or only to a very low extent

incorporated into sulfide minerals, Hf should behave conservative during sulfide precipitation, which implies that leaching of sulfide minerals would not contribute significantly to the Hf budget of the solutions.

Pure Fe oxides sampled from an inactive chimney (272 ROV) carry a strong mantle Hf signal (+8.1). This is in contrast to the Os signature of the same sample, which is dominated by seawater Os and could argue for a primary precipitate.

Overall, the relative amount of mantle Nd, Os, and Hf depends on the concentrations in the two principle sources (i.e., at very low seawater concentrations relative to the mantle source a small fraction of hydrothermal fluid can contribute large quantities of the element with a mantle signature, as for example Nd), and the addition or removal of an element during fluid mixing and reaction with solid phases. Whereas the majority of Os in the crusts originates from a mantle source (more than 80%), only about 22% of Nd and 28% of Hf in the stratified Mn crusts are mantle-sourced. This shows that the relative contribution of different sources to the elemental content within the crusts might be quite different, depending on the concentrations in the endmember fluids and their different geochemical behavior in aqueous solutions.

Among the three elements Nb, Os, and Hf, Os has the highest partition coefficient for MnO_2 , related to the speciation in solution. The discrepancy of apparent hydrothermal fluid proportions based on Nd and Os isotopes can likely be attributed to both removal of Nd (reaction with oxides or anhydrite) and addition of Os (due to leaching of Cu-sulfide minerals and/or ultramafic host rocks) during mixing. Furthermore, Nd is in exchange equilibrium with surrounding solution and continued sorption and desorption reactions would result in isotopic re-equilibrium with the (changing) parental fluid, while Hf and Os are probably not exchangeable.

6.4.3 Transition metal accumulation in hydrothermal Fe-Mn deposits

Copper: The Mn crusts are strongly enriched in metals like Cu, Co, Zn, Ni, which are commonly rather depleted in hydrothermal Mn deposits. Especially Cu shows exceptional high concentrations with up to 2% in stratified Mn crusts. As evident from SEM-analyses, the Cu is bound to the Mn phase and not present in minor sulfide grains. As shown by Sherman et al. (2010), Cu in 7 Å manganates is present as inner-sphere complexes but also to a significant amount structurally incorporated into the MnO_2 layer at pH8, a similar enrichment process as described for Ni (Peacock et al., 2007). The strong enrichment in Cu relative to hydrogenetic crusts may thus partly be related to the presence of 7 Å manganates. The relatively small amounts of Cu in hydrogenetic Fe-Mn crusts (<1000 ppm) are probably a function of both the organic complexation of Cu in seawater preventing extensive scavenging and the smaller proportion of well-crystalline Mn minerals. Manganese nodules, in contrast, contain Cu

concentrations of more than 1%, related to its mobilization during diagenesis. As previously described, hydrothermal Mn crusts without any relation to a high-temperature hydrothermal vent site generally have very low concentrations of Cu (<500 ppm), additional factors besides the mineralogy are required, favoring the Cu enrichment. At Logatchev-1, the high Cu content can be related to the circulation of high-temperature hydrothermal fluids containing significant amounts of dissolved Cu, which precipitates as chalcopyrite/isocubanite due to cooling and mixing below or at the seafloor. Massive sulfides from the Logatchev field occurring in so-called smoking crater settings, are dominated by Cu sulfide minerals, which has been related to the regional and local geological setting in an ultramafic-hosted location. Between the different types of Fe and Mn deposits at the Logatchev field, the highest amounts of Cu were observed in the stratified Mn crusts. As deduced from the isotopic composition of Os and REY distribution, these deposits are formed by fluids containing variable amounts of metals leached from the host rocks. Copper is most likely delivered via the leaching of Cu sulfides, which has been discussed as possible source of Os enrichment in the same deposit. Evidence for a redistribution of Cu within the Logatchev field comes from the observation of secondary Cu sulfides formed from the reaction of cooled hydrothermal fluid with primary Cu sulfides below a silicified cap rock at the Irina II mound (Petersen et al., 2009). Although most Cu will immediately be incorporated into secondary sulfides again, some Cu probably stays in solution. Leaching of massive sulfides as process leading to the enrichment of metals like Cu, Zn, Pb in hydrothermal Mn crusts has also been proposed for various island arc and backarc settings deposits (e.g., Yap arc (Hein, 1992), Mariana arc (Hein et al., 2008). However, the Cu concentration in such deposits is still more than 1 magnitude lower compared to the Logatchev field, whereas Zn and Ni are partly higher. This may be related to the mineralogy of the leached sulfides; Logatchev only contains minor amounts of ZnS, but massive Cu sulfides.

Th Cu enrichment in group II Mn oxides is variable but generally lower compared to group I, which indicate less contribution from low-temperature hydrothermal fluid.

Vanadium: Vanadium in seawater is present as oxyanion HVO_2^- , and is in hydrogenetic crusts mainly associated with the FeOOH phase (Koschinsky and Hein, 2003). Its relatively strong enrichment in the hydrothermal Mn deposits at Logatchev is likely related to the presence of more reduced vanadyl species like VO_2^+ , which would preferentially bind to the Mn oxide phase. Similar phase associations were observed in hydrothermal crusts from the North Fiji Basin (Koschinsky and Hein, 2003). It can also be speculated that V gets enriched via reductive scavenging on Mn oxide minerals.

Molybdenum: Molybdenum is closely associated with the Mn oxide phase and similarly strong enriched in all Mn oxide crusts including the Mn-rich coatings of group III, being much higher than in hydrogenetic crusts and Mn nodules formed by diagenetic processes. The

concentration of Mo in Fe-rich coatings is similar compared to hydrogenetic crusts. The enrichment of Mo in hydrothermal Mn crusts has been recognized before (Rodgers et al., 2001, Kuhn et al., 2003), being attributed to its different speciation in reduced, acidic hydrothermal fluids relative to seawater (Kuhn et al., 2003). Its speciation in acidic, low-temperature hydrothermal fluids as octahedrally coordinated heptamolybdate, may allow for its preferential adsorption onto Mn oxides via the formation of inner-sphere surface complexes (Kuhn et al., 2003). Further, Mo^{6+} could substitute for Mn^{4+} in the crystal lattice due to similar ionic radii. Whereas Mo is highly mobile in oxic seawater, its mobility is strongly reduced at anoxic conditions like hydrothermal fluids, and its concentration in such fluids is below seawater concentration (e.g., Schmidt et al., in press). As primary hydrothermal fluids at Logatchev-1 are depleted in Mo, the Mo enrichment in the Mn crusts might be derived from sulfide leaching or from low-temperature alteration of the underlying rocks. In addition, the relatively well crystallinity of manganates at Logatchev with their high sorption capacity probably further supports the enrichment of Mo. The Mo concentration clearly distinguishes these deposits from those formed by hydrogenetic processes.

Lithium: Lithium is strongly enriched in all Mn-rich oxide deposits in the Logatchev field, with concentrations up to 1500 ppm, being much higher compared to Mn nodules and hydrogenetic ferromanganese crusts (for comparison see Jiang et al., 2007; Hein et al., 1997). Iron-rich coatings of group III are strongly depleted. Besides Mo, Li concentrations in Fe-Mn oxide deposits indicate best a hydrothermal formation environment. Similarly high Li contents as in the Logatchev field were reported from other hydrothermal localities (Rodgers et al., 2001; Chan and Hein, 2007; Jiang et al., 2007), associated with 10Å manganates. Hydrated Li ions in seawater and hydrothermal fluids are almost exclusively sorbed on the negatively charged surface of MnO_2 by coulombic force (loosely bound). Lithium is typically enriched in high-temperature hydrothermal fluids (e.g., Schmidt et al., 2007) and is characterized by a conservative mixing behavior. However, the Li concentration in hydrothermal Mn crusts cannot simply be related to the Li concentration in hydrothermal fluids: Li in diffuse fluids is only slightly higher concentrated compared to seawater. At low-temperature rock alteration at high water-rock ratios, Li is rather removed from solution and bound to secondary alteration minerals. Further, Li concentrations are surprisingly similar in hydrothermal Mn deposits from different geological settings, independent of high-temperature fluid venting. Considering these, the Li enrichment in Mn oxide precipitates of hydrothermal environments may dominantly be related to the different mineralogy and crystallography of Mn oxides, rather than to the hydrothermal fluid source. However, the strong contrast of Li concentrations between Fe-rich and Mn-rich oxide coatings is not only a function of the preferential adsorption of Li to Mn oxides but indicates a Li-enriched source during the formation of the Mn oxide particles. The discrepancy is not yet fully understood.

Nickel: Similar to Mo and Li, Ni is generally enriched in all Mn-rich deposits from the Logatchev field. In the lower parts of the stratified Mn crust, however, Ni concentrations are low. Depending on solution pH, Ni is both substituted isomorphically for Mn in the manganese layer and sorbed at vacant Mn layer sites in the interlayer, with a strong preference for the first site at circumneutral pH and for the second at acidic pH (Manceau et al., 2007). The transformation from surface complexation to structural incorporation into phylломanganate provides a potentially irreversible sink for Ni in seawater (Peacock and Sherman, 2007). Nickel concentration in the Logatchev hydrothermal fluid is not known. The ultramafic host rock nature suggests a preferential leaching of Ni, however, Herzig et al. (2007) have shown, that Ni might be preferentially mobilized from mafic rocks (gabbro-norites), similar to Cu and Zn.

Cobalt: Similar to Ce, oxidative scavenging is evident for Co, which is oxidized to Co(III) by Mn oxides (Murray and Dillard, 1979, Mannheim and Lane-Bostwick, 1988). Co(III) is substituted isomorphically for Mn in the manganese layer (Manceau et al., 1997), and the steric match between Co(III) (0.54Å) and Mn(IV) (0.53Å) is believed to be responsible for the selective enrichment of cobalt in manganese oxides (Burns, 1976). The Co content generally decreases with increasing growth rate from hydrogenetic to hydrothermal crusts. As soon as the particles are in contact with bottom seawater, the Co concentration is controlled by the growth rate (group II, group III). The strongly Co-enriched hydrothermal Mn oxides of group I in the Logatchev field suggest an additional Co source, which argues against hydrogenetic sorption as main enrichment process. In contrast, Fe-Mn oxide coatings have been shown to be mainly influenced by hydrogenetic sorption and the relatively high Co concentration in these precipitates rather indicates slow accumulation rates. A detailed discussion of growth rates is given below.

Zinc: While the Zn concentration in Fe-Mn oxide coatings is relatively low and independent of the relative amount of Fe or Mn oxides, its concentration in pure Mn crusts varies between low and very high concentrations (about 2 orders of magnitude) being highest in the top layers of stratified Mn crusts and in Mn crusts of group II. As hydrated cation, Zn is preferentially attracted by Mn oxides. Zinc is sorbed in the interlayer at vacant Mn layer sites, forming inner-sphere surface complexes with the three surface oxygen surrounding a vacancy (Manceau et al., 2007). In addition, Zn may occur as loosely bound metal similar to Cu and Ni, as been shown in leaching experiments by Cronan et al. (2002). Its decoupling from Cu concentrations suggests that Zn is not sequestered from sulfides, in agreement with the low abundance of Zn sulfides in massive sulfides at Logatchev-1 (except for Irina II). Group II Mn oxides are strongly enriched in Zn. Assuming a hydrothermal source of Zn, the different Zn concentrations in botryoidal and laminated layers of group I and those in the top layers and in Mn oxides of group II may result from different mixing ratios of hydrothermal fluid and

seawater and/or different Zn concentrations in the fluid. Otherwise, enhanced scavenging of Zn from seawater in group II can alternatively cause the enrichment of Zn.

Al, P, Ti, U, Th, HFSE, Pb

The strong affinity of this group of elements to Fe-oxyhydroxide particles in the Logatchev field is in agreement with their association with the Fe oxyhydroxide fraction in hydrogenetic ferromanganese crusts (Koschinsky and Hein, 2003) and can be related to their speciation in solution. In addition, detrital minerals can contribute significant amounts of Al, Ti, HFSE and Th. Except for Pb, their concentration in hydrothermal fluids is low. Lead and U occur mainly as negatively charged carbonate complexes in seawater, whereas P occurs as oxyanion (Byrne, 2002). Thorium, Ti, and HFSE form neutrally and negatively charged hydroxide complexes, likely enriched via the formation of surface precipitates. For a more detailed discussion of solid phase associations, see Koschinsky and Hein (2003).

6.4.3.1 Implications of REY composition

The rare earth element distribution in the diverse ferromanganese and manganese deposits of group I, group II and group III at the Logatchev-1 hydrothermal field is relatively similar with respect to the relative fractionation between LREE, MREE and HREE, despite huge differences in the absolute concentrations. However, the variable Ce anomaly ranging from strongly negative to positive, as well as subtle but significant differences in the Pr/Gd ratio and the size of the Eu anomaly indicate differences in the growth conditions.

The REY composition of Fe- and Mn oxyhydroxide minerals is controlled by competitive solution and surface complexation of REY, which in turn depend on pH, Eh, T, solution composition, and the relative amount of Fe and Mn oxides. In oxic seawater, the REY speciation is dominated by carbonate complexes with stronger HREE complexation relative to LREE (at pH8: $\text{REY}(\text{CO}_3)_2^-$). The competition between REY-complexing carbonate ligands in solution and REY^{3+} -and REY-carbonate-complexing hydroxyl ligands on the mineral surface (Quinn et al., 2006) defines an equilibrium and results in the fractionated incorporation of REY, with the lowest partition coefficients for HREE and Y. Seawater-normalized REY patterns of ferromanganese crusts thus generally show a decrease from LREE to HREE. The fractionation of REY during surface complexation is different for coexisting Fe oxyhydroxides and Mn oxides, resulting in different REY distributions with preferential scavenging of La, Y, Gd, and Lu on Mn oxides (Bau and Koschinsky, 2009).

In contrast to trivalent REY, the Ce enrichment in Fe and Mn oxide particles is directly controlled by the growth rate of the ferromanganese oxide, with oxidative sorption of

dissolved Ce(III) on Fe and Mn oxide minerals being the main pathway of Ce incorporation in ferromanganese oxides (Bau and Koschinsky, 2009; Takahashi et al., 2007). Since Ce(IV) is sparingly soluble (De Baar et al., 1988; Byrne, 2002), the sorbate remains at the surface of the Fe–Mn oxide after oxidation took place, progressively leading to Ce enrichment. Cerium (IV) is likely retained in the interlayer on top of vacant Mn layers sites (Takahashi et al., 2007). The Ce oxidation might be pH dependent (Tanaka et al., 2010). The role of biological activity controlling the size of the Ce anomaly has recently been investigated by Tanaka et al. (2010), demonstrating that under circumneutral pH conditions soluble ($<0.2 \mu\text{m}$) Ce(IV) can be stabilized in natural environments, where microorganisms are ubiquitously distributed. This process would reduce the Ce-anomaly in the solids showing that microbial activities can cause specific redox mechanisms for trace elements, which cannot be explained by inorganic chemical processes.

Fe-Mn oxide coatings:

The absolute concentrations and the general shale-normalized REY distribution of Fe-rich Fe-Mn oxide coatings on rock substrate closely resemble those of hydrogenetic ferromanganese crusts: an increase from the LREE to MREE, a positive Ce anomaly and a negative Y anomaly. The only difference is the subtle depletion from the middle to the heavy rare earth elements. Some samples apparently display a small positive Eu anomaly (above those resulting from the Eu depletion in shales relative to its neighbors Sm and Gd); however, this may also result from a positive Gd anomaly. The relative REY distribution implies that REY accumulation is mainly controlled by equilibrium sorption of REY from oxic seawater, which is in agreement with Nd isotopic data showing $\epsilon\text{Nd}(0)$ values mostly indistinguishable from hydrogenetic ferromanganese crusts from the NE Atlantic (Abuchami et al., 1999; Bogdanov et al., 2008).

The lower REY content and the smaller Ce anomaly in Mn-rich oxide coatings relative to the Fe-rich coatings is likely be caused by differences in the source fluid composition/physico-chemical conditions/growth rate during sorption on Fe oxyhydroxides and Mn oxides and cannot be explained by different distribution coefficients of REY in Fe oxyhydroxides and Mn oxides, as discussed in Bau and Koschinsky (2009). The latter has been attributed to a combination of complex REY speciation in oxic seawater and mineral-specific surface complex stabilities (Bau and Koschinsky, 2009; Ohta et al., 2009). As oxidative Ce adsorption is not preferentially associated with one phase or the other, the size of the Ce anomaly in the Fe-Mn oxide coatings, being quite different between both types, rather indicates different formation conditions. This implies that the Fe oxyhydroxide particles and the Mn oxide particles making up the Fe-Mn oxide coatings are formed in different environments or at different growth rates. The lower REY concentrations and lower Ce anomalies are correlated with a slightly more radiogenic Nd composition in Mn-rich coatings which seems to confirm

that the Mn oxides and the Fe oxides in these deposits are formed in somewhat different growth environments although both Fe oxides and Mn oxides almost exclusively scavenge seawater-derived REY. It has to be mentioned that the differences in isotopic composition are within the standard error of the measurement.

The Fe oxyhydroxides accumulating in these coatings are likely formed in the hydrothermal plume, although some contribution of background material cannot be excluded (see also discussion of growth rates). The chemical composition of these particles is very similar to those making up ferromanganese crusts, without any significant contribution of hydrothermally sourced elements. In contrast to the REY distribution in fresh plume particles from the Rainbow field, TAG field and EPR site 9°45'N (Edmonds and German, 2004; German et al., 1990; Sherell et al., 1999), which show more seawater-like REY distribution patterns, Fe oxide particles in rock coatings from Logatchev are characterized by an equilibrium sorption of REY. Assuming that plume-derived Fe-oxyhydroxide particles accumulate in these coatings, this difference might be attributed to long-term continuous scavenging/sorption-desorption, thereby progressively changing the LREE/HREE fractionation and the relative Ce enrichment from a non-equilibrium pattern to an equilibrium distribution. Similar relationships between the age of the particles and the relative fractionation of REY have been observed within the TAG plume. Alternatively, the apparent relationship between particle age and REY distribution could simply result from mixing with background Fe oxyhydroxide material with more fractionated REY distribution, as discussed in Sherell et al. (1999). Although the experimentally determined equilibrium exchange between solution and fresh Fe oxide particles is reached within 15 min (Bau, 1999; Quinn et al., 2006), arguing against a temporal effect on LREE/HREE fractionation, REY sorption onto Fe oxyhydroxides in natural systems may be kinetically controlled, or the REY uptake in hydrothermal plumes is limited by the dissolved REY concentration, leading to a quantitative scavenging. On the basis of the REY distribution, the Fe oxide fraction in the Logatchev oxide coatings could be both derived from the plume or be dominated by background material not derived from the recent hydrothermal plume but being much older. As also the Fe oxyhydroxide particles in hydrogenetic crusts far away from any hydrothermal plume are thought to ultimately been formed in hydrothermal plumes (Bau and Koschinsky, 2006), this might be a rather philosophic differentiation.

Mn oxide particles are likely formed in an environment somewhat more influenced by low-temperature hydrothermal fluids and at faster precipitation rates with less time to accumulate Ce(IV). As discussed before, Mn oxide particles are unlikely to have been formed in the recent hydrothermal plume but rather precipitate in the bottom water close to or at the emanation sites of low-temperature hydrothermal fluids.

All Fe-Mn oxide coatings display a size of the Ce anomaly being significantly lower relative to hydrogenetic ferromanganese crusts, likely resulting from faster accumulation time of the crust and thus less time to enrich Ce(III) via surface oxidation to Ce(IV), which is in agreement with the significantly lower Co contents compared to the range of Co concentrations in hydrogenetic crusts (see below).

Mn crusts:

In contrast to Fe-Mn coatings on rock substrates, the Mn crusts in the Logatchev hydrothermal field are more influenced by low-temperature hydrothermal fluids and partly formed at much faster accumulation rates (see below).

Stratified Mn crusts display REY distributions with a decrease from the MREE to HREE, negative Y anomalies, positive Ce anomalies and LREE depletion. The two principle sources of REY in Mn crusts of the Logatchev hydrothermal field - seawater and diffuse hydrothermal fluids – display PAAS-normalized HREE enrichment and positive Y anomalies (Fig. 18). The relative HREE+Y depletion in the Mn crusts from the Logatchev field thus indicates equilibrium fractionation, with smaller partition coefficients for HREE and Y from a solution with similar REY speciation as normal seawater (indicates carbonate solution complexation) and cannot be used to trace the influence of a hydrothermal REY source. The decoupling of Ce, as obvious from the positive Ce anomalies, is evident for an oxidative scavenging enrichment. While the overall REY distribution and speciation in the source solution is likely similar to seawater (as also discussed in detail below), the small but significant positive Eu anomaly in all samples of the profile indicate a contribution of Eu from a high-temperature fluid source. Europium can only be decoupled from its REE neighbors in high-temperature (>250°C), reducing hydrothermal solutions, where Eu is stable as Eu^{2+} . The reduced Eu has a different geochemical behavior during fluid-mineral interactions, which commonly leads to strong positive Eu anomalies in high-temperature hydrothermal fluids. Diffuse hydrothermal fluids often show even larger Eu anomalies, attributed to the precipitation of sulfide and sulfate minerals in the subsurface, discriminating Eu^{2+} during REY incorporation (Mills and Elderfield, 1995). The Eu anomaly in solution is a relatively sensitive tracer of high-temperature hydrothermal circulation. In low-temperature hydrothermal fluids, thermodynamic calculations predict Eu to be present in its oxidized, trivalent state, and the Eu anomaly of the solution should be inherited in the crust due to the non-fractionated incorporation of Eu relative to its neighbors Sm and Gd (as for example also observed in mussel shells growing at the emanation sites of diffuse fluids in the Logatchev field – Bau et al., 2010). The small Eu anomaly in the Mn oxide precipitates apparently indicate a very

small contribution of hydrothermally-derived Eu in the Mn oxide precipitates from the Logatchev field, which is in contrast to estimations based on Nb isotopes.

The pure Mn coatings and the massive Mn crusts of group II have similar REY distributions as stratified Mn crusts of group I, but display strongly negative to neutral Ce anomalies, which can be attributed to the precipitation of Mn oxides from a Ce-depleted source fluid with fast precipitation rates, and only very small positive Eu anomalies.

As derived from the isotopic signature of Nd, the contribution of mantle Nd range from 10% to 20% in the stratified Mn crusts, with lowest contribution on top. The massive Mn crusts of group II at least partly have somewhat higher contributions of around 30%. If one assumes a conservative mixing behavior of all REY, and that all mantle Nd is gained from the high-temperature hydrothermal fluid, simple mixing calculations using the relative contributions of high-temperature fluid and seawater based on the mantle Nd result in an REY distribution of the hypothetical parental fluid with seawater-like pattern but less depletion of LREE to MREE, neutral or small negative Ce anomalies and significant positive Eu anomalies, a pattern typical for diffuse hydrothermal fluids from various high-temperature hydrothermal locations (see Bau et al., 2010; Fig. 18). The most mantle-influenced mixing scenario is quite similar to diffuse fluids sampled at the Irina II vent site except for the neutral Ce anomaly in the diffuse fluid (which indicates higher fluid proportion in the low-temperature fluid). When normalizing the REY concentrations in the different Mn crusts to their abundances in deep seawater, all samples show positive Ce anomalies. As mixtures of high-temperature hydrothermal fluids and seawater will be variably less depleted in Ce relative to seawater, variable Ce anomalies in the Mn oxide deposits do not automatically mean different accumulation rates, but may also be explained by variable Ce anomalies in the source fluid. The sample with the strongest negative Ce anomaly (0.23, group II) must have been accumulated very fast from almost pure seawater (with respect to REY composition), having a Ce anomaly of about 0.20. In contrast, the Ce anomaly in calculated fluid mixture with about 30% mantle Nd (0.62) is similar to those in the respective Mn crust sample (225 GTV-3 B2, 0.61) which would imply a very fast precipitation and accumulation without major oxidative Ce enrichment but equilibrium fractionation with respect to HREE. One has to mention, that the REY distribution in the low-temperature hydrothermal fluid might have been modified before by the precipitation of sulfide and/or sulfate minerals in the subseafloor however, this would not strongly affect the Ce depletion. Stratified Mn crusts of group I with positive Ce anomalies are generally precipitated at lower growth rates than Mn oxides of group II.

The calculated Eu anomaly in a conservative fluid mixture with 10-30% Nd derived from a high-temperature hydrothermal source is far bigger than the Eu anomaly measured in the Mn crusts. This disagreement of hydrothermal fluid contributions calculated from Nd isotopes and

those based on the size of the Eu anomaly in the crust requires either a depletion of Eu from solution before crust deposition (not evident from diffuse fluids from the Logatchev field) or a discrimination of Eu during REY incorporation (different speciation, some Eu^{2+} present) or an additional source of mantle REY without a Eu anomaly. The latter could be represented by the rocks hosting the Logatchev field, leached at low temperatures.

The group II Mn crusts with negative Ce anomalies are characterized by a stronger Pr/Gd fractionation relative to group I and III samples. This general trend has also been observed for hydrothermal plume particles (see above, German et al., 1990) and could indicate that fast-growing Mn oxides accumulate LREE without full equilibrium fractionation (i.e., inherited signature of parental solution).

In the stratified Mn crust profile, the Ce anomaly co-varies with the total REY concentrations. This relationship is not easily explained by the growth rate but may imply differences in the crystallinity of the Mn oxides. The size of the Eu anomaly co-varies with the size of the Ce anomaly. Using the Eu anomaly as an independent measure of hydrothermal fluid contribution, the most hydrothermally influenced layer is characterized by the lowest REY enrichment and strongest Ce anomaly. This is in agreement with Nd isotopes. The strongest mantle Nd signal is correlated with the lowest Nd concentration and increasing REY concentrations are accompanied by decreasing proportion of mantle Nd (and decreasing Eu anomaly). This could be related to an overprint of a primary signal by continuous sorption from a more seawater-like source, possibly in conjunction with recrystallization processes, or a simple change in the parental fluid composition. The smallest Ce anomaly in the top layer, which shows the lowest contribution of hydrothermal Nd and Eu can be related to slow precipitation from a strongly Ce depleted solution, whereas the layer with strongest positive Ce anomaly likely have been more affected by hydrothermal solutions (i.e., smaller negative Ce anomaly in the solution). The differences in absolute REE concentrations could be related to differences in the crystallinity. There is also an apparent co-variation of REY and Zr in the stratified Mn crusts, which are both thought to be exclusively or dominantly bound to the Mn oxide phase. Although this co-variation may indicate dependence from the growth rate, it can also be related to variable crystallinity or surface area with implications mainly for hydroxide forming elements like REE and HFSE.

Considering the different lines of evidence, it can reasonably be concluded that the majority of REE origins from seawater (Nd isotopes, small Eu, relative distribution of REY indicate fractionated sorption from solution with carbonate complexation), but with variable contributions from a high-temperature hydrothermal source. Mn crusts of type II must be immediately precipitated from variable mixtures of low-temperature hydrothermal fluid and more oxygenated seawater, without major Ce enrichment. Stratified Mn crusts of type I

formed at slower precipitation rates, with equilibrium fractionation of REY between solution and mineral surface.

Unresolved questions arise from the correlation of Ce anomaly and Y/Ho ratio and the low Eu anomalies especially in those group II Mn oxides having the highest mantle Nd. Further, microbial activity can significantly modify the REY distribution in solids, as shown by Tanaka et al. (2010) and Takahashi et al. (2010). Taking organic complexation of Ce^{4+} into consideration, microbial activity might explain the negative Ce anomalies in group II Mn oxides.

The pure Fe oxide crusts are characterized by very low REE concentrations, with depletion in LREE, flat to slightly increasing MREE to HREE, variably negative Ce anomalies, positive Eu anomalies and neutral to positive Y anomalies. This REY distribution is very similar to Fe oxide plume particles from TAG, 9°50'N, EPR, and Rainbow (German et al., 1990; Sherrell et al., 1999; Edmonds and German, 2004) and could represent unfractionated REY uptake from seawater or dilute hydrothermal fluids. Fresh Fe-oxide particles filtered from a cooled hydrothermal fluid mixed with seawater in a ratio of about 1:10 displays a REY distribution and concentration identical to the calculated REY distribution in the fluid (no Ce anomaly, pos. Eu anomaly, small pos. Y anomaly), evident for a quantitative uptake of dissolved REY during oxide formation (unpublished data).

6.4.3.2 Implications of HFSE signature

[1] Little is known about the aqueous geochemistry of the HFS elements Zr, Hf, Nb and Ta. The distribution of HFSE in hydrogenetic ferromanganese crusts and deduced implications for the geochemical behavior of these elements in seawater is discussed in detail elsewhere (Schmidt et al., in prep.). *Chapter 7* provides a summary of the major findings of this study. The concentration and distribution of HFSE excludes a dominant enrichment via the incorporation of detrital aluminosilicates but proves scavenging of dissolved complexes from seawater. As for other highly charged trace elements that easily hydrolyze in seawater (e.g., Th, Ti) scavenging of Zr, Hf, Nb, Ta likely occurs via the initial formation of inner-sphere surface complexes with hydroxyl groups, followed by surface precipitation of specific hydroxyl compounds (Farley et al., 1985). Non-chondritic Zr/Hf and Nb/Ta ratios in seawater prove the independent geochemical behavior of homolog elements in aqueous environments. It has been shown, that hydrogenetic ferromanganese crusts are characterized by strongly fractionated elemental ratios both relative to chondrite and relative to seawater (Schmidt et al., in prep). The fractionated incorporation of HFSE from solution can be related to differences in (hydroxide) complex stabilities in solution and on mineral surfaces between the two elements (Baes and Mesmer, 1986; Pershina, 1998, 2002), resulting from differences in the specific electron structures of the hydrolyzed species (which determines the type and strength

of chemical bonding). An influence of simple mixing of two endmembers with different elemental ratios cannot be excluded. The HFSE enrichment in ferromanganese crusts is thought to co-vary with growth rate (Godfrey et al., 1997), related to the formation of surface precipitates. Figures 19-21 display the HFSE systematics in hydrogenetic and hydrothermal Fe-Mn oxide deposits.

[2] No data are published about the fluxes of HFSE in high-temperature mid-ocean ridge hydrothermal systems and the respective Zr/Hf and Nb/Ta ratios in the hydrothermal fluids, which complicate a discussion of the HFSE signature of hydrothermal Mn and Fe-Mn crusts in the Logatchev field. Concentrations of HFSE in hydrothermal fluids are probably quite low, as HFSE are rather immobile, but their mobility may be enhanced in high-temperature, acidic hydrothermal solutions. However, a single measurement yields lower than seawater concentrations of Zr. Deep seawater is characterized by strongly fractionated Zr/Hf ratios, which vary according to the short residence time of HFSE (Zimmermann et al., 2009) between the different ocean basins (NE Atlantic >90 (w/w); Godfrey et al., 1996). While a single measurement of Zr and Hf in Logatchev hydrothermal fluids indicate chondritic Zr/Hf ratios (by weight: ~40, unpublished data, this study), Zr/Hf ratio inferred from an Fe oxyhydroxide crust with almost mantle-like Hf isotopic signature is strongly superchondritic (~87). A mixture of hydrothermal fluid and seawater would always display superchondritic Zr/Hf ratios. The Nb/Ta ratios in seawater are not well-constrained and range from chondritic to moderately superchondritic (Firdaus et al., 2008, pers. comm.). High field strength elements enriched in stratified Mn crusts are at least partly derived from a mantle source (up to 28% of total Hf), as evident by Hf isotopes, although this may also comprise mobilization during low-temperature fluid-rock interaction. The Hf isotopic composition of the Fe-Mn oxide coatings is similar to seawater, which indicates seawater a dominant source of dissolved HFSE in the deposits.

[3] In hydrogenetic ferromanganese crusts, HFSE are usually almost exclusively associated with the Fe oxyhydroxide fraction (Koschinsky and Hein, 2003; Bau and Koschinsky, 2009). This preferential association is also evident in the different deposits of the Logatchev field, with highest HFSE concentration in Fe-rich oxide coatings of group III. Here, the HFSE concentration is similar to those in hydrogenetic ferromanganese crusts, whereas pure Mn oxides of group I and II are much less enriched in these elements. Whereas Zr/Hf ratios are not significantly different between the groups but vary within the individual deposits, Nb/Ta ratios are clearly different in the separate groups. Both ratios range between chondritic and moderately to strongly superchondritic values, which proves a fractionation of Zr-Hf and Nb-Ta also in hydrothermal environments.

[4] As the HFSE do not correlate with Fe in stratified Mn crusts of group I, they are likely not associated with an Fe oxyhydroxide phase but must be bound to the Mn oxides or detrital

minerals. The elements do not correlate with Fe, but with Al. The contribution of detrital aluminosilicates to the HFSE budget in these Mn crusts, as indicated by the results of different digestion methods and the correlation of HFSE with Al, is significant and will be discussed below. Group II, which has similar HFSE contents as group I, is characterized by a strong association of all HFSE with Fe. The Al/Fe ratio in Mn oxide crusts (0.2-0.9, decreasing with increasing Fe) is smaller than in the UCC (~2), which is evident for an additional Fe enrichment in these crusts. This can be a separate Fe oxyhydroxide phase or Fe being incorporated into the Mn oxide structure (as in vernadite). The co-variance of Fe and Al in group II can be explained by parallel enrichment of detrital and Fe oxyhydroxide particles (although some Al might also be incorporated in the Fe oxyhydroxide phase), whereas Fe and Al are decoupled in stratified Mn crusts with Fe likely been incorporated into the Mn oxide minerals. The Fe content in group II Mn oxides is not higher than in group I Mn oxides (max. 2%), but is likely representing a distinct Fe oxyhydroxide phase.

[5] The Al/Zr ratio in average upper continental crust (UCC) is about 400 (Rudnick and Gao, 2003). In the stratified Mn crusts, the Al/Zr ratio ranges from 320-570, with the lowest value in the most HFSE-depleted layer 3 and a strong correlation of Al and Zr. It is assumed that at least part of the Al in the Mn crusts is detrital Al, although Al may also be scavenged to Fe and Mn oxide minerals (derived from a leaching study of Nod-P1: about 40% of Al bound to oxide phase, 60% is detrital, A. Koschinsky, pers. comm.). As Fe is almost quantitatively leached with the HCl digestion in the stratified Mn crust, this indicates that either more than 50% of Al must be bound to the Mn oxide phase, or the presence of a Fe-depleted detrital phase. The digestion only with HCl has shown that about 60% of the Al content is not leached with the oxides. This already indicates a strong contribution of detrital aluminosilicates to the Zr budget of the stratified Mn crust. The below-UCC Al/Zr ratio in the most Zr-depleted layer 3 is evident for some Zr bound to the Mn oxide phase. The Hf isotopic composition is in agreement with this interpretation, that some Hf in the stratified Mn crust is mantle-sourced (i.e., Hf is not exclusively bound to the detrital mineral phase). The increasing Zr and Al concentrations with increasing Al/Zr ratio (Fig. 22) results from the overprint of the small, fluid-sourced Zr contribution with detritus material, likely containing most of the Zr incorporated into these deposits. This is in agreement with the results from the digestion study, showing that in the top layer with the highest amount of Al more Zr is bound to the detritus phase relative to the layer with the lowest Al content. The above UCC ratios in the top layers are either attributed to lower Zr concentrations in the detritus material relative to UCC or Al being preferentially sorbed in the crust. The decreasing Zr/Hf ratio in stratified Mn crusts with increasing Zr (and Al) content is related to the increasing dominance of detrital material with chondritic Zr/Hf ratios, whereas higher, superchondritic Zr/Hf ratios in the most Zr-depleted layers, which contain the highest relative amount of Zr bound to Mn oxide, proves the decoupling of Zr and Hf. It can only be speculated about the relative fractionation of Zr-Hf during sorption, as the ratio in the parental solution not known. The Zr/Hf ratios

cluster around chondritic to slightly superchondritic ratios, independent on the relative enrichment of Zr (except for group I). As seawater has strongly superchondritic Zr/Hf ratios, this would imply the preferential adsorption of Hf relative to Zr. the influence of detritus, the enhanced Zr (and Al) concentrations in the top layers could partly result from a lower growth rate, associated with continuous accumulation.

Whereas in stratified Mn crusts the relative enrichment of Zr over Al is restricted to the parts with lowest Zr concentration, the relative Zr enrichment over Al in massive crusts of group II increases with increasing Fe. Massive Mn oxide deposits of group II show a good correlation of HFSE with Fe, in contrast to group I. The Al/Zr ratio ranges between 250 and 500, being generally lower than in group I samples and decreasing with increasing Zr concentration. This proves an additional Zr enrichment relative to Al, bound on Fe-oxyhydroxide particles with lower Al/Zr ratio. The decreasing Al/Zr ratio with decreasing Al/Fe ratio, together with the Zr-Fe correlation, is evident for the enrichment of Zr on Fe-oxyhydroxide particles (Fig. 23).

In contrast to Mn oxide deposits, the Fe-Mn coatings of group III are strongly enriched in HFSE, with the majority being scavenged from solution and not present in detritus material. This becomes evident when comparing the Al/Zr ratios ranging from 40-80, which is much lower than the UCC ratio and is in agreement with Hf isotopes. As seawater has a strongly superchondritic Zr/Hf ratio, the close-to-chondritic ratios in Fe-Mn oxide coatings suggest the preferential scavenging of Hf relative to Zr.

[6] Niob and Ta behave differently than Zr and Hf: In the stratified Mn crust profile, the Al/Nb ratio is lowest at highest Nb concentration in the top layer (about 4200), which indicates some additional Nb enrichment due to adsorption from seawater towards top relative to those derived from detrital aluminosilicates (UCC: Al/Nb=6666; Rudnick and Gao, 2003), overprinting the detrital signature. The highest Al/Nb ratio in the most Nb-depleted layer (about 8000) may indicate that some Al is bound to the Mn phase. In contrast to Nb, Ta seems to be exclusively bound to the detritus phase, with relatively constant Al/Ta ratios over the profile independent of Ta concentration. The preferential enrichment of Nb over Ta in the top layers explains the increasing Nb/Ta ratios changing from chondritic to superchondritic towards top. It is possible, that some Ta is also bound to the Mn oxide phase, but this contribution cannot be quantified. The above-UCC Al/Ta ratios suggest lower Ta concentrations in the hypothetical detritus minerals. Some Al may also be bound to the Mn oxide (hydrothermal fluids are enriched in Al).

In the massive Mn oxide crusts of group II, smaller Al/Nb ratios of 500-2700 prove the enrichment of dissolved Nb, although the contribution of Nb from detritus material is still significant. Niob is preferentially sorbed in the Fe oxyhydroxide phase in these deposits, as evident from the close Nb-Fe association similar to the other HFSE. Aluminium/Ta ratios are

similar to UCC, which implies that most Ta included in the crusts is derived from detrital material. Relative to stratified Mn crusts, Nb/Ta ratios are enhanced due to the relative higher proportion of oxide-bound Nb and get increasingly superchondritic with increasing Nb content (i.e., at increasing Fe content).

Iron-manganese oxide coatings of group III are characterized of strongly superchondritic Nb/Ta ratios and high Nb concentrations, which cannot be explained by the incorporation of detrital minerals but require adsorption of dissolved Nb from solution ($Al/Nb=250-500$). In contrast, a major proportion of Ta is bound to the detrital minerals ($Al/Ta=40000-60000$), decreasing with increasing Ta concentration. The strongly fractionated Nb/Ta ratios in these deposits can thus be explained by the preferential enrichment of Nb over Ta on Fe oxyhydroxide particles. The Nb/Ta ratios increase with increasing Fe and Nb concentration in group II and III. The lower Nb/Ta ratio in Mn-rich oxide samples could result from the higher relative contribution of detrital aluminosilicates compared to Fe oxyhydroxides (as indicated by higher Al/Nb and Al/Ta ratios), or, alternatively, from a different Nb/Ta fractionation on Mn oxides relative to Fe oxyhydroxides (see below).

It can be concluded, that group II Mn oxides are somewhat more enriched in seawater-scavenged HFSE than group I, with decreasing relative contribution in the order of $Nb > Zr > Hf > Ta$. Iron-rich oxide coatings are dominated by seawater-scavenged HFSE except for Ta, which is dominantly bound to detritus material. The contribution of detrital material is highest in the stratified Mn crust and lowest in Fe-Mn oxide coatings. The calculation of the relative amount of scavenged HFSE in the individual samples depends on the composition of the detritus material (volcanic glass would deliver less HFSE and thus, the relative contribution of scavenged elements would be higher) and on the amount of Al being sorptively enriched in the crusts.

[7] Depending on the relative concentrations of Zr, Hf, Nb, and Ta in detrital material and in Fe oxyhydroxides, increasing contributions of Fe oxyhydroxides will either increase or dilute the absolute concentrations of these elements. This becomes apparent from increasing Zr with decreasing Al/Zr ratio, but decreasing Hf with decreasing Al/Hf in group II Mn oxides. Assuming a mixing of aluminosilicates with Fe oxyhydroxides containing more Zr but less Hf than the aluminosilicate (which implies higher Zr/Hf ratios) this should be expressed in a correlation of Zr/Hf ratio with Fe. As this is not the case, Zr and Hf may additionally be scavenged on Mn oxides with different ratios. As Al and Fe co-vary, an apparent relationship of Hf and Fe may in fact result from the higher amount of Al in the crust. A genetic relationship between Hf and Fe, for example can only be proven by the correlation of Al/Hf with Al/Fe .

[8] Although the Zr-Hf distribution in the stratified Mn crust can be explained by a major contribution from detrital material, increasing towards top and overprinting a primary, Mn-bound Zr-Hf signature with higher Zr/Hf ratio, an alternative explanation is possible: The relation of Zr/Hf ratio decreasing with increasing Zr concentration in stratified Mn crust may be related to a change from unfractionated incorporation from a solution with high Zr/Hf ratio, which becomes progressively overprinted by further enrichment with preferential enrichment of Hf. This trend is also evident for Y/Ho ratios, which are seawater-like in plume-particles (German et al., 1990; Sherell et al., 1999), but strongly fractionated in hydrogenetic crusts (although this ratio is controlled by equilibrium between solution complexes and surface complexes). The change from non-fractionated to fractionated incorporation could be explained by increasing surface loading leading to surface precipitation, which follows surface complexation with changing complex stabilities.

[9] While the strongly different Nb/Ta ratios in Fe oxide rich coatings and in Mn crusts are attributed to the relative proportion of detrital Nb and Ta in the different genetic types and a preferential enrichment of Nb on Fe oxyhydroxides, further parameters may influence the distribution of Nb and Ta in the deposits: different sources with different Nb/Ta ratios or different relative fractionation of Nb and Ta on different oxide phases, which is shown by different Y/Ho ratios in Fe oxyhydroxides and Mn oxides, with Y/Ho less fractionated on Mn oxides than on Fe oxides.

[10] The HFSE content in group III is not correlated with Fe in Fe-rich samples, but only in Mn-rich samples, being lowest in most-Mn-enriched sample. The weak correlation of HFSE and Fe shows that these elements are not simply controlled by the presence of Fe oxyhydroxides, but, as evident from variable Zr/Fe ratios, other factors like growth rate and accumulation in Mn oxides also play a role. Furthermore, Fe is also contained in detrital minerals. Although Zr-Hf will be preferentially bound to the Fe oxyhydroxide phase also in Mn-rich oxides, the Zr/Hf ratio varies depending on the relative amount of Fe oxyhydroxides and Mn oxides in the coatings: The most superchondritic Zr/Hf ratios are observed in the Mn-rich samples, decreasing with increasing Fe concentration. This could result from a different fractionation of Zr and Hf during sorption on Fe oxyhydroxides and Mn oxides implying that Zr and Hf are not exclusively bound to the Fe phase. The enrichment of HFSE in ferromanganese crusts generally increase with the time of exposure to the solution, due to the formation of surface precipitates continuously enriching the elements. However, this is not proven in the Logatchev hydrothermal oxide deposits: the HFSE concentration in group I and group II Mn oxides is similar, despite much faster precipitation rates of group II Mn oxides. Group III oxides show a general correlation of Fe-normalized Zr concentration (Zr/Fe increases with Zr concentration) and Ce/Ce*, which may indicate continuous sorption on Fe oxyhydroxide particles. One has to mention that Ce is bound to both Mn and Fe oxides, whereas Zr is likely mainly bound to the Fe oxyhydroxide phase, and thus a straight

correlation of Zr and Ce/Ce* is not expected even in case of similar relation to the accumulation time.

6.4.4 Growth rate:

The age and the growth rate of hydrothermal ferromanganese crusts are usually determined using the empirical approach of Manheim and Lane-Bostwick (1988):

$$GR = 0.68 / (Co^*)^{1.67} \quad \text{Equation 2}$$

Where GR is the growth rate in mm/Myr and Co^n is the normalized Co calculated as follows:

$$Co^n = \frac{w_{Co} \times 50}{w_{Fe+Mn}} \quad \text{Equation 3}$$

where w_{Co} denotes mass of Co in weight%.

As Co in ferromanganese deposits is enriched via surface oxidation of Co (II) to Co (III), its absolute concentration is directly controlled by the exposure time of the mineral surface to the solution, i.e., the growth rate. Hydrothermal Mn crusts are generally characterized by fast growth rates based on low Co contents in these deposits relative to hydrogenetic ferromanganese crusts. However, this approach assumes a constant Co flux for all ferromanganese deposits and relates fast growth rates to local bottom water enrichment of Fe and Mn relative to Co close to hydrothermal emanation sites.

This approach fails in case of an additional hydrothermal Co flux, as it is evident in high-temperature hydrothermal systems. A strong hydrothermal contribution of Co to the total Co content of the crust would strongly enhance the Co/(Fe+Mn) ratio resulting in apparent growth rates much slower than the real ones. This becomes obvious in case of the stratified Mn crusts of group I, which have apparent growth rates of only a few mm/Ma. However, this would imply ages for the 3 cm-thick deposits being much older than the oceanic crust the Mn deposits were hosted on. To form the mm-thick Fe-Mn coatings on rock substrates, between 100 000 and 200 000 years would be required, which is still older than the oldest hydrothermal activity in the Logatchev field (60 000a; Lalou et al., 1996). So either these deposits also contain a significant amount of hydrothermal Co (as can be suggested for the Mn oxide part, compare discussion on Os isotopes and Cu concentration), or the Fe-oxyhydroxide particles actively scavenge Co over a longer time period as the hydrothermal activity in the Logatchev-1 vent field. As the Co concentration is generally correlated with the Mn concentration the former explanation seems to be more convincing, although a combination of both is possible. In contrast, the extremely low Co content in group II Mn oxides, which are generally enriched in other trace metals, indicate a very fast growth rate with only short exposure times to the parental fluid. Applying the above formula, the 3-4 cm-

thick deposits (225 GTV-3) would be precipitated over about a time of 10000-20000 years, which would be within the hydrothermal activity period of the Logatchev field, whereas the 1 cm thick, pure Mn oxide coating on a rock fragment (225 GTV-1F) would be formed within about 1000 years. These ages represent maximum ages, as additional, hydrothermally sourced Mn may be incorporated into these deposits. The strongly contrasting growth rates at the surface of one rock piece (225 GTV-1F, 1000 and 100 000 years) implies short-space variations of hydrothermal fluid fluxes, possibly influenced by biological activity.

6.4.5 Model of oxide deposit formation at Logatchev-1

Based on geochemical and mineralogical observations, a model for the formation of the various types of Fe-Mn deposits in the Logatchev-1 field has been developed. On the basis of their occurrence and mineralogy, the Mn crusts are considered to be hydrothermal, but the elemental content is derived from dilute hydrothermal fluids as well as from seawater.

The isotopic signatures deviating from normal seawater values prove that Mn crust formation is influenced by dilute hydrothermal fluids carrying mantle sourced elements, while the Fe-Mn oxide coatings are more typical for hydrogenetic formation in the open water column. The close spatial association of group II Mn oxides and Fe-Mn oxide coatings at station 225 GTV east of the *Quest* site and of group I Mn oxides and Fe-Mn oxide coatings at station 78 GTV west of *Quest* indicate that small-scale, local variations of hydrothermal flow.

Fe-Mn oxide coatings

The good correlation of Fe/P, Fe/V, and Fe/U in these deposits indicates scavenging of oxyanions from seawater on Fe oxyhydroxide particles in hydrothermal plumes. Because of the different oxidation kinetics of Fe and Mn in hydrothermal plumes (Feely et al., 1994), Fe oxyhydroxide particles and Mn oxide particles composing the Fe-Mn coatings are likely not formed in the same environment. It is proposed that the Fe oxyhydroxide particles in these deposits are formed in the buoyant and non-buoyant plume or as background material in the open ocean and settled down, mixing with Mn oxide particles rather formed close to the emanation sites of rising diffuse fluids. At high-temperature vent sites, Fe(II) is precipitated as sulfide close to the emanation site, followed by the oxidation of the remaining Fe to form insoluble Fe (III) oxyhydroxide phases during plume rise (Field and Sherrell, 2000). These Fe oxide particles continuously scavenge elements from seawater (e.g., Edmonds and German, 2004) and hydrothermal plumes are known to be a sink for elements forming oxyanion complexes in solution, like P, V, U, Os. The composition of Fe-rich oxide coatings is similar to hydrogenetic ferromanganese crusts, except for higher Cu (sulfide inclusions) and somewhat lower Co and Ni and does not require any significant contribution from a hydrothermal source. In contrast, the formation of Mn oxide particles in the deposits is likely coupled to local outflow of low-temperature hydrothermal fluids, enriching the bottom water

with dissolved Mn. Precipitation of Mn oxides is possibly microbial mediated or catalyzed on pre-existing Fe oxide particles. As soon as the particles are in contact with bottom seawater, the Co concentration is controlled by the growth rate; high Co concentrations are evident for a slow accumulation of these deposits. In agreement with isotopic data, the majority of elements accumulated in the Mn-rich oxide particles are scavenged from seawater (hydrogenetic enrichment), although small amounts of some elements (Nd and Os) are hydrothermally sourced, evident for an enrichment of those elements in bottom water due to hydrothermal outflow. Despite the similarity of Fe-rich Fe-Mn oxide coatings and hydrogenetic ferromanganese crusts, the lower Co content together with the smaller positive Ce anomaly are attributed to shorter accumulation rate with less time for oxidative sorption. Fe-Mn oxide coatings from 8°18'S (diffuse vent field) show almost identical chemical signatures as Fe-Mn oxide coatings in the Logatchev-1 field (except for higher Cu content). The formation of the Lilliput oxide deposits is dominated by hydrogenetic enrichment processes, leading to high concentrations of Co and Ni. Thus it seems valid to attribute the high Ni concentrations observed in Mn-rich oxide coatings and possibly those in Mn oxides of group II to a hydrogenetic enrichment process.

Although the chemical composition of Mn-rich coatings is similar to the pure Mn coatings and crusts of group II, they do not form a continuum but are clearly separated by the relative concentration of Co and Ce. The chemical characteristic are evident for a rapid precipitation of the latter, which is in agreement with the thickness. The close association becomes most evident in the sample 225 GTV-1F, where rock fragments are covered by relatively Fe-rich coatings containing high amounts of detrital material, but with niches of thick, pure Mn coatings.

Massive Mn crusts

This group of Mn oxides, occurring as thick coatings on rock substrates or as individual slabs, represents very young deposits, formed by fast accumulation of MnO₂ without much time of enrichment. These deposits are supposed to have been formed at the discharge sites of low-temperature hydrothermal fluids. Once a low-temperature fluid enters the seawater, forming Mn oxide particles are exposed to seawater and scavenge elements from seawater. Although the crusts are considered to be hydrothermal, they contain elements sourced from seawater *and* from oceanic crust. The Mn crusts are strongly enriched in elements associated with Mn oxides, like Li, Mo, Ni, and Zn. In the preferred model, those elements are dominantly scavenged from seawater (hydrogenetic enrichment) and are not mantle-derived. Their concentration is mainly determined by the presence of well-crystalline manganate minerals, rather than by their absolute concentration in the parental solutions. Further physico-chemical parameters like pH and Eh may also play a role. The isotopic composition of Nd indicates relatively high mantle REY contributions in at least one sample, whereas others accumulated

in almost pure seawater (as evident from large negative Ce anomaly). A higher seawater influence relative to Mn oxides of group I is also derived from the HFSE signatures. The strong correlation of Th, Ti, U, Zr, Pb, and REY with the relative amount of Fe indicate the presence of a separate Fe oxide phase, hosting these elements. An additional detrital component is evident for Al, Zr, Ti and the other HFSE. This is in contrast to group I Mn oxides, where Fe might be bound to the Mn phase like in Fe-vernadite. Vanadium is not correlating with Fe, which implies, that V is bound to the Mn oxides, similar to group I Mn oxide crusts. The association of V with the Mn phase is linked to the presence of reduced V sourced from the hydrothermal fluid.

Despite similar or even higher mantle contributions for Nd and Os in some group II Mn oxides relative to group I, they apparently were formed under different conditions, resulting in fast precipitation in open seawater. The fast precipitation is likely related to the mixing of low-temperature hydrothermal fluid with oxygenated seawater, resulting in strong oversaturation of dissolved Mn.

The decoupling of Ni and Co indicates different sources. However, if it is assumed that the high metal contents are rather sourced from hydrothermal fluid and not from seawater, a change in the composition of the parental fluid of group II Mn oxides relative to group I cannot be excluded, but it implies that group II Mn crusts precipitate from a fluid which is enriched in Ni and Zn but depleted in Co, which is rather unlikely.

Stratified Mn crusts:

Variations in the concentrations of hydrothermally enriched metals within individual deposits reflect temporal variations in the compositions of hydrothermal fluids from which they were precipitated (Rodgers et al., 2001). However, many elements are of mixed origin and compositional variations may simply reflect different mixing ratios of hydrothermal fluid and seawater. This makes a careful investigation of geochemical signals necessary.

A relation of stratified Mn crust formation to the high-temperature hydrothermal activity in the Logatchev hydrothermal field is evident by field relations, microscopic textures as well as geochemical fingerprints, like positive Eu anomaly, high Cu, Co, and Mo concentrations. The influence of seawater as source of scavenged elements becomes evident by the isotopic composition of Nd. Assuming that the layering in the stratified Mn crusts is primary, changing chemical composition is either attributed to a change in the high-temperature fluid source or/and more local variations in the mixing scenarios between fluid and seawater and changing relative contributions of hydrogenetic scavenging.

The top layers of group I and the Mn-rich coatings of group III are similar in their macroscopic texture and elemental composition suggesting similar formation processes. The

top layers are more influenced by hydrogenetic scavenging implying, that these layers were in contact with seawater for a long time after deposition, continuously adsorbing elements and maybe also more Mn oxides. It is assumed that the massive Mn oxide layers have been precipitated first, at the sediment-seawater interface. Beneath this cap, laminated and botryoidal Mn oxides were formed, precipitating out from upwelling, Cu- and Co-enriched low-temperature hydrothermal fluids, which have already lost all Fe. This model of formation is consistent with Mn-crusts from other localities (Mariana-Bonin-Arc, Tonga Ridge, Hodgkinson et al., 1994) and implies that the hydrothermal flux is higher during the formation of layers 2 and 3 than during the formation of layer 1, reflected in higher Cu, Co, but low Ni, Zn. The low-temperature hydrothermal fluids are significantly enriched in Cu and Co, due to leaching of Cu-sulfides. The concentrations of Ni and Zn are coupled, with rather low concentration in the botryoidal and laminated layers, but strong enrichments towards top. This may be attributed to stronger hydrogenetic contribution in the top layers, in agreement with Nd isotopes. In analogy to Mn-rich oxide coatings and massive Mn crusts, the high Ni and Zn concentrations in the upper layers were probably mainly accumulated from seawater. Layer 3, which is characterized by a pronounced depletion of REY, Ni, Li, Zr, Th, Al, Ti but pronounced enrichments of V, (Os) and Cu in conjunction with highest Ce anomaly (U, Co, Fe keep unchanged), indicate a change in the formation environment and is likely formed at the most limited seawater access (i.e., highest fluid contribution) and lowest detritus content. It could be speculated that the redox state of the fluid changed over time of crust growth, as indicated by the co-variance of Ce/Ce*, Co, V, Cu, (Fe). Although a higher amount of H₂O incorporated into the manganate crystal structure in this layer can cause changes in the absolute concentrations of adsorbed metals, this would not explain enrichments of specific elements. The concentrations of Zr, Th, Ti co-vary with Al over the profile. These elements have among the lowest partition coefficients for a Mn oxide phase and are probably very low concentrated in hydrothermal fluids. As discussed above, the content of HFSE and Ti is probably affected by detritus material, with the highest relative input in granular top layers. Li concentrations do not vary strongly over the profile, but only slightly decrease at top. This indicates that Li is not affected by the major changes in relative amounts of different sources and/or variable fluid compositions as evident by other elements and suggests a primary control by the presence of well-crystalline MnO₂. Small-scale variations of chemical composition and microscopic textures may result from different Eh, pH, T, and chemical composition of parental fluid.

Deduced from the model of crust formation, the growth direction of stratified Mn crusts is downward for the botryoidal and laminated layers and possibly upward in the top layers. The formation of laminated and botryoidal layers as upward growth in open seawater can be excluded, as this would imply that the high Co contents would have been mainly scavenged from seawater requiring absolute ages of several million years. Alternatively to the model presented above including hydrogenetic trace metal accumulation in the top layers, variable

hydrothermal fluxes with different concentrations of Zn, Ni, Co (and REY) during the formation of the crusts could also cause the observed changes over the crust profile and the differences between group I and group II. Furthermore, a different crystallinity and changing physic-chemical conditions could maybe also explain different Zn and Ni concentrations.

Fe-oxide deposits from the Logatchev field

[1] The Fe oxide deposits occur in different varieties ranging from pure Fe oxide crusts (group V) recovered from ancient chimneys to semi-consolidated, massive Fe crusts in close proximity to smoking crater structures (group IV). Two possible formation conditions have to be considered: primary, low-temperature deposition of Fe oxyhydroxides at the seafloor or in the outer sites of chimneys and formation due to oxidation of massive sulfides. Plume fallout accumulation being responsible for the formation of these deposits can be excluded, as they are not enriched in Zr, Th, REY. The genesis of these Fe oxyhydroxide deposits at Logatchev-1 is only shortly discussed, as a detailed evaluation is beyond the scope of this thesis.

[2] Pure Fe crusts, occurring in form of hollow tubes (fluid channels), being characterized by low abundances of Zr, Th, V, REY, Ca, Mg, Ni, and Co but high contents of U, Zn and Pb are likely formed at limited seawater access. The high U contents indicate redox processes during formation (co-precipitation of U). The crusts are likely formed by oxidation of primary (Zn-rich) sulfide chimneys, as partly common at *Irina II*. A primary precipitate as Fe oxyhydroxide chimney from cooled hydrothermal fluids is rather unlikely, as the SiO₂ content in the hydrothermal fluids required to stabilize such structures is rather low. Furthermore, primary precipitates are expected to show large positive Eu anomalies, as observed at TAG (Petersen, 2000). The enrichment in U, which is commonly observed in oxidized sulfides, can be referred to a change of the oxidation state of U during recrystallization.

[3] The majority of Fe oxyhydroxides is likely formed due to the oxidation of primary sulfides, in agreement with field observations (close association of sulfide debris and Fe oxyhydroxides at stations 32 GTV and 33 GTV). The reaction with seawater leads to the formation of acidic pore fluids leaching Fe from the sulfides and precipitating them as amorphous Fe oxyhydroxides, which are immediately altered to goethite (Hannington and Jonasson, 1992). Atacamite forms as secondary mineral during this process and is commonly closely associated with the Fe oxyhydroxides. The negative Ce anomalies are evident for seawater interaction, whereas small positive Eu anomalies are inherited from primary sulfides. Such deposits are commonly enriched in S, Cu, Zn, Co, Pb, whereas the REY concentrations are very low and characterized by non-equilibrium incorporation from seawater during recrystallization.

[4] The massive Fe oxyhydroxides at stations 32 GTV and 33 GTV could also be formed as low-temperature exhalations of hydrothermal fluids which were conductively cooled or

mixed with seawater in the subseafloor, containing high Fe concentrations but low H₂S. Such deposits often form during waning stages and at the periphery of sulfide-forming vent sites (Hannington and Jonasson, 1992) and are characterized by very low trace metal contents, no Ce anomaly but large positive Eu anomalies. At the TAG field, upwelling diffuse fluids have been shown to significantly contribute to the formation of metalliferous sediments (Petersen, 2000). Leaching of Cu sulfides below these deposits will eventually mobilize Cu, which precipitates as atacamite in the Fe oxyhydroxide deposits (S. Petersen, pers. Comm.). At Logatchev, Fe oxyhydroxide deposits are highly diverse in their chemical composition. On the basis of the existing data it is not possible to exclude one process or the other, although the generally small Eu anomalies and negative Ce anomalies argue against a deposition from cooled hydrothermal fluids. A combination of both (precipitation from low-temperature fluids formed due to mixing with seawater and oxidation of primary sulfides) is also possible. A variability of the concentrations of Pb, Cu, and Zn within the massive Fe oxyhydroxide deposits of stations 32 GTV and 33 GTV and the low REY abundances rather indicate the formation via sulfide oxidation. But the considerable amounts of Mn in some of the massive Fe oxyhydroxide deposits are not easily explainable by sulfide oxidation. Thus, deposits containing more Mn could rather be formed as direct precipitates of low-temperature hydrothermal fluids.

[5] Bogdanov et al. (2004) attributed Fe oxyhydroxide crusts associated with sulfide chimneys in the Logatchev-1 field, containing high amounts of high Cu and Zn, to the horizontal flow of highly saline hydrothermal solutions without strong seawater mixing. As the Logatchev-1 hydrothermal fluids have seawater-like salinities (Douville et al., 2002) and bottom-parallel flow of black hydrothermal plumes is rather caused by strong bottom currents especially in the craters, this explanation is probably not valid.

6.4.6 Comparison of Mn oxide deposits from Logatchev-1 and other localities – ultramafic signature?

Previously investigated “hydrothermal” Mn deposits in island arc and backarc settings are characterized by a strong fractionation of Fe and Mn and a generally low trace metal content, with some exceptions as occasional enrichment of Zn (Mariana Arc), Ni and Cr (Hawaii rift zone), Ni, Cu, Zn, Cr (Yap Arc) as well as common enrichments of Mo and Li.

In comparison, the Logatchev-1 Mn oxides are all strongly enriched in Cu and Mo, accompanied by variable enrichments of Co, Ni, and Zn (Fig. 24, Table 6). Lithium concentrations are similar in the different deposits. The enrichment of transition metals can reasonably be related to high-temperature hydrothermal circulation with formation of massive sulfides; similar signatures were recently reported from other hydrothermal fields at the MAR (Davydov et al., 2007, 2009).

Table 6: Comparison of geochemical composition of hydrothermal Mn crusts from different locations

		Logatchev-1, Group I, bottom I.	Logatchev-1, Group I, top lay.	Logatchev-1, Group II	Logatchev-1, Group III	Ashadze-1 (Davidov et al., 2009)	Logatchev-2 (Davidov et al., 2009)	North Fiji Basin (Kuhn et al., 2003)	Yap Arc (Hein, 1992)	TAG (Toth, 1980)	Tonga-Kermadec- Ridge (Rodgers et al., 2001)	Mariana Arc (Hein et al., 2008)
Ca	%	1.84	1.76	1.99	6.68	1.43	1.71	1.44			1.63	1.59
Mg	%	1.93	2.06	2.62	1.45	1.51	1.46	0.22	2.20		1.08	2.15
Na	%	2.95	2.98	2.65	1.24							
Fe	%	1.43	1.19	1.73	24.9	4.4	1.9	0.3	2.0	0.1	0.5	0.7
Mn	%	41.9	39	37.5	11.7	38.7	35.1	44.0	40.7	44.2	40.2	49.8
Al	%		1.01			0.440	0.460	0.060		0.430	0.780	0.327
Cu	%	1.46	2.08	0.37	1.17	0.342	2.915	0.023	0.240		0.005	0.073
Co	ppm	3470	1680	57	1550	573	110	n.m.	410	31	11	70
Ni	ppm	817	3830	3870	593	975	1400	155	4119	782	115	534
Zn	ppm	173	1380	1380	728	822	3100	341	1477	460	158	8388
Mo	ppm	1910	3030	2730	133	331.0	600.0	826.0	297.0		958.0	501.0
Li	ppm	1140	993	1390		474	415		100		458	
Pb	ppm	8.53	12	26		6.3	27	15	80	4	<10	142
Zr	ppm	13.6	18.4	24	307							
Th	ppm	1.07	1.3	2	34.5	0.6	1.4					
U	ppm	0.877	0.855	0.7	11.7	3.4	1.4					
V	ppm	409	328	381	1110			193	487		88	
Ti	ppm		523		4520	479	958					
P	ppm											
Os	ppt	240	175									
S	%											
Ba	ppm	334	274	424	1020	1258	1200	1195	2843	1010	390	708
Cs	ppm	0.382	0.423	0.253	0.311							
Sc	ppm				9.39							
W	ppm				29.9	4.00	15.4					
Mn/Fe		29.3	32.7	21.7	0.468							
U/Th		0.817	0.657	0.35	0.339							

Stratified Mn oxide crusts formation is controlled by the circulation of low-temperature, diffuse fluids. Depending on whether such fluid origins from low-intensity hydrothermal flow at low temperatures and high w/r ratios unsuitable for leaching of base metals except for Fe and Mn, or from cooling/dilution of high-temperature hydrothermal fluids associated with massive sulfide deposits they are variably enriched in metals.

Bogdanov and coworkers (2004) described similar Fe-Mn oxide coatings as investigated during this study from the *Sad Ani* site in the Logatchev field (W of Irina II), possibly close to the 225 GTV sampling site from this study. Their interpretation as product of diffuse discharge of low-temperature hydrothermal solutions at the seafloor are in general agreement with own work, except that the chemical signature of Fe oxyhydroxide particles rather indicate a formation within the ocean water column independent of fluid discharge.

The Cu enrichment in hydrothermal Mn crusts seems to be a common feature in all proximal Mn crusts at high-temperature venting sites. Similar Cu enrichments were recently reported for Mn deposits of the ultramafic-hosted Ashadze-1 and the Logatchev-2 hydrothermal fields (Davydov et al., 2007), with Co concentrations up to <500 - 1000 ppm. The same study also presents graphical data showing high Cu contents above 1% in the TAG mound and from deposits at Lucky Strike, with similar Co contents as reported from Ashadze and Logatchev-2. This would imply that the high Cu concentrations are not a unique feature of ultramafic-hosted hydrothermal systems. As no further information on the major element geochemistry, the mineralogy and macroscopic and microscopic textures are given, these data cannot be further evaluated.

As there are no compiled geochemical data for ferromanganese deposits from high-temperature vent sites on MAR other than for the ultramafic-hosted hydrothermal fields Ashadze-1 and Logatchev-2 are available, it will be difficult to determine whether Logatchev-1 hydrothermal crusts reflect an ultramafic fingerprint or not. Indicators could be Co, Ni, Cr, however, all these elements are influenced by several processes superimposing a primary ultramafic signature. Herzig and co-workers (2007) reported moderate Ni enrichments in active, chalcopyrite-rich chimneys but suggested that Ni is dominantly sourced from mafic rather than ultramafic rocks. No information is available on Ni contents in high- or low-temperature hydrothermal fluids from the Logatchev-1 hydrothermal field. Nickel is strongly enriched in the massive Mn crusts of group II and in the top layers of group I Mn oxides, but also in Mn rich Fe-Mn coatings and clearly associated with the Mn phase. The decoupling of Ni and Co, as observed in the Mn crusts, indicates contrasting geochemical behavior during Mn crust formation in hydrothermal environments. The model of crust formation as discussed above suggests two different sources for these elements, with Ni being strongly enriched via hydrogenetic scavenging, while high Co concentrations are related to the leaching of chalcopyrite in the subseafloor. Bogdanov and coworkers (2008) suggested that enhanced Co

and Ni contents up to 2000 ppm and 4700 in Fe-Mn deposits of Logatchev-2 and Rainbow could potentially be used as indicators of the alteration of ultramafic host rocks, however, the available literature data presented so far does not specify the type of deposits. (Bogdanov et al., 2004). Fe-Mn oxide coatings from other vent areas in basaltic host rock settings at 5°S (high-temperature field) and at 8°18'S (diffuse vent field) are also characterized by high Co and Ni contents up to 2600 ppm and 4700 ppm. At least the latter is dominated by hydrogenetic enrichment processes. Whether or not the almost identical chemical signature of Fe-Mn oxide coatings in the Logatchev-1 field (except for higher Cu content) were developed by hydrogenetic enrichment, the signature in this group is not restricted to ultramafic vent sites. The high Cu and Co concentrations in the stratified Mn crusts could possibly be used as tracers for fluid-ultramafic rock interaction, but data for proximal, pure Mn oxides from basaltic-hosted vent fields are presently not available to validate this hypothesis. Ultramafic-hosted hydrothermal fields were shown to be dominated by Cu-sulfides, which are enriched in Co. Transition metal contents in hydrothermal fluids are more controlled by sulfide precipitation and temperature-dependent solubility rather than host rock composition (Schmidt et al., 2010a) and thus, clear ultramafic fingerprint in oxide deposits of diluted hydrothermal fluids in such geological settings are not expected. However, the high Cu concentration, decoupled from Zn enrichments could reflect the chalcopyrite-dominance in massive sulfides, which were leached by lower-temperature hydrothermal fluids. Similar oxide deposits from TAG and Lucky Strike seem to be characterized by Cu enrichments as well (Davydov et al., 2007).

Manganese oxide deposits from other locations are often enriched in HREE relative to MREE in shale-normalized patterns (Mills et al., 2001; Kuhn et al., 2003; Hein et al., 2008; Hodkinson et al., 1994; Frank et al., 2005; Scholten et al., 2008), together with a negative Ce anomaly (Fig. 25). This has often been referred to fast growth rates and deposition from low-temperature hydrothermal fluids modified by leaching of arc volcanic rocks and basaltic rocks. The Logatchev hydrothermal Mn and Fe-Mn oxide deposits are characterized by REY distributions typical for hydrogenetic enrichments except for negative Ce anomalies in group II Mn oxides, which indicates equilibrium fractionation of REY between solution and forming oxide deposits.

6.5 Conclusion

This study presents mineralogical and chemical data for different genetic types of Fe- and Mn oxide deposits in the Logatchev-1 hydrothermal field. This includes the first detailed geochemical dataset for proximal hydrothermal Mn crusts in spatial association with high-temperature fluid circulation.

Despite close spatial associations, the textures as well as mineralogical and chemical compositions of Fe-Mn oxide deposits in the Logatchev hydrothermal field are highly variable, which can be attributed to different formation environments of the deposits. This demonstrates that different chemical composition cannot solely be related to general differences in hydrothermal circulation.

Differences in redox chemistry between Fe and Mn lead to the strong fractionation of both elements in hydrothermal environments, which is reflected in the formation of pure Mn oxide crusts at Logatchev-1. Radiogenic isotope signatures of Mn oxide crusts prove variable influences by dilute hydrothermal fluids, laden with mantle-derived elements, during the formation of these crusts and during elemental scavenging from the surrounding solution. The geochemical signature of hydrothermal Mn crusts from is clearly linked to high-temperature hydrothermal activity. Strong Cu enrichments are related to the mobilization of Cu by leaching of massive Cu sulfides in the subseafloor, which makes such deposits valuable as tracers for hidden sulfide deposits. A clear fingerprint for ultramafic host rock alteration could not be proven, as no chemical data for Mn oxide deposits from other, basaltic-hosted high-temperature vent sites are available. Promising key parameters could be Co, Os, and Cu. The relative hydrothermal component in single deposits is variable between individual elements and depends on the relative concentrations in the principle sources (seawater and hydrothermal fluid) and the partition coefficients during adsorption. While Mn is solely hydrothermal-derived, other elements are of mixed origin. Copper, Co, and Os are likely directly delivered from hydrothermal fluids (the Os budget is dominated by mantle-derived Os with up to 85%), while Nd is dominantly sourced from seawater with maximum fluid contributions of 30%. Compositional variations in the crust profiles of pure Mn crusts indicate changes in source fluid composition during the formation of the crusts over time, but not stringently general changes in the high-temperature fluid circulation.

In contrast to stratified Mn crusts, mixed Fe-Mn oxide deposits forming thin coatings on rock substrates, are dominated by hydrogenetic scavenging in the open ocean. Fe oxyhydroxides partly generated in the hydrothermal plume, while high Co concentrations indicate a long history of scavenging (>100 000a) implying, that some Fe particles probably represent background material similar to hydrogenetic ferromanganese crusts.

In comparison to hydrogenetic ferromanganese crusts, pure Mn crusts are enriched in Cu, Li, Mo, but depleted in Pb, Co, Ni, and Zn, whereas Fe-rich Fe-Mn oxide coatings are in principle hydrogenetic deposits scavenging elements from the open seawater. Mn-rich Fe-Mn oxide coatings are somewhat more influenced by hydrothermal fluids and are likely formed at the seafloor.

With increasing elemental concentrations of Os, Nd and Hf from stratified pure Mn crusts over massive Mn crusts containing small amounts of Fe oxyhydroxides to mixed Fe-Mn oxide

coatings, the mantle-derived contributions decrease, associated with increasing hydrogenetic scavenging. All these elements are preferentially associated with the Fe phase, which shows that Fe oxyhydroxide particles dominantly scavenge seawater Os, Nd, and Hf. Thus, continentally derived Os, Nd, and Hf dominate the elemental budgets in the ocean water close to the high-temperature vent sites. From the few data obtained so far it seems that hydrothermal Hf is not exported into the open ocean via high-temperature fluids. However, fresh plume particles would provide more information on this topic, as the isotopic composition of Hf in plume particles should reflect the isotopic composition of dissolved element. Iron oxyhydroxide particles sampled at Logatchev continuously scavenged Hf over long times, which might have overprinted any primary hydrothermal signal.

Elements like Al, Ti, and HFSE are of mixed origin in the pure Mn oxides, with variable contributions of detrital aluminosilicates. Extreme fractionations of the Nb/Ta ratio in the Fe-Mn oxide deposits can be related to seawater-derived Nb being preferentially scavenged relative to Ta, whose detrital component is significant. In contrast, the Zr-Hf distribution in Fe-Mn oxides indicates preferential scavenging of Hf relative to Zr.

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Appendix Table 1: Literature reference values and measured element concentrations for CRMs analyzed within JUB Geochemistry Lab with ICP-OES, data are in mg/kg, if not stated otherwise

JMn-1	Imai et al. (1999) comp. data	range (includes unpublished data)	JUB single measurements														Method Precision		Accuracy
																	Average <i>n</i> =14	%RSD	% Diff.
Al%	2.28	2.35-2.42	2.28	2.48	2.33	2.22	2.25	2.29	2.28	2.23	2.21	2.27	2.22	2.28	2.19	2.21	2.27	3.1	0.4
Ca%	2.08	2.00-2.15	2.00	2.13	2.01	1.97	2.02	2.09	2.10	2.04	2.04	2.08	2.04	2.11	2.04	2.04	2.05	2.2	1.4
Co	1730	1692-1740	1620	1760	1640	1700	1720	1750	1740	1700	1640	1700	1660	1710	1650	1670	1690	2.5	2.3
Cu	11100	10500-12004	9800	10400	9820	9760	9480	10300	10300	9960	11100	11500	11200	11700	11200	11200	10600	6.7	4.5
Fe%	10.1	9.97-10.06	10.3	10.9	10.1	10.5	10.2	10.4	10.2	9.84	9.64	9.90	9.66	10.0	9.61	9.73	10.1	3.5	0.0
Li	71.7	69-74	58.2	62.5	58.2	65.0	62.5	63.0	61.0	59.9	65.0	67.1	65.2	68.1	64.3	64.0	63.1	4.6	12.0
Mg%	1.87	1.74-2.05	1.96	2.09	1.93	1.91	1.85	1.94	1.93	1.89	1.84	1.90	1.85	1.91	1.85	1.86	1.91	3.3	2.1
Mn%	25.6	25.19-25.39	25.6	26.9	25.0	25.7	23.7	25.1	24.3	23.8	23.4	24.0	23.4	24.1	23.4	23.6	25.2	3.8	1.6
Mo	318	314-316	301	305	288	304	315	291	289	294	293	307	300	318	292	301	300	3.0	5.7
Na%	2.08	2.11-2.14	2.02	2.16	2.04	1.94	1.95	2.11	2.11	2.07	2.04	2.10	2.05	2.13	2.06	2.03	2.06	2.9	1.0
Ni	12600	12500-12552	12600	13400	12500	12600	11700	12100	11900	11500	11800	12100	11900	12400	11800	12000	12200	3.9	3.2
P	2350	2359-3802	2480	2590	2340	2130	2310	2000	2100	1970	2270	2340	2320	2410	2230	2320	2270	7.4	3.4
S	940	800-1080	1240	1370	1290		1310	1400	1450		1280	1340	1300	1460	1300	1320	1340	4.9	42.6
Sr	792	737-808	759	805	761	771	803	807	805	777	755	775	758	786	757	753	777	2.6	1.9
V	424	397-458	390	430	397	396	425	392	396	389	402	416	405	420	400	410	405	3.2	4.5
Zn	1070	1042-1090	1080	1180	1090	1130	1110	1130	1120	1100	1090	1130	1100	1160	1110	1140	1120	2.5	4.7

Appendix Table 1, continued

Nod-A-1	Axelsson et al. (2002)	Govindaraju (1994) comp.	Kuhn et al. (2003)	Nayak and Vijayan (2005)	Range	JUB single measurements			Method Precision	Accuracy	
									Average %RSD		
									<i>n</i> = 3		
Al%	2.08	2.05	2.26		2.05-2.26	2.23	2.07	2.05	2.12	3.8	1.9
Ca%	11.4	11.0	10.8	11.4	10.7-11.4	11.2	11.3	11.1	11.2	0.8	1.5
Co	3180	3110	3260	2986	2990-3260	3190	3050	3070	3110	1.9	0.0
Cu	1130	1110	1310	1173	11.1-13.1	1070	1190	1170	1140	4.7	0.9
Fe%	11.2	10.9	10.6	11.0	10.6-11.2	11.7	10.7	10.7	11.0	4.4	0.9
Li	76.1				76.0	71.9	76.6	75.2	74.6	2.6	2.0
Mg%	2.83	2.87		3.30	2.83-3.3	3.08	2.81	2.80	2.90	4.5	2.5
Mn%	18.3	18.5	17.3	18.6	17.3-18.6	19.4	17.5	17.5	18.1	5.1	2.3
Mo	390	448	418		390-448	365	360	367	364	0.8	21.5
Na%	0.866	0.772			0.77-0.87	0.827	0.824	0.813	0.822	0.8	5.8
Ni	6450	6360	6730	6208	6210-6730	6670	6150	6160	6330	3.9	0.5
P	5920	5973			5920-5970	5640	5350	5330	5440	2.6	9.0
S	3350				3350	3690	3550	3530	3590	2.0	7.2
Sr	1630	1748	1730	1692	1630-1750	1540	1500	1480	1510	1.7	14.6
V	660	770	709	644	644-770	627	602	602	611	1.9	24.1
Zn	800	587	698	582	582-800	604	609	614	609	0.7	2.8

Appendix Table 1, continued

GSMC-1	Wang et al. (2003)	JUB single measurements			Method Precision	Accuracy		Nod-P-1	Axelsson et al. (2002)	Govindaraju (1994) comp.	Terashima et al. (1995)	Range	JUB single measurements				Method Precision	Accuracy	
					Average <i>n</i> =3	%RSD	% Diff.										Average <i>n</i> =4	%RSD	% Diff.
Al%	1.11	1.09	1.07	1.07	1.08	0.9	1	Al%	2.46	2.55	2.57	2.46-2.57	2.39	2.53	2.46	2.52	2.48	2.2	3
Ca%	3.29	3.11	3.26	3.26	3.21	2.2	3	Ca%	2.24	2.19	2.21	2.1-2.24	2.07	2.19	2.13	2.19	2.14	2.4	2
Co	13000	13200	12800	13000	13000	1.2	1	Co	2290	2240	2280	2240-2290	2170	2320	2200	2240	2230	2.5	0.4
Cu	1400	1330	1410	1430	1390	3.3	5	Cu%	1.12	1.15	1.17	1.12-1.17	1.12	1.17	1.29	1.32	1.23	6.6	7
Fe%	17.2	17.5	16.3	16.5	16.8	3.0	4	Fe%	5.89	5.77	5.81	5.77-5.89	5.67	5.90	5.66	5.84	5.77	1.8	0
Li			3.08	3.09	3.09	0.0		Li	140		142	140-142	128	133	136	140	134	3.3	4
Mg%	1.11	1.09	1.09	1.10	1.09	0.5	0	Mg%	2.03	1.99	2.00	1.99-2.03	1.90	1.99	1.95	1.99	1.96	1.8	1
Mn%	23.2	23.5	21.6	22.2	22.4	3.5	4	Mn%	29.6	29.1	29.2	29.1-29.6	27.4	28.4	27.6	28.1	27.9	1.4	4
Mo	493	490	481	492	488	1.0	0	Mo	675	762		675-762	591	631	606	635	616	2.9	22
Na%	1.09	0.999	1.06	1.07	1.04	3.0	4	Na%	1.71	1.64	1.66	1.64-1.71	1.59	1.67	1.61	1.66	1.63	2.2	1
Ni	4400	4530	4430	4520	4500	1.0	1	Ni	13500	13400	13800	13400-13800	12200	12900	12900	13100	12800	2.7	4
P	6932	6500	6760	6890	6720	2.4	3	P	2060			2060	1650	1800	2040	2040	1880	8.8	9
S	1200		1510	1540	1530	1.1		S	1000			1000	1090	1230	1220	1230	1190	5.1	19
Sr	1481	1440	1460	1480	1460	1.1	2	Sr	670	680	678	670-680	629	657	622	640	637	2.1	6
V	617	605	617	628	617	1.5	2	V	510	570	586	510-586	425	456	465	479	456	4.4	22
Zn	676	708	721	738	722	1.7	2	Zn	2020	1595	1590	1590-2020	1550	1650	1670	1690	1640	3.2	2

Appendix Table 2: Literature reference values and measured element concentrations for CRMs analyzed within JUB Geochemistry Lab with ICP-MS, data are in mg/kg

Element	NOD-A-1 Dulski (2001)	NOD-A-1 Axelsson (2002)	NOD-A-1 Govindaraju (1994)	CRM average	CRM (Sd)	CRM (%RSD)	Average JUB, single meas. (n=10)	Element	JMn-1 Dulski (2001) meas.	JMn-1 Imai et al. (1999) comp.	JMn-1 Terashima et al. (1995) meas.	CRM average	CRM (Sd)	CRM (%RSD)	Average JUB, control std. (n=20)	Method precision (%RSD)	Average JUB, single meas. (n=27)
Sc		12.4					11.9	Sc		13.0					12.3	8.7	13.0
Ti		3030					2910	Ti		6360					6140	2.1	6380
Co		3180	3110	3150	35.0	1.1	2410	Co		1730	1690	1710	20.0	1.2	1690	2.0	1580
Ni		6450	6360	6410	45.0	0.7	6300	Ni		12600	12600	12600	40.0	0.3	12100	2.1	10200
Rb	9.70	10.6		10.2	0.450	4.4	10.3	Rb	11.6	10.9	11.0	11.2	0.302	2.7	10.7	5.3	11.3
Sr	1470	1630	1750	1620	115	7.1	1350	Sr	800	792	737	776	28.0	3.6	752	8.8	746
Y	116	120	116	117	1.89	1.6	117	Y	114	111	106	110	3.09	2.8	107	3.4	109
Zr	233	310		272	38.5	14.2	313	Zr	392	344	350	362	21.4	5.9	354	3.6	359
Nb		43.1		43.1			47.0	52 Nb		22.3-33*	27.4	27.4			29.0	4.4	29.2
Mo		390	448	419	29.0	6.9	378	Mo		318	316	317	1.00	0.3	307	2.8	308
Cs	0.560	0.610		0.585	0.0250	4.3	0.586	Cs	0.370	0.600	0.410	0.460	0.100	21.8	0.357	6.3	0.354
Ba	1350	1530	1670	1520	130	8.6	1490	Ba	1510	1710	1700	1640	93.0	5.7	1570	4.1	1610
La	112	115	118	115	2.45	2.1	115	La	121	122	125	123	1.64	1.3	116	4.4	121
Ce	743	720	732	732	9.39	1.3	792	Ce	271	277	286	278	6.16	2.2	278	11.4	277
Pr	24.3	25.0		24.7	0.350	1.4	24.8	Pr	32.0	31.4	29.7	31.0	0.965	3.1	30.4	4.3	31.4
Nd	93.0	98.0	94.0	95.0	2.16	2.3	103	Nd	123	137	128	129	5.80	4.5	128	4.1	131
Sm	19.8	21.9	21.1	20.9	0.865	4.1	22.3	Sm	27.0	30.2	29.3	28.8	1.34	4.7	28.7	3.9	29.1
Eu	5.40	5.20	4.96	5.19	0.180	3.5	5.51	Eu	7.53	7.60	7.26	7.46	0.147	2.0	7.15	4.5	7.33
Gd	24.9	25.4	26.1	25.5	0.492	1.9	26.1	Gd	32.1	29.8	26.1	29.3	2.49	8.5	30.1	5.1	31.4
Tb	3.90	4.00		3.95	0.0500	1.3	3.98	Tb	4.92	4.80	4.42	4.71	0.213	4.5	4.67	4.6	4.85
Dy	23.5	23.8	22.8	23.4	0.419	1.8	24.0	Dy	28.6	28.3	26.1	27.7	1.14	4.1	27.5	4.0	28.1
Ho	4.90	5.00		4.95	0.0500	1.0	5.06	Ho	5.58	5.80	5.49	5.62	0.130	2.3	5.33	4.1	5.55
Er	14.6	14.4	11.7	13.6	1.32	9.8	15.1	Er	15.6	14.6	13.3	14.5	0.959	6.6	14.9	4.2	15.6
Tm	2.09	2.00		2.05	0.0450	2.2	2.20	Tm	2.21	2.10	2.04	2.12	0.0704	3.3	2.06	6.4	2.23
Yb	13.7	13.9	13.8	13.8	0.0816	0.6	14.1	Yb	14.4	13.8	12.9	13.7	0.634	4.6	13.7	4.1	14.2
Lu	2.20	2.10	2.24	2.18	0.0589	2.7	2.27	Lu	2.16	2.10	2.06	2.11	0.0411	2.0	2.07	3.9	2.12
Hf	4.00	5.80		4.90	0.900	18.4	6.38	Hf	6.40	6.20	6.10	6.23	0.125	2.0	5.87	7.1	6.45
Ta		0.760		0.760			0.911	Ta		0.635	0.680	0.658	0.0225	3.4	0.611	9.1	0.620
W		87.0		87.0			85.4	W		45.3	37.5	41.4	3.91	9.4	40.2	4.5	
Pb	797	860	846	834	27.0	3.2	796	Pb	434	430	444	436	5.89	1.4	445	1.3	439
Th	23.0			23.0			22.2	Th	13.0	11.7	11.9	12.2	0.566	4.6	12.2	1.0	12.3
U	7.00			7.00			6.91	U	5.30	5.00	4.81	5.04	0.202	4.0	5.24	2.7	4.98

Appendix Table 2, continued

GSMC-1 Wang et al. (2003) comp.	GSMC-1 (SD)	GSMC-1 (%RSD)	Average JUB, single meas. (n=7)	Nod-P-1 Dulski (2001)	Nod-P-1 Axelsson (2002)	Nod-P-1 Govindaraju (1994)	CRM average	CRM (Sd)	CRM (%RSD)	Average JUB, control std. (n=2)	Method precision (%RSD)	Average JUB, single meas. (n=23)
13.0	2.00	15.4	11.2		9.70					9.31	1.1	10.2
13200			12500		2720					2610	0.2	2920
13000	900	6.9	8990		2290	2240	2270	25.0	1.1	1430	3.6	2280
4400	200	4.6	4540		13500	13400	13500	50.0	0.4	8060	5.1	12800
11.0	1.00	9.1	10.4	24.5	23.7		24.1	0.400	1.7	25.2	4.5	24.5
1480	71.0	4.8	1460	649	670	680	666	12.9	1.9	513	8.9	627
239	9.00	3.8	244	91.0	90.0	94.0	91.7	1.70	1.9	85.9	0.1	87.4
656	43.0	6.6	655	298	280		289	9.00	3.1	277	1.7	280
58.0	9.00	15.5	64.9		21.3		21.3			20.4	3.2	21.4
493	21.0	4.3	497		675	762	719	43.5	6.1	617	1.9	641
0.600	0.100	16.7	0.650	1.75	1.80		1.78	0.0250	1.4	1.69	2.4	1.69
1850	65.0	3.5	1830	2450	2690	3350	2830	380	13.4	2520	1.1	2890
352	22.0	6.3	349	110	105	104	106	2.62	2.5	105	1.0	110
1320	66.0	5.0	1370	329	305	294	309	14.6	4.7	320		341
72.0	6.00	8.3	71.0	33.0	31.0		32.0	1.00	3.1	31.2	1.3	31.2
293	14.0	4.8	293	128	130	119	126	4.78	3.8	133	1.9	134
61.0	2.00	3.3	60.3	30.0	31.0	29.5	30.2	0.624	2.1	31.9	0.6	32.1
15.0	2.00	13.3	15.2	8.00	7.60	7.50	7.70	0.216	2.8	7.63	0.3	7.65
65.0	8.00	12.3	68.4	31.7	30.4	28.2	30.1	1.44	4.8	30.6	2.7	30.2
9.50	0.960	10.1	10.3	4.88	4.90		4.89	0.0100	0.2	4.69	0.7	4.76
58.0	6.00	10.3	60.1	27.5	27.1	26.8	27.1	0.287	1.1	26.4	0.4	26.7
11.3	0.900	8.0	12.1	5.13	5.00		5.07	0.0650	1.3	4.92	0.2	4.98
32.0	3.00	9.4	34.1	14.2	13.6	12.5	13.4	0.686	5.1	13.5	0.1	13.7
4.60	0.400	8.7	4.72	2.03	1.90		1.97	0.0650	3.3	1.95	3.3	1.93
31.0	1.00	3.2	30.9	13.3	12.9	12.7	13.0	0.249	1.9	12.7	0.4	12.7
4.50	0.300	6.7	4.68	1.99	1.80	1.78	1.86	0.0946	5.1	1.91	0.9	1.92
9.30	2.20	23.7	10.2	4.20	4.20		4.20			4.06	6.4	3.99
			1.10		0.330		0.330			0.326	7.2	0.360
88.0	5.00	5.7	90.3		57.8		57.8			56.4	3.1	59.3
1500	100	6.7	1320	451	475	555	494	44.5	9.0		4.6	464
25.0	4.00	16.0	18.8	16.6	16.7		16.7	0.0500	0.3		5.2	16.4
12.0	1.00	8.3	11.3	4.21	4.00		4.11	0.105	2.6		1.9	4.28

Appendix Table 2, continued

Element	GSPN-3 Dulski (2001)	GSPN-3 Wang et al. (1998)	Ref. average	GSPN-3 (Sd)	GSPN-3 (%RSD)	Average JUB, control std. (n=9)	Method precision (%RSD)	Average JUB, single meas. (n=18, Nb,Ta=4)
		9.40						9.86
		3240						3050
		1700	1700					1700
		15500	15500					13900
	18.8	17.0	17.9	0.900	5.0	18.2	3.5	18.1
	565	561	563	2.00	0.4	540	15.6	563
	87.4	84.0	85.7	1.70	2.0	81.6	2.3	83.3
	274	256	265	9.00	3.4	269	6.6	276
		21.0	21.0					21.4
		622	622					672
	1.26	1.20	1.23	0.0300	2.4	1.22	5.0	1.17
	2320	2400	2360	38.5	1.6	2470	7.8	2460
	97.0	96.0	96.5	0.500	0.5	91.6	3.2	95.9
	262	249	256	6.50	2.5	278	18.0	267
	30.9	29.0	30.0	0.950	3.2	28.6	3.9	29.1
	120	121	121	0.500	0.4	122	4.2	124
	29.0	31.0	30.0	1.00	3.3	30.5	4.1	31.0
	7.95	7.60	7.78	0.175	2.3	7.34	4.9	7.46
	30.8	28.0	29.4	1.40	4.8	28.3	5.4	29.6
	4.87	4.60	4.74	0.135	2.9	4.57	3.8	4.68
	27.4	27.0	27.2	0.200	0.7	25.8	4.8	26.8
	5.00	5.10	5.05	0.0500	1.0	4.88	3.7	4.92
	13.9	13.0	13.5	0.450	3.4	13.4	4.3	13.8
	2.00	1.90	1.95	0.0500	2.6	1.93	4.0	1.97
	13.2	12.0	12.6	0.600	4.8	12.6	4.0	12.9
	1.95	1.80	1.88	0.0750	4.0	1.86	3.9	1.90
	4.10	3.90	4.00	0.1000	2.5	3.89	4.5	4.01
								0.315
		61.0	61.0					73.0
	318	328	323	5.00	1.6		8.0	331
	16.2	15.0	15.6	0.600	3.9		7.8	15.8
	3.99	3.80	3.90	0.0950	2.4		9.6	4.02

Appendix Table 3: Comparison of Zr, Hf, Nb, Ta concentrations determined in different Fe-Mn oxide samples by different methods: JUB: acid pressure digestion, Münster: matrix separation method (Münker et al., 2001)

Sample type	Sample ID	Nb (Münster)	Nb (JUB)	Ta (Münster)	Ta (JUB)	Nb/Ta (Münster)	Nb/Ta I(UB)	Zr (Münster)	Zr (JUB)	Hf (Münster)	Hf (JUB)	Zr/Hf (Münster)	Zr/Hf (JUB)
Fe-Mn oxide group III	M 64/2 09	31.6	35.3	0.302	0.318	105	111	236	266	6.07	6.19	39	43
Fe oxyhydroxide group IV	M 60/3 21	0.856	0.920	0.0281	0.0290	30	32	16.1	16.1	0.257	0.240	63	67
Mn crust group I	M 60/3 37	0.966	0.850	0.0488	0.0460	20	18	7.32	8.68	0.164	0.165	45	53
CRM	JMn-1	25.5	29.2	0.510	0.607	50	48	321	359	5.64	6.4	57	56

Chapter 7: Further scientific contributions as co-author

This chapter summarizes my contributions to various other published papers and one submitted manuscript, which deal with different aspects of hydrothermal activity at the MAR. Those studies have been conducted within the frame of SPP1144 or are closely related to this program.

The paper “*Geochemical and physical structure of the hydrothermal plume at the ultramafic-hosted Logatchev hydrothermal field at 14°45'N on the Mid-Atlantic Ridge*” intended to investigate the hydrothermal plume above the Logatchev I hydrothermal field in order to characterize the hydrothermal fluxes at an ultramafic-hosted hydrothermal system. Besides physico-chemical parameters, concentrations of dissolved H₂, CH₄, Fe, and Mn determined in individual water plume samples were used for evaluation. My contribution to this study was conducting part of the field work as well as the responsibility for analytical determinations of Fe and Mn.

1. Marbler, H., Koschinsky, A., Pape, T., Seifert, R., Weber, S., Baker, E.T., de Carvalho, L.M., **Schmidt, K.**, 2010. Geochemical and physical structure of the hydrothermal plume at the ultramafic-hosted Logatchev hydrothermal field at 14°45'N on the Mid-Atlantic Ridge. *Marine Geology* 271(3-4): 187-197.

Abstract:

The hydrothermal plume generated in deep waters above the Logatchev hydrothermal field (LHF) about 15°N on the Mid-Atlantic Ridge was investigated and mapped for its 3D distributions using a combination of in situ optical light scattering data, temperature and salinity data, as well as concentrations of hydrogen, methane, total dissolvable Fe, and total dissolvable Mn. Based on the results obtained for these meaningful parameters, we report the geochemical and physical characteristics of the fluids expelled from the ultramafic LHF and the chemical structure of its hydrothermal plume in the water column. The hydrothermal plume is sourced by at least seven distinct vent sites and possibly additional diffusive fluid and gas discharge. It comprises a water body characterized by strong nephelometric anomalies (expressed as ΔNTU , nephelometric turbidity units) and high concentrations of Fe and Mn (>5 times seawater concentration), and the gas plume with several times the H₂ and CH₄ concentrations of normal seawater. Up to three plume levels with a total vertical extension of about 350 m from the seafloor were classified in the hydrothermal plume. The ΔNTU plume could be followed to approximately 2.5 km to the north and to the south from the vent site while the gas plume spread several km farther from the hydrothermal source. High concentrations of H₂ (up to 1598 nmol l⁻¹) and CH₄ (up to 323 nmol l⁻¹) accompanied by relatively low dissolvable Fe concentrations (up to 270 nmol l⁻¹) as well as low concentrations of dissolvable Mn (112 nmol l⁻¹) compared to basaltic hydrothermal systems are the characteristics of the plume. The low metal/gas ratios showed a decrease with increasing distance from the vent site. Our data demonstrate that ultramafic systems such as the LHF serve as both sources and sinks for elements, with respect to metal and gas inputs

into the oceanic water column. The relevance of such systems is underlined by the discovery (and postulated frequency) of further ultramafic-hosted hydrothermal systems on slow-spreading ridges.

In another study, entitled “*Iron isotope fractionation in a buoyant hydrothermal plume, 5°S Mid-Atlantic Ridge*”, S. Bennett and co-workers investigated the Fe isotopic composition of venting hydrothermal fluids and buoyant plumes from 5°S, MAR. The study intended to investigate the Fe inputs from a basalt-hosted, deep-sea hydrothermal system and the isotopic fractionation processes that occur as Fe enters the ocean. My contributions to this paper result from chemical analyses of fluid samples, together with my colleague from Kiel, Dr. Garbe-Schönberg.

2. Bennett, S.A., Rouxel, O., **Schmidt, K.**, Garbe-Schönberg, D., Statham, P.J., German, C.R., 2009. Iron isotope fractionation in a buoyant hydrothermal plume, 5°S Mid-Atlantic Ridge. *Geochimica et Cosmochimica Acta* 73(19): 5619-5634.

Abstract

Fe isotopes are a potential tool for tracing the biogeochemical redox cycle of Fe in the ocean. Specifically, it is hypothesized that Fe isotopes could enable estimation of the contributions from multiple Fe sources to the dissolved Fe budget, an issue that has received much attention in recent years. The first priority however, is to understand any Fe isotope fractionation processes that may occur as Fe enters the ocean, resulting in modification of original source compositions. In this study, we have investigated the Fe inputs from a basalt-hosted, deep-sea hydrothermal system and the fractionation processes that occur as the hot, chemically reduced and acidic vent fluids mix with cold, oxygen-rich seawater. The samples collected were both end-member vent fluids taken from hydrothermal chimneys, and rising buoyant plume samples collected directly above the same vents at 5°S, Mid-Atlantic Ridge. Our analyzes of these samples reveal that, for the particulate Fe species within the buoyant plume, 25% of the Fe is precipitated as Fe-sulfides. The isotope fractionation caused by the formation of these Fe-sulfides is $\delta\text{Fe(II)-FeS} = +0.60 \pm 0.12\text{‰}$. The source isotope composition for the buoyant plume samples collected above the Red Lion vents is calculated to be $-0.29 \pm 0.05\text{‰}$. This is identical to the value measured in end-member vent fluids collected from the underlying "Tannenbaum" chimney. The resulting isotope compositions of the Fe-sulfide and Fe-oxyhydroxide species in this buoyant plume are $-0.89 \pm 0.11\text{‰}$ and $-0.19 \pm 0.09\text{‰}$, respectively. From mass balance calculations, we have been able to calculate the isotope composition of the dissolved Fe fraction, and hypothesize that the isotope composition of any stabilized dissolved Fe species exported to the surrounding ocean may be heavier than the original vent fluid. Such species would be expected to travel some distance from areas of hydrothermal venting and, hence, contribute to not only the dissolved Fe budget of the deep-ocean but also its dissolved Fe isotope signature.

The REY distribution of high-temperature hydrothermal fluids is characterized by distinct positive Eu anomalies, which can be attributed to a decoupling of Eu in reducing solutions at

temperatures above 200°C (a remarkable exception is discussed in chapter 4). Diffuse fluids, resulting from cooling/mixing of high-temperature hydrothermal fluids often display even enhanced Eu anomalies, which been related to the discrimination of Eu^{2+} during incorporation into sulfides/sulfates in the subseafloor. The paper “*Rare earth elements in mussel shells of the Mytilidae family as tracers for hidden and fossil high-temperature hydrothermal systems*” by M. Bau and coworkers investigated the REY composition of *Bathymodiolus* mussel shells living at the emanation sites of diffuse hydrothermal fluids in order to evaluate their potential to trace high-temperature hydrothermal activity. As could have been demonstrated, the mussel shells from Logatchev I reflect the strong positive Eu anomalies of the fluids, related to the unfractionated incorporation of Eu, being present as Eu^{3+} , relative to its neighbors, which makes them a powerful tracer for hidden or fossil high-temperature hydrothermal systems. In case of the diffusively venting Lilliput vent field at 9°S, MAR, the small but significant positive Eu anomaly in the mussel shells is evident for hidden high-temperature hydrothermal activity in the subseafloor, which has been suggested but could not be proven before. My contribution to this study comprises the modification/testing of the REY separation method for mussel shells and the separation and analyses of REY in diffuse fluids from different locations.

3. Bau, M., Balan, S., **Schmidt, K.**, Koschinsky, A., 2010. Rare earth elements in mussel shells of the Mytilidae family as tracers for hidden and fossil high-temperature hydrothermal systems. *Earth and Planetary Science Letters* 299(3-4): 310-316.

Abstract

Bathymodiolus mussels of the *Mytilidae* family live in ecological niches at marine vent sites where hydrothermal fluids discharge at the seafloor and mix with ambient seawater. We report the first concentration data for rare earth elements and yttrium (REY) of *Bathymodiolus* shells and of low-temperature diffuse hydrothermal fluids venting in their respective habitat at three hydrothermal vent fields along the Mid-Atlantic Ridge (MAR) and for littoral *Mytilus edulis* shells from the western North Atlantic, Dingle Bay, Ireland, and from the southern North Sea, German Bight, Germany. Similar to high-temperature hydrothermal solutions expelled in the respective area, the low-temperature diffuse fluids from the hydrothermal vent sites display positive Eu anomalies. These indicate that the fluids carry a component previously involved in high-temperature water–rock interaction, as decoupling of Eu from neighbouring REY requires temperatures above about 200 C. While the *Bathymodiolus* shells from the hydrothermal vent fields reflect these positive Eu anomalies, the littoral *M. edulis* shells studied for comparison, do not show Eu anomalies, consistent with the lack of any high-temperature hydrothermal activity in their coastal environments. Shells of mussels of the *Mytilidae* family, such as *Bathymodiolus* and *M. edulis*, therefore, are archives whose REY distribution can be used as a proxy for the Eu anomaly of the waters in which the mussels grew. Although the Ca carbonate of a mussel shell is precipitated from the extrapallial fluid of the mussel and not directly from seawater, the Eu/Eu* ratio of seawater is not significantly modified under the low-temperature conditions prevailing during vital

processes and biomineralization. This allows one to use the positive Eu anomalies in the REY distribution patterns of *Bathymodiolus* shells as a tracer for hidden or fossil high-temperature hydrothermal systems where other indicators of high-temperature hydrothermalism are not available.

One focus of the SPP1144 program was on the geo-bio interactions at hydrothermal vent sites. Dr. M. Perner investigated the occurrence of microbial communities at different vent sites in dependence of the host rock composition of the hydrothermal field. One study focused on bacterial communities at the Logatchev-1 vent field, which is characterized by extremely high concentrations of hydrogen and methane to find out, whether the fluid composition directly determines the type of bacteria and which other factor may play a role. For this study, the fluid geochemistry group including myself provided the analytical data of vent fluid composition.

4. Perner, M., Kuever, J., Seifert, R., Pape, T., Koschinsky, A., **Schmidt, K.**, Strauss, H., Imhoff, J.F., 2007. The influence of ultramafic rocks on microbial communities at the Logatchev hydrothermal field, located 15°N on the Mid-Atlantic Ridge. FEMS Microbiology Ecology 61, 97-109.

Abstract

The ultramafic-hosted Logatchev hydrothermal field (LHF) on the Mid-Atlantic Ridge is characterized by high hydrogen and methane contents in the seafloor, which support a specialized microbial community of phylogenetically diverse, hydrogen-oxidizing chemolithoautotrophs. We compared the prokaryotic communities of three sites located in the LHF and encountered a predominance of archaeal sequences affiliated with methanogenic *Methanococcales* at all three. However, the bacterial composition varied in accordance with differences in fluid chemistry between the three sites investigated. An increase in hydrogen seemed to coincide with the diversification of hydrogen-oxidizing bacteria. This might indicate that the host rock indirectly selects this specific group of bacteria. However, next to hydrogen availability further factors are evident (e.g. mixing of hot reduced hydrothermal fluids with cold oxygenated seawater), which have a significant impact on the distribution of microorganisms.

In the context of studies regarding hydrothermal fluxes from the lithosphere to the hydrosphere, one study by my colleague V. Klevenz and coworkers investigated the particle formation during initial hydrothermal fluid-seawater mixing in ultramafic- (Logatchev-1) and mafic-hosted (5°S vent field) hydrothermal systems, entitled “*Geochemistry of particle formation during initial hydrothermal fluid - seawater mixing at the emanation sites of MAR vent fluids*”. The study aimed to investigate the mineralogical and chemical composition of fluid particles forming during initial fluid-seawater mixing, in dependence of host rock composition and mixing grade, and determined fluid-particle partition coefficients of elements. My contribution to this project results from field work and chemical sample

analyses (fluids and particles) as well as from discussions on the geochemical processes controlling the composition of fluid particles. Furthermore, I investigated the mineralogy of some particle samples with REM in collaboration with Dr. S. Petersen.

5. V. Klevenz, **K. Schmidt**, W. Bach, M. Hentscher, A. Koschinsky, S. Petersen:
Geochemistry of particle formation during initial hydrothermal fluid - seawater mixing
at the emanation sites of MAR vent fluids – manuscript in preparation

8. Conclusion

The work presented in chapters 2 to 8 has been conducted in the research field of mass transfer between the lithosphere and the hydrosphere at high-temperature hydrothermal vent sites at the slow-spreading MAR within the research program SPP1144 and deals with different aspects of hydrothermal fluid geochemistry. For this, chemical analyses of hydrothermal fluids and solid deposits were performed and complemented by mineralogical studies and reaction path modeling. The results contribute to the research in the framework of the SPP1144 program in that fluids are the medium to transfer energy and mass from the crust in the hydrosphere and biosphere. The study aimed to: (1) characterize hydrothermal fluid composition, and to deduce geochemical processes defining the hydrothermal fluid composition in different geological environments at the slow-spreading MAR, in dependence of pressure and temperature, (2) to resolve time scales of hydrothermal activity at slow-spreading ridges, and (3) to investigate the potential of hydrothermal oxide deposits to record hydrothermal export fluxes. With this, the study extends the data record for hydrothermal systems at the MAR in space and time and substantiate the relevance of hydrothermal activity at slow-spreading ridges for geochemical exchange budgets.

The manuscripts of this study deal with different aspects of mass transfer between the hydrosphere and the lithosphere in submarine hydrothermal systems and investigated the geochemical behavior of trace metals in the course of hydrothermal circulation. The first manuscript (Chapter 2 of this thesis) focused on the characterization of vent fluid geochemistry at the ultramafic-hosted Logatchev I hydrothermal field, discussing the spatial variability within this complex, hydrothermal field. Comparison with previously published data (Douville et al., 2002) further allowed a time series study, the first in an ultramafic-hosted hydrothermal system. The discovery of a new, off-axis hydrothermal system influenced by ultramafic rocks in 2006, the Nibelungen field, offered the possibility to compare both fields and define similarities and differences in the compositional signatures, and to deduce geochemical processes determining the fluid composition (Chapter 5). Fluid-mobile elements and stable isotopes have been used to constrain type and extent of fluid-rock interaction and to quantify fluid-rock interaction in the seafloor. The annual sampling campaigns at the 5°S vent system provided data not only for the first mafic-hosted systems venting at p-T conditions above the critical point of seawater (>407°C, >298 bars), representing a completely different type of hydrothermal activity at slow-spreading ridges (Chapter 3), but also allowed to investigate the temporal evolution of chemical output in

response to a magmatic event over several years (Chapter 3 and 4) and on shorter time scales of minutes to days (Chapter 4). Chapter 4 more specifically focused on the trace metal (REY) variation in this highly dynamic, actively phase-separating hydrothermal system. While the first five chapters of the thesis concentrated on the fluid geochemistry of high-temperature vents and related geochemical processes in the subseafloor, chapter 6 addresses the chemical composition of proximal Fe and Mn oxide precipitates in the ultramafic-hosted Logatchev I field und their spatial and medium-term temporal variability and evaluates the relative contributions of hydrothermal and other sources for individual elements dependent on the formation conditions.

In recent years, slow-spreading ridges received more attention in hydrothermalism-related research (Bach and Früh-Green, 2010). About 50% of the global ridge-axis length are slow and ultraslow spreading ridges (Sinha and Evans, 2004) and thus it has been recognized that the mass, heat, and chemical fluxes at hydrothermal systems along these ridges likely contribute significantly to the overall exchange between lithosphere and hydrosphere (e.g., German et al., 2010). The MAR is characterized by slow plate separation and variable lithosphere compositions ranging from “typical” layered oceanic crust (e.g., 5°S) to thinned basaltic crust with mantle rock exposures containing gabbroic intrusions along deep-rooted detachment faults, as often observed at segment ends. The water depth of the axial valley is greater compared to fast-spreading ridges. Both, the different lithologies and the water depth make this spreading axis unique relative to fast-spreading ridges and affect the hydrothermal activity. While fast-spreading ridges are often characterized by small and short-lived hydrothermal systems with a composition defined by basalt-seawater interaction, hydrothermal activity at slow-spreading ridges is more variable with respect to fluid composition between different localities (linked to variety of lithologies in different geological settings), but generally more stable considering the temporal evolution of individual fields. The MAR hosts the hottest hydrothermal system found so far (basaltic rocks, Turtle Pits, 5°S) as well as hydrothermal systems operating in mantle rocks. The variety of previously known and newly discovered hydrothermal fields at the MAR investigated during this study allowed to systematically investigate the effect of host rock composition (Logatchev/Niblelungen/Red Lion) and the effect of temperature/phase separation processes (Red Lion/Turtle Pits) at similar water depths of 3000 m. The possibility to revisit target sites several time during numerous cruises allowed to investigate the temporal evolution of hydrothermal systems depending on their geological setting and physical conditions.

One focus of this study was the question which geochemical processes and mechanisms control the elemental and isotopic compositions of hydrothermal fluids in heterogeneous, mafic-ultramafic lithosphere settings as typically found at slow-spreading ridges. Previous studies in ultramafic rock settings have shown that associated high-temperature hydrothermal fluids are characterized by distinct fluid compositions with strong enrichments of dissolved hydrogen and methane but lower H_2S and Si concentrations relative to basaltic-hosted hydrothermal systems (Douville et al., 2002). The Nibelungen vent field represents a new vent system at the southern MAR, whose occurrence is tectonically controlled and its fluid composition is controlled by a hybrid alteration of mafic and ultramafic rocks. It could be shown that compositional key parameters of Nibelungen, together with those of the Logatchev I hydrothermal field and the Rainbow vent field (dissolved gases, Si, trace alkali elements, B, and $\Delta^2\text{H}_{\text{H}_2\text{O}}$) collectively define a unique geochemical fingerprint that is typical for hot fluids venting in heterogeneous, ultramafic-bearing lithosphere settings at slow-spreading ridge axes. In contrast, the concentrations of transition metals like Fe, Cu, Zn, Co, Sn, strongly differ between Nibelungen and Logatchev I and depend on the fluid temperature enhancing the solubility, the fluid pH, redox conditions, and on H_2S activity, rather than on the rock composition. While these metals are extremely enriched in the 372°C hot Nibelungen fluids with metal/ H_2S ratios >5 , 350°C hot Logatchev I hydrothermal fluids show rather moderate metal concentrations, comparable to high-temperature mafic-hosted hydrothermal systems.

A major progress in the study of fluid-rock interaction in ultramafic-hosted hydrothermal systems is the quantification of geochemical processes in the subseafloor, as it has been discussed in chapter 3. Fluid geochemical constraints have been used to infer the alteration sequence of the lithosphere below the Nibelungen field (or rather along the fluid pathway) encompassing a low- to medium-temperature alteration of gabbroic rocks, pervasive serpentinization at moderate- to high-temperatures and limited high-temperature interaction with basaltic rocks during ascent in agreement with field observations, (seafloor covered by altered pillow lava), at a low integrated water-rock ratio <0.5 . The lithosphere below the Nibelungen hydrothermal field is probably disrupted by deep-rooted faults and consists of a thin basaltic layer (pillow lava and lava flows) overlying peridotite with gabbro intrusions typical for segment ends (Searle and Escartin, 2004). Due to tectonic stretching of the crust resulting in the formation of normal faults, seawater may get access to mantle rocks.

This study provides important implications about the mode of hydrothermal alteration in off-axis settings. These parts of the spreading ridges are still under-explored, and probably have a

profound impact on heat and mass exchange between the lithosphere and the hydrosphere. The distinct fluxes of elements and isotopes in heterogeneous lithosphere settings like Logatchev I and Nibelungen might be important for the budgets of specific elements in the ocean and geo-bio interactions at the vent sites. Different exchange budgets at high-temperature, ultramafic-hosted compared to mafic-hosted hydrothermal systems at similar p-T conditions are evident for B, Li, H₂O, Cl and possibly some more elements, for which ultramafic-hosted hydrothermal systems act as sink for these compounds. Furthermore, enhanced metal/H₂S ratios $\gg 1$ in hydrothermal fluids like Nibelungen (and Rainbow) have important implications for the flux of dissolved and particulate metals into the ocean: Reduced sulfide precipitation close to the vent sites enhances the amount of Fe available to form Fe(III) oxyhydroxide particles, which in turn has consequences for the removal flux of particle-reactive elements in the hydrothermal plume (c.f., German et al., 2010), and likely also the hydrothermal flux of other dissolved metals like Cu. Organic complexation and stabilization of the reduced metal species may significantly contribute to the export flux of dissolved metals in the ocean, in dependence of the concentration of the elements in the fluids (e.g., Koschinsky and Sander, in revision).

Opposite to the Logatchev I and Nibelungen vent fields located in fault-controlled settings and characterized by mantle rock alteration, which become possible by tectonic stretching, the 5°S vent system is hosted in young oceanic crust at the ridge axis. The three individual high-temperature vent fields are located in basaltic lava settings, with two of them (Two Boats and Comfortless Cove) being influenced by a recent lava eruption (Haase et al., 2007). Hydrothermal fluids from the Turtle Pits and Comfortless Cove fields vent at p-T conditions close to or above the CP_{SW} as chloride-depleted, vapor-like single-phase fluids or vapor-phase fluids. Phase separation by brine condensation above the CP_{SW} and p-T venting conditions close to the CP_{SW} makes this field unique at mid-ocean ridges. Post-eruptive hydrothermal systems associated with young lava flows are known from the EPR where they are often characterized by significant changes in the fluid geochemistry and heat fluxes over time. Vapor phase fluids sampled in such settings are often strongly depleted in metals. The fluid chemistry data of TP and CC show that vapor phase fluids forming above the CP behave differently compared to vapor phase fluids formed by boiling, stabilizing high dissolved metal concentrations. Physico-chemical properties of hydrothermal fluids change with increasing p and T and determine elemental speciation; complex stabilities and high Fe contents at 5°S can be explained by strong complexation of metals like Fe at high temperatures close to the CP_{SW} , and a high capability of vapor-phase fluids which are formed due to exsolution of a brine

phase to transport metals, leading to minor relative fractionation to chloride between vapor and brine during phase separation. The high venting temperatures of 405-425°C are related to the depth of the seafloor and the depth of the reaction zone generally favoring hotter hydrothermal fluids, and are close to the 420°C temperature of maximum energy transport (Geiger et al., 2005). Chloride and Si concentrations can be used to constrain the depth of the reaction zone, indicating a relatively shallow heat source less than 500 m below the seafloor at Turtle Pits (350 bars; based on equilibrium relations as given in Foustoukos and Seyfried, 2007 and Fontaine et al., 2009). As this is based on the assumption that Cl and Si concentrations do not change during fluid ascent (which is not the case if fluid upflow occurs in the two-phase region), such calculations should be used with caution. On the other hand, the high fluid temperatures themselves indicate a relatively shallow heat source in the crust, as long upwelling pathways would lead to substantial cooling of the fluids.

Temporal evolution of vent fluid geochemistry

The temporal evolution of chemical fluxes between the lithosphere and the hydrosphere at high-temperature vent fields has important implications for the quantification of hydrothermal contributions to elemental budgets in the ocean. It has been recognized that the chemical composition of MAR vent fields can remain stable over long time periods (e.g., TAG). Time series studies conducted within the SPP1144 resolve stable chemical compositions with respect to major elements in all investigated hydrothermal fields over a period of several years. The chemical composition at Logatchev-1 has been stable for the past 13 years (1996-2009), and the Nibelungen fluids remained unchanged between 2006 and 2009 (Fig. 9.1). The stability refers to all elements behaving conservative during initial fluid seawater mixing (Cl, Br, Na, K, Ca, Si, Li, B, Mn, Rb, Sr, Cs, W). Elements easily precipitating as sulfides during cooling and/or seawater mixing (like Cu, Zn, Pb, Cd, Sn, Tl) show larger variations. While stable fluid emanations in tectonically controlled vent settings can be explained by limited magmatic activity in areas with mantle rock exposures, in favor of stable convection plumes not affected by changes in the permeability (Coumou et al., 2006), the stability of the 5°S vent system between 2005 and 2009 is remarkable (Fig. 9.1). Hydrothermal activity has been triggered by a volcanic eruption, and comparable hydrothermal systems at the EPR usually display cooling and transition to brine phase emanation within months or a few years (e.g., Butterfield et al., 1994; von Damm et al., 1995). These results show that hydrothermal systems at the MAR behave differently compared to those on fast-spreading ridges. The water depth of slow-spreading ridge axes is generally deeper than that of fast-spreading ridges. The

hydrostatic pressure above the magmatic heat source and the depth of the seafloor probably play a critical role for the temporal evolution of a hydrothermal system (Coumou et al., (2009). More specifically, phase separation and the depth at which it occurs appear to be first order controls on the salinity of vent fluids and its variation in space and time. Coumou and co-workers (2009) conducted fluid flow simulations at 35 MPa seafloor pressure with a magma chamber depth 1000 m below the seafloor and could show, that a single-phase upflow zone develops, consisting of fluids resulting from dilution of seawater by a 1.0 wt % vapor phase which condensed out a brine at depth. On its way to the top, this single-phase fluid is progressively mixed with more and more seawater, moving through the top as a 2.1 ± 0.1 wt % NaCl fluid with a temperature of $407 \pm 7.0^\circ\text{C}$. Such systems are expected to emanate fluids with constant salinity and temperature over years and decades, while at lower pressures fully developed vapor and liquid upflow zones form, which results in simultaneous or succeeding emanations of low-salinity vapors and high-salinity brines as observed at $9^\circ 50' \text{N}$, EPR. Pressure conditions at 5°S are somewhat lower than in the high-pressure simulations of Coumou et al. (2009) but these simulations clearly demonstrate how systems like 5°S may evolve. While the fluids of about 407°C at Turtle Pits vent exactly at the 2-phase boundary, hotter fluids with stable temperatures up to 425°C in 2009 represent vapor-phase fluids. The often observed “gas bubbles” most likely represent vapor-phase fluids within a single-phase fluid of slightly lower temperature. A full discussion of the phase relations including extremely hot vapor exsolutions observed at Turtle Pits are beyond the scope of this thesis but will be continued in an upcoming manuscript. At Red Lion, the third vent field at 5°S , the fluid seems to evolve between 2005 and 2009 from a single-phase fluid with seawater-like salinity (Koschinsky et al., 2008) to a condensed vapor phase with decreased salinity, which is accompanied by a decrease in the concentrations of Ca, Na, Si, Mn, Fe, and H_2S . This may indicate changes in the depth of the heat source driving the circulation and onset of phase separation (Fig. 9.1).

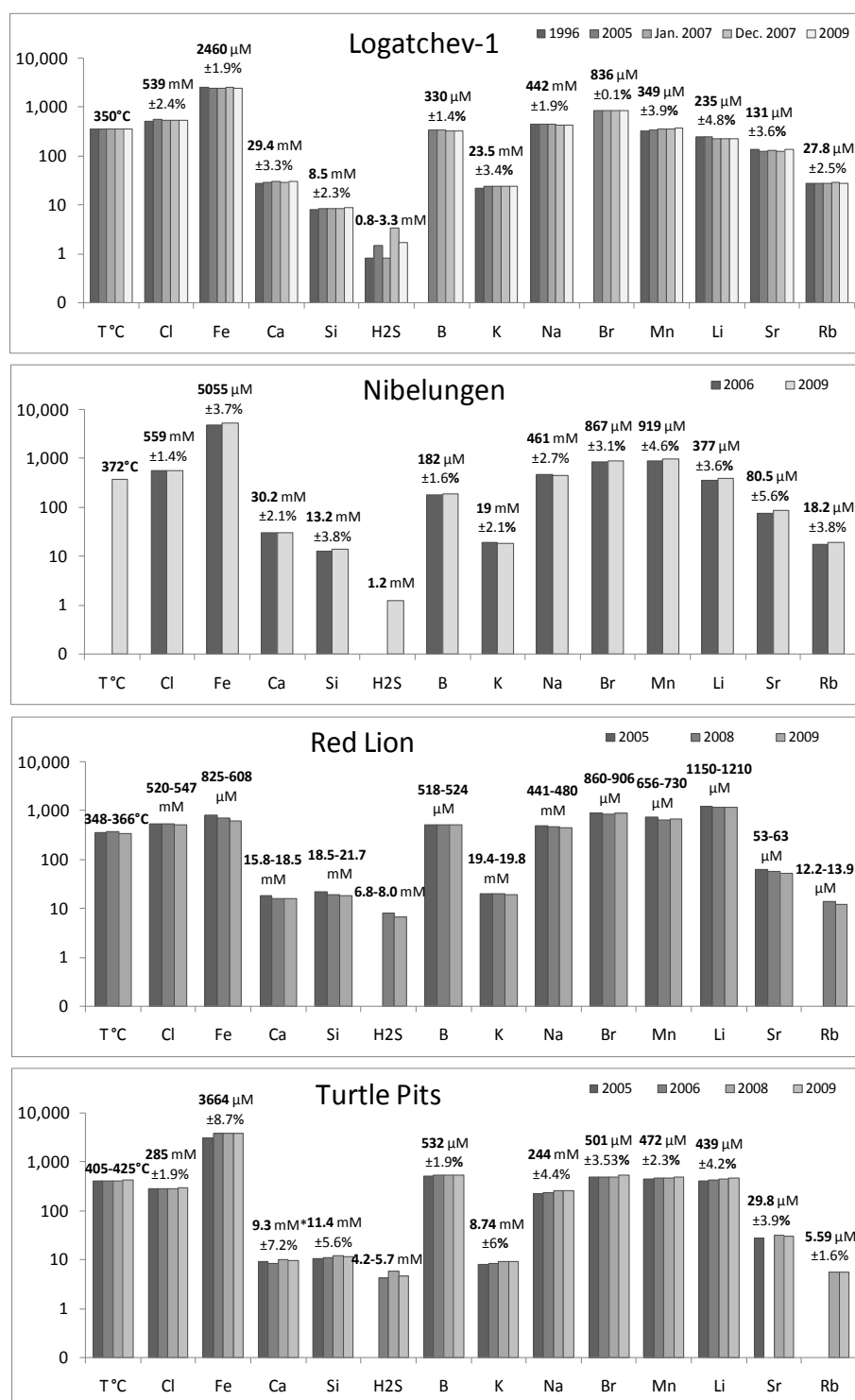


Figure 9.1: Temporal evolution of the elemental composition of hydrothermal fluids of Logatchev-1, Nibelungen, Red Lion and Turtle Pits over several years, with average values and %RSD, *Ca is highly variable between individual fluid samples of sampling campaign, see text for discussion, no average values are given for Red Lion, as there seems to be a systematic trend indicating changes in the fluid composition between 2005 and 2009

The Turtle Pits and Comfortless Cove vent fluids have distinct elemental and dissolved gas compositions, which are mainly attributed to the high fluid temperature, and are stable with respect to temperature and salinity. This type of venting as observed at 5°S is different than

formerly investigated hydrothermal fields affected by phase separation at fast-spreading ridges. At these physico-chemical conditions high fluid temperatures of 400°C and more are possible, and vapor-phase fluids can transport high amounts of dissolved elements over time periods of (6) years at least, increasing the heat and elemental flux into the hydrosphere. The continuous heat supply with stable fluid convection might also be controlled by the dimensions of a magmatic intrusion providing the heat source, with generally greater magma reservoirs anticipated at slow-spreading ridges.

While the overall fluid composition of phase-separating fluids of Turtle Pits and Sisters Peak remains stable, individual fluid samples are characterized by highly variable trace metal signatures specifically of REY on time scales of minutes to years. The vapor-phase fluids are partly quite different in their REY distribution, most prominently demonstrated by the Eu anomaly which is absent in some samples. Independent of the major element composition, the REE + Y concentrations fluids display a strong temporal variability in accordance with changes in the Ca concentrations and can be correlated with a strong variability in fluid flow dynamics. The compositional changes in REY distribution can be related to the formation of anhydrite, being a common phase formed due to seawater mixing with rising hot fluids. As shown in fluid flow simulations, seawater mixing in the subseafloor might be common in high-pressure circulation systems (Coumou et al., 2008, 2009). The paper presents two conclusive models in order to explain the variable REY fluid signature. Both models involve fluid-anhydrite interaction and underline the importance of secondary processes as mineral precipitation in defining the REE pattern of hydrothermal fluids. One model discusses the unusual REY distribution in some fluids as signal of a primary reaction zone fluid with short migration pathways at very high fluid temperatures and limited water-rock interaction. This activity state might be common at hydrothermal sites of high magmatic activity, but the primary fluid REE signature will later be completely modified by anhydrite precipitation, in addition to the effects of solution complexation and sorption/incorporation onto/into alteration minerals resulting in the more common REY distribution. Irrespective of whether or not the REY signature represents a primary reaction zone fluid signature, this study has shown that the REY hydrothermal flux in such settings is different to what has been observed at more moderate systems (with respect to temperature), which might have implications for the interpretation of REY signatures in chemical precipitates. In contrast to previous assumptions, hot hydrothermal fluids in mid-ocean ridge settings are not always characterized by large Eu anomalies. This unusual type of REY distribution is probably restricted to young, post-eruptive stages of hydrothermal venting.

The temporal and spatial variation of trace metals at the Logatchev I and Nibelungen vent fields can be related to sulfide precipitation prior, during or after sampling and does not imply differences in the primary geochemical signature as obtained in the reaction zone.

Fe-Mn oxide deposits

The hydrothermal contribution to ocean chemical budgets depends on the composition and flux of hydrothermal fluids at low- and high-temperature emanation sites and the geochemical behavior while fluids enter the ocean. Elements are, depending on their geochemical behavior and the specific conditions, fixed close to the emanation site either as sulfides or in oxides/hydroxide precipitates or are transported into the open ocean (dissolved or colloidal), defining the hydrothermal contribution to the elemental budget. Biogeochemical processes in hydrothermal plumes determine the net hydrothermal flux from high-temperature hydrothermal fluids into the oceans. As Fe oxyhydroxide particles forming due to oxidation of dissolved Fe^{2+} , effectively scavenge dissolved particle-reactive elements from the seawater and also those derived from the hydrothermal source, hydrothermal plumes are *net sinks* for many elements (e.g., REY; Edmonds and German, 2004). Organic complexation likely increases the flux of dissolved components from hydrothermal sources (e.g., Koschinsky and Sander, in revision, Bennett et al., 2008), but the influence on trace metals other than Fe and Cu remains unexplored.

Hydrothermal Fe and Mn oxide precipitates forming in close proximity to the high- and low-temperature emanation sites trace the hydrothermal input into the ocean at the seafloor and can be used as archives of hydrothermal activity. While scavenging dissolved elements, the oxide mineral surfaces are exposed to seawater or to low-temperature hydrothermal fluids, depending on the growth environment. The Fe oxyhydroxide particles and the Mn particles record removal fluxes from different parts of the system: while Mn oxide deposits were rather formed in close association to circulating low-temperature hydrothermal fluids, Fe oxyhydroxide particles were formed in the open ocean water column, probably in the hydrothermal plume. Elements were scavenged from the seawater (hydrogeneous enrichment) and from the low-temperature fluid (hydrothermal enrichment), which does not necessarily reflect the original sources. Using the isotopic composition of radiogenetic elements in hydrothermal deposits of the Logatchev I field, the relative input from hydrothermal and other sources could be quantified for individual groups of elements.

The investigation of hydrothermal Fe- and Mn oxide deposits has implications for hydrogenetic ferromanganese crusts. Ferromanganese crusts consist of Fe oxyhydroxide and Mn oxide particles. While Mn oxides form due to oxidation of dissolved Mn^{2+} in the water column above the precipitates, at least part of the Fe oxyhydroxide particles are thought to represent aggregates of colloidal and particulate Fe^{3+} -oxyhydroxides dispersed in the ocean and originating from hydrothermal sources (e.g., Bau and Koschinsky, 2006). For some elements, the hydrothermal contribution to the elemental budget is controversially discussed, as in the case of Hf (Bau and Koschinsky, 2006; Van de Fliert et al., 2007) and oxide particles forming in close distance to the emanation sites may provide information on the hydrothermal fluxes, as they accumulate elements without isotopic fractionation. As Hf isotopes are used to constrain global variations of continental weathering (e.g., Van de Fliert et al., 2004), the investigation of hydrothermal fluxes of Hf provides important information.

Low-temperature hydrothermal Mn oxide deposits record variable hydrothermal fluxes in space and time. These fluxes are different for individual elements and depend on the relative concentrations in the principle sources (hydrothermal solution and seawater), and the geochemical behavior during crust formation. The differentiation of relative contributions from different sources is crucial for the interpretation of geochemical signals in hydrothermal Mn crusts and Fe-Mn oxide deposits. This study contributes to the understanding of chemical signatures in hydrothermal Mn crusts, which were previously mainly investigated at low-temperature sites. The main conclusions derived from this part of the PhD thesis can be formulated as:

1. The geochemistry of pure Mn crusts found at the Logatchev I hydrothermal field differs significantly compared to texturally and mineralogically similar deposits in distal hydrothermal settings in island arcs and mid-ocean ridge valleys. These deposits record geochemical signals of high-temperature hydrothermal activity, and trace the leaching of massive Cu sulfide deposits in the subseafloor by low-temperature fluids.
2. Individual types of oxide deposits represent different formation environments and thus record different chemical fluxes. While Fe-Mn oxide coatings are grown in contact with seawater, stratified pure Mn oxides were mainly exposed to circulating, low-temperature fluids and record fluxes at low-temperature emanation sites. However, transitions between hydrothermal enrichment processes and hydrogenetic scavenging are smooth and the relative contributions of the different principle sources (low-

temperature fluid, seawater, and detritus) vary in dependence of the source concentrations and the enrichment process.

3. Significant hydrothermal contributions are recorded in the stratified Mn crusts formed in contact with low-temperature hydrothermal fluids, being highest for Os, Cu, but also high for Hf, and, to a lower extent, REY. Fe oxyhydroxide particles do not carry any significant amount of mantle Hf and mantle REY, but small amounts of mantle Os. With increasing hydrogenetic scavenging, the primary signals get overprinted.
4. Depth profiles of stratified Mn crusts resolved strong temporal changes in the composition. This variability has only limited significance with respect to the evaluation of long-term changes of hydrothermal circulation at Logatchev I, as too many factors influence the trace metal signature, and rather reflects local variations in the growth environment and the relative contribution of hydrothermal and hydrogenous scavenging processes.
5. While the strong Cu concentrations in the Mn crusts may document ultramafic mantle rock alteration with the formation of massive Cu sulfide deposits in the subseafloor of Logatchev-1. Nickel contents are strongly influenced by hydrogenetic enrichment and are not capable of tracing ultramafic rock alteration, as has previously been suggested.
6. Hafnium isotopes of mature Fe oxyhydroxide particles sampled at Logatchev I do not show any evidence of a significant hydrothermal flux of Hf via high-temperature hydrothermal fluids. Particle-reactive Hf in Fe oxyhydroxides, which are at least partly influenced by processes in the plume, has a similar isotopic composition as seawater. Even if there is some hydrothermal Hf scavenged by fresh Fe oxyhydroxide plume particles, this signature would immediately be overprinted by continuous sorption of seawater Hf. It cannot, however, be excluded, that dissolved mantle Hf might be stabilized by organic ligands, contributing to the dissolved Hf budget in the ocean.
7. The calculation of growth rates applying the empirical formula of Manheim and Lane-Bostwick (1988) is not valid for hydrothermal Mn deposits, which are strongly influenced by hydrothermal fluids, if these contain high dissolved concentrations of Co. Relative age relations for the different types of oxide deposits indicate very fast growth rates for Mn crusts formed in contact with seawater, lower growth rates for stratified Mn crusts, and very long exposure times to seawater for Fe-rich oxide coatings. Small hydrothermal contributions of some elements in the latter are in agreement with estimated age of hydrothermal activity in the Logatchev hydrothermal field (about 60 000 a, Cherkashev et al., 2008; Lalou et al., 1996).

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