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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.

Keywords: Ultramafic-hosted hydrothermal systems; Serpentinization; Hydrothermal fluids; Temporal variability; Logatchev field

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;

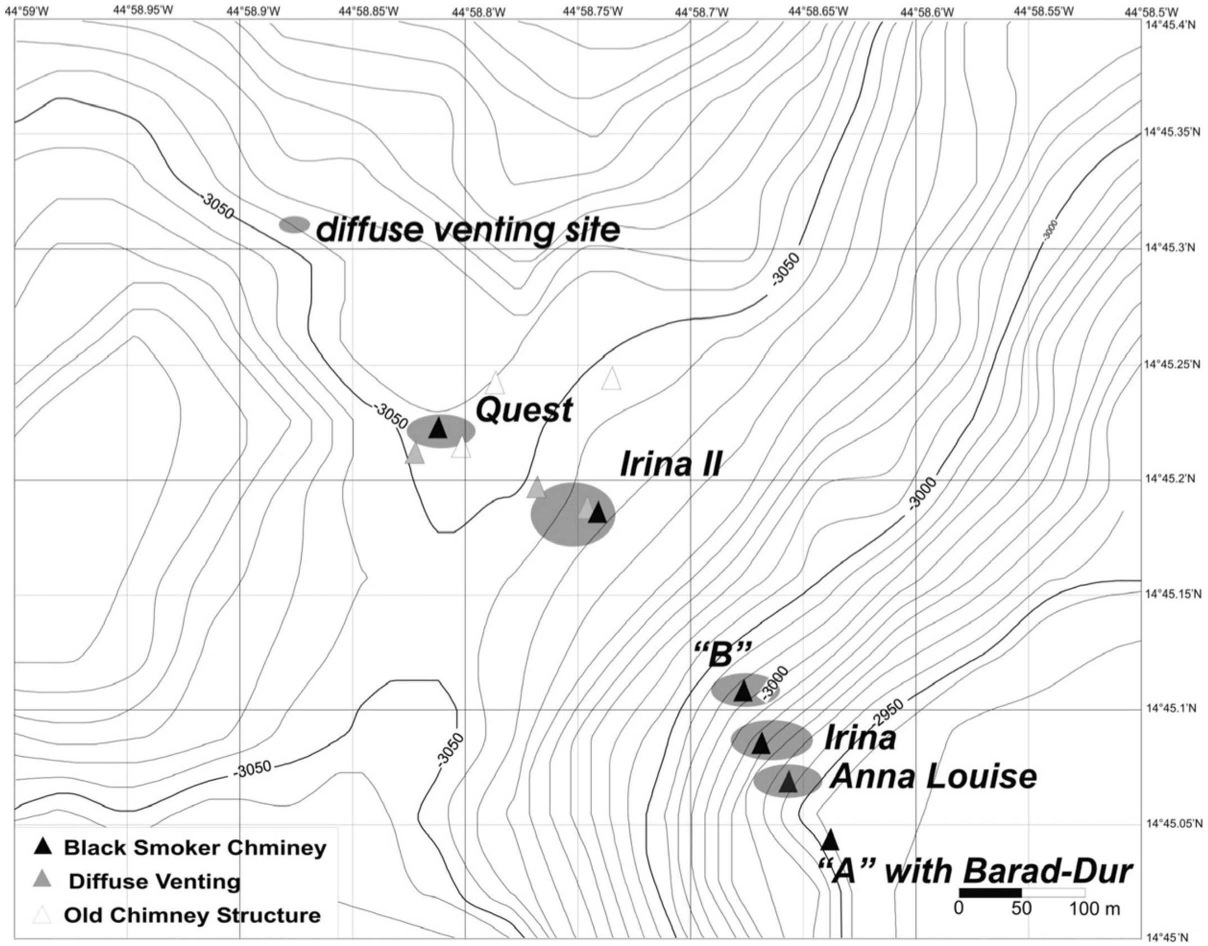

Fig. 2. Sketch map of vent sites in the Logatchev hydrothermal field.

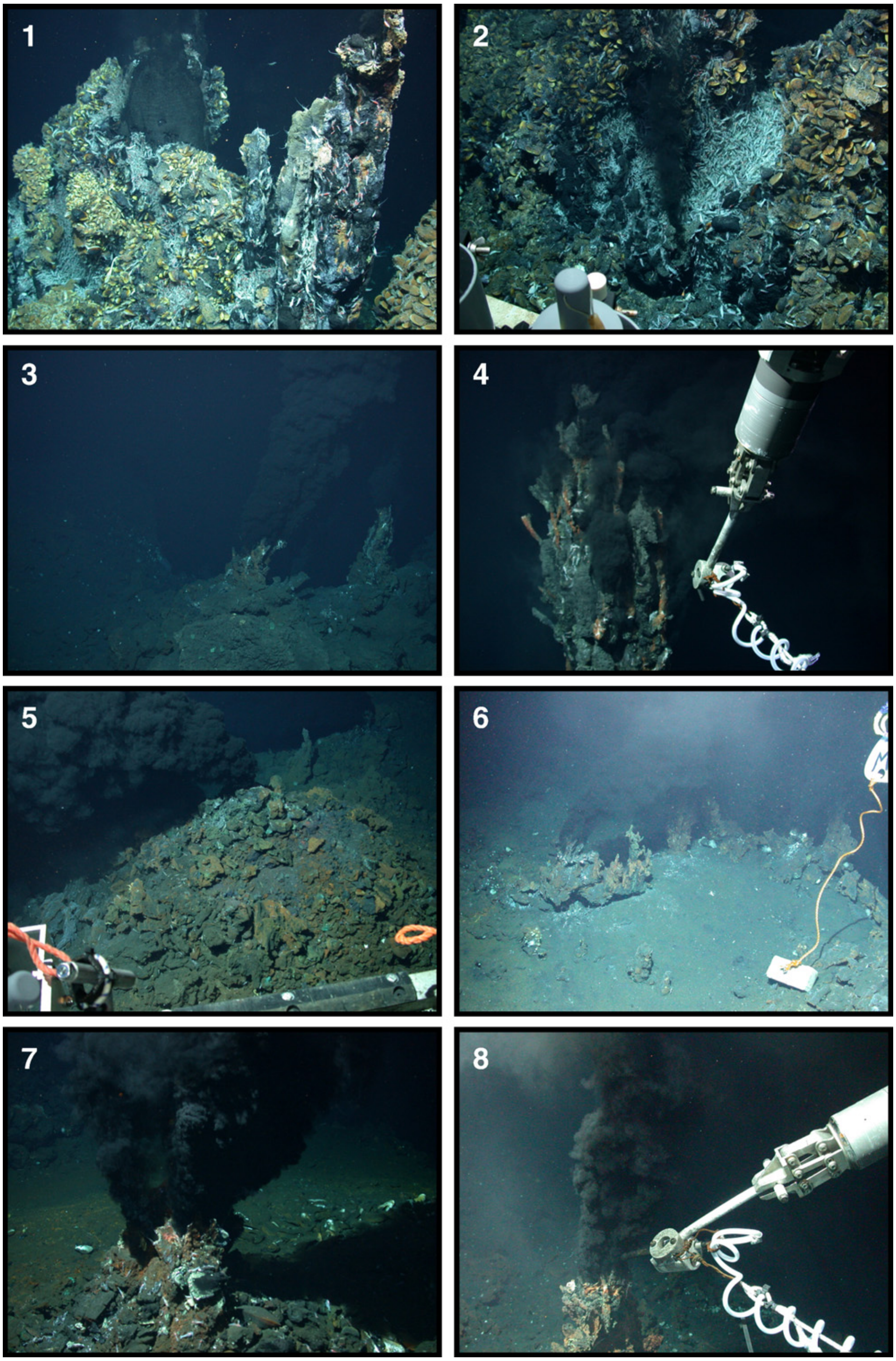

Fig. 3. Photo plate of sampling sites: 1) IRINA II main complex with chimney and beehive structures, dense mussel inhabitation; 2) Sampled fluid emanation at the base of IRINA II main complex (samples 277 ROV-5; 283 ROV-5), dense shrimp mat; 3) Site B smoking crater, sample 257 ROV-8 was taken from the 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	*T* (°C)	Endmember fluid (%)	Description
IRINA II				
Main complex	277 ROV-5	170	20	Emanating grey smoke from a small fissure at the base of the sulfide complex (eastern side), dense shrimp mat
3034 m			55	
	283 ROV-5			
Single black smoker	224 ROV	225	75	Free-standing black smoker chimney SE of IRINA II
3034 m				
Mussel bed				
	232 ROV-3			Diffuse fluids
	232 ROV-7			Diffuse fluids
	266 ROV-7			Diffuse fluids
	277 ROV-4			Diffuse fluids
QUEST	281 ROV-5	280	55	Black smoker chimney approx. 1 m high, Marker MC
3042 m				
				Diffuse fluids
Mussel bed	281 ROV-2			
IRINA	261 ROV-6		70	Black smoker chimney at the southeastern crater rim of the smoking crater, Marker MD
2963 m				
Site B	266 ROV-10	300	75	Black smoker chimney 1, southeastern crater rim of the smoking crater (right)
2983 m				
	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” (Lakschewitz 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 (Lakschewitz 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 ultiport 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 HNO_3 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 $AgNO_3$ 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 Al_2O_3) 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:

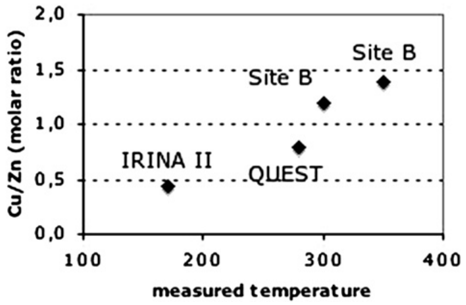

Fig. 4. Cu/Zn ratios in sampled fluids vs measured emanation temperatures for different vent sites; not plotted are Cu/Zn for IRINA (2.2) and IRINA II black smoker (0.8) because of unknown emanation temperatures.

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, SO_4, 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_2S 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 ferroin 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. Unsoluble 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 H_2S, 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 CH_4 and H_2 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_2S, (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 $1.52 * 10^{-3}$ ($1.50 * 10^{-3}$ 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 endmember 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 1996	Rainbow
	TAG	IRINA II BS	Quest	IRINA I	Site B	IRINA II	Site B		
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

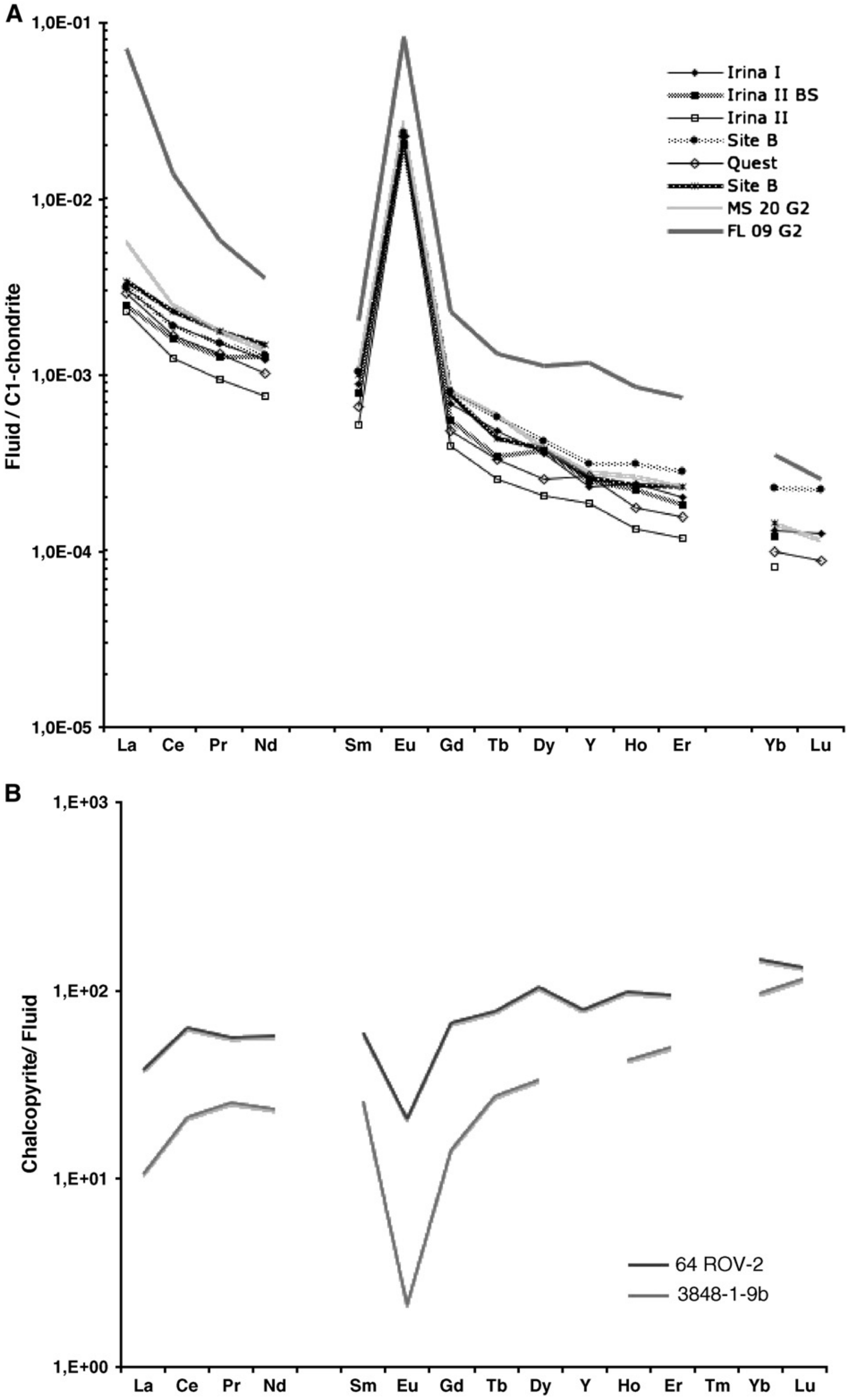

Fig. 5. A) Endmember REE-Y composition for different hydrothermal fluid samples (Site B: 257 ROV-8, 266 ROV-10; black smoker (BS) at IRINA II: 224 ROV, Quest: 281 ROV-5; IRINA I: 261 ROV-6; IRINA II: 283 ROV-5) in the Logatchev field in comparison to endmember data from Douville et al. (2002) for the 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; Rimskaya-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 ±5%: Mg, Ca, Na, K, Sr; CH_4 and H_2 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_2S (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 CH_4, H_2, and H_2S (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

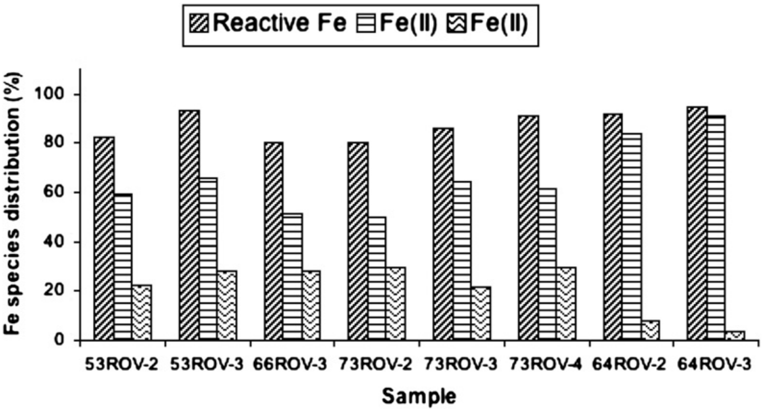

Fig. 6. Distribution of Fe species in hydrothermal fluids taken in 2004 at Sites IRINA (53 ROV-2, 53 ROV-3, 66 ROV-3); IRINA II (73 ROV-2, 73 ROV-3, 73 ROV-4), and ANNA Louise (64 ROV-2, 64 ROV-3).

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 H_2 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 H_2 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, CH_4 is formed from the reaction of H_2 with CO_2, explaining the typical high H_2 and CH_4 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 H_2 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 H_2 concentrations of more than 30 mM (Lilley et al., 2003). As the concentrations of H_2 (and H_2S) 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 H_2 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 SiO_2 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 H_2S 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 °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, (ii) lower Li concentrations compared to basaltic systems, (iii) 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.

Table 7
REE-Y concentrations (in ppm) in two hydrothermal chalcopyrite (cp) samples from the Logatchev field (Cruise M64/2) and the Rainbow field (Rimskaja-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

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 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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