



HAL
open science

Mineral and gas chemistry of hydrothermal fluids on an ultrafast spreading ridge: East Pacific Rise, 17° to 19°S (Naudur cruise, 1993) phase separation processes controlled by volcanic and tectonic activity

Jean Luc Charlou, Yves Fouquet, Jean Pierre Donval, Jean Marie Auzende, Philippe Jean-Baptiste, Michel Stievenard, Stéphane Michel

► **To cite this version:**

Jean Luc Charlou, Yves Fouquet, Jean Pierre Donval, Jean Marie Auzende, Philippe Jean-Baptiste, et al.. Mineral and gas chemistry of hydrothermal fluids on an ultrafast spreading ridge: East Pacific Rise, 17° to 19°S (Naudur cruise, 1993) phase separation processes controlled by volcanic and tectonic activity. *Journal of Geophysical Research: Solid Earth*, 1996, 101 (B7), pp.15899-15919. 10.1029/96JB00880 . hal-03334885

HAL Id: hal-03334885

<https://hal.science/hal-03334885v1>

Submitted on 5 Sep 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Mineral and gas chemistry of hydrothermal fluids on an ultrafast spreading ridge: East Pacific Rise, 17° to 19°S (Naudur cruise, 1993) phase separation processes controlled by volcanic and tectonic activity

Jean Luc Charlou, Yves Fouquet, Jean Pierre Donval, and Jean Marie Auzende¹

Département Géosciences Marines, IFREMER Centre de Brest, Plouzané, France

Philippe Jean-Baptiste and Michel Stievenard

CEA Saclay, DSM/LMCE, Gif sur Yvette, France

Stéphane Michel

Université de Bretagne Occidentale, Brest, France

Abstract. During the Naudur cruise in December 1993, 23 dives using the French submersible *Nautilus* were conducted on the axis of the East Pacific Rise between 17° and 19°S where the spreading rate is among the fastest in the ocean (14 to 16 cm/yr). Twenty hydrothermal fluids located at the topographic high of each segment in the axial domain were collected between 2573 and 2669 m depth on three segments centered, respectively, at 17°25'S, 18°15'S, and 18°26'S. The fluids exhibit a very wide range of temperature, chemical, and gas compositions. On the 17°25'S and 18°26'S segments, fluids have quite uniform compositions, low chlorinities, are gas-enriched and are low in dissolved metals relative to fluids from the 18°15'S segment which show high chlorinities, are less gas-enriched and show high-metal concentrations. Chloride and metal depletion associated with gas enrichment is consistent with phase separation. Whereas CH₄ end-members show large variations between sites, the ¹³CH₄ data are very similar, with ¹³C values in a narrow range -22.0 to -23.9 ‰ versus peee-belemnite (PDB). δ¹³CO₂ measured in fluids within the 18°15'S and 18°26'S segments are, respectively -7.9 and -5.8 ‰ versus PDB, similar to ¹³C of CO₂ trapped in mid oceanic ridge basalts, suggesting a magmatic origin. The variability in fluid composition is linked to the variability of the accretion process observed on the three segments. The uniform venting of low-chlorinity fluids in the 17°25'S and 18°26'S segments is connected with volcanic activity which causes boiling with preferential venting of vapor-enriched fluids. High-salinity fluids are emitted on the 18°15'S segment where the ridge is tectonics-dominated and subsurface circulation controlled by faults. Phase-separated effluents induced by volcanic and tectonic activity are delivered to the deep ocean in this area, as previously observed on the Juan de Fuca Ridge or in the North Fiji Basin Ridge.

Introduction

Submarine hydrothermal springs are now known to be a common phenomenon along tectonic structures in different geodynamical environments. The first discovery of hot metalliferous brines was along the slow spreading (half rate 1 cm/yr) axis of the Red Sea [Miller *et al.*, 1966]. After the first discovery in 1977 [Corliss *et al.*, 1979] of submarine hydrothermal vents on the Galapagos Spreading Center (half rate 3 cm/yr), vent fluids with a wide range of chemical compositions have been collected from a variety of tectonic settings [Von Damm, 1990]. These seafloor hot springs differ widely and are found over a wide range of geological settings: ultrafast to slow spreading mid-ocean ridges (MOR), back arc basins, and sedimented ridges. Fluids have been collected at fast spreading

ridges (half rate 6 - 10 cm/yr) such as the East Pacific Rise (EPR) at 9°, 13°, 21°N [RISE Project Group, 1980; Von Damm *et al.*, 1985; Michard *et al.*, 1984; Campbell *et al.*, 1988a; Bowers *et al.*, 1988] and the Juan de Fuca Ridge [Von Damm and Bischoff, 1987; Butterfield *et al.*, 1990; Butterfield *et al.*, 1994; Butterfield and Massoth, 1994], slow spreading ridges (3 cm/yr) such as the Mid-Atlantic Ridge (MAR) at MARK (Snake Pit) (23°N) [Campbell *et al.*, 1988b; Jean-Baptiste *et al.*, 1991], TAG (26°N) [Rona *et al.*, 1986; Campbell *et al.*, 1988b], Broken Spur (29°N) [Elderfield *et al.*, 1993; James *et al.*, 1995], and more recently at Lucky Strike (37°17'N) [Colodner *et al.*, 1993] and Menez Gwen (37°50'N) [Fouquet *et al.*, 1994a,b; Donval *et al.*, 1994], or back arc environments such as the North Fiji Basin [Grimaud *et al.*, 1991; Ishibashi *et al.*, 1994a,b] and Lau Basin [Fouquet *et al.*, 1991a,b; Charlou *et al.*, 1991a]. Important differences in vent fluid composition between ridge crest sites [Von Damm, 1990], and large gradients in composition within single vent fields have been noted and explained by different mechanisms [Massoth *et al.*, 1989; Butterfield *et al.*, 1990, 1994].

We report here on the chemistry of hydrothermal fluids collected for the first time along three segments of an ultrafast spreading ridge between 17° and 19°S on the EPR. During the

¹Now at Institut Français de Recherche Scientifique pour le Développement en Coopération, ORSTOM, Nouméa, Nouvelle Calédonie.

Copyright 1996 by the American Geophysical Union.

Paper number 96JB00880.
0148-0227/96/96JB-00880\$09.00

Naudur cruise, a series of 23 dives using the French submersible *Nautille* supported by the R/V *Nadir* was conducted in this area. The objectives of this cruise (December 3 - 30, 1993) were to carry out geological explorations along the different segments (Figure 1), in order to study the interaction between magmatic, tectonic, and hydrothermal processes [Auzende *et al.*, 1994a] at an ultrafast spreading axis. Dives were conducted along and across axis in different areas of segments centered around 17°25'S, 18°15'S, and 18°26'S. The explored segments (Figure 1) are at different stages of their tectonic-volcanic cycle, and clearly illustrate the evolution of the accretion processes and the relationships between magmatism, tectonism, hydrothermal processes [Auzende *et al.*, 1994b; Fouquet *et al.*, 1994c] and biological colonisation [Geisdoerfer *et al.*, 1995]. Sixty-nine new hydrothermal areas grouped into 14 hydrothermal fields were discovered, and diffuse and hot fluids were sampled [Charlou *et al.*, 1994]. We discuss here the mineral and gas composition of these fluids and compare them to other fluids sampled in other active fields.

Geological Setting

The Garrett Fracture Zone (13°S) and the Easter Microplate limit a large segment of the EPR where the full accretion rate (141 to 162 mm/yr) is among the fastest ever measured at the present day [Naar and Hey, 1989; DeMets *et al.*, 1990; Perram *et al.*, 1993] (Figure 1). Between 17° and 18°S, the spreading axis consists of a 2600-m deep ridge. Between 18° and 19°S, the "Hump" zone is formed by three 25- to 40-km-long segments separated by relatively small oceanic spreading center offsets, at 18°22'S and 18°37'S. The whole area has been extensively surveyed since 1982 with Seabeam and Seamark II by French, German, and American Institutions [Renard *et al.*, 1985; Backer *et al.*, 1985; Lonsdale, 1989; MacDonald *et al.*, 1988; Scheirer *et al.*, 1993]. The ridge axis in this region varies from a shallow axial dome less than 2600-m deep to an axial graben a few hundred meters wide and a few tens of meters deep cutting the top of the dome. A very shallow (less than 1-km deep) seismic reflector interpreted as the top of the magma chamber has been identified by multichannel seismic surveys [Detrick *et al.*, 1993] at 17°22'S. In 1984, the submersible *Cyana* carried out eight dives between 17°30'S and 21°30'S, with the discovery of hydrothermal mineralization in collapsed lava lakes [Renard *et al.*, 1985; Backer *et al.*, 1985], but no active venting was observed.

Hydrothermal sites studied during the Naudur cruise occur along axial fissure systems and related collapsed lava lakes. Along the segment centered around 17°25'S and particularly at 17°10'S, 17°25'S, and 17°37'S, the ridge crest is dominated by volcanic activity with occurrences of recent lava. Three types of hydrothermal discharge are distinguished [Fouquet *et al.*, 1994c]. First, diffuse discharges (<50°C), without sessile animals, due to heating of seawater by recent volcanic extrusions are located at the bottom of the collapsed lava lakes. Surrounding waters are often milky and turbid. These sites are very similar to the 9°50'N East Pacific Rise (EPR) site [Haymon *et al.*, 1993]. Second, diffuse discharges with sessile animals and active chimneys are associated with older lava away from the axial collapsed lava lakes. The largest site at 17°25'S (Nadir, Rehu-Marka vents) is nearly continuous for more than 1-km and shows young chimneys up to 6 m high starting to grow on the lobate flows in the middle of large fields of animals. The 1984 observations [Renard *et al.*, 1985] at the same site did not show the large fields of animals visible today. From the 1984 and 1994 dive observations, the

mussels are therefore estimated to be 10 years old. In many places recent lava flow coming from the axial lava lakes is observed. The third type of hydrothermal material consists of inactive chimneys partially buried under lava flows.

The northern Hump segment (18°02'S to 18°22'S) centered around 18°15'S is characterized by a very wide (800-m) and deep (50-m) axial graben with no recent lava. Tectonic activity is dominant along the graben [Auzende *et al.*, 1994a,b]. Only two active black smokers (Akorta, >305°C) were found among 20 hydrothermal sites discovered along 20-km of the eastern wall at 2669-m depth. This site is characterized by abundant silicic chimneys and the scarcity of macrofauna.

The central Hump segment (18°22'S to 18°37'S) has an asymmetric graben. The bottom of this graben is covered with very recent lava related to the beginning of a new volcanic episode [Auzende *et al.*, 1994b], with warm water discharging through lobate flows. At the northern part of the segment at 18°26.5'S, among the 17 hydrothermal sites without recent lava found on a 2-km survey along the east graben wall, three types of sites are distinguished. First, inactive sulfide mounds with spires (up to 20-m high) correspond to an old hydrothermal episode. Chimneys are often tilted away from the wall toward the graben, and outcrops of stockwork occur in many places. Second, shimmering waters (up to 55°C), without sulfide chimneys, discharge through the talus along the faults. Third, young active chimneys (Stockwork, Fromveur, Le Stiff, up to 310°C) are growing on the talus of the graben wall. The absence of sessile animals on diffuse discharges and the abundance of shimmering waters suggest a very recent start of the hydrothermal activity.

Between 18°22'S and 18°34'S, a uniform sedimentary cover with a thickness of a few millimeters was observed. On the southern Hump segment (18°37'S to 19°S), the axial graben narrows and its aspect resembles that of the 17°25'S segment. Hydrothermal activity in this part of the Hump segment is concentrated along a narrow ridge of pillow debris close to the eastern wall of the graben. On the northern tip of the segment, hydrothermal activity consists of black smokers on active white mounds venting diffuse discharge (up to 150°C), covered with animals, and without mineral deposits on recent lobate flows. Most of the sites are small and the coverage by recent lava flows indicates a high degree of temporal instability of the hydrothermal systems on this ultrafast-spreading ridge. This is particularly true on volcanically active ridges where no major faults are present to focus sites of discharge of subsurface circulation. The hydrothermal fluids collected along the segments surveyed during the Naudur cruise are listed in Table 1.

Methods

Hydrothermal fluids were collected in 750-mL titanium syringes deployed in pairs and operated by the hydraulic arm of the *Nautille*. Dead volumes in syringes were filled with deep seawater collected during the first dive in the area. Before hot fluid sampling, the temperature was measured with a high-temperature probe (50° to 600°C). The accuracy of the high-temperature probe is generally better than +/- 2% up to at least 400°C, and temperature measurements of vent fluids using this system are accurate to about +/- 2% when working properly. Unfortunately, the high-temperature probe did not permit precise measurements to be obtained in some vents (Soupape, Stockwork, Akorta, Rehu-Marka) due to electronic problems. Hydrothermal fluids were processed on board the ship as quickly

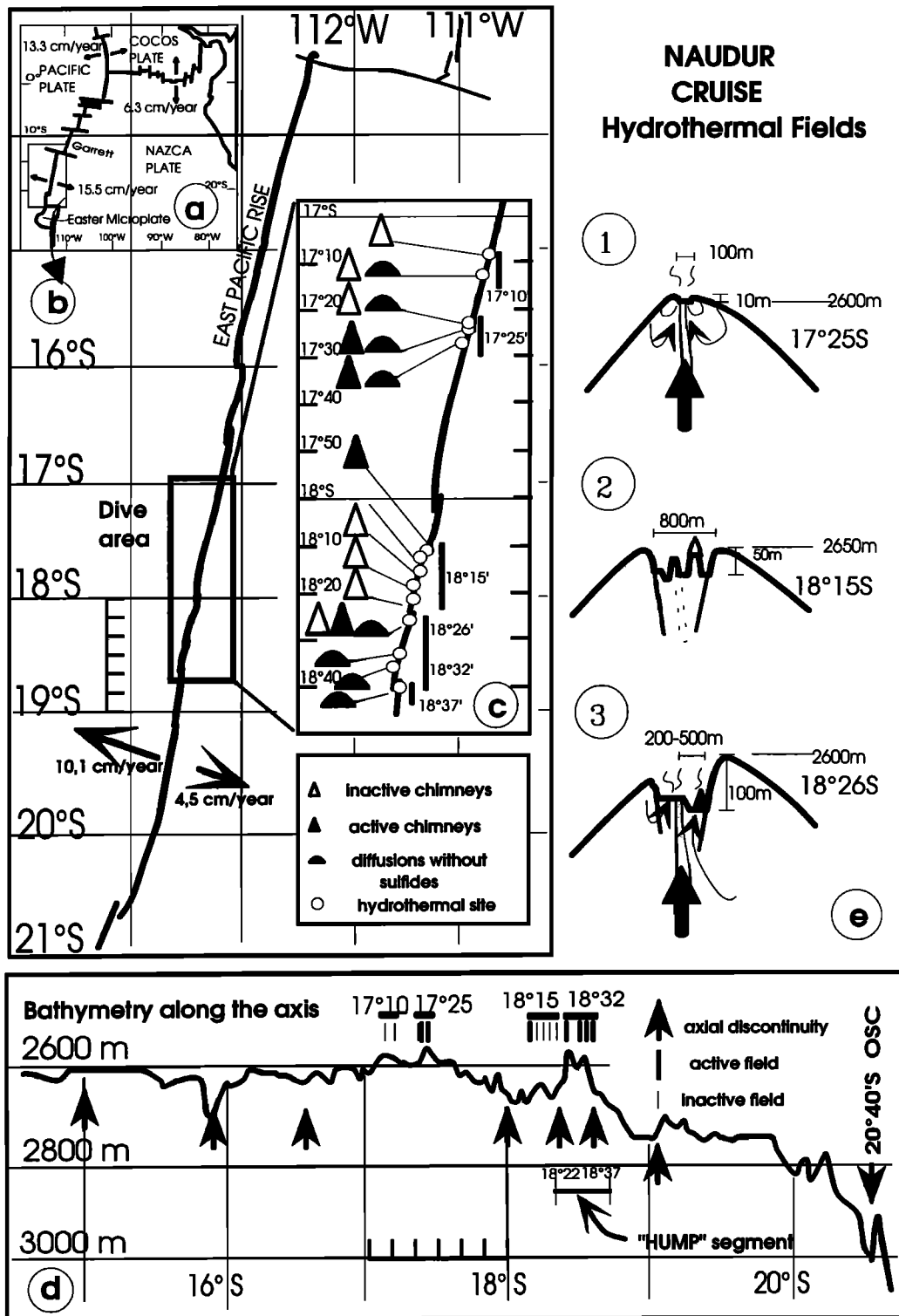


Figure 1. (a) Regional map of South Pacific Ridge between 15° and 21°S. (b) *Nautilid* dives were located between 17° and 19°S on four volcanic axial ridge segments with contrasting morphologies. All studied areas are close to the highest point of the ridge. Hydrothermal fields were discovered on the four segments. High-temperature venting is confined to the ridge axis and hot hydrothermal samples were collected on active sites from the three segments, respectively, centered around 17°25'S, 18°15'S, and 18°26'S. (c) Open circles indicate hydrothermal sites. Solid circles indicate hot fluid chimneys. All fluids studied in this work are listed. (d) Figure shows depth of the ridge along the axis. Solid arrows represent axial discontinuities. The explored areas, with their active (I) and inactive fields (II) as observed from *Nautilid* dives, are located on the topographic highs of the ridge: 17°10'S, 17°25'S, and on the "HUMP" segment between 18°15'S and 18°32'S. (e) Geologic cross sections of the axis at 17°25'S, 18°15'S, and 18°26'S schematically show successive relations between volcanism, tectonics, and hydrothermal activity [after Fouquet et al., 1994c].

Table 1. Hydrothermal Fluids Collected During the Naudur 1993 Cruise

Number	Sample	Vent Name	Lat., S	Long., W	Depth, m	T, °C	pH	Comments
1	ND-03-D	Tanio	17°25'70	113°12'35	2576	33	7.58	On ridge top, recent lava; D, diffusion.
2	ND-03-G	Nadir	17°25'80	113°12'35	2574	340	3.11	On ridge top; G, black smoker.
3	ND-04-D	Rehu-Marka	17°24'85	113°12'15	2573	318	7.36	Recent lava; ND-04-D and G sampled
4	ND-04-G	Rehu-Marka	17°24'85	113°12'15	2573	318	3.78	on the same black smoker.
5	ND-05-D	Soupape	17°22'43	113°11'42	2591	<150	7.40	Black smoker without chimney.
6	ND-06-D	Rehu-Marka	17°24'85	113°12'15	2573	260	7.53	ND-06-D and G sampled on the same
7	ND-06-G	Rehu-Marka	17°24'85	113°12'15	2573	260	7.31	white smoker.
8	ND-08-G	Stockwork	18°25'80	113°23'35	2630	>210	3.17	Black smoker on the wall.
9	ND-09-D	Fromveur	18°25'90	113°23'35	2620	310	3.06	Close to the graben wall; ND-09-D and G
10	ND-09-G	Le Stiff	18°25'62	113°23'30	2621	-	7.21	sampled on 2 different vents.
11	ND-10-D	(diffusions)	18°30'38	113°24'83	2636	-	7.51	Diffusions without chimney; ND-10-D and
12	ND-10-G	(diffusions)	18°30'38	113°24'83	2636	-	7.15	G sampled on the same site.
13	ND-11-D	(diffusions)	18°33'28	113°24'93	2647	150	7.63	Diffusions in fresh hot lobated lava.
14	ND-13-G	Fromveur	18°25'90	113°23'35	2620	310	4.81	Same vent as ND-09-D.
15	ND-15-D	Tchao	18°16'14	113°22'02	2659	<200	7.77	Diffuse black fluid.
16	ND-17-D	Akorta	18°10'20	113°20'66	2669	>305	3.35	ND-17-D and G sampled on the same
17	ND-17-G	Akorta	18°10'20	113°20'66	2669	>300	3.34	smoker.
18	ND-19-D	Rehu-Marka	17°24'85	113°12'15	2573	300	3.56	D sampled on smoker.
19	ND-19-G	Rehu-Marka	17°24'85	113°12'15	2573	>305	7.22	G sampled on broken diffusor.
20	ND-20-D	Kihi	17°27'27	113°12'79	2575	60	4.75	Diffuse fluid, without chimney.

Numbers of samples and vent names are indicated with their coordinates calculated from acoustic navigation and global positioning system (GPS). Vent temperatures were measured with the Nautilie high-temperature probe and pH was measured on board. All samples are numbered from 1 to 20 in the first column. These numbers appear on Figures 2, 3, 4, 5, and 6 to identify individual hydrothermal fluids.

as possible after the submersible recovery. A titanium fitting connected to a length of Tygon tubing was fixed on the titanium stopcock of the syringe and rinsed with approximately 20 mL of the sample. A 10-mL copper tube with clamps in line with an evacuated 125-mL glass bulb with Teflon stopcocks and containing sodium azide poison to stop bacterial action was fixed on the syringe outlet and filled for helium and other gas analyses on shore. We know that leakage of gases is possible from titanium syringes between sampling at 2660-m depth and their arrival on board after the dive. So, all gas data have to be considered as a minimum. However, CO₂ versus Mg shows good linearity (Figure 6) for samples collected on the different sites, permitting the discussion of gas data together with other elements. Samples were all enriched in H₂S, but unfortunately H₂S was not measured on board. Aliquots for pH (also measured on board), silica, major, and minor elements were drawn directly into acid-cleaned polyethylene bottles. Trace metal samples were acidified to pH<1.8 with ultrapure HNO₃, thus redissolving any precipitates. Some black deposit observed when demounting the titanium bottles indicates a slight loss of trace metals by precipitation in the samplers. All measurements were performed on shore. Aliquots for silica determination were immediately diluted 100- to 200-fold on board, and analysed by automatic colorimetry on shore. These silica measurements were compared to silica measurements obtained from nondiluted aliquots treated with 10 M NaOH solution to recover silica polymerized in samples during storage, and showed a good agreement. Major elements including anions (Cl, Br, SO₄) and cations (Na, Mg, K, Ca) were measured by ion chromatography (Dionex DX100), after appropriate dilutions. Li and Rb were measured by flame atomic emission spectrometry using standard additions. Minor elements (Ba, Sr) and dominant metalliferous elements (Fe, Mn, Cu, Zn) were determined by Inductively Coupled Plasma Emission Spectrometry (ICP-ES) after appropriate dilution of samples, in the laboratory of Joseph Cotten, at the University of Brest, France.

Gases were extracted on shore from the samples held in glass bulbs after connecting the glass bulbs to a gas extractor [Charlou *et al.*, 1993]. Only samples containing more than 30% of hydrothermal fluid (except for ND-13-G and ND-20-D which have, respectively, only 23 and 8% of hydrothermal fluid) were considered. Each sample was transferred into a titanium decantor placed in an ultrasonic bath to accelerate degassing. Laboratory tests and calculations show that more than 95 % of all gases in solution are extracted from the fluid solution. Pressure of total extracted gas was measured with a previously calibrated pressure gauge. All gases were enriched by compression and transferred into 100-mL gas sampling flasks or 10-mL copper tubes, at a pressure above the atmospheric pressure to avoid air entry in samples. Some samples contaminated by air were eliminated. All gases were analysed with a Hewlet Packard 5890 gas chromatograph using Plot columns and micro-catharometer (TCD) associated to a flame ionization detector (FID). Mass balance of quantified gases matches the global gas pressure of the samples. Carbon isotope analyses, ¹³CO₂ and ¹³CH₄, were carried out at Saclay on a Mat-Finnigan 252 mass spectrometer coupled to a gas chromatograph.

Results

The concentrations of all major and minor elements found in the samples are shown in Table 2. Composition of pure hydrothermal end-member solutions have been determined by extrapolating fluid concentrations to Mg=0 mmol/kg, based on laboratory observations that complete removal of Mg occurs during high-temperature basalt-seawater interactions [Bischoff and Dickson, 1975; Mottl and Holland, 1978; Seyfried and Bischoff, 1979]. The mixing lines of all elements versus magnesium, representing linear least squares regressions fitted to data for the different vents, are drawn on Figures 2, 3, 4, 5. We report zero-magnesium end-members for all high-temperature fluids in Table 3. Only samples containing more than 30% of

Table 2. Chemical Composition of the Samples Collected During the 1993 Naudur Cruise

Component	sw	03-D	03-G	04-D	04-G	05-D	06-D	06-G	08-G	09-D	09-G	10-D	10-G	11-D	13-G	15-D	17-D	17-G	19-D	19-G	20-D
T, °C	2	50	340	320	320	-	260	260	>210	310	-	(diff.)	-	150	310	<210	>305	>300	300	>305	60
pH, NBS, 25°C	7.6	7.58	3.11	7.36	3.78	7.40	7.53	7.31	3.17	3.06	7.21	7.51	7.15	7.63	4.81	7.77	3.35	3.34	3.56	7.22	4.75
Si, mmol/kg	0.178	2.70	9.95	2.35	3.74	2.20	2.00	1.82	11.00	10.20	2.00	2.00	2.00	1.48	3.39	1.91	15.30	14.7	6.43	1.30	1.56
Cl, mmol/kg	546	546	212	544	491	554	539	540	438	251	528	541	542	563	457	573	821	830	390	538	534
Br, mmol/kg	838	863	350	838	888	813	813	826	483	400	826	813	838	838	703	900	1276	1200	638	851	838
SO ₄ , mmol/kg	28.2	28.0	1.65	26.8	22.2	28.5	26.4	26.6	1.5	7.4	25.8	28.7	27.4	28.2	24.5	28.5	3.0	4.0	7.5	27.6	29.0
Li, μmol/kg	27.5	27.4	173.7	21.0	87.5	45.0	33.8	32.2	173.3	42.6	30.6	27.4	27.4	27.4	32.7	41.8	629	599	227	30.6	25.8
Rb, μmol/kg	1.4	1.3	2.0	0.54	2.0	1.48	1.4	1.4	1.4	0.65	1.0	1.20	1.30	1.20	1.17	1.30	6.30	5.90	3.70	1.30	1.30
Na, mmol/kg	468	465	146	462	409	477	464	444	255	220	469	472	463	479	392	474	659	657	345	480	468
K, mmol/kg	10.2	9.8	6.9	9.6	10.5	10.6	10.2	9.9	6.4	4.7	10.3	10.3	10.1	10.2	8.5	10.9	19.4	19.4	12.0	10.5	10.5
Mg, mmol/kg	53.2	49.0	3.3	46.3	39.2	49.6	47.6	47.6	4.9	13.1	48.0	49.0	49.4	51.8	41.1	48.3	4.9	6.6	16.0	49.6	48.9
Ca, mmol/kg	10.3	10.3	5.5	10.5	11.9	11.4	10.6	10.5	8.4	7.2	10.6	10.6	11.0	10.2	9.6	11.3	43.6	43.1	11.7	11.2	11.1
Sr, μmol/kg	87	91.3	17.9	89.6	79.3	91.3	87.3	88.5	21.5	29.5	88.5	89.3	89.6	91.3	70.2	91.3	171.5	176.4	56.1	91.3	86.6
Ba, μmol/kg	0.14	0.27	5.78	0.43	2.08	0.43	0.46	0.31	3.24	1.27	0.09	0.17	0.07	0.20	0.49	0.53	15.80	16.30	3.06	0.20	0.23
Fe, μmol/kg	0.003	3	556	1	535	4	8	8	511	1960	3	0.7	0.3	-	792	1	11080	11060	2550	7	3
Mn, μmol/kg	0.002	2	230	27	153	60	14	8	348	367	15	5	6	3	94	15	1570	1560	517	15	5
Cu, μmol/kg	0.004	0.53	9.6	0.04	3.0	0.04	-	-	3.1	9.3	-	1.57	1.09	0.21	3.10	-	80.2	81.3	7.03	0.016	7.2
Zn, μmol/kg	0.010	0.87	-	8.38	15.2	4.28	1.80	5.36	81.7	84.9	-	0.93	0.45	0.04	11.0	4.0	285.3	291.2	90.4	3.37	2.0

The sample number represents the number of the dive followed by the D or G letters which are, respectively, the right and left part of the titanium syringes pair. Analytical method (precision): Ion chromatography (Na, 2%; K, 2%; Mg, 2%; Ca, 2%; Cl, 2%; Br, 3%; SO₄, 2%), flame atomic emission (Li, 2%; Rb, 2%), ICP-AES, inductively coupled plasma atomic emission spectrometry, (Ba, 4%; Sr, 2%; Fe, 4%; Mn, 4%; Cu, 5%; Zn, 5%), silica was analyzed by automatic silicomolybdate method (1%). For all these methods, appropriate dilutions were made before analysis.

hydrothermal fluids are considered, allowing greater confidence in the end-member values.

Anions (Figure 2)

Chloride. Chloride, which is the dominant anion in hydrothermal fluids clearly shows multiple mixing lines for vent fluids sampled on the three ridge segments (Figure 2). The highest end-member chloride concentration (871 mmol/kg) is seen in Akorta fluids at 18°15'S, and the lowest (155 mmol/kg) in Fromveur fluids at 18°26'S. Other fluids (Nadir and Rehu-Marka near 17°25'S) show intermediate chlorinities (190-323 mmol/kg). These fluids show separate and distinct mixing lines between the two extremes Akorta and Fromveur (Figure 2, Table 3). However, Nadir and Rehu-Marka fluids show chemical properties closer to Fromveur fluid which has a chloride content among the lowest of the hydrothermal fluids yet sampled in the oceans. Such large variations in chlorinity have been observed within a single vent field on the Juan de Fuca Ridge at Axial Seamount [Butterfield et al., 1990]. Larger variations (155-871 mmol/kg) are observed here between fluids sampled on different neighbouring ridge segments. Cl⁻ variability may be influenced by many mechanisms such as changes in the pressure and temperature of the reaction zone, nature of plumbing, rock hydration, trapping of Cl⁻ in hydrous minerals, phase separation with variable unmixing (segregation) of brine and vapor phases, tapping a brine either of magmatic origin or produced through phase separation, and subseafloor mixing of hydrothermal fluids (brine or vapor) with seawater [Edmond et al., 1882; Seyfried et al., 1986; Von Damm and Bischoff, 1987; Campbell and Edmond, 1989; Von Damm, 1990; Berndt and Seyfried, 1990; Seyfried et al., 1991]. It should be noted that only phase separation processes are likely to alter the chlorinity of the vented fluids by more than ~ 10%.

Bromide. Bromide concentrations follow the same pattern as chloride (Figure 2). The highest values are also observed at Akorta (1.32 mmol/kg, 157% of seawater Br concentration). Low-Br concentrations are found at Fromveur (0.26 mmol/kg, 31% of seawater Br concentration). The Br/Cl ratio of all vent fluids varies from 0.00144 at Akorta to 0.00171 at Rehu-Marka compared to a Br/Cl of 0.00153 found in normal seawater. However, with an uncertainty in the Br/Cl ratio of the order of 8%, the small variations observed in the Br/Cl ratio are not really significant. The lack of significant Br/Cl variability is consistent with a phase separation process.

Sulfate. In the Figure 2, sulfate concentrations are plotted versus magnesium concentrations for all vent fluids. Sulfate is observed to decrease to zero with magnesium, following a linear regression, [SO₄] = 0.576 [Mg] - 0.428 (r² = 0.994), indicating that there is no significant sulfate increase in samples due to the hydrogen sulfide oxidation during sample storage. Standard seawater values are from the literature and are taken in account in the regression line calculation. No deep seawater sample unaffected by hydrothermal input was available for SO₄ and Mg measurements.

The Alkali Metals (Figure 3)

Lithium. Standard seawater contains generally 27.5 μmol/kg. All fluids are highly enriched relative to seawater. The highest values are observable in Akorta fluids (690 μmol/kg) and the lowest values in Fromveur fluids (48 μmol/kg). All other samples show intermediate values. High-temperature alteration of the oceanic crust is well known to be a source for Li in seawater. In this case, Li is leached into seawater reacting with basaltic rocks

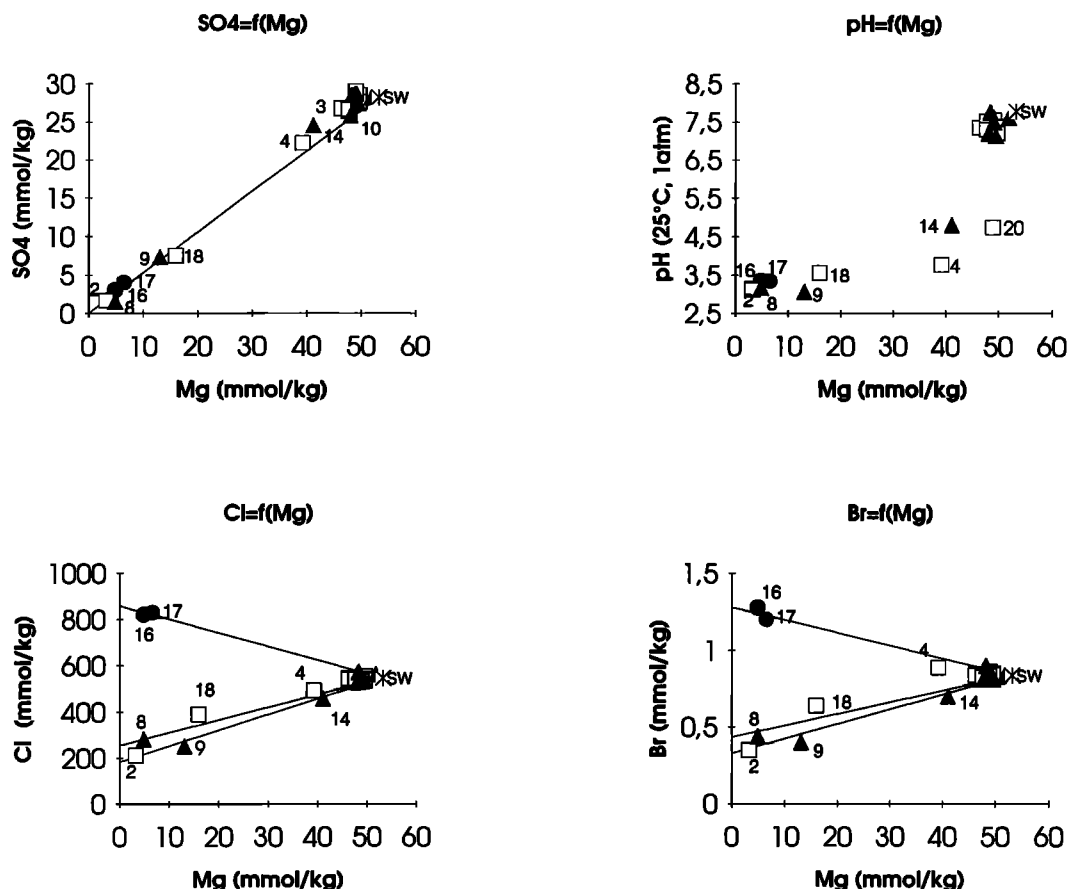


Figure 2. Plot of sulfate, chloride, bromide, and pH versus magnesium for Naudur fluids. Lines drawn represent linear least squares regressions fitted to data for Nadir, Rehu Marka fluids (open squares) on the 17°25'S segment, Akorta fluids (solid circles) on the 18°50'S segment, and Stockwork, Fromveur fluids (solid triangles) on the 18°26'S segment. SO_4 and Mg data are fitted with linear regression, $[\text{SO}_4] = 0.576 [\text{Mg}] - 0.428$, with $r^2 = 0.994$. Anions show distinct trends for vents located on each segment with significant positive and negative chloride and bromide anomalies. Vent numbers from 1 to 20 are taken from Table 1.

at low water/rock ratios (as long as chlorite, which can be a sink for Li [Seyfried *et al.*, 1984], is not a major product of alteration). So, Li is a potential indicator of the intensity of water/rock interaction. It has been demonstrated that Li mobilization is a temperature-dependent process and Li release can begin at relatively low temperature and increases with heating [Chan and Edmond, 1988]. Therefore, some of the differences observed in lithium concentration between vents may be attributed to variations in the water/rock ratio. However, the highest concentrations are observed in the Cl-rich fluids of the 18°15'S vents (Akorta), a fact which again points to Li partitioning between brine and vapor phases during phase separation [Berndt and Seyfried, 1990; Bischoff and Rosenbauer, 1987].

Sodium and potassium. Sodium and potassium follow the same trend as chloride, with high values (respectively up to 686 mmol/kg and 20.7 mmol/kg) in Akorta fluids, and much lower values elsewhere. Except for Nadir and Akorta vents, all other vents show a Na/Cl ratio higher than that in seawater (0.857), demonstrating a preferential loss of Cl with respect to Na in these fluids.

Rubidium. Rubidium is among the mobile elements which are efficiently extracted from basalt by high-temperature hydrothermal fluids. Rubidium end-members (0.39 to 6.80 $\mu\text{mol/kg}$) are very low in all Naudur fluids compared to fluids

sampled at the present day on the EPR, MAR, or southwest Pacific, where rubidium ranges from 15 to 70 $\mu\text{mol/kg}$ in hydrothermal fluids [Bowers *et al.*, 1988; Campbell *et al.*, 1988a; Von Damm, 1990]. Very low values (0.39 to 0.96 $\mu\text{mol/kg}$) lower than the Rb content of seawater (1.4 $\mu\text{mol/kg}$) are found in Fromveur and Stockwork vents (18°26'S segment), indicating that Rb has been lost from these solutions. The highest value (6.8 $\mu\text{mol/kg}$) is observed in Akorta vents. This low-Rb anomaly is also found in south EPR basalts, which show very depleted Rb concentrations (between 0.3 and 1 ppm) compared to normal mid-ocean ridge basalts (MORBs) [Mahoney *et al.*, 1994]. Hence, the low-Rb concentrations observed here suggest that hydrothermal fluids are actually leaching Rb-poor basalt.

The Alkaline Earths (Figure 4)

Magnesium. All end-members are consistent with the theory that Mg is removed from the fluid during hydrothermal circulation. Mg concentration is a good indicator of the proportion of mixing with surrounding seawater during sampling. The purest fluids were at Nadir (ND-03-G, 3.3 mmol/kg) and at Akorta (ND-17-G, 6.6 mmol/kg).

Calcium. Calcium is enriched 5 times relative to seawater (10.3 mmol/kg) in the high-chlorinity Akorta fluids. Except in Rehu-Marka fluid (12.3 mmol/kg, close to seawater content), all

Table 3. End-Member Composition of the Naudur Fluids

Component	sw	17°25'S		18°15'S		18°26'S		
		Nadir 03-G	Rehu-Marka 19-D	Akorta 17-D	Akorta 17-G	Stockwork 08-G	Fromveur 09-D	Fromveur 13-G
Temp.max (°C)*	2	340	300	>305	>300	>210	310	310
pH, NBS, 25°C	7.6	3	3.1	3.25	3.25	3.1	3	3
Si, mmol/kg	0.178	10.6	9.1	16.8	16.8	12.1	13.6	14.3
Cl, mmol/kg	546	190	323	848	871	256	155	155
Br, µmol/kg	838	318	552	1320	1251	397	257	245
Li, µmol/kg	27.5	183	313	690	680	148	48	50
Rb, µmol/kg	1.4	2	4.7	6.8	6.5	0.96	0.4	0.39
Na, mmol/kg	468	125	292	686	677	233	139	135
K, mmol/kg	10.2	6.7	12.8	20.3	20.7	6.0	2.9	2.7
Ca, mmol/kg	10.3	5.2	12.3	47	47.7	8.2	6.1	7.2
Sr, µmol/kg	87	13.3	42.8	187	189	14.8	10.7	13
Ba, µmol/kg	0.14	6.1	4.3	17.4	18.6	3.6	1.64	1.7
Fe, µmol/kg	0.003	590	3600	12200	12600	560	2600	3480
Mn, µmol/kg	0.002	250	740	1730	1780	380	480	410
Cu, µmol/kg	0.004	10	10	88	93	3.4	12	13.6
Zn, µmol/kg	0.010	90	130	314	332	90	113	48
Fe/Mn	1.5	2.36	4.90	7.05	7.07	1.47	5.42	8.50
Br/Cl x 1000	1.53	1.67	1.71	1.55	1.44	1.55	1.66	1.58
Na/Cl	0.857	0.658	0.904	0.808	0.777	0.910	0.896	0.871
Ca/Na x 1000	22.0	41.6	42.1	68.5	70.4	35.1	43.9	53.3
Sr/Ca x 1000	8.44	2.55	3.48	3.98	3.96	1.80	1.75	1.80
Rb/K x 1000	0.137	0.298	0.367	0.335	0.314	0.160	0.138	0.140
Li/K x 1000	2.7	27.4	24.5	34.0	32.8	24.7	16.4	18.6
Li/Cl x 1000	0.05	0.96	0.97	0.81	0.78	0.58	0.31	0.32

The latitudes 17°25'S, 18°15'S, and 18°26'S represent the middle of the three segments where hot fluids were collected. All these samples contain more than 30% of hydrothermal fluid. Temperatures (Temp. max.*) are not end-member temperatures but the temperature maxima measured in vents with the *Nautille* probe. The uncertainty on temperature measurements do not permit to obtain the end-member temperatures precisely. End-members are calculated by extrapolation of data for individual vents to zero magnesium. Elements and element ratios found in standard seawater are given for comparison.

the other fluids are depleted 2 times relative to seawater. The increase in Ca in high-chlorinity solutions strongly suggests that Cl complexing plays an important role in the mobility of Ca in these solutions [Bowers *et al.*, 1988].

Strontium. In a way similar to Ca, Sr is enriched by 217% relative to seawater (87 µmol/kg) in Akorta fluids (189 µmol/kg) and significantly depleted (10.7 to 14.8 µmol/kg) in Nadir, Stockwork, and Fromveur fluid. A very low Sr/Ca ratio (0.00175) is found at Fromveur. The highest ratios (0.00396) are found at Akorta and have the same order of magnitude as those found at 21°N (EPR) or on the Endeavour segment [Butterfield *et al.*, 1994].

Barium. Barite is known to precipitate at temperatures lower than 20°C and is found indeed to be enriched in low-temperature silica chimneys [Fouquet *et al.*, 1994c]. Therefore, barium is subject to barite solubility control during dilution with seawater and is under estimated by linear extrapolation to zero magnesium [Von Damm *et al.*, 1985]. The highest calculated Ba end-member, considered as a minimum because of possible precipitation of barite in the vent itself or later in the titanium sampler, is found in Akorta fluids (18.6 µmol/kg). The lowest values are observed at Stockwork and Fromveur (1.64-3.60 µmol/kg, whereas Nadir and Rehu-Marka fluids have intermediate values (4.3-6.1 µmol/kg). In all cases, an enrichment relative to seawater (0.14 µmol/kg) is observed.

Silica and Dominant Metals: Fe, Mn, Cu, Zn (Figure 5)

Silica and transition metals are all enriched in the Naudur fluid end-members compared to seawater. The metals are correlated

with chloride, though not perfectly. The measurements suggest that metal and chloride data cannot simply be explained by phase separation of a common end-member. There are probably differences due to a combination of other factors, including variable hydrogeological and thermodynamical conditions between segments.

Silica. Similarly to major elements, highest silica concentrations (16.8 mmol/kg) are found in the high-chlorinity fluids (Akorta), and lowest values (9.1 to 12.1 mmol/kg) in the low-chlorinity fluids. However, Figure 8h lacks to show a clear trend of increasing silica with increasing chloride content.

Iron. Fe reaches concentrations of 12.6 mmol/kg in Akorta on the 18°15'S segment while concentrations of 0.56 to 3.6 mmol/kg (4 to 20 times lower) are found in all fluids collected on the two other segments. Iron shows a positive correlation with chlorinity classically observed in many sites, except on the Endeavour vent field on the Juan de Fuca Ridge where a trend of increasing Fe and Mn concentration with decreasing chlorinity was observed across the vent field [Butterfield *et al.*, 1994] in contrast to the other major elements. Iron depletions in vapor-rich fluids (low Cl) are probably due to iron-sulfide precipitation during phase separation and primarily to partitioning of Fe and Cl into the brine phase.

Manganese. Mn is also highest at Akorta (1.78 mmol/kg) on the 18°15'S segment and lowest at Nadir (0.25 µmol/kg) on the 17°25'S segment and also at Stockwork (0.38 µmol/kg), and Fromveur (0.48 µmol/kg) on the 18°30'S segment. The Fe/Mn ratio is very high and variable (from 1.47 up to 8.50) in fluids collected in this South Pacific area compared to the ratios found

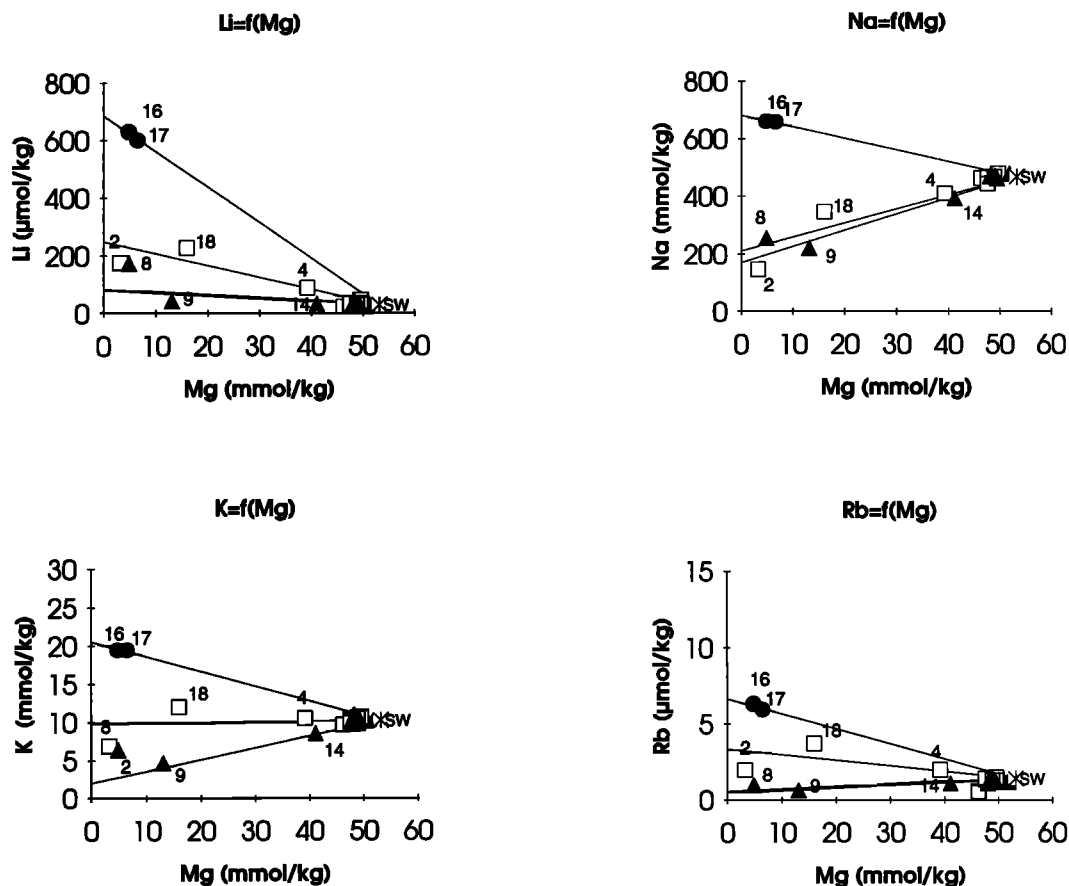


Figure 3. Plots of alkali metals (Li, Na, K, Rb) versus magnesium for Naudur fluids. Lines drawn represent linear least squares regressions fitted to data for Nadir, Rehu Marka fluids (open squares) on the 17°25'S segment, Akorta fluids (solid circles) on the 18°15'S segment, and Stockwork, Fromveur fluids (solid triangles) on the 18°26'S segment. All these elements are strongly enriched in Akorta fluids. Lithium is enriched over seawater in all fluids collected on the three segments from 1.8 times seawater content at Fromveur to 25 times seawater content at Akorta. Sodium ranges from 146% of seawater concentration in Akorta down to 26.7% of seawater in Nadir. Potassium ranges from 26.4% of seawater concentration in Fromveur to 203% of seawater at Akorta. Rubidium is only 7.1% of seawater concentration at Fromveur but is enriched 4.8 times seawater concentration at Akorta. Vent numbers from 1 to 20 are taken from Table 1.

in other areas [Butterfield *et al.*, 1990; Von Damm, 1990]. Only cleft segment vent fluids on the Juan de Fuca Ridge have ratios of the same magnitude (1.52 to 3.86) [Von Damm and Bischoff, 1987; Butterfield *et al.*, 1994]. In addition, the Fe/Mn ratio is here relatively variable: 7.05 to 7.07 in Akorta Cl-rich fluid, 5.42 to 8.50 in Fromveur low-Cl fluid, 2.36 in Nadir and 4.90 in Rehu-Marka. The lowest value (1.47) is found in Stockwork fluid due to a higher subseafloor precipitation of iron probably as iron sulfides. The higher iron content (12.7 mmol/kg) associated to a high Fe/Mn ratio (7.06) observed at Akorta may be also related to the more evolved ferrobaltic composition of the lavas in these areas [Melson *et al.*, 1976; Sinton *et al.*, 1991; Mahoney *et al.*, 1995].

Copper and Zinc. Enrichment is correlated with chloride in all fluids. Both metals are particularly enriched in Akorta fluids on the 18°15'S segment, with respective end-members of 93 $\mu\text{mol/kg}$ and 332 $\mu\text{mol/kg}$. In other fluids, Nadir and Rehu-Marka on the 17°25'S segment or Stockwork and Fromveur on the 18°26'S segment, Cu and Zn concentrations are lower, in the range 3.4 to 13.6 $\mu\text{mol/kg}$ for Cu and 48 to 130 $\mu\text{mol/kg}$ for Zn.

Gases

Fluids sampled along the 18°26'S segment (Stockwork, Fromveur) show very distinct gas enrichments (806 to 1438 mL STP/kg) compared to other Naudur fluids. Akorta fluid on the 18°15'S segment also contain a significant quantity of gas (404 mL STP/kg), but are depleted by a factor of 3, compared to Stockwork and Fromveur. Slightly higher gas contents (500 to 518 mL STP/kg) are found in Nadir and Rehu-Marka fluids on the 17°25'S segment. The highest gas volumes are found in samples with the lowest chlorinity, whereas the lowest gas volumes are in samples of highest chlorinity (Table 3 and 4), clearly pointing to phase separation.

Carbon dioxide. Total dissolved CO_2 is the major gas in the vent waters and is highly enriched relative to standard seawater (2.30 mmol/kg), with a maximum concentration of 22 mmol/kg in the Fromveur fluids. CO_2 concentrations in low-Cl fluids up to 20 times higher than those of the high-Cl fluids was observed at Axial Seamount Hydrothermal Emissions Study (ASHES) on the Juan de Fuca Ridge [Butterfield *et al.*, 1990] and in the 9°-10°N

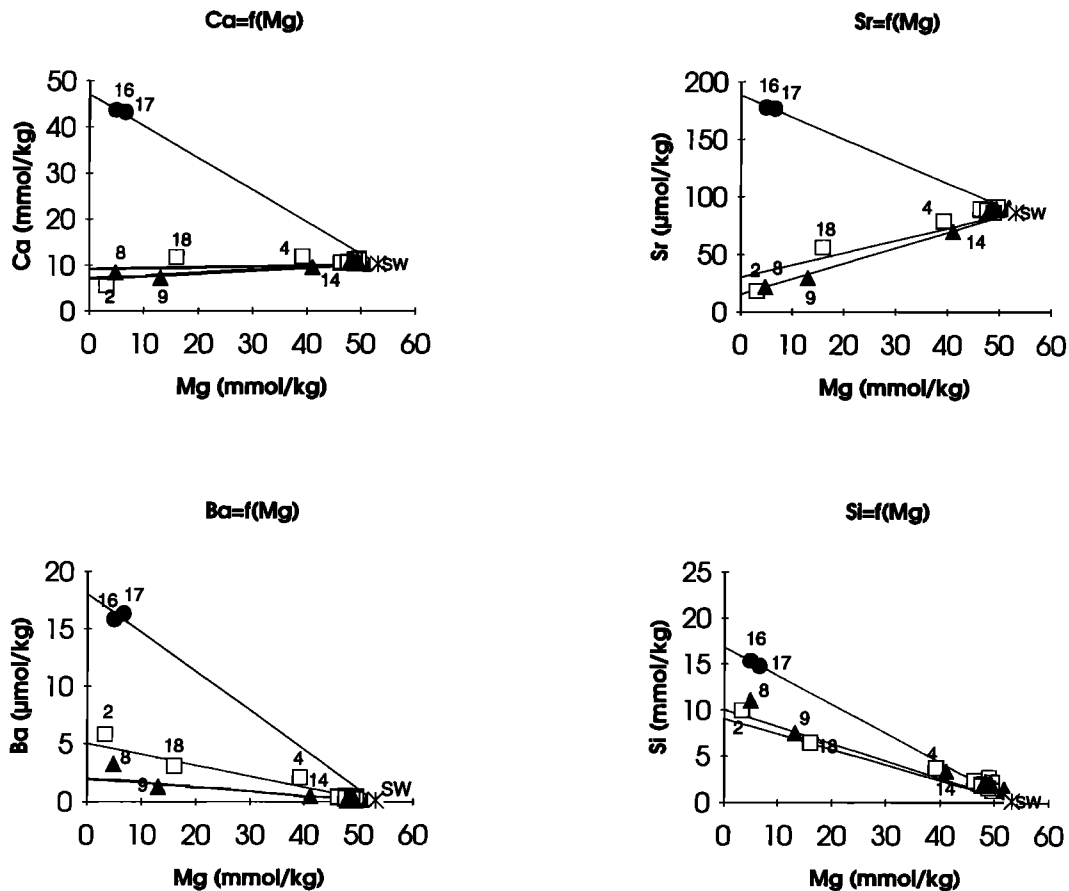


Figure 4. Plots of alkaline earth metals (Ca, Sr, Ba) and silica versus magnesium for Naudur fluids. Lines drawn represent linear least squares regressions fitted to data for Nadir, Rehu Marka fluids (open squares) on the 17°25'S segment, Akorta fluids (solid circles) on the 18°15'S segment, and Stockwork, Fromveur fluids (solid triangles) on the 18°26'S segment. Vent numbers from 1 to 20 are taken from Table 1.

fluids on the EPR [Lilley *et al.*, 1991; Lupton *et al.*, 1991] (Table 5). The lowest CO₂ content (8.5 mmol/kg) is found in Akorta fluids on the 18°15'S segment, whereas intermediate values (13.1-14 mmol/kg) are found in fluids on the 17°25'S segment. CO₂ versus magnesium shows three different linear correlations (Figure 6). This confirms the different nature of fluids emitted on the three contrasted ridge segments. The carbon isotopic composition, δ¹³C_{CO₂}, measured in Akorta and Fromveur fluids, is -7.9 and -5.8 ‰ respectively. This range of values is quite similar to other known hydrothermal sites on the East Pacific Rise and to the ¹³C value of CO₂ trapped in MORB (Table 5), pointing to a magmatic origin of CO₂.

Hydrogen. Although some hydrogen may be produced by redox reactions of the hydrothermal fluid with titanium during sampling [Merlivat *et al.*, 1987], this phenomenon is likely to remain marginal compared to the H₂ content of the fluids (Lilley, personal communication, 1994). H₂ concentrations in the Naudur fluids are high compared to seawater and relatively uniform (0.05 to 0.15 mmol/kg) in all samples, with an especially high value (1.30 mmol/kg) in sample ND-09-D. In most samples, the H₂ concentration compare well to that found in many other hydrothermal fields, such as 13°N (EPR) [Merlivat *et al.*, 1987], Juan de Fuca Ridge [Evans *et al.*, 1988], or Mid-Atlantic Ridge [Charlou *et al.*, 1993; Charlou and Donval, 1993; Donval *et al.*, 1994] (Table 5). However, we speculate that the relatively high

H₂ composition found in fluids collected within the 17°25'S and 18°26'S segments does not result solely from the release of magmatic gas but may also be due to freshly erupted lava-seawater reactions [Christie *et al.*, 1986]. Lava flows, pillow lavas, and volcanic ejecta are observed within these segments [Auzende *et al.*, 1994a; Fouquet *et al.*, 1994c.]. High H₂ concentrations are generally observed in seawater reacting with hot lavas, and the contribution of H₂ likely produced by lava-seawater reactions is probably more elevated than magmatic H₂ [Sansone *et al.*, 1991].

Nitrogen and Argon. N₂ and Ar are assumed to behave conservatively in hydrothermal systems [Welhan and Craig, 1983], and the N₂/Ar ratio of fluids is generally close to the N₂/Ar ratio of the recharge seawater. It is difficult to interpret the Ar data since all the values are close to the standard value (16 μmol/kg). An enrichment in Ar is observed in one sample (ND-13-G: 83 μmol/kg). To explain the Ar and N₂ variations, noble gases and their isotopic measurements may be necessary [Evans *et al.*, 1988].

Methane and other hydrocarbons. CH₄ is well known to be variably enriched in all hydrothermal fluids [Welhan, 1981; Welhan *et al.*, 1984; Welhan and Lupton, 1987; Evans *et al.*, 1988; Lilley *et al.*, 1993] (Table 5). Generally, deep seawater contains only 0.4 nmol/kg. Compared to CO₂ content (8.5 to 22 mmol/kg), hydrothermal fluids typically contain much lower low-

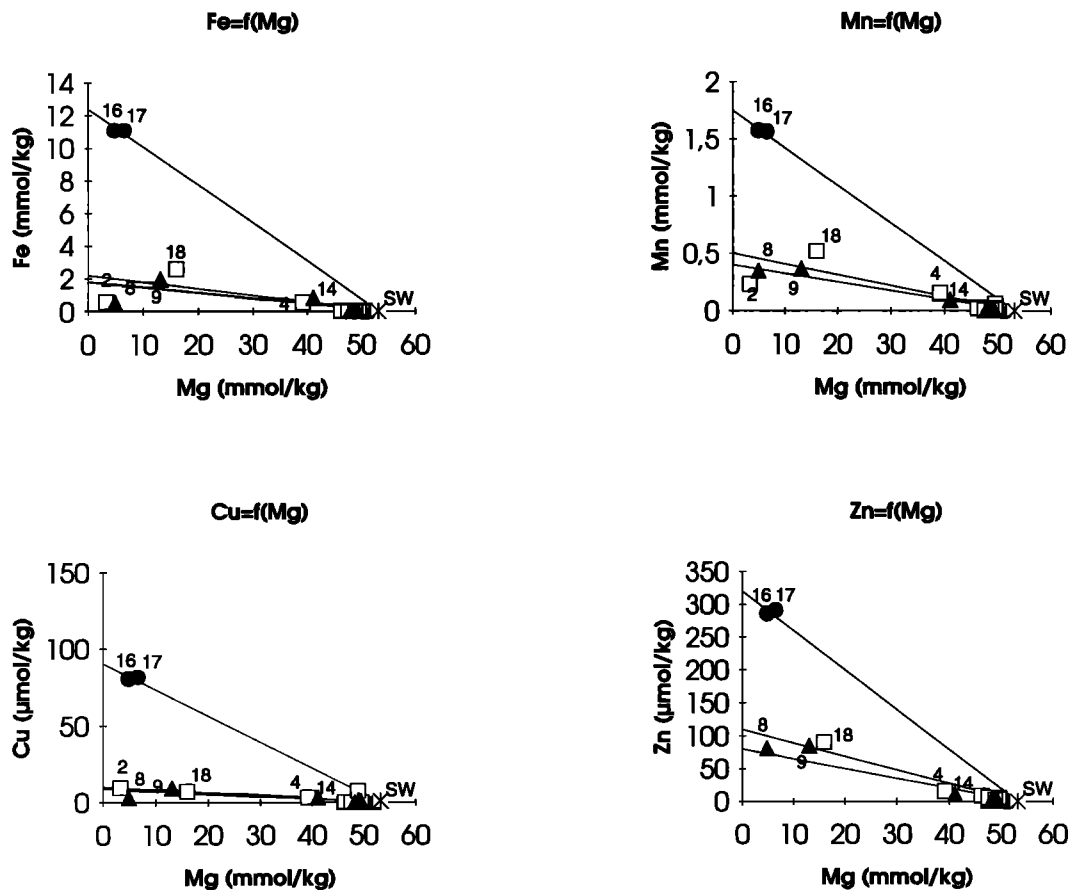


Figure 5. Plots of transition metals (Fe, Mn, Cu, Zn) versus magnesium for Naudur fluids. Lines drawn represent linear least squares regressions fitted to data for Nadir, Rehu Marka fluids (open squares) on the $17^{\circ}25'S$ segment, Akorta fluids (solid circles) on the $18^{\circ}15'S$ segment, and Stockwork, Fromveur fluids (solid triangles) on the $18^{\circ}26'S$ segment. Vent numbers from 1 to 20 are taken from Table 1.

CH_4 concentrations, ranging from 50 to 120 $\mu\text{mol/kg}$, except in some areas such as the Endeavour segment, where CH_4 concentrations reach 1.8 to 3.4 mmol/kg [Lilley *et al.*, 1993], many times greater than those measured previously at any unsedimented mid-ocean ridge. Recently, similar CH_4 concentrations ranging from 1.35 to 2.63 mmol/kg were found at the new Menez-Gwen hydrothermal site at $37^{\circ}50'N$, south of the Azores on the MAR [Donval *et al.*, 1994]. Between 17° and $19^{\circ}S$ on the south East Pacific Rise, CH_4 is found to be enriched in all fluids collected on the three segments. The lowest values are found in Nadir and Rehu-Marka fluids (7.5 to 8.5 $\mu\text{mol/kg}$) on the $17^{\circ}25'S$ segment. CH_4 values are higher in Stockwork and Fromveur fluids on the $18^{\circ}30'S$ segment (32 to 95 $\mu\text{mol/kg}$), and the highest values, as for N_2 , are found in Akorta fluids (133 $\mu\text{mol/kg}$), where total extracted gas and CO_2 content are the lowest. CH_4 is thus enriched in the high-salinity solutions, whereas CO_2 is enriched in the low-salinity fluids, indicating that CH_4 and CO_2 behave differently in the hydrothermal system. Whereas methane end-member concentrations show large variations, the ^{13}C data are very similar in fluids on all three sites, with $\delta^{13}\text{C}$ values in a narrow range -22.9‰ to -23.9‰ similar to other available carbon isotope data at sediment-free hydrothermal sites, with the exception of Endeavour (Table 5), suggesting a similar mantle origin for methane at these different sites. Saturated hydrocarbons C_2 and C_3 are also detected in all Naudur samples but at low concentrations, whereas traces of

unsaturated hydrocarbons are only detected in Fromveur fluids (Table 4).

Discussion

Evidence of Phase Separation

Between 17° and $19^{\circ}S$ (EPR) hydrothermal fluids exhibit a very wide range of chemical and gas composition. In the $17^{\circ}25'S$ and $18^{\circ}26'S$ hydrothermal fields, fluids have rather uniform composition and exhibit low chlorinities (155-323 mmol/kg , 28-59 % of seawater), major gas enrichment and low dissolved metal concentrations relative to typical hydrothermal fluids. In contrast, on the $18^{\circ}15'S$ segment, fluids show high chlorinities (up to 871 mmol/kg , 159 % of seawater) and high metal concentrations while being much less gas-enriched (Table 3).

Chloride enrichment or depletion influences the behavior of other elements and is generally the result of a combination of mineralization and phase separation related processes [Seyfried *et al.*, 1986; Delaney *et al.*, 1987; Von Damm and Bischoff, 1987; Campbell and Edmond, 1989; Von Damm, 1988, 1990; Berndt and Seyfried, 1990; Seyfried *et al.*, 1991]. Increased gas concentration in hydrothermal vents can be the result of processes involving phase separation, direct injection of magmatic gases, rapid initial stripping of gas from volcanic glass, and for some gases, bacterial activity within the hydrothermal system, or

Table 4. Gas End-Members in Naudur Hydrothermal Fluids

Sample	17°25'S		18°15'S	18°26'S		
	Nadir	Rehu-Marka	Akorta	Stockwork	Fromveur	Fromveur
	ND-03-G	ND-19-D	ND-17-D	ND-08-G	ND-09-D	ND-13-G
T (°C), max.*	340	300	>305	>210	310	310
pH, NBS, 25°C	3.00	3.10	3.25	3.10	3.00	3.00
Total gas volumes mL STP/kg fluid	518	500	404	806	1438	1143
H ₂ S**, mM	8.6	7.8	8.4	15.5	(35)	27.3
H ₂ , mM	0.15	0.10	0.04	0.15	1.30	0.05
CO ₂ , mM	13.1	14.0	8.5	19.6	22.0	20.4
δ ¹³ (CO ₂), ‰ vs. PDB	-	-	-7.9	-	-5.8	-
Ar, μM	26	14	-	27	14	83
N ₂ , mM	1.27	0.36	0.92	0.61	(5.2)	3.04
CH ₄ , μM	7.5	8.5	133	41	32	95
δ ¹³ (CH ₄), ‰ vs. PDB	-23.9	-	-22.0	-	-23.5	-
C ₂ H ₄ , μM	-	-	-	-	0.091	0.013
C ₂ H ₆ , μM	0.062	0.086	0.041	0.105	0.156	0.204
C ₃ H ₆ , μM	-	-	-	-	-	0.0086
C ₃ H ₈ , μM	0.0074	0.0114	-	0.025	0.036	0.039

T(°C), max.* are maxima temperatures measured in vents and not end-members. Reported gas values are zero-magnesium end-members. The latitudes 17°25'S, 18°15'S, and 18°26'S represent the middle of the three segments where hot fluids were collected. Gas extraction was performed by using a gas extractor [Charlou *et al.*, 1993]. Total gas volume was compressed between 1 and 2 atm in 200-mL metallic flasks, which were connected immediately after the extraction to a chromatographic system with catharometer and flame ionization detectors in line. Gas volumes are measured at ambient temperatures (25°C). Reported gas values are zero-magnesium end-members. Concentrations are in millimoles (mM) or micromoles (μM) per kilogram of hydrothermal fluid. H₂S** endmember concentrations are estimated by difference between total gas volume extracted and the sum of permanent analyzed gases. Gas concentrations in deep seawater unaffected by hydrothermal input are, respectively, CO₂: 2.30 mmol/kg; N₂: 0.59 mmol/kg; Ar: 16 μmol/kg; CH₄: 0.4 nmol/kg; H₂: 0.4 nmol/kg. The ¹³C isotope in CO₂ and CH₄ is relative to the Peedee belemnite (PDB) carbon isotope standard.

serpentinization reactions as seawater circulates through ultramafic rocks. In general, the composition of gases is very variable and dependent on the geological environment and the nature of the hydrothermal circulation [Lilley *et al.*, 1983, 1989, 1993; Welhan *et al.*, 1984; Evans *et al.*, 1988; Charlou *et al.*, 1991a,b; Charlou *et al.*, 1993; Charlou and Donval, 1993; Donval *et al.*, 1994] (Table 5).

The large chlorinity, metal, and gas variations observed in the Naudur fluids support the hypothesis that vent fluids have experienced boiling during hydrothermal circulation through the oceanic crust. From the temperature-pressure-composition

diagram showing the two-phase curve for a seawater analogue aqueous solution of 3.2-3.5 wt % NaCl [Sourirajan and Kennedy, 1962; Bischoff and Rosenbauer, 1984, 1985, 1988; Bischoff and Pitzer, 1985], the boiling temperature at the 260 atm pressure, which is the hydrostatic pressure at the hydrothermal sites on the 17°-19°S segments, is 392°C. All temperatures measured in this study were fluctuating and lower (max ~340°C) than the boiling temperature, due to the difficulty to sample the end-member. Generally, the vent temperatures are observed to be lower than the boiling temperature, suggesting always conductive cooling associated with some subsurface mixing of the hydrothermal fluid with cool seawater leading to a diversity of vent fluid composition. As shown by Von Damm [1990] and Edmonds and Edmond [1995] for hydrothermal fluids from the Galapagos Spreading Center, 21° and 13°N on the East Pacific Rise, the southern Juan de Fuca Ridge or the Guaymas Basin, hydrothermal solutions released in these areas where phase separation has taken place are in fact the result of mixing between separate components of brine, vapor, and hydrothermal seawater. Variable degrees of mixing are therefore able to account for the observed variability.

Low-chlorinity Fluids

With respect to their chemical properties, fluids collected within the 17°25'S and 18°26'S segments show a similar tendency to the 9°N EPR, ASHES, and North Fiji basin fluids. Their chemical composition indicates that they experienced phase separation and segregation (generation of vapor-rich and brine-rich fluids) during hydrothermal circulation and subsequent seafloor cooling by admixture of cold seawater while

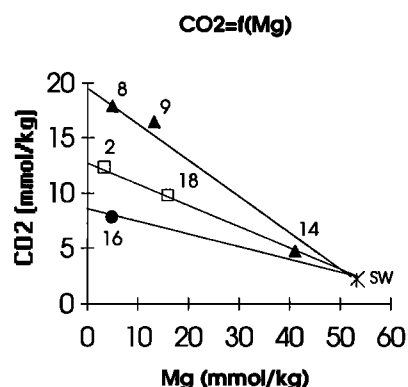


Figure 6. Carbon dioxide versus magnesium showing three different linear correlations. This suggests conservative behavior during mixing of vent fluids with seawater and confirms the different nature of fluids emitted from the three contrasted 17°25'S (open squares), 18°15'S (solid circles), and 18°26'S (solid triangles) ridge segments.

Table 5. Comparison of Gas Concentrations From Different Hydrothermal Systems

Site	T (°C), max.	H ₂ S, mM	CO ₂ , mM	δ ¹³ CO ₂ , ‰	Ar, μM	N ₂ , μM	H ₂ , μM	CH ₄ , μM	δ ¹³ CH ₄ , ‰
Std sw	2	0	2.30	-5.1/-5.9	16	590	0.0004	0.0003	-
Galapagos ^a	30	-	-	-	-	-	0.080	3.5	-
East Pacific Rise									
9 - 10°N ^b	300/400	> 65	2.6/65	-	-	-	100/1800	10/300	-
11°N ^c	347	4.4/12.2	10.8/16.7	-	-	-	446/499	67/117	-
13°N ^d	354	2.9/8.2	11.8/18.4	-4.1/-5.5 ^e	-	-	143	27/54	-16.6/-19.6
21°N ^e	355	6.6/8.4	5.7	-7.0	-	-	357/1610	54/94	-15.0/-17.6
17°-19°S (this work)	340	7.8/35	8.4/22.0	-5.8/-7.9	14/40	360/3000	40/1300	7/133	-22.0/-23.9
Guaymas Basin ^f	315	3.8/6	-	+2.7/-6.0	-	-	-	16650	-43.2/-50.8
Juan deFuca Ridge									
Endeavour (NJDF) ^g	350	6	5/11	-	-	-	160/420	500/1500	-48.4/-55.0
southern JDFR ^h	285	1.95/4.12	3.92/4.36	-6.8/-9.7	10.1	440	270/527	82/118	-17.8/-20.8
Axial seamount ⁱ	350	7/19	50/285	-	-	-	-	25	-
Mid-Atlantic Ridge									
Mark (23°N) ^j	335/345	6	-	-	-	-	-	45/62	-
TAG (26°N) ^k	321/390	6.7	2.9/3.4	-	20/40	800/890	152/370	124/147	-
Lucky Strike (37°17'N) ^l	152/320	2.5/3.0	13/28	-	20/98	610/970	20/726	500/970	-
Menez Gwen (37°50'N) ^l	280	1.5	17/20	-	11/41	600/1900	24/48	1350/2630	-
Southwest Pacific									
Okinawa (JADE) ^m	320	12.3	198	-	-	-	-	2400	-
North Fiji Basin ⁿ	285	2/4	14.5	-5.7/-6.2	-	-	-	30.4/43.5	-18.0/-20.0
Lau Basin ^o	334	-	5.9/7.8	-	3.1/3.7	1800/6200	24/49	3.5/5.0	-
Loihi seamount ^p	30	-	300	-1.7/-5.5	-	-	-	7	-
MORB basalt glass ^q	-	-	3.5/5.2	-5.3/-7.6	-	9/90	45/160	4.5/7.2	-

End-member concentrations are in millimoles (mM) or micromoles (μM) per kilogram of hydrothermal fluid. Gas concentrations in deep seawater unaffected by hydrothermal input are, respectively, CO₂: 2.30 mmol/kg; N₂: 0.59 mmol/kg; Ar: 16 μmol/kg; CH₄: 0.4 nmol/kg; H₂: 0.4 nmol/kg. The ¹³C isotope in CO₂ and CH₄ is relative to the Pee Dee belemnite (PDB) carbon isotope standard.

^a Lilley et al., [1983], Welhan, [1981].

^b Lilley et al., [1991], Lupton et al., [1991], Haymon et al., [1993].

^c Kim et al., [1984], Welhan et al., [1984].

^d Welhan et al., [1984], Von Damm et al., [1985], Merlivat et al., [1987].

^e Welhan and Craig, [1983], Lilley et al., [1983], Von Damm, [1990].

^f Welhan and Lupton, [1987].

^g Lilley et al., [1993].

^h Von Damm and Bischoff, [1987], Evans et al., [1988].

ⁱ Butterfield et al., [1990].

^j Jean-Baptiste et al., [1991], Charlou and Donval, [1993b].

^k Charlou and Donval, [1993a,b].

^l Donval et al., [1994].

^m Sakai et al., [1990a,b], Ishibashi et al., [1995].

ⁿ Ishibashi et al., [1994a,b].

^o Charlou et al., [1991a].

^p Sedwick et al., [1992], Sedwick et al., [1994].

^q Pineau et al., [1976]; Moore et al., [1977], Welhan and Craig, [1983], Welhan, [1988b].

^r data not corrected for the involvement of seawater bicarbonate.

ascending in the upflow zone. Strong arguments speak in favor of this interpretation. In the fluids collected along the 18°26'S segment (Stockwork, Fromveur), the Cl end-member represents only 28 % of the Cl concentration of seawater and is among the lowest values reported to date for ridge crest fluids. Rock hydration and precipitation of Cl-bearing minerals can only explain small Cl variations (<10% of Cl concentration of seawater) [Seyfried et al., 1986]. In addition, these processes would lead to significant Br/Cl ratio variations, which are not observed in our data. Actually, the Br/Cl ratio does not vary significantly with chloride concentration in the 18°26'S fluids (Table 3; Figure 7), as also observed in ASHES fluids by Butterfield et al., [1990]. Hence rock hydration or precipitation of

Cl minerals are not adequate to explain the magnitude of the 18°26'S Cl depletion.

Evidence for phase separation is further given by the inverse correlation of CO₂ versus chloride in the fluids collected on the 17°25'S and 18°26'S segments, with CO₂ enrichment (13.1 to 22 mmol/kg) corresponding to strong Cl depletion (155 to 323 mmol/kg). In contrast, as will be discussed in the next section, Akorta fluids on the 18°15'S segment show a high chlorinity (848 to 871 mmol/kg) associated with a lower CO₂ content (8.5 mmol/kg). These observations are consistent with a phase separation process in which gases are preferentially transferred into the vapor phase and all non volatile elements are concentrated in the liquid phase. The mixing lines (Figure 8)

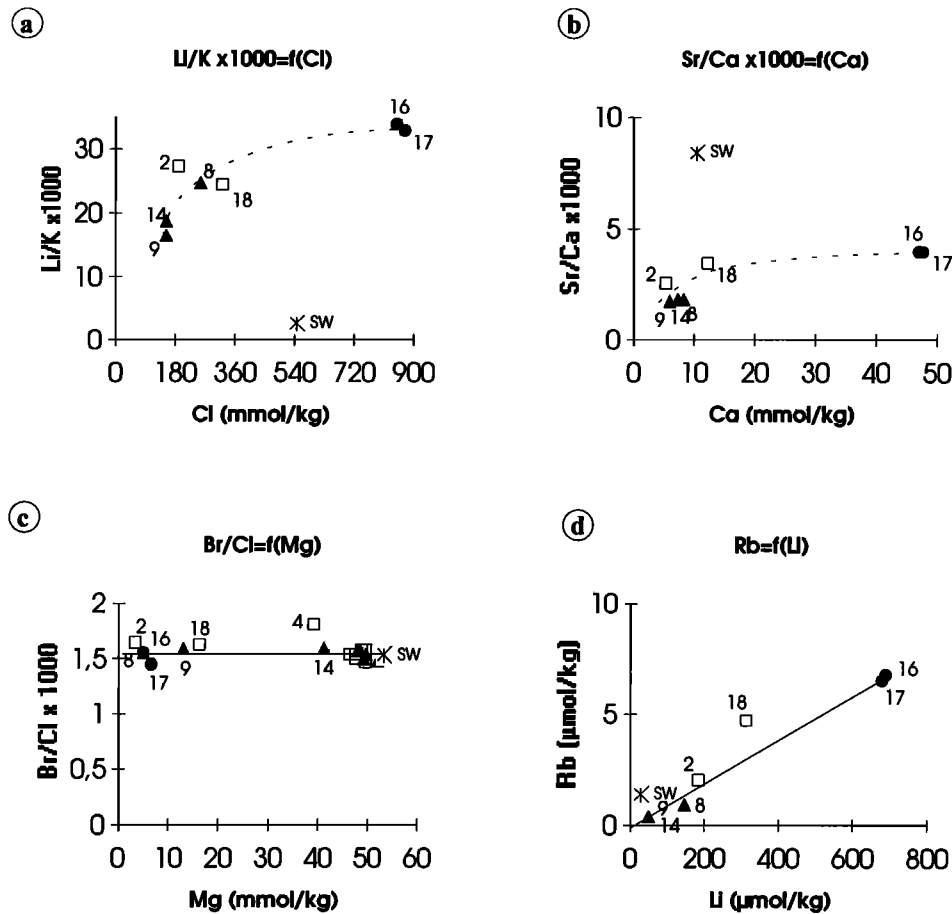


Figure 7. (a) Li/K versus Cl concentration in Naudur fluids: Nadir, Rehu Marka fluids (open squares) on the 17°25'S segment, Akorta fluids (solid circles) on the 18°10'S segment, and Stockwork, Fromveur fluids (solid triangles) on the 18°26'S segment. The increase in Li/K in the high-chlorinity fluids is consistent with continued leaching of extractable elements from the rocks into the high-chlorinity, vapor-poor fluids relative to the lower-chlorinity fluids. (b) Sr/Ca versus Ca content. In the 17°-19°S (EPR) fluids, the Sr/Ca ratio is noticeably higher in the Cl-enriched phase, than in the Cl-depleted phase, in good agreement with experimental observations of liquid-vapor partitioning by *Berndt and Seyfried*, [1990]. (c) Br/Cl ratio versus magnesium. The Br/Cl ratio in all fluids between 17° and 19°S are close to the seawater Br/Cl ratio (1.540×10^{-3}). (d) Rb versus Li in fluids from 17°-19°S (EPR). The Rb-Li trend characterize fluids typically collected on a volcanic-hosted mid-oceanic ridge, as shown by *Butterfield et al.*, [1994]. The lowest Rb/Li ratios are observed in fluids from the 17°25'S and 18°26'S ridge segments where volcanism is dominant, as observed during *Nautile* dives [*Auzende et al.*, 1994; *Fouquet et al.*, 1994c].

show that most of the non volatile elements (Br, Na, K, Li, Rb, Ca, Sr, Ba, Fe, Mn) are correlated with chloride. Total gas volume is also inversely correlated with chloride with the indication of three distinct families of fluids related to the three distinct ridge segments (17°25'S, 18°15'S, and 18°26'S).

High-chlorinity Fluids

Brine production mechanisms. High-chlorinity fluids were found on the 18°15'S segment. There is no evidence that low-Cl fluids were equally present on that segment. This suggests that phase separation was not in progress at the Akorta hydrothermal field at the time of the cruise. As discussed above, dissolution of chloride-bearing minerals cannot explain the strong Cl enrichment in Akorta fluids. We think that phase separation occurred at 18°15'S at some time in the past, producing a residual brine at depth in the hydrothermal system, as previously observed

on the southern Juan de Fuca Ridge [*Von Damm and Bischoff*, 1987]. These high salinities are likely to be the counterpart, in the phase separation process, of the low-salinity fluids seen on the two other segments. Presumably, brine segregation occurs early in a magmatic event and stabilizes the system thereafter. Given their higher densities and lower buoyancies, the brines may remain stored in the oceanic crust during the quiescence periods between thermal pulses. However, *Bischoff and Rosenbauer* [1989] have recently suggested the existence of very deep saline hydrothermal circulation cells. Although the data are still limited, there is some evidence in the literature [*Vanko*, 1988] that very high salinity fluids may occur at greater depths in the oceanic crust than those depths at which axial hot springs are currently believed to circulate. Supercritical phase separation (at $T > 400^\circ\text{C}$, $P > 300$ atm) can generate fluids of very high salinity (2 to 10 times that of seawater) as observed for example in some fluid inclusions from deep gabbros near the Kane fracture zone in the

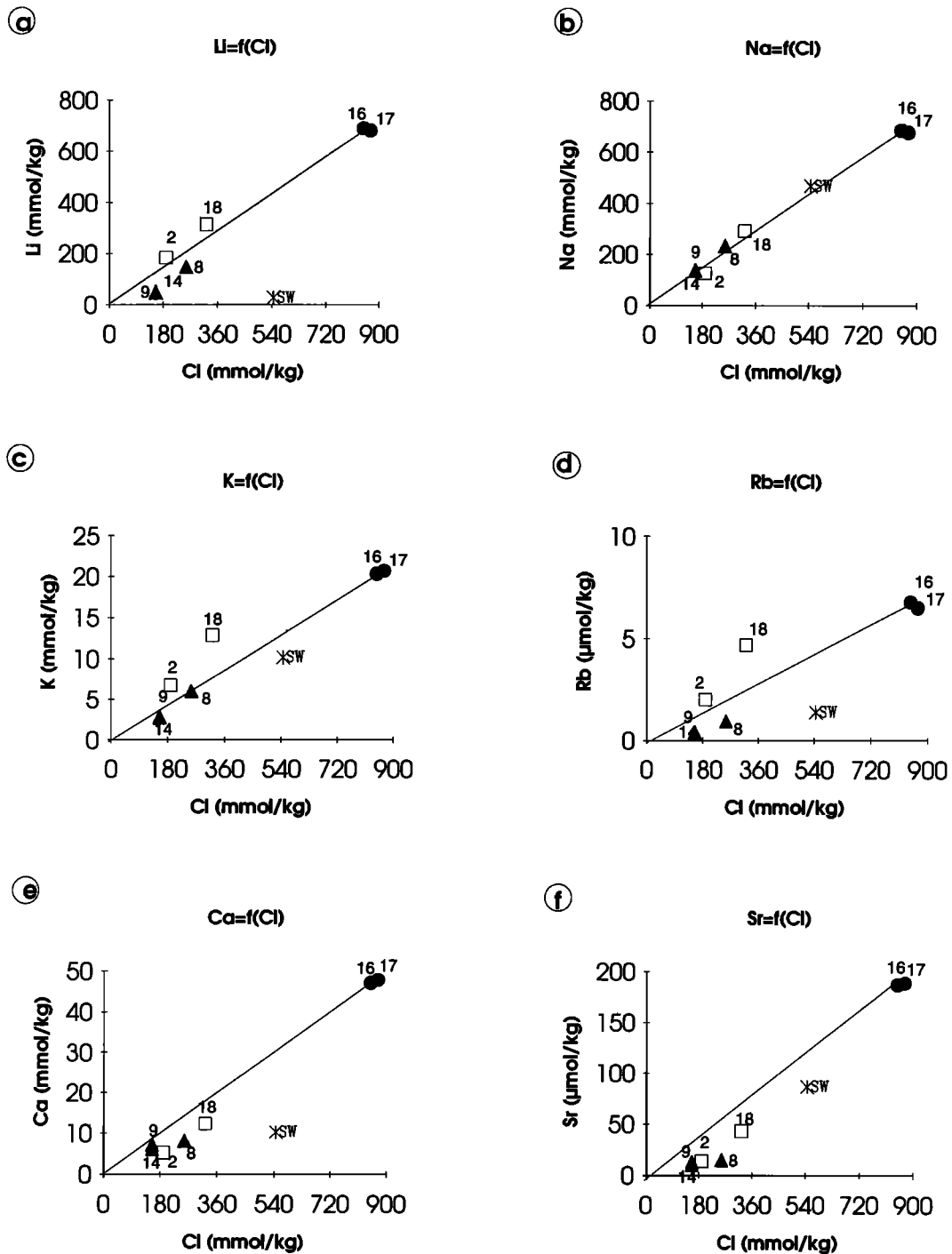


Figure 8. Plot of endmember major and minor element concentrations versus end-member chloride for individual vents: Nadir, Rehu Marka fluids (open squares) on the 17°25'S segment, Akorta fluids (solid circles) on the 18°15'S segment, and Stockwork, Fromveur fluids (solid triangles) on the 18°26'S segment. (a) lithium, (b) sodium, (c) potassium, (d) rubidium, (e) calcium, (f) strontium, (g) barium, (h) silica, (i) iron, (j) manganese, (k) bromide, and (l) total extracted gas. All elements show a positive correlation with chloride, consistent with phase separation, chloro-complexing, and unmixing of vapor and brine. For many elements, the end-members are very close to a line connecting the Akorta brine composition with the origin, consistent with the mixing of a brine with a vapor of near-zero salinity. All end-members have to be on this mixing line if a simple boiling model is considered. Loss or gain of elements by the hydrothermal fluids are given by deviations from this ideal mixing line.

Atlantic [Delaney et al., 1987], or in fluid inclusions trapped in the ore-forming discharge zone in many other areas [Fournier, 1987; Kelley and Delaney, 1987; Goldfarb and Delaney, 1988; Vanko, 1988; Nehlig, 1991]. This suggestion is in agreement with

the three-component mixing model for ridge crest hydrothermal fluids [Edmonds and Edmond, 1995]. These brines may be reinjected periodically into the hydrothermal circulation through fractured rocks. Episodes of brine accumulation in the deeper

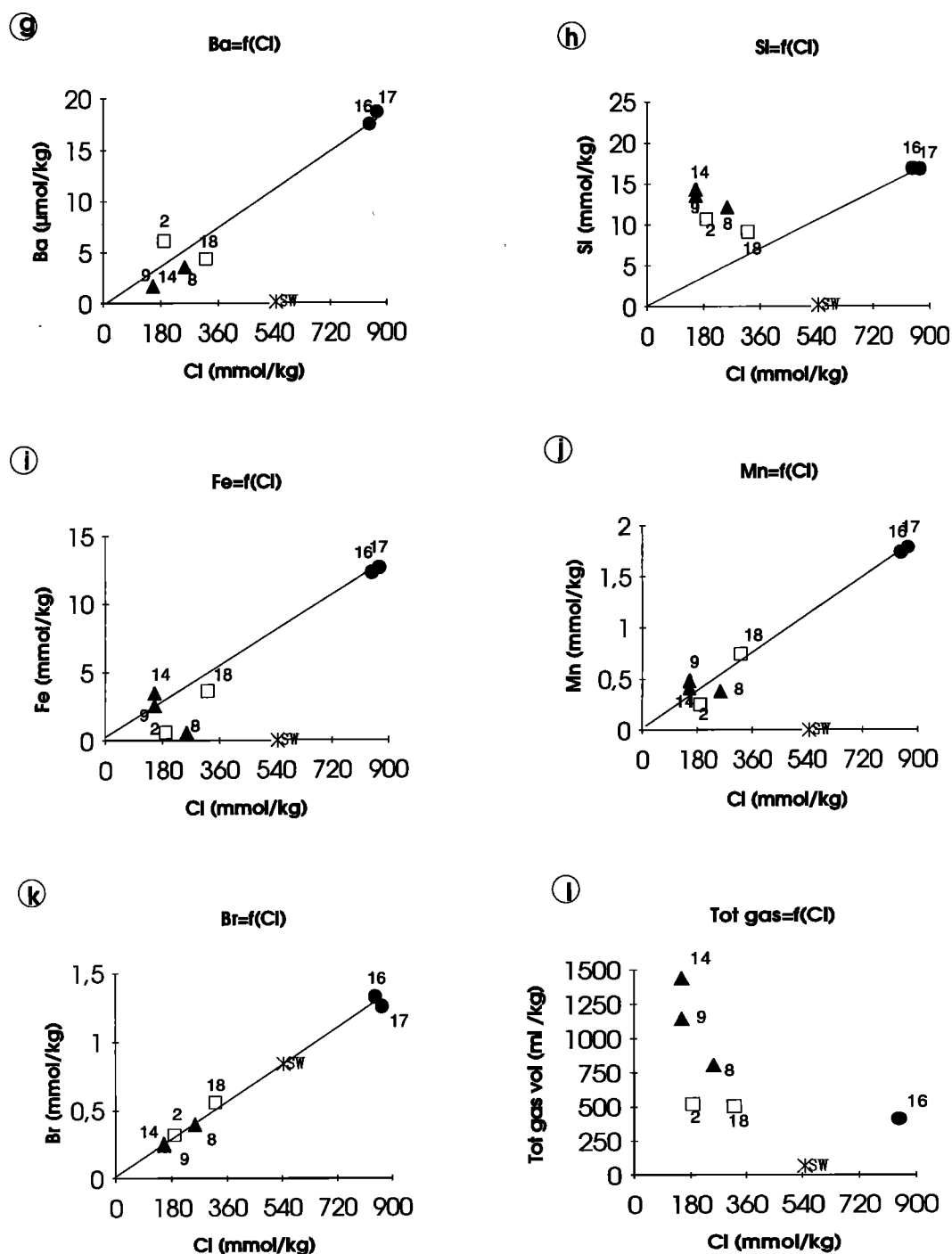
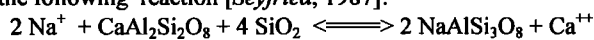


Figure 8 (continued).

layer may alternate with episodes of brine transport to the seafloor. Therefore we cannot totally exclude the possibility that these Cl-enriched fluids encountered at 18°15'S on the south EPR could also originate from this brine formation process deeper in the crust.

These brines are primarily responsible for the albitization of the oceanic crust [Seyfried, 1987; Von Damm, 1990]. The Ca/Na ratio (~0.07) found in the high-Cl fluids from the 18°15'S segment is twice the value measured on the two other segments (Table 3) and supports this mechanism of albitization of the crust. High-Cl concentrations of Akorta fluids increase the complexing of divalent cations more than monovalent cations. So, at salinities

higher than 600 mmol/kg [Von Damm et al., 1985], Na⁺ may be exchanged with Ca⁺⁺ to produce albit (NaAlSi₃O₈), whereas Ca⁺⁺ issued from dissolved anorthite is liberated in solution, in the following reaction [Seyfried, 1987]:



In addition, there is a clear evidence of other rock alteration processes by this brine phase, as indicated by the increase of Li/K and Li/Cl ratios in Cl-enriched fluids (Akorta) (Table 3).

Enrichment of CH₄ in brines. CO₂ and CH₄ are enriched both in low- and high-Cl fluids (Table 4). However, these two gases show different trends versus chlorinity on the three different segments (Figure 9). CO₂ is always higher in the low-

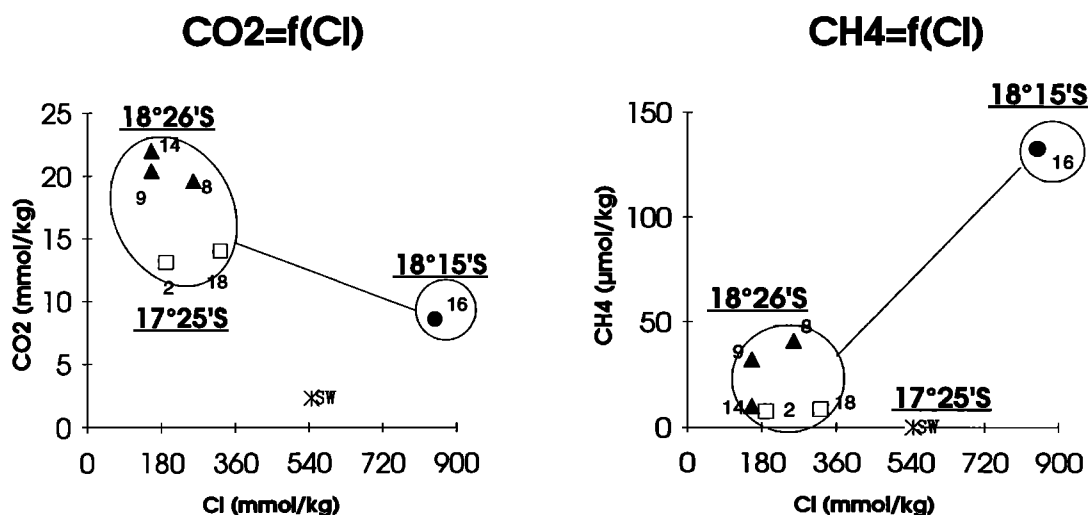


Figure 9. CO₂ and CH₄ versus Cl in fluids collected on the three segments 17°25'S (open squares), 18°15'S (solid circles) and 18°26'S (solid triangles) (south East Pacific Rise). The enrichment of CO₂ in the low-chlorinity fluids (Stockwork, Fromveur, Nadir, Rehu-Marka) is consistent with phase separation. CO₂ and CH₄ show different trends versus chloride. CO₂ content is higher in low-chlorinity fluids, whereas CH₄ content is higher in high-chlorinity fluids. Both gases are partitioned into the vapor phase during phase separation. On the 18°15'S segment there is no evidence of present-day phase separation. Emitted fluids consist only of CH₄-enriched brines. CH₄ enrichment is explained by alteration of CH₄-enriched rocks and reduction of primary magmatic CO₂.

chlorinity fluids than in the high-chlorinity fluids. In contrast, CH₄ is higher in high-chlorinity fluids (Akorta) located on the 18°15'S segment than in low-chlorinity fluids sampled on the 17°25'S and 18°26'S segments. Carbon isotopic measurements suggest these gases, enriched in all hydrothermal fluids, have a mantle origin (P. Jean-Baptiste *et al.*, Helium and oxygen isotopes in hydrothermal fluids from the East Pacific Rise between 17°S and 19°S, submitted to *Geo-Marine Letters*, 1996), from outgassing of juvenile CO₂ and CH₄ and inorganic synthesis [Welhan, 1988]. Both gases are strongly fractionated into the vapor phase during phase separation [Drummond, 1981]. Therefore the differences in CH₄ concentration have to be due to reactions occurring in the brine phase after phase separation has occurred. Recently, CH₄ concentrations up to 40 times those of occluded gases in basaltic glasses and of hydrothermal vents were detected in gabbro-hosted fluid inclusions [Kelley and Delaney, 1987; Kelley, 1996]. Hence this CH₄ enrichment in brines may well be produced by the leaching of gabbroic rocks containing CH₄-rich inclusions. In addition, CH₄ production may also arise from reduction by H₂ of primary magmatic CO₂ in the plumbing system. Indeed, H₂ is commonly found to be anomalously high along active faults [Wakita *et al.*, 1980] and to show large temporal changes possibly related to earthquake activity [Sugisaki *et al.*, 1983]. H₂ is produced by different mechanisms including deep crustal outgassing, high-temperature reaction between water and silica radicals on freshly cleaved surfaces of silicates in active tectonic areas [Sugisaki *et al.*, 1983], reduction of water by hot (>800°C) ferrous rocks in extrusive magmas [Apps, 1985], inorganic generation by stressed rocks [Giardini *et al.*, 1976; Sugisaki *et al.*, 1985], reaction of water with carbon of mantle origin in magma source regions and in deep magma chambers when intrusions may form [Sato, 1978], and low-temperature reaction in the shallow crust (serpentinization of olivine) with direct outgassing from mantle or lower crust along fracture zones [Apps, 1985; Charlou *et al.*, 1991b; Charlou and Donval, 1993].

Magmatism and Fault Controls on the Hydrothermal Fluid Composition

The 17°-19°S ridge section studied during the Naudur cruise displays geologically contrasted segments (20 to 45 km long). The style of the hydrothermal activity appears to vary with axis morphology and to be related to how recently the area has been volcanically active [Auzende *et al.*, 1994; Fouquet *et al.*, 1994c]. Fluid composition is rather uniform within each segment, but very different from one segment the other (Tables 3 and 5). The contrasting fluid compositions observed on the 17°25'S, 18°15'S, and 18°26'S segments is likely to be related to the geological setting and narrowly dependent on interactions between magmatism, faulting, and hydrothermal circulation.

17°25'S segment. Observations between *Cyana* 1984 dives and *Nautile* 1993 dives in the same area of the axis near 17°25'S show substantial volcanic eruptions have occurred in this area during the last decade [Auzende *et al.*, 1994a]. The extensive collapsed lava lake discovered in 1984 has disappeared, to give way to fresh lavas that have only collapsed along a discontinuous fissure zone. Now, on this volcanics-dominated ridge, shimmering waters are milky and turbid and directly associated with new lava flows. The thermal anomalies recorded by the submersible *Nautile* in the seawater layer, 1 to 3 m above the seafloor, are probably linked to the cooling of young lavas. High temperature discharges start to produce black smoker chimneys outside the axial lava lake area (Nadir, Rehu-Marka) with highly reducing fluids related to deeper hydrothermal convection controlled by the cooling dike system [Fouquet *et al.*, 1994c]. We believe that phase separation which was previously initiated (perhaps by a magma eruption episode) is continuing, but, due to the progressive cooling of the intrusion, is diminishing, with an associated increase in the chlorinity (up to 323 mmol/kg) and metal content and a decrease in the proportion of the gas phase (500 mL STP/kg) in the hydrothermal circulation. The result is

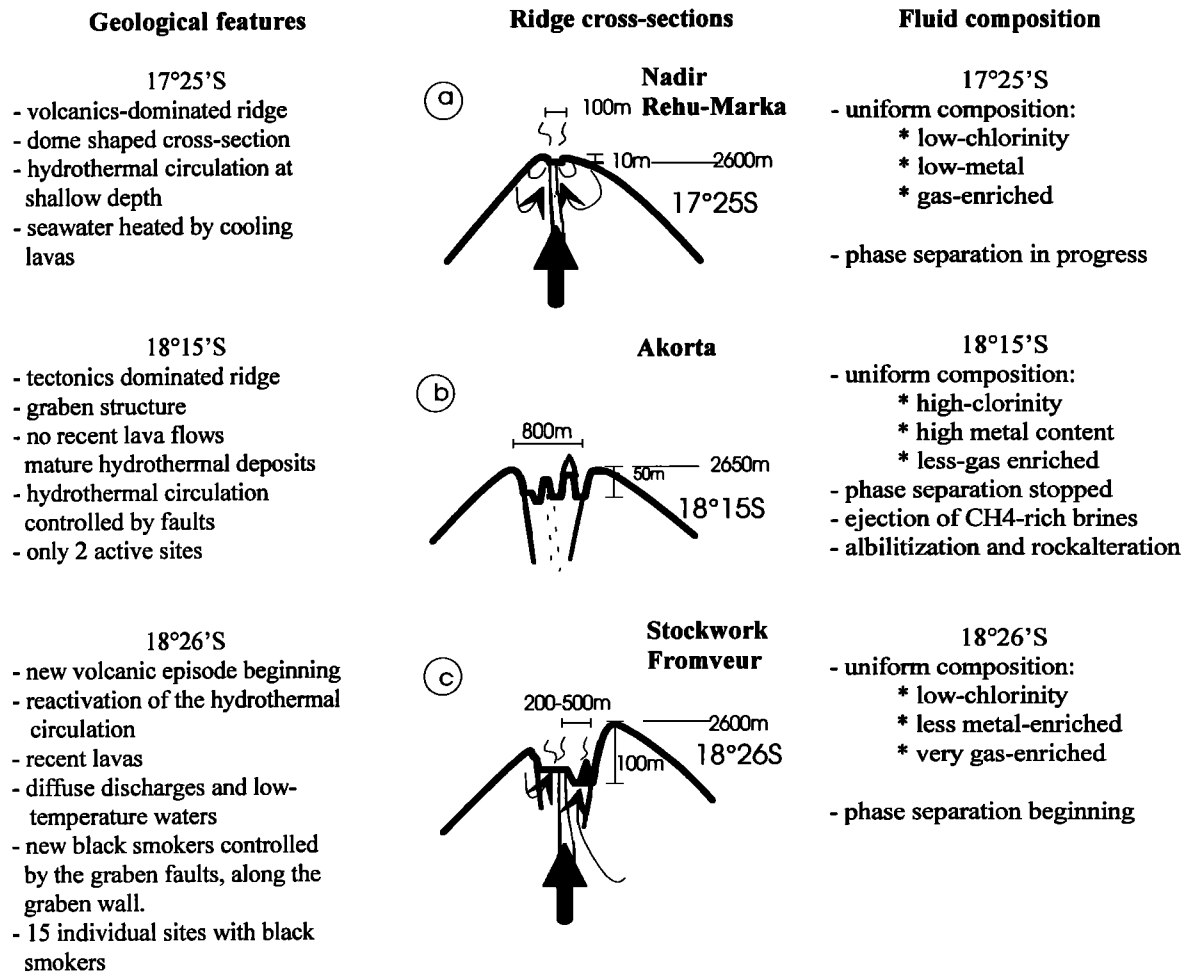


Figure 10. Variability of geological settings related to variability in fluid composition on the three 17°25'S, 18°15'S, and 18°26'S segments. Geological features are taken from *Auzende et al.*, [1994b]. Ridge cross sections are adapted from *Fouquet et al.*, [1994c].

consistent with a progressive mixing of the vapor-enriched phase with dense brine accumulated in the deeper parts of the system, giving more and more Cl-enriched, gas-depleted fluids. In many aspects, these sites are similar to the site at 9°50'N [*Haymon et al.*, 1993].

18°15'S segment. This segment, north of the "Hump" segment is characterized by an axial graben. No recent lava was observed, and tectonic activity is dominant along the graben [*Auzende et al.*, 1994a]. The Akorta fluids are thus located on a tectonics-dominated ridge, controlled by faults, in a graben structure without evidence of recent lava flows, absence of diffuse flows on the large surfaces of lava, with more mature deposits and an abundance of silicic material [*Fouquet et al.*, 1994c]. This may indicate stable and deep hydrothermal systems focused along the major faults. Active sites are less numerous than on the adjacent volcanically active segments. The active sites are related to the main faults, while the other small faults have been obtruded by recent lava flows [*Auzende et al.*, 1994a; *Fouquet et al.*, 1994c]. The continuation of tectonic activity along major faults has resulted in the exposure of stockwork areas. Very few vents are active and the hydrothermal circulation appears to be in a decreasing phase. The Akorta fluids circulating through more mature hydrothermal deposits have high salinities

(up to 871 mmol/kg), and are metal-enriched and less gas-enriched (404 mL STP/kg). The higher density brines which accumulated within the deeper layer of the hydrothermal plumbing saturating the microfractured rocks above the magma chamber, are now expelled. As discussed above, we think that these fluids have evolved to high-chlorinity fluids after earlier venting of vapor-enriched fluids, initially caused by a boiling event. High Fe and metal levels, low Na/Cl and low Sr/Ca suggest that the high-chlorinity brines further react with altered basalt after the episode of phase separation and segregation before and/or while being entrained upward through the hydrothermal system. A period of vapor-dominated venting preceding a brine-dominated phase with a continuous alteration of ocean crust by the brines was previously postulated for the northern cleft segment [*Butterfield and Massoth*, 1994].

18°26'S segment. The 18°26'S segment is characterized by very low chlorinity (155 mmol/kg) and gas-enriched fluids (up to 1438 mL STP/kg) (Stockwork, Fromveur). From the submersible observations reported by *Auzende et al.*, [1994a] and *Fouquet et al.*, [1994c], we believe that black smokers are probably related to the reactivation of the hydrothermal system by the onset of a new volcanic episode further south (18°34'S to 18°37'S) on the segment, whereas diffuse warm water is related to the cooling of

the recent lava [Fouquet *et al.*, 1994c]. This 18°34'–18°37'S area is characterized by lobate lavas, lava lakes, and massive lavas with intense shimmering waters and without sessile animals, favouring the hypothesis of very recent hydrothermal activity. The heat released by this new activity may reactivate the deep hot water circulation along the graben faults. As already discussed above, the low salinities and high concentrations of gases in fluids suggest that subcritical phase separation is occurring. During this ongoing widespread phase separation, vapor-dominated fluids are discharged along the segment, while brines may be accumulating in the deeper parts of the hydrothermal system, as also shown for the Endeavour segment [Butterfield *et al.*, 1994] and at 9°46'N on the East Pacific Rise [Von Damm *et al.*, 1995].

As pointed out in the above discussion, the different chemical patterns of the hydrothermal fluids in the whole area appear to be strongly related to the geological settings (Figure 10). This suggests that the spacial variability in fluid composition is linked to the variability through time of the accretion process on the three segments. We speculate that our observations on these three segments, associated with the geological and petrological data [Auzende *et al.*, 1994b; Fouquet *et al.*, 1994c], display the influence of the different temporal stages of the magmato-tectonic cycle of the ridge on the hydrothermal circulation, thermodynamics, and chemistry of the fluids. Enhanced hydrothermal activity is related to areas of inflated ridge cross sections and to the presence of a shallow axial magma chamber [Urabe *et al.*, 1995]. As the spreading rate increases, the minimum depth of the axial chamber rises closer to the seafloor, presumably increasing the frequency, the extent, and duration of magmatic intrusions [Detrick *et al.*, 1993]. The variations in cross-sectional width of the axis with latitude suggest significant along-axis variations in the magma supply [Scheirer *et al.*, 1993]. Hence hydrothermal activity varies from one segment to the other and produces fluids of different composition, according to the predominant type of activity that is occurring at a specific period of time, that is, mainly tectonic or mainly volcanic. The lowest salinity fluids are generally related to recent magmatic expulsion. The highest salinity fluids are produced later by expulsion of brines previously accumulated in deep conduits of the hydrothermal system.

Conclusions

We have reported the chemistry of the first hydrothermal fluids collected with *Nautile* between 17° and 19°S on three contiguous ultrafast spreading ridge segments centered, respectively, at 17°25'S, 18°15'S, and 18°26'S on the southern East Pacific Rise.

Both enrichments and depletions of elements relative to seawater are observed in those fluids. Three distinct trends are observed, particularly related to chloride concentration, corresponding to the three geologically contrasted segments previously described by Auzende *et al.*, [1994b] and Fouquet *et al.*, [1994c]. Hydrothermal fluids chloride content ranges from 28% to 159% of seawater chlorinity. All major elements are strongly correlated with chlorinity. Chlorinity varies from one segment to the other, but vents sampled within each segment have a rather uniform composition.

Major element, CO₂ and metal data show that fluid chemistry is affected by phase separation. This process, which occurs or occurred over the whole area, is the most plausible one to explain

the large differences in fluid composition and gas content between hydrothermal vents present on the three successive segments. Chlorinity and CO₂ content are inversely correlated on the three segments, supporting the phase separation hypothesis. End-member concentrations of most of the major and minor elements are positively correlated with chloride in the Naudur fluids due to the combined effects of phase separation/physical segregation of the vapor and liquid phases and chloro-complexing. Silica, lithium, barium, and metals are very enriched in all fluids compared to seawater. The trend of increasing transition metal content with increasing chlorinity suggests that chloride complexing is the dominant control on metal solubility in the Naudur fluids.

Lithium levels in low-chlorinity fluids (17°25'S and 18°26'S segments) suggest that water/rock interaction has not taken place in the upflow zone subsequent to phase separation. This means that low-chlorinity fluids produced by phase separation have reacted with surrounding rocks only to a limited extent. In contrast, on the 18°15'S segment, high-Cl fluids seem to have reacted more intensively with deeper rocks given the enrichment observed in silica and extractable elements. CH₄ is also enriched in the 18°15'S fluids compared to the low-Cl fluids from the other segments. We speculate that a part of the CH₄ in these brines originates from gabbroic fluid inclusions that would be leached by these high-salinity fluids.

Carbon isotopes suggest a magmatic origin for CO₂ and CH₄ in the hydrothermal fluids collected on the three ultrafast spreading ridge segments. The spacial variability in fluid composition appears to be related to the temporal variability of the accretion process, including interactions between magmatism, faulting, and hydrothermal circulation. Venting of low-chlorinity fluids over the 17°25'S and 18°26'S ridge segments is favoured by ongoing volcanic activity which causes boiling with preferential discharge of vapor-enriched fluids, whereas high-salinity fluids are emitted on the 18°15'S ridge segment which is tectonics-dominated and fault-controlled. On fast and ultrafast spreading ridges, hydrothermal circulation is characterized by successive volcanic/tectonic/hydrothermal cycles, resulting in fluids controlled by phase separation processes and related to sudden volcanic episodes which can spontaneously modify their composition.

Acknowledgments. We thank Captain Thébaud and the crew of the *Nadir* for their help during Naudur cruise. The *Nautile* Team under the direction of Jean-Pierre Labbé accomplished perfect work. We thank Ken Macdonald for providing us compiled multibeam bathymetric maps of the area and Jérôme Chappelaz (CNRS-LGGE) for the use of his carbon isotope chromatographic equipment. We are also grateful to Joel Knoery and Pamela Murphy for their comments, suggestions, and discussions on this manuscript. The manuscript was greatly improved by the thoughtful reviews of Dave Butterfield, Robert Lowell, and an anonymous reviewer. The Naudur cruise was funded by IFREMER.

References

- Apps, J. A., Methane formation during hydrolysis by mafic rocks, *Ann. Rept.* pp. 13-17, Univ. of Calif., Lawrence Berkeley Lab., Berkeley, Calif., 1985.
- Auzende, J. M., J. Sinton, and Scientific Party, Submersible observations at Superfast spreading. NAUDUR program, East Pacific Rise, 17-19°S, *Eos Trans. AGU*, 75, (16), Spring Meet. Suppl., 329, 1994a.

- Auzende, J. M., V. Ballu, R. Batiza, D. Bideau, M. H. Cormier, P. Geisdoerfer, Y. Lagabrielle, J. Sinton, and P. Spadea, Activité magmatique, tectonique et hydrothermale actuelle sur la Dorsale Est Pacifique entre 17° et 19°S (campagne NAUDUR), *C. R. Acad. Sci. Paris*, 319, Série II, 811-818, 1994b.
- Backer, H., J. Lange, and V. Marchig, Hydrothermal activity and sulfide formation in axial valleys of the East Pacific Rise crest between 18° and 22°S, *Earth Planet. Sci. Lett.*, 72, 9-22, 1985.
- Berndt, M. E., and W. E. Seyfried Jr, Boron, bromine, and other trace elements as clues to the fate of chlorine in mid-ocean ridge fluids, *Geochim. Cosmochim. Acta*, 54, 2235-2245, 1990.
- Bischoff, J. L., and F. W. Dickson, Seawater-basalt interaction at 200°C and 500 bars: Implications for origin of seafloor heavy metal deposits and regulation of seawater chemistry, *Earth Planet. Sci. Lett.*, 25, 385-397, 1975.
- Bischoff, J. L., and R. J. Rosenbauer, The critical point and two-phase boundary of seawater, 200°C-500°C, *Earth Planet. Sci. Lett.*, 68, 172-180, 1984.
- Bischoff, J. L., and R. J. Rosenbauer, An empirical equation of state for hydrothermal seawater (3.2 percent NaCl), *Am. J. Sci.*, 285, 725-765, 1985.
- Bischoff, J. L., and K. Pitzer, Phase relations and adiabats in boiling seafloor geothermal systems, *Earth Planet. Sci. Lett.*, 75, 327-338, 1985.
- Bischoff, J. L., and R. J. Rosenbauer, Phase separation in seafloor geothermal systems: An experimental study of the effects on metal transport, *Am. J. Sci.*, 287, 953-978, 1987.
- Bischoff, J. L., and R. J. Rosenbauer, Liquid-vapor relations in the critical region of the system NaCl-H₂O from 380 to 415°C: A refined determination of the critical point and two-phase boundary of seawater, *Geochim. Cosmochim. Acta*, 52, 2121-2126, 1988.
- Bischoff, J. L., and R. J. Rosenbauer, Salinity variations in submarine hydrothermal systems by layered-double-diffusive convection, *J. Geol.*, 97, 613-623, 1989.
- Bowers, T. S., A. C. Campbell, C. I. Measures, A. J. Spivack, M. Khadem, and J. M. Edmond, Chemical controls on the composition of vent fluids at 13° - 11°N and 21°N, East Pacific Rise, *J. Geophys. Res.*, 93, 4522-4536, 1988.
- Butterfield, D. A., G. J. Massoth, R. E. Mc Duff, J. Lupton, and M. Lilley, Geochemistry of hydrothermal fluids from Axial Seamount Hydrothermal Emissions Study vent field, Juan de Fuca Ridge: Subseafloor boiling and subsequent fluid-rock interaction, *J. Geophys. Res.*, 95, 12895-12921, 1990.
- Butterfield, D. A., and G. Massoth, Geochemistry of North Cleft segment vent fluids: Temporal changes in chlorinity and their possible relation to recent volcanism, *J. Geophys. Res.*, 99, 4951-4968, 1994.
- Butterfield, D. A., R. E. Mc Duff, M. J. Mottl, M. D. Lilley, J. Lupton, and G. J. Massoth, Gradients in the composition of hydrothermal fluids from the Endeavour segment vent field: Phase separation and brine loss, *J. Geophys. Res.*, 99, 9561-9583, 1994.
- Campbell, A. C., T. S. Bowers, C. I. Measures, K. K. Falkner, M. Khadem, and J. M. Edmond, A time series of vent fluid compositions from 21°N, East Pacific Rise (1979, 1981, 1985) and the Guaymas basin, Gulf of California (1982, 1985), *J. Geophys. Res.*, 93, 4537-4549, 1988 a.
- Campbell, A. C., M. R. Palmer, G. P. Klinkhammer, T. S. Bowers, J. M. Edmond, J. L. Lawrence, J. F. Casey, G. Thompson, S. Humphris, P. Rona, and J. A. Karson, Chemistry of hot springs on the Mid-Atlantic Ridge, *Nature*, 335, 514-519, 1988b.
- Campbell, A. C., and L. M. Edmond, Halide systematics of submarine hydrothermal vents, *Nature*, 342, 168-170, 1989.
- Chan, L. H., and J. M. Edmond, Variation of lithium isotope composition in the marine environment: a Preliminary report, *Geochim. et Cosmochim. Acta*, 42, 1711-1717, 1988.
- Charlou, J. L., J. P. Donval, J. Erzinger, Y. Fouquet, and U. Von Stackelberg, Hydrothermal activity in the Lau Back-Arc Basin: plumes and hot fluid chemistry, *Terra Abstr.*, 3, 1, 406, 1991a.
- Charlou, J. L., H. Bougault, P. Appriou, T. Nelsen, and P. Rona, Different TDM/CH₄ hydrothermal plume signatures: TAG at 26°N and serpentinized ultrabasic diapir at 15°05'N on the Mid-Atlantic Ridge, *Geochim. Cosmochim. Acta*, 55, 3209-3222, 1991b.
- Charlou, J. L., J. P. Donval, P. Jean-Baptiste, R. Mills, P. Rona, and D. von Herzen, Methane, nitrogen, carbon dioxide and helium isotopes in vent fluids from TAG hydrothermal field, 26°N-MAR (abstract), *Eos Trans. AGU*, 74 (43) Fall Meet. Suppl., 99, 1993.
- Charlou, J. L., and J. P. Donval, Hydrothermal methane venting between 12°N and 26°N along the Mid-Atlantic Ridge, *J. Geophys. Res.*, 98, 9625-9642, 1993.
- Charlou, J. L., J. P. Donval, Y. Fouquet, and J. M. Auzende, Variability of hydrothermal fluids composition on ultra fast spreading segments between 17° and 19°S on the EPR (NAUDUR cruise), *Eos Trans. AGU*, 75, (44), Fall Meet. Suppl., 320, 1994.
- Christie, D. M., I. S. Carmichael, and C. H. Langmuir, Oxidation states at mid ocean basalt glasses, *Earth Planet. Sci. Lett.*, 79, 397-411, 1986.
- Colodner, D., J. Lin, K. L. Von Damm, L. Buttermore, R. Kozlowski, J. L. Charlou, J. P. Donval, C. Wilson, the Lucky Strike Team, Chemistry of Lucky Strike fluids: Initial results (abstract), *Eos Trans. AGU*, 74, (43), Fall Meet. Suppl., 99, 1993.
- Corliss, J. B., J. Dymond, L. I. Gordon, J. M. Edmond, R. P. von Herzen, R. D. Ballard, K. Green, D. Williams, A. Brainbridge, K. Crane, and T. H. van Andel, Submarine thermal springs on the Galapagos Rift, *Science*, 203, 1073-1083, 1979.
- Delaney, J. R., D. W. Mogk, and M. J. Mottl, Quartz cemented breccias from the mid-Atlantic Ridge: Samples of a high-salinity hydrothermal upflow zone, *J. Geophys. Res.*, 92, 9175-9192, 1987.
- Demets, C., R. G. Gordon, D. F. Argus, and S. Stein, Current plate motions, *Geophys. J. Int.*, 101, 425-478, 1990.
- Detrick, R. S., A. J. Harding, G. M. Kent, J. A. Orcutt, J. C. Mutter, and P. Buhl, Seismic structure of the southern East Pacific Rise, *Science*, 259, 499-503, 1993.
- Donval, J. P., J. L. Charlou, J. Knoery, Y. Fouquet, I. Costa, N. Lourenço, H. Ondreas, H. Pellé, M. Segonzac, and M. K. Tivey (DIVA 1 scientific team), Compared chemistry of hydrothermal fluids collected with the Nautila at Lucky-Strike (37°17'N) and the new Menez-Gwen (37°50'N) sites on the Mid-Atlantic Ridge (DIVA 1 cruise - May 1994), *Eos Trans. AGU*, 75, (44), Fall Meet. Suppl., 309, 1994.
- Drummond, S. E., Boiling and mixing of hydrothermal fluids: chemical effects on mineral precipitation, Ph. D. dissertation, 380 pp., Penn. State, University Park, 1981.
- Edmond, J. M., K. L. Von Damm, R. E. Mc Duff, and C. I. Measures, Chemistry of hot springs on the East Pacific Rise and their effluent dispersal, *Nature*, 297, 187-191, 1982.
- Edmonds, H. N., and J. M. Edmond, A three-component mixing model for ridge-crest hydrothermal fluids, *Earth Planet. Sci. Lett.*, 134, 53-67, 1995.
- Elderfield, H., C. German, M. Palmer, C. Chin, M. Greaves, E. Gurvich, R. James, G. Klinkhammer, E. Ludford, R. Mills, M. Rudnicki, J. Thomson, and A. Williams, Preliminary geochemical results from the Broken Spur hydrothermal field, 29°N, Mid-Atlantic Ridge (abstract), *Eos Trans. AGU*, 74, (43), Fall Meet. Suppl., 99, 1993.
- Evans, W. C., L. D. White, and J. B. Rapp, Geochemistry of some gases in hydrothermal fluids from the Southern Juan de Fuca Ridge, *J. Geophys. Res.*, 93, 15,305-15,313, 1988.
- Fouquet, Y., U. Von Stackelberg, J. L. Charlou, J. P. Donval, J. Erzinger, J. P. Foucher, P. Herzig, R. Muhe, S. Sokai, M. Wiedicke, and H. Whitechurch, Hydrothermal activity and metallogenesis in the Lau back-arc basin, *Nature*, 379, 778-781, 1991a.
- Fouquet, Y., Von Stackelberg, J. L. Charlou, J. P. Donval, J. P. Foucher, J. Erzinger, P. Herzig, R. Muhe, M. Wiedicke, S. Soakai, and H. Whitechurch, Hydrothermal activity in the Lau back-arc basin: Sulfides and water chemistry, *Geology*, 19, 303-306, 1991b.
- Fouquet, Y., J. L. Charlou, I. Costa, J. P. Donval, J. Radford-Knoery, H. Pellé, H. Ondreas, N. Lourenço, M. Segonzac, and M. K. Tivey, A detailed study of the Lucky-Strike hydrothermal site and discovery of a new hydrothermal site: "Menez-Gwen". Preliminary results of DIVA 1 cruise (5-29 May, 1994), *Inter-Ridge News*, 3, 2, 14-17, 1994a.
- Fouquet, Y., J. L. Charlou, J. P. Donval, J. Radford-Knoery, H. Pellé, H. Ondreas, M. Segonzac, I. Costa, N. Lourenço, and M. K. Tivey, Geological setting and comparison of the Menez-Gwen and Lucky-Strike vent fields at 37°17'N and 37°50'N on the Mid-Atlantic Ridge (MAR, DIVA 1 diving cruise), *Eos Trans. AGU*, 75, (44), Fall Meet. Suppl., 313, 1994b.
- Fouquet, Y., J. M. Auzende, V. Ballu, R. Batiza, D. Bideau, M. H. Cormier, P. Geisdoerfer, Y. Lagabrielle, J. Sinton, and P. Spadea, Variabilité des manifestations hydrothermales actuelles le long d'une dorsale ultra-rapide: Exemple de la Dorsale Est Pacifique entre 17° et 19°S (campagne NAUDUR), *C. R. Acad. Sci. Paris*, 319, Série II, 1399-1406, 1994c.
- Fournier, R. O., Conceptual models of brine evolution in magmatic-hydrothermal systems, *U. S. Geol. Surv. Prof. Pap.*, 1350, 487-506, 1987.
- Fox, C. G., Consequences of phase separation on the distribution of

- hydrothermal fluids at ASHES vent field, Axial Volcano, Juan de Fuca Ridge, *J. Geophys. Res.*, *95*, 12,923-12,926, 1990.
- Geisdoerfer, P., J. M. Auzende, R. Batiza, D. Bideau, M. H. Cormier, Y. Fouquet, Y. Lagabrielle, J. Sinton, and P. Spadea, Hydrothermalisme et communautés animales associées sur la Dorsale du Pacifique Oriental entre 17°S et 19°S (campagne NAUDUR, Décembre 1993), *C. R. Acad. Sci. Paris*, *320*, Série IIa, 47-54, 1995.
- Giardini, A. A., G. E. Subbrarayuda, and C. E. Melton, The emission of occluded gas from rocks as a function of stress: its possible use as a tool for predicting earthquakes, *Geophys. Res. Lett.*, *3*, 355-358, 1976.
- Goldfarb, M. S., and J. R. Delaney, Response of two-phase fluids to fracture configurations within submarine hydrothermal systems, *J. Geophys. Res.*, *93*, 4585-4594, 1988.
- Grimaud, D., J. I. Ishibashi, Y. Lagabrielle, J. M. Auzende, and T. Urabe, Chemistry of hydrothermal fluids from the 17°S active site on the North Fiji Basin Ridge (SW Pacific), *Chem. Geol.*, *93*, 209-218, 1991.
- Haymon, R. M., et al., Volcanic eruption of the mid-ocean ridge along the East Pacific Rise crest at 9°45'-52'N: Direct submersible observations of seafloor phenomena associated with an eruption event in April, 1991, *Earth Planet. Sci. Lett.*, *119*, 85-101, 1993.
- Ishibashi, J. I., D. Grimaud, Y. Nojiri, J. M. Auzende, and T. Urabe, Fluctuation of chemical compositions of the phase-separated hydrothermal fluid from the North Fiji Basin Ridge, *Mar. Geol.*, *116*, 215-226, 1994a.
- Ishibashi, J. I., H. Wakita, Y. Nojiri, D. Grimaud, P. Jean-Baptiste, T. Gamo, J. M. Auzende, and T. Urabe, Helium and carbon geochemistry of hydrothermal fluids from the North Fiji basin spreading ridge (southwest Pacific), *Earth Planet. Sci. Lett.*, *128*, 183-197, 1994b.
- Ishibashi, J. I., Y. Sano, H. Wakita, T. Gamo, M. Tsutsumi, and H. Sakai, Helium and carbon geochemistry of hydrothermal fluids from the Mid-Okinawa Trough Back Arc Basin, southwest of Japan, *Chem. Geol.*, *123*, 1-15, 1995.
- James, R. H., H. Elderfield, and M. R. Palmer, The chemistry of hydrothermal fluids from the Broken Spur site, 29°N Mid-Atlantic Ridge, *Geochim. Cosmochim. Acta*, *59*, 4, 651-659, 1995.
- Jean-Baptiste, P., J. L. Charlou, M. Stievenard, J. P. Donval, H. Bougault, and C. Mével, Helium and methane measurements in hydrothermal fluids from the mid-Atlantic ridge: The Snake Pit at 23°N, *Earth Planet. Sci. Lett.*, *106*, 17-28, 1991.
- Kelley, D. S., and J. R. Delaney, Two-phase separation and fracturing in mid-ocean ridge gabbros at temperatures greater than 700°C, *Earth Planet. Sci. Lett.*, *83*, 53-66, 1987.
- Kelley, D. S., Methane-rich fluids in the oceanic crust, *J. Geophys. Res.*, *101*, 2943-2962, 1996.
- Kim, K. R., J. A. Welhan, and H. Craig, The hydrothermal vent fields at 13°N and 11°N on the EPR: Alvin 1984 results (abstract), *Eos Trans. AGU*, *65*, 973, 1984.
- Lilley, M. D., J. A. Baross, and L. I. Gordon, Reduced gases and bacteria in hydrothermal fluids: The Galapagos spreading center and 21°N, East Pacific Rise, in *Hydrothermal Processes at Seafloor Spreading Centers*, edited by P. A. Rona, K. Bostrom, L. Laubier, and K. L. Smith, Jr., pp. 411-419, Plenum, New York, 1983.
- Lilley, M. D., J. A. Baross, D. A. Butterfield, E. J. Olson, R. E. Mc Duff, S. A. Macko, J. A. Welhan, and C. N. Dahn, Volatile in Endeavour vent fluids, *Eos Trans. AGU*, *70*, 1163, 1989.
- Lilley, M. D., E. J. Olson, and E. Mc Laughlin, Methane and Carbon dioxide in vent fluids from the 9°N hydrothermal system, *Eos Trans. AGU*, *72*, 481, 1991.
- Lilley, M. D., D. A. Butterfield, E. J. Olson, J. E. Lupton, S. A. Mackos, and R. E. Mc Duff, Anomalous CH₄ and NH₄⁺ concentrations at an unsedimented mid-ocean-ridge hydrothermal system, *Nature*, *364*, 45-47, 1993.
- Londsdale, P., Segmentation of the Pacific-Nazca spreading center, 1°N - 20°S, *J. Geophys. Res.*, *94*, 12,197-12,226, 1989.
- Lupton, J. E., M. Lilley, E. Olson, and K. von Damm, Gas chemistry of vent fluids from 9°-10°N on the East Pacific Rise, *Eos Trans. AGU*, *72*, 481, 1991.
- MacDonald, K. C., R. M. Haymon, S. P. Miller, and J. C. Sempere, Deep-Tow and Sea Beam studies of dueling propagating ridge on the East Pacific Rise near 20°40'S, *J. Geophys. Res.*, *93*, 2875-2898, 1988.
- Mahoney, J. L., J. M. Sinton, M. D. Kurtz, J. D. Macdougall, K. J. Spencer, and G. W. Lugmair, Isotope and trace element characteristics of a super-fast spreading ridge: East Pacific Rise, 13-23°S, *Earth Planet. Sci. Lett.*, *121*, 173-193, 1994.
- Masotho, G. J., D. A. Butterfield, J. E. Lupton, R. E. Mc Duff, M. D. Lilley, and J. R. Jonasson, Submarine venting of phase-separated hydrothermal fluids at axial Volcano, Juan de Fuca Ridge, *Nature*, *340*, 702-705, 1989.
- Melson, W. G., T. L. Vallier, T. L. Wright, G. Byerly and J. Nelsen, Chemical diversity of abyssal volcanic glasses erupted along Pacific, Atlantic and Indian Ocean seafloor spreading centers, in *The Geophysics of the Pacific Ocean Basin and its margin*, Geophys. Monogr. Ser., vol. 19, edited by G. H. Surton, pp. 351-367, Washington D. C., 1976.
- Merlivat, L., F. Pineau, and M. Javoy, Hydrothermal vent waters at 13°N on the East Pacific Rise: Isotopic composition and gas concentration, *Earth Planet. Sci. Lett.*, *84*, 100-108, 1987.
- Michard, G., F. Albarede, A. Michard, J. F. Minster, J. L. Charlou, and N. Tan, Chemistry of solutions from the 13°N East Pacific Rise hydrothermal site, *Earth Planet. Sci. Lett.*, *67*, 297-307, 1984.
- Miller, A. R., C. D. Densmore, E. T. Degens, F. C. Hataway, E. T. Manheim, P. F. McFarlen, H. Pocklington, and A. Jokela, Hot brines and recent deposits in deeps of the Red Sea, *Geochim. Cosmochim. Acta*, *30*, 341-359, 1966.
- Moore, J.G., J.N. Batchelder, and C.G. Cunningham, CO₂-filled vesicles in Mid-Ocean Basalt, *J. Volcanol. Geothermal Res.*, *2*, 309-327, 1977.
- Mottl, M. J., and H. D. Holland, Chemical exchange during hydrothermal alteration of basalt by seawater, I, Experimental results for major and minor components of seawater, *Geochim. Cosmochim. Acta*, *42*, 1103-1115, 1978.
- Naar, D. F., and R. N. Hey, Recent Pacific-Easter-Nazca plate motions, *Evolution of Mid-Ocean Ridges*, I. U. G. C. Geophysical Monograph Ser., vol. 57, edited by J. M. Sinton, 1989.
- Nehlig, P., Salinity of oceanic hydrothermal fluids: a fluid inclusion study, *Earth Planet. Sci. Lett.*, *102*, 310-325, 1991.
- Perram, L. J., M. H. Cormier, and K. MacDonald, Magnetic and tectonic studies of the dueling propagating spreading centers at 20°40'S on the East Pacific Rise: Evidence for crustal rotations, *J. Geophys. Res.*, *98*, 13,850-13,885, 1993.
- Pineau, F., M. Javoy, and Y. Bottinga, ¹³C/¹²C ratios of rocks and inclusions in popping rocks of the Mid-Atlantic Ridge and their bearing on the problem of isotopic composition of deep-seated carbon, *Earth Planet. Sci. Lett.*, *29*, 413-421, 1976.
- Renard, V., R. Hekinian, J. Francheteau, R. D. Ballard, and H. Backer, Submersible observations at the axis of the ultra-fast-spreading East Pacific Rise (17°30' to 21°30'S), *Earth Planet. Sci. Lett.*, *75*, 339-353, 1985.
- RISE Project group, East Pacific Rise. Hot springs and geophysical experiments, *Science*, *207*, 1421-1433, 1980.
- Rona, P. A., G. Klinkhammer, T. A. Nelsen, J. H. Trefry, and H. Elderfield, Black smokers, massive sulfides and vent biota at the Mid-Atlantic Ridge, *Nature*, *321*, 33-37, 1986.
- Sakai, H., T. Gamo, E-S. Kim, et al., Unique chemistry of the hydrothermal solution in the mid-Okinawa Trough back-arc basin, *Geophys. Res. Lett.*, *17*, 2133-2136, 1990a.
- Sakai, H., T. Gamo, E-S. Kim, et al., Venting of carbon dioxide-rich fluid and hydrate formation in the mid-Okinawa Trough back arc basin, *Science*, *248*, 1093-1096, 1990b.
- Sansone, F. J., J. A. Resing, G. W. Tribble, P. N. Sedwick, K. M. Kelly, and K. Hon, Lava-seawater interactions at shallow water submarine lava flows, *Geophys. Res. Lett.*, *18*, 1731-1734, 1991.
- Sato, M., Oxygen fugacities of basaltic magmas and the role of gas-forming elements, *Geophys. Res. Lett.*, *5*, 447-449, 1978.
- Scheirer, D. S., K. C. MacDonald, and D. W. Forsyth, Widespread volcanic and tectonic activity on the southern East Pacific Rise and its flanks, *Ridge Events*, *4*, 1-2, 8-10, 1993.
- Sedwick, P. N., G. M. McMurtry, and J. D. McDougall, Chemistry of hydrothermal solutions from Pelé's Vents, Loihi seamount, Hawaii, *Geochim. Cosmochim. Acta*, *56*, 3643-3667, 1992.
- Sedwick, P. N., G. M. McMurtry, D. R. Hilton, and F. Goff, Carbon dioxide and helium in hydrothermal fluids from Loihi Seamount, Hawaii, USA: Temporal variability and implications for the release of mantle volatiles, *Geochim. Cosmochim. Acta*, *58*, 1219-1227, 1994.
- Seyfried, W., and J. L. Bischoff, Low temperature basalt alteration by seawater: An experimental study at 70°C and 150°C, *Geochim. Cosmochim. Acta*, *43*, 1937-1947, 1979.
- Seyfried, W. E., D. R. Janecky, and M. J. Mottl, Alteration of the oceanic crust: Implications for the geochemical cycles of lithium and boron, *Geochim. Cosmochim. Acta*, *48*, 557-69, 1984.

- Seyfried, W. E., M. E. Berndt, and D. R. Janecky, Chloride depletions and enrichments in seafloor hydrothermal fluids: Constraints from experimental basalt alteration studies, *Geochim. Cosmochim. Acta*, *50*, 469-75, 1986.
- Seyfried, W. E., Experimental and theoretical constraints on hydrothermal alteration processes at mid-ocean ridges, *Ann. Rev. Earth. Sci.*, *15*, 317-35, 1987.
- Seyfried, W. E., Jr, K. Ding, and M. E. Berndt, Phase equilibria constraints on the chemistry of hot spring fluids at mid-ocean ridges, *Geochim. Cosmochim. Acta*, *55*, 3559-3580, 1991.
- Sinton, J. M., S. M. Smaglik, J. J. Mahoney, and K. C. Macdonald, Magmatic processes at superfast Mid-Ocean Ridge glass compositional variations along the East Pacific Rise 13° - 23°S, *J. Geophys. Res.*, *96*, 6133-6155, 1991.
- Sourirajan, S., and G. C. Kennedy, The system H₂O-NaCl at elevated temperatures and pressures, *Am. J. Sci.*, *260*, 115-41, 1962.
- Sugisaki, R., M. Ido, H. Takeda, Y. Isobe, Y. Hayashi, N. Nakamura, H. Satake, and Y. Misutani, Origin of hydrogen and carbon dioxide in fault gases and its relation to fault activity, *J. Geol.*, *91*, 239-258, 1983.
- Sugisaki, R., Relation between hydrogen emission and seismic activity, *Pure Appl. Geophys.*, *122*, 175-184, 1985.
- Urabe, T. et al., The effect of magmatic activity on hydrothermal venting along the super-fast spreading East Pacific Rise, *Science*, *269*, 1092-1095, 1995.
- Vanko, D. A., Temperature, Pressure and composition of hydrothermal fluids, with their bearing on the magnitude of tectonic uplift at Mid-Ocean Ridges, inferred from fluid inclusions in Oceanic Layer 3 rocks, *J. Geophys. Res.*, *93*, 4595-611, 1988.
- Von Damm, K. L., J. M. Edmond, B. Grant, C. I. Measures, B. Walden, and R. F. Weiss, Chemistry of submarine hydrothermal solutions at 21°N, East Pacific Rise, *Geochim. Cosmochim. Acta*, *49*, 2197-220, 1985.
- Von Damm, K. L., and J. L. Bischoff, Chemistry of hydrothermal solutions from the Southern Juan de Fuca Ridge, *J. Geophys. Res.*, *92*, 11,334-11346, 1987.
- Von Damm, K. L., Systematics of and postulated controls on submarine hydrothermal solution chemistry, *J. Geophys. Res.*, *93*, 4551-561, 1988.
- Von Damm, K. L., Seafloor hydrothermal activity: Black smoker chemistry and chimneys, *Ann. Rev. Earth. Sci.*, *18*, 173-04, 1990.
- Von Damm, K. L., S. E. Oosting, R. Kozlowski, L. G. Buttermore, D. C. Colodner, H. N. Edmonds, J. M. Edmond, and J. M. Grebmeler, Evolution of East Pacific Rise hydrothermal fluids following a volcanic eruption, *Nature*, *375*, 47-0, 1995.
- Wakita, H., Y. Nakamura, J. Kita, N. Fujii, and K. Notsu, Hydrogen releases: New indication of fault activity, *Science*, *210*, 188-190, 1980.
- Welhan, J. A., Carbon and hydrogen gases in hydrothermal systems: The search for a mantle source, PhD dissertation, Univ. of Calif., San Diego, 1981.
- Welhan, J. A., and H. Craig, Methane, hydrogen, and helium in hydrothermal fluids at 21°N on the East Pacific Rise, in *Hydrothermal Processes at Seafloor Spreading Centers*, edited by P. A. Rona et al., pp. 391-409, Plenum, New York, 1983.
- Welhan, J. A., K. R. Kim, and H. Craig, Hydrothermal gases at 11°N and 13°N on the East Pacific Rise, *Eos Trans AGU*, *65*, 973, 1984.
- Welhan, J. A., and J. E. Lupton, Light hydrocarbon gases in Guaymas Basin hydrothermal fluids: Thermogenic vs. abiogenic origin, *AAPG Bull.*, *71*, 215-223, 1987.
- Welhan, J. A., Origin of methane in hydrothermal systems, *Chem. Geol.*, *71*, 183-198, 1988.
-
- J. M. Auzende, ORSTOM, BPA5, Nouméa, Nouvelle Calédonie (email: auzende@noumea.orstom.nc)
- J. L. Charlou, J. P. Donval, and Y. Fouquet, IFREMER Centre de Brest, Département Géosciences Marines, B. P. 70, 29280 Plouzané cedex, France (email: charlou@ifremer.fr; jpdonval@ifremer.fr; fouquet@ifremer.fr)
- P. Jean-Baptiste and M. Stievenard, CEA Saclay, DSM/LMCE, Gif-sur-Yvette, France (email: pjb@asterix.saclay.cea.fr; misti@asterix.saclay.cea.fr)
- S. Michel, Université de Bretagne Occidentale, Avenue Le Gorgeu, Brest, France

(Received March 22, 1995; revised March 4, 1996; accepted March 13, 1996.)