



Direct observation of the evolution of a seafloor ‘black smoker’ from vapor to brine

K.L. Von Damm^{a,*}, L.G. Buttermore^a, S.E. Oosting^{a,1}, A.M. Bray^a, D.J. Fornari^b,
M.D. Lilley^c, W.C. Shanks, III^d

^a Department of Earth Sciences University of New Hampshire, James Hall, Durham, NH 03824-3589, USA

^b Marine Geology and Geophysics Department, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA

^c School of Oceanography, University of Washington, Seattle, WA 8195, USA

^d U.S. Geological Survey, Branch of Geochemistry, MS 973, Denver, CO 80225, USA

Received 25 October 1996; revised 21 February 1997; accepted 24 February 1997

Abstract

A single hydrothermal vent, ‘F’ vent, occurring on very young crust at 9°16.8’N, East Pacific Rise, was sampled in 1991 and 1994. In 1991, at the measured temperature of 388°C and seafloor pressure of 258 bar, the fluids from this vent were on the two-phase curve for seawater. These fluids were very low in chlorinity and other dissolved species, and high in gases compared to seawater and most sampled seafloor hydrothermal vent fluids. In 1994, when this vent was next sampled, it had cooled to 351°C and was venting fluids ~ 1.5 times seawater chlorinity. This is the first reported example of a single seafloor hydrothermal vent evolving from vapor to brine. The 1991 and 1994 fluids sampled from this vent are compositionally conjugate pairs to one another. These results support the hypothesis that vapor-phase fluids vent in the early period following a volcanic eruption, and that the liquid-phase brines are stored within the oceanic crust, and vent at a later time, in this case 3 years. These results demonstrate that the venting of brines can occur in the same location, in fact from the same sulfide edifice, where the vapor-phase fluids vented previously.

Keywords: black smokers; hydrothermal processes; mid-ocean ridges; East Pacific Rise

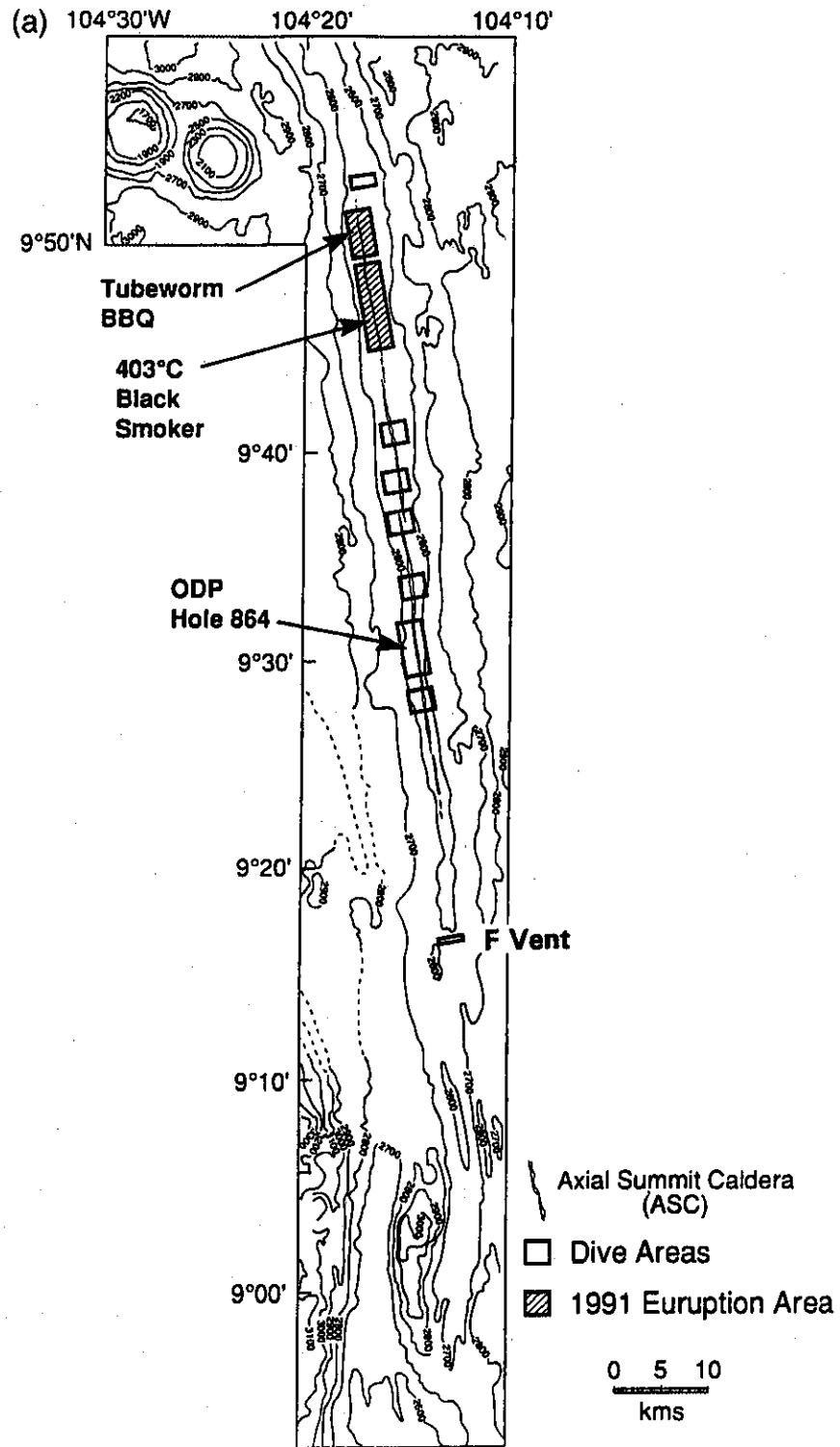
1. Introduction

Phase separation is now accepted as the primary mechanism causing large ($> \pm 10\%$) variations in the chloride content of seafloor hydrothermal fluids compared to ambient seawater. Fluids with chlorini-

ties approaching twice the seawater value were first sampled from vents on the southern end of Cleft Segment, Juan de Fuca Ridge (JdFR) in 1984 [1] and even higher chlorinity fluids have been more recently reported from the northern end of Cleft Segment [2]. Of the ~ 77 vents sampled worldwide, ~ 28 (or 36%) have chlorinities exceeding the seawater value by $> 10\%$ [3]. While fluids with chlorinities less than the seawater value have been reported since the initial discoveries [4,5], the most extreme depletions in chlorinity yet measured are associated with volcanic eruptions in 1991 between

* Corresponding author. Also at: Institute for the Study of Earth, Oceans and Space. Tel: +1 603 862 0142. Fax: 603 862 2649; E-mail: kvd@christa.unh.edu

¹ Present address: GEI Consultants, Inc., 1021 Main Street, Winchester, MA 01890, USA.



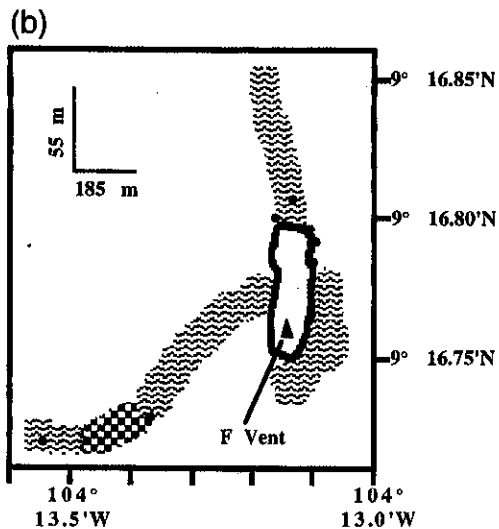


Fig. 1 (continued). (b) Detailed geologic map of the setting of F vent. F vent (▲) is located within a 3 m deep collapse pit (heavy solid line) lined by lobate and curtain-folded lavas. Change in lava types observed during dives 2365 and 2739 are shown with lobate lavas (wavy pattern), hackled flows (checked pattern) as well as the locations where basalt samples were collected (●). The depth increases from 2582 m in the collapse to 2609 m at the western end of the traverse.

9° and 10° north latitude on the East Pacific Rise (EPR) [6]. With the exception of Axial Volcano [7], in no case have vapors and brines been found venting at the same time within a single vent area, thus creating a mass balance problem. Based on their results from South Cleft, JdFR, Von Damm and Bischoff [1] and Von Damm [8] initially proposed a model of phase separation with brine storage occurring within the oceanic crust, followed by later venting of this phase. Butterfield and Massoth [2] have subsequently invoked a similar model for North Cleft, where a general increase from low to higher chlorinity fluids with time has been observed.

The distribution of hydrothermal activity between 9° and 10°N EPR, was determined with *ARGO-I* in late 1989 [9]. When the site was first visited with *Alvin* in 1991, it became obvious that a volcanic eruption had occurred on the ridge north of 9°45'N after the *ARGO* program, and just prior to the dives [10–14]. To date, most discussion of the new erup-

Table 1

Analytical methods and precisions

Element/Species	Method	Precision
Cl ^a	Potentiometric titration	±0.5%
Li	FAAS ^b /Ion chromatography	±1%
Na	FAAS	±2%
K	FAAS	±1%
Mg	FAAS	±1%
Ca	FAAS	±1%
Sr	FAAS	±2%
Fe	FAAS	±1%
Mn	FAAS	±1%
pH (25°C, 1 atm)	Potentiometry	±0.01
Alkalinity _{total}	Potentiometric titration/Gran plot	±0.5%
H ₂ S	Colorimetry/Starch titration	±5%
SO ₄	Ion chromatography	±1%
Br	Ion chromatography	±3%
Si	Colorimetry	±1%
CO ₂	Gas chromatography	±5%
H ₂	Gas chromatography	±5%
δD	Mass spectrometry	±0.5‰
δ ¹⁸ O	Mass spectrometry	±0.05‰

^a Major elements were standardized to IAPSO seawater; NIST traceable standards were used for all analyses except H₂S and silica, for which absolute standardization is based on Dilut-it[®] standard solutions. Isotopic values are relative to VSMOW.

^b FAAS = Flame atomic absorption spectrophotometry.

tive vent chemistry at 9–10°N EPR has focused on the vents north of 9°45'N [6]. However, there is also very young crust at ~9°14–20'N, and the single vent found in this area, 'F' (at 9°16.8'N), when sampled in 1991, had a temperature and composition similar to the vapor-phase low chlorinity vent fluids north of 9°45'N. By 1994, when this vent was next sampled, it was venting a high chlorinity brine. Here we report the first example of a single hydrothermal vent whose fluid compositions have evolved from vapor to brine, within a relatively brief 3 year period. Even more remarkable is that the particular vapor and brine compositions sampled appear to be the conjugate pair to one another.

2. Geologic setting

Haymon et al. [9] have identified 10 fourth-order ridge segments on the EPR between 9°03'N and

Fig. 1. (a) Location of F vent in relationship to the axial summit caldera, new eruption area, and other vents between 9° and 10°N EPR. After Haymon et al. [10].

Table 2
The chemical composition of 'F' vent hydrothermal fluids

Element	Units ^a	F 1991 ^b	F 1994 ^b	Seawater	21°N OBS 1981 ^c
T	°C	388	351	2	350
Depth (P)	m (bars)	258	258	251	260
Cl	mmol	46.5	846	540	489
Br	mmol	0.0748	1.35	0.84	17.6
Si	mmol	5.93	20.0	0.155	891
Li	μmol	18	1620	26	432
Na (calc)	mmol	38.4	683	464	23.2
K	mmol	1.16	41.5	10.1	0
Mg	mmol	0	0	52.7	15.6
Ca	mmol	1.83	45.6	9.95	81
Sr	μmol	2.32	167	87	1.66
Fe	mmol	1.49	12.1	0	0.960
Mn	mmol	0.174	3.28	0	3.4
pH	(25°C, 1 atm)	2.8	2.6	7.8	−0.40
Alkalinity	meq	−1.4	−1.8	−2.4	5.7 ^d
CO ₂	mmol	15.5	11.4	2.3	1.7 ^e
H ₂	mmol	1.8	0.30	0.3 × 10 ^{−6}	7.3
H ₂ S	mmol	41	8.71	0	0.5
SO ₄	mmol	−1.07	0.86	28.2	
δD	‰	1.4	−0.1	0	1.6 ^e
δ ¹⁸ O	‰	1.46	1.54	0	0.88
Na/Cl		0.826	0.807	0.859	1.82
Li/Cl	μ/m	0.387	1.91	0.0481	0.047
K/Cl		0.0249	0.0491	0.0187	38.4
Li/K	μ/m	15.5	39.0	2.57	0.0319
Ca/Cl		0.0394	0.0539	0.0184	0.166
Sr/Cl	μ/m	0.0499	0.197	0.161	5.19
Sr/Ca	μ/m	1.27	3.66	8.74	0.0034
Fe/Cl		0.0320	0.0143	0.0000	0.0020
Mn/Cl		0.0037	0.0039	0.0000	1.73
Fe/Mn		8.56	3.69	−	0.23
Fe/H ₂ S		0.0363	1.39	−	0.0149
H ₂ S/Cl		0.882	0.0103	0.0000	

^a Units are all per kilogram. mmol = millimol/kg; μmol = micromol/kg; meq = milliequivalents/kg.

^b A total of 10 water samples were collected from F vent in 1991, and 11 in 1994. Minimum Mg = 5.54 in 1991 and 4.33 mmol/kg in 1994.

^c Data from [5]. This vent fluid has been shown to be in water–rock equilibrium [23] and has often been used as a comparator for other vent fluids.

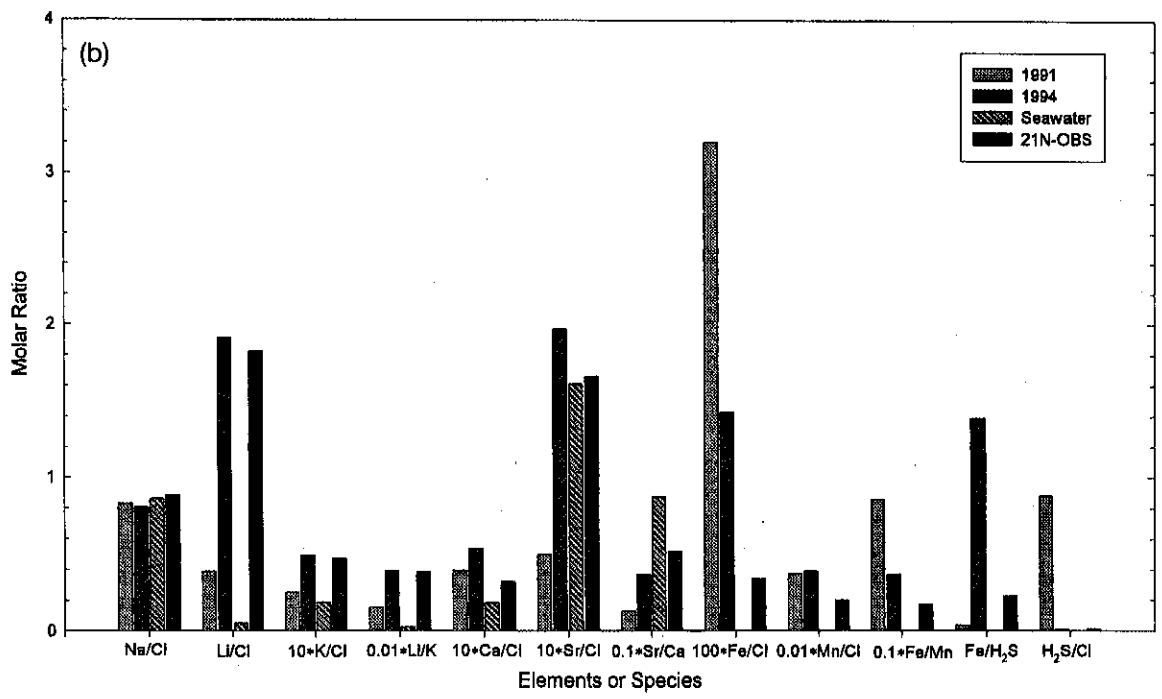
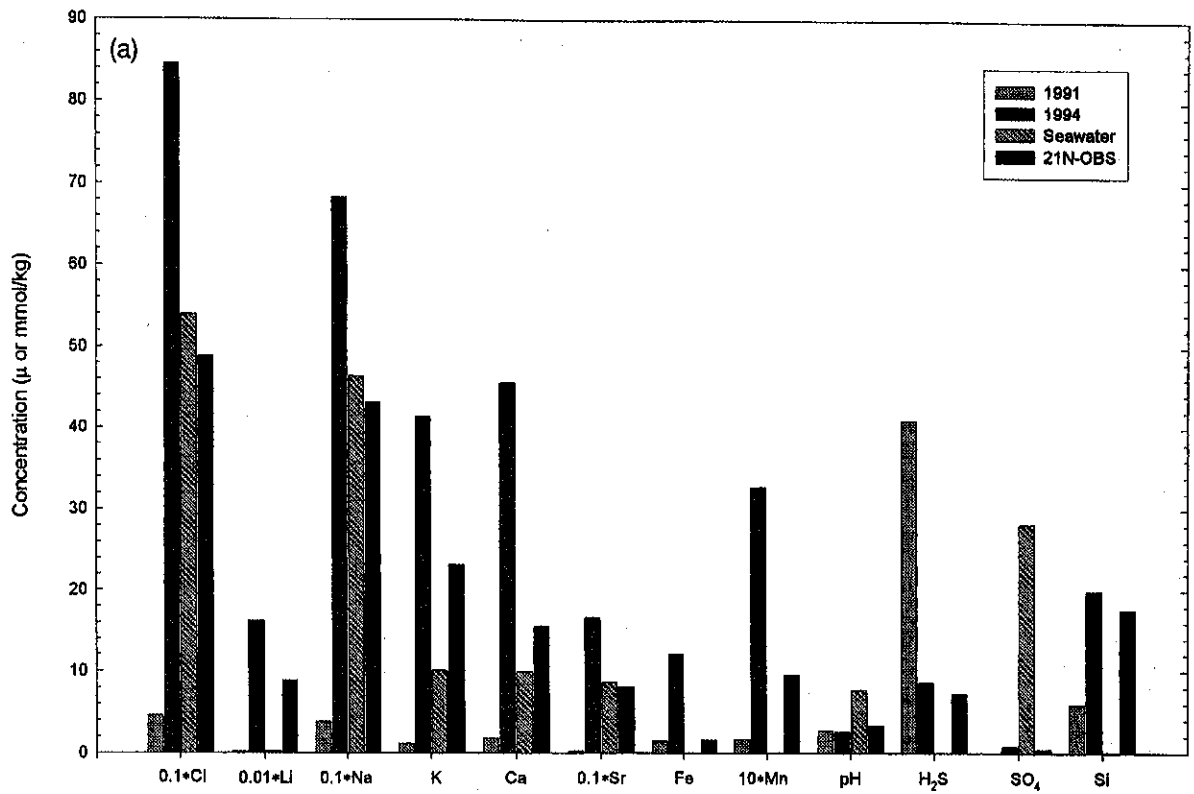
^d Craig and Welhan [29], 1979 average value for all 21°N vents.

^e Welhan et al. [15], 1979 value for OBS (H₂) and 1979 average value for all 21°N vents (δ¹⁸O).

9°54'N, and F vent occurs on segment G, at 9°16.8'N, 104°13.1'W at a depth of 2582 m (Fig. 1). This segment is not characterized by an axial summit

caldera (ASC) but, instead, by a series of elongate collapse pits and F vent is located within one of these collapses. During the November–December

Fig. 2. Comparison of F vent compositions in 1991 and 1994, with seawater and OBS vent from 21°N EPR as measured in 1981. Variable multipliers have been applied to the data from Table 2 so they can be plotted on a single scale. These multipliers are noted in the x axis labels. (a) Concentration of individual elements or species. (b) Molar ratios of particular elements or species.



mol/kg in
other vent

elongate
one of
ecember

Variable
the x axis

1989 *ARGO-I* cruise, black smoke, but no sulfide-sulfate constructional feature, was observed on very glassy young basalts at this location [10]. On April 16, 1991 (*Alvin* dive 2365) F vent was a 3–5 m tall sulfide chimney, some diffuse fluids were exiting from nearby basalt, and a syntactic foam marker was deployed. On March 15, 1994 (*Alvin* dive 2739) the sulfide edifice was of a similar height, the diffuse fluid flow had ceased, and the syntactic foam marker was still in place. No other hydrothermal vent was found in this area in either 1991 or 1994.

3. Sampling and analytical methods

Fluid samples were collected from DSV *Alvin* using the 755 ml 'majors' water samplers [5] and the 160 ml 'gas tight' samplers (M.D. Lilley and J.E. Lupton, pers. commun.). On both cruises the NOAA Manifold sampler [16], with discrete 'majors' and 'gas tight' samplers attached, was also used to sample fluids. Temperature measurements were made with both the *Alvin* high temperature probe and the manifold sampler temperature probe. During both cruises the probes were independently calibrated and were found to agree within the precision of the measurement (a few degrees Celsius). Analytical methods and precisions are summarized in Table 1.

4. Results

In April 1991 the measured temperature of 388°C at the seafloor pressure of 258 bar puts this fluid on the two-phase curve for seawater. The fluid should therefore have been boiling subcritically and the low Cl and high H₂S concentrations (Table 2) suggest the vapor phase was indeed sampled. At this time Cl and H₂S were almost equimolar. The low alkali and alkaline earth cation concentrations were reflective of the low Cl content of the fluid. In contrast, in spite of the low Cl and high H₂S relative to seawater, the level of Fe exceeded 1 mmol/kg. The concentration of iron therefore exceeded the concentration of K, and was only 0.27 mmol/kg less than the concentration of Ca. Manganese, although not as enriched as Fe, was significantly higher in concentration than Li or Sr. Carbon dioxide and H₂ were also

quite high with respect to seawater. The low pH in 1991 is consistent with what we have observed north of 9°45'N for similar fluids [17]. Silica was also enriched with respect to seawater, but was approximately a factor of three lower than is typically observed in seafloor hydrothermal fluids. The negative sulfate calculated for the end-member hydrothermal fluid may indicate that mixing had occurred, either during the sampling process or within the hydrothermal system itself, resulting in deposition of sulfate-containing minerals.

By March 1994 the measured temperature of F vent had decreased to 351°C, placing the fluids within the single phase region. The chlorinity had increased by a factor of 18 to a value > 50% higher than the local seawater value (Fig. 2). While the H₂S had dropped markedly, at 8.71 mmol/kg the level was still high compared to most sampled 'black smoker' fluids (e.g., [3]). Although the Fe level had increased by a factor of eight, in conjunction with the increase in chlorinity, Na, K, and Ca had also increased and were now present in much higher concentrations than was Fe. Li and Sr now exceeded the concentrations in local seawater, and Mn had reached millimolar levels. While CO₂ and H₂ had dropped significantly by 1994, they were still quite elevated, especially CO₂. The continued low pH in 1994 may be indicative of precipitation of some sulfide minerals, and, in fact, preliminary calculations show that pyrite is supersaturated in these fluids. The sulfate end-member was now positive and the silica a more typical 20.0 mmol/kg.

Within a 3 year period extreme chemical changes have therefore occurred in the fluids exiting from a single hydrothermal vent.

5. Discussion

5.1. Changes in chlorinity

At the 1991 measured seafloor conditions of pressure and temperature, the F vent fluids were on the two-phase curve of seawater, below the critical point of 407°C and 298 bar. In compiling data on the PVTx properties of seawater (NaCl–H₂O), based on experimental studies and literature data, Bischoff [18] reported that when seawater phase separates at

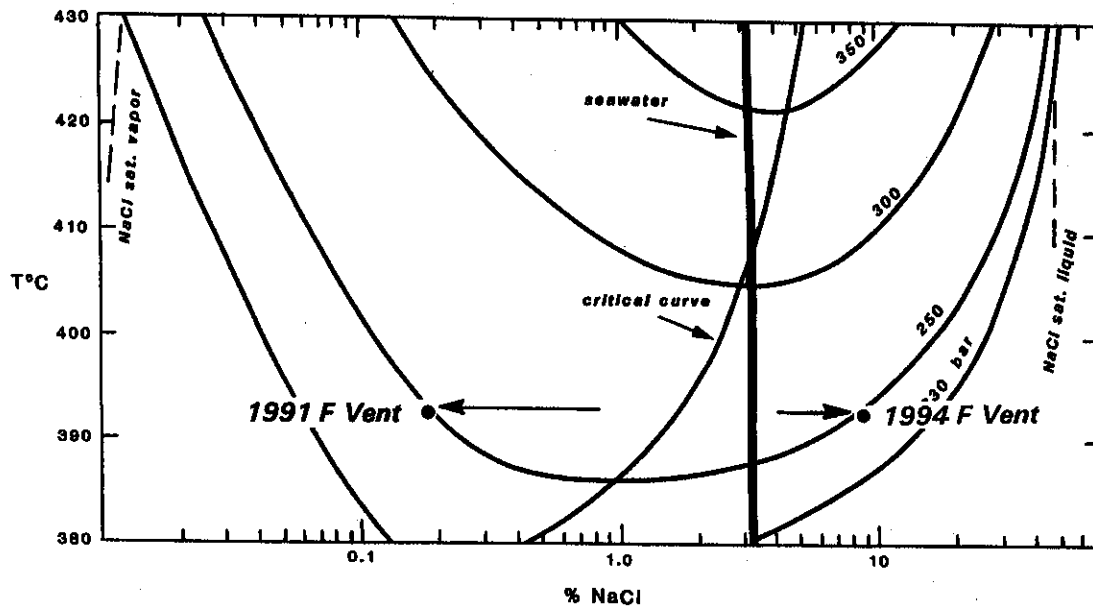


Fig. 3. Weight percent NaCl as a function of temperature for co-existing vapor and brine phases formed by phase separating fluids of starting seawater chlorinity. The composition of F vent fluids in 1991 (vapor) and 1994 (brine) is noted on the 250 bar isobar, the approximate seafloor pressure for this vent. Figure modified from [28].

390°C and 250 bar, a vapor containing 0.240 wt% NaCl (40.5 mmol/kg Cl) and a brine containing 5.00 wt% NaCl (844 mmol/kg Cl) should be produced, in the ratio of 38% vapor and 62% brine (Fig. 3). These compositions are virtually identical to the 1991 and 1994 fluids, respectively, suggesting that they are the conjugate pairs to one another. Although it could be mere chance that the two fluids appear to be (chemical) conjugate pairs to one another, a more likely explanation is that the brine, formed while the vapor was being expelled, was stored within the oceanic crust at this site until it was later vented. Although more complex models could also be invoked to derive the compositions of these two fluids, there is no data to constrain such models of fluid evolution. In fact, data from two other locales support this simple model. At 9°33.5'N on the East Pacific Rise, two vents ('D' and 'E') had been venting brines of similar chlorinities from 1991 through 1994, although some of the other chemical characteristics differ, most likely due to the lower temperatures of D and E relative to F [17]. Charlou et al. [19] report chemical data from vents on the EPR at 17°S that also have similar chlorinities. Al-

though the timing of the last eruption at these other sites has not been documented, and the vapor phase fluids have not been sampled, all of these vents are at similar depths and hence may have undergone phase separation at similar pressure (and temperature) conditions to 9°16.8'N, as all three now appear to be venting the conjugate brine that may have formed under these conditions.

The vents north of 9°45'N EPR that were affected by eruptions in 1991 (and also in 1992 for some vents) [11], have generally been increasing in chlorinity since that time [6,20]. As of early 1996, none of these vents had chlorinities as high as what we have observed at F vent, and each appears to be increasing in Cl at a different rate.

5.2. Changes in elemental ratios

While it seems clear that subcritical phase separation was the primary process forming the F vent fluids, water-rock interaction and equilibrium are likely to affect and control the relative concentrations of the cations, and other species besides Cl. As the 1981 fluid compositions from OBS vent at 21°N

EPR [5] have been used as a comparison in numerous experimental (e.g., [21,22]) and geochemical modeling [23] studies, we have also used it as a comparison to our results from F vent. The results from these studies suggest that the OBS fluids are probably at water–rock equilibrium, as is also suggested by the compositional stability of the fluids from this vent over ~ 10 years [24].

5.2.1. Ratios to Cl

As Cl is the major anion, and at elevated pressure and temperature most of the cations will be transported as chloro-complexes, examination of changes in ratios to Cl (1) with time, (2) in comparison to seawater, and (3) in comparison to other hydrothermal fluids, can provide information on the extent of water–rock interaction (Fig. 2b). The Na/Cl (molar) ratio in seawater is 0.86, and ratios significantly less than this in hydrothermal fluids most likely reflect albitization, where Na is taken up by the rock and Ca is released to solution. Unfortunately, we do not know if the Na/Cl seawater ratio is exactly maintained during subcritical phase separation. In F vent fluids the Na/Cl ratio is below the seawater value in both years, although the lower ratio in 1994 may suggest albitization is occurring. The Ca/Cl ratio in both years is greater than the seawater value, suggesting water–rock interaction is occurring, and its increase with time is consistent with albitization. The Ca/Cl ratio in seafloor hydrothermal fluids is more variable than for some other species, and the values in both years are within the range of values observed elsewhere, although not as high as, for example, in South Cleft JdFR samples which have the clearest signature of ongoing albitization [1]. The K/Cl ratio in most hydrothermal fluids is quite uniform at ~ 0.04 (e.g., [3]), significantly higher than the seawater value of 0.0184, reflecting addition of K from the rock. Although this ratio in the 1991 F vent fluids is higher than that in seawater, it is significantly lower than what was measured in 1994, which is a typical hydrothermal fluid value. This is consistent with some water–rock reaction occurring in 1991, and suggests that perhaps water–rock equilibrium (or steady state) was achieved by 1994. The Li/Cl ratio in 1991 is also greater than the seawater value, but is significantly below the 1994 value, which is again more typical of seafloor hydrothermal

fluids. The Sr/Cl ratio in seafloor hydrothermal fluids is quite variable, often less than the ratio in seawater, but the 1991 value in F vent fluids is unusually low. The 1994 Sr/Cl ratio is within the range of more typically observed values. The Mn/Cl ratio is relatively constant between the two samplings but the Fe/Cl ratio shows a pronounced drop, as does the H₂S/Cl ratio.

The Br/Cl in the F vent fluids is the same as the seawater ratio in both years. This is in contrast to the below-seawater ratios noted in vents with chlorinities < 250 mmol/kg north of 9°45'N EPR by Oosting and Von Damm [20]. These authors suggested this was a result of subcritical phase separation in an open system but experimental data for the appropriate conditions were lacking for Br, and hence for the Br/Cl ratio. In recent experiments Berndt and Seyfried [25] have shown that Br and Cl will not fractionate under these conditions and have suggested instead that the low Br/Cl ratios are due to halite dissolution. As the Br/Cl ratios in F vent fluids are equal to the seawater value, this suggests that halite dissolution (or precipitation) was not an active process in this vent in either 1991 or 1994.

5.2.2. Other elemental ratios

The Fe/Mn ratio observed in seafloor hydrothermal vent fluids is typically 5:1 to 1:1, clustering around the 3:1 ratio found in metalliferous sediments. The 1991 ratio of 8.6:1 was therefore unusually high, confirming the preferential mobilization of Fe during the early phase of hydrothermal activity. Seyfried and Ding [21] have shown that more Fe will be mobilized when in situ conditions are more reducing, more acid, and higher in temperature (i.e., buffered by pyrite–pyrrhotite–magnetite rather than hematite–magnetite–pyrite). This describes the 1991 fluids compared to 1994, and the high Fe concentrations relative to Cl and Mn that we have observed early in the eruptive cycle are consistent with the high measured H₂S and temperature, and low pH. The Fe/H₂S ratio also showed a large increase from 1991 to 1994, due to both the increase in Fe and the decrease in H₂S. In 1991 the concentration of H₂S greatly exceeds that of Fe, but by 1994 this had reversed. Previous workers have suggested when H₂S > Fe, excess H₂S will be available making the locale favorable to organisms; but when Fe > H₂S

organisms will not survive because little or no H_2S will be available to them after Fe–S compounds have precipitated. Around F vent in 1991 a community of animals was beginning to establish itself but by 1994 only the dead animal tubes remained covered by an orange, Fe-rich floc. This further supports the critical nature of the molar relationship between Fe and H_2S to vent biology.

Other elemental ratios of interest are for elements with similar geochemical behaviors, such as the alkalis (e.g., Li/K) or the alkaline earths (e.g., Sr/Ca). Examining these elemental (concentration) ratios eliminates some of the uncertainties inherent in dealing with concentrations rather than activities, because the activity coefficients for these elements should be similar and in effect cancel out in the ratio. The Li/K ratio was significantly greater than seawater in both 1991 and 1994. The 1991 value was at the low end of what has been observed at other sites, although low chlorinity vents do tend to have lower Li/K ratios. The 1994 value is more typical of what is observed in hydrothermal fluids with chlorinities equal to or greater than the seawater value. The Sr/Ca ratio was lower than that in seawater in both years. The extremely low ratio in 1991 was much lower than what has been observed elsewhere, and likely reflects the low Sr with respect to Cl noted above. Berndt et al. [22] note that reaction with basalt will produce a lower Sr/Ca ratio (1.67) than will reaction with diabase (4.58), and the increase in the ratio between 1991 and 1994, to a value more typical of other sites, may suggest a deepening of the reaction zone.

The various elemental ratios therefore indicate that water–rock interaction, not just phase separation, was an important process in determining the fluid compositions in 1991, but also suggest the system had not yet having achieved the steady-state or equilibrium compositions typical of other hot springs. By 1994 the elemental ratios are more similar to those measured elsewhere, and it is more likely that the F vent fluids are now in equilibrium with the rock.

5.3. Gases and isotope systematics

The gases CO_2 , H_2S and H_2 were much higher in 1991 than in 1994, as would be expected in a vapor

versus a brine phase. The concentrations reflect water–rock interaction processes as well as phase separation and the 1994 values for CO_2 , in particular, are too high to be explained simply by phase separation.

Many of the vapor phase fluids north of $9^{\circ}45'N$ EPR have negative δD values, which Shanks et al. [26] suggest may reflect a small input of magmatic water. To produce this isotopic signature at appropriate pressure and temperature conditions during phase separation experiments [27] requires open system conditions, and is also dependent on whether the phase separation occurs by isobaric heating or by adiabatic decompression. F vent vapors, however, have positive δD values and the brines have values that are essentially zero, and could therefore be produced by either mechanism of phase separation. The δD and $\delta^{18}O$ values observed in the F vent fluids are consistent with fluids that have equilibrated with gabbro under greenschist facies conditions [26].

5.4. Silica content

Von Damm et al. [6] have suggested, based on the silica content of the fluids, that the depth of reaction has deepened with time at the 'A' vent, which is in the area of the 1991 eruption north of $9^{\circ}45'N$. The Si data from F vent are also suggestive of a shallow, perhaps dike-driven reaction zone at ≤ 200 m below the seafloor in 1991, deepening to a depth more indicative of the magma chamber by 1994.

5.5. Comparison with experimental results

Bischoff and Rosenbauer [28] conducted a water–rock interaction experiment in which they phase separated natural seawater fluid at $392^{\circ}C$ and 251 bar, conditions very similar to those observed at F vent. The duration of their experiment was 20 days. Difficulties with sampling both the pure vapor and pure brine phase from the experimental apparatus in these experiments preclude a rigorous element-by-element comparison of our data to these experiments. The experimental difficulties are most obvious in the anomalously high Cl concentration reported by these authors for their brine phase (1555 mmol/kg as opposed to the 844 predicted by the equation of state for seawater). We have therefore

not included this data in Table 2 for comparison with the sampled vent chemistry. The general enrichments and depletion trends of elements in the experimental data set agree with our field results, and the concentration of silica in the experimental vapor phase agrees within the error of the measurements with our vapor-phase fluid data.

6. Conclusions

Between 1991 and 1994 a single vent, F, located at 9°16.8'N on the East Pacific Rise evolved in composition from a vapor to a brine. This evolution has not been previously observed in the fluids from a single seafloor hydrothermal vent. In addition, the vapor and the brine are, compositionally, the conjugate pairs to one another, which provides direct evidence that the brine was stored within the oceanic crust at this site. The other chemical data from this vent suggest that water–rock interaction was an ongoing process, continuing after the phase separation, and that the fluids have more likely equilibrated (or reached steady state) with the rock in 1994. In 1991, although the effect of water–rock reaction on the composition is noted in every elemental ratio, the extent of water–rock interaction was more limited than in 1994, perhaps as a result of kinetics and a shorter residence time of the fluids within the hydrothermal system. A model inferring storage of brine requires that these brines have had a significantly longer residence time within the oceanic crust, in this case 3 years, which, based on experimental results, should be sufficient time in which to achieve chemical equilibrium or steady state.

Acknowledgements

We thank the *Alvin* Group, and the captain, officers and crew of the *Atlantis II* for their skillful operations at sea, and the cooperation and collaboration of the AdVenture I and AdVenture 4 scientific parties. We thank R.M. Haymon for providing her original for Fig. 1a, and J.L. Bischoff for providing his original for Fig. 3. M. Berndt, T. Plank and C. German provided constructive reviews that helped to improve the manuscript. This research was supported

by the National Science Foundation through grants OCE-9101440 (KVD), OCE-9300508 (KVD), OCE-9100503 (DJF), OCE-9100804 (MDL), and OCE-9307295 (MDL). [CL]

References

- [1] K.L. Von Damm, J.L. Bischoff, Chemistry of hydrothermal solutions from the Southern Juan de Fuca Ridge, *J. Geophys. Res.* 92 (1987) 11334–11346.
- [2] D.A. Butterfield, G.J. Massoth, Geochemistry of North Cleft segment vent fluids: temporal changes in chlorinity and their possible relation to recent volcanism, *J. Geophys. Res.* 99 (1994) 4951–4968.
- [3] K.L. Von Damm, Controls on the chemistry and temporal variability of seafloor hydrothermal fluids, in: J. Lupton, L. Mullineaux, R. Zierenberg (Eds.), *Physical, Chemical, Biological and Geological Interactions Within Hydrothermal Systems*, AGU Monogr. 91 (1995) 222–247.
- [4] J.M. Edmond, C. Measures, R. McDuff, L.H. Chan, R. Collier, B. Grant, L.I. Gordon, J.B. Corliss, Ridge crest hydrothermal activity and the balances of the major and minor elements in the ocean: the Galapagos data, *Earth Planet. Sci. Lett.* 46 (1979) 1–18.
- [5] K.L. Von Damm, J.M. Edmond, B. Grant, C.I. Measures, B. Walden, R.F. Weiss, Chemistry of submarine hydrothermal solutions at 21°N, East Pacific Rise, *Geochim. Cosmochim. Acta* 49 (1985) 2197–2220.
- [6] K.L. Von Damm, S.E. Oosting, R. Kozlowski, L.G. Buttermore, D.C. Colodner, H.N. Edmonds, J.M. Edmond, J.M. Grebmeier, Evolution of East Pacific Rise hydrothermal fluids following a volcanic eruption, *Nature* 375 (1995) 47–50.
- [7] D.A. Butterfield, G.J. Massoth, R.E. McDuff, J.E. Lupton, M.D. 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 (1990) 12895–12921.
- [8] K.L. Von Damm, Systematics and postulated controls on submarine hydrothermal solution chemistry, *J. Geophys. Res.* 93 (1988) 4551–4661.
- [9] R.M. Haymon, D.J. Fornari, M.H. Edwards, S. Carbotte, D. Wright, K.C. McDonald, Hydrothermal vent distribution along the East Pacific Rise crest (9°09'–54'N) and its relationship to magmatic and tectonic processes on fast-spreading mid-ocean ridges, *Earth Planet. Sci. Lett.* 104 (1991) 513–534.
- [10] R.M. Haymon, D.J. Fornari, K.L. Von Damm, M.D. Lilley, M.R. Perfit, J.M. Edmond, W.C. Shanks III, R.A. Lutz, J.M. Grebmeier, S. Carbotte, D. Wright, E. McLaughlin, M. Smith, N. Beedle, E. Olson, 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 (1993) 85–101.

- [11] K.H. Rubin, J.D. MacDougall, M.R. Perfit, $^{210}\text{Po}/^{210}\text{Pb}$ dating of recent volcanic eruptions on the sea floor, *Nature* 468 (1994) 841–844.
- [12] K.L. Von Damm, J.M. Grebmeier, J.M. Edmond, Preliminary chemistry of hydrothermal vent fluids from 9–10°N East Pacific Rise, *EOS Trans. AGU 72 Fall Meet. Suppl.* (1991) 480.
- [13] W.C. Shanks III, J.K. Böhlke, R.R. Seal, Stable isotope studies of vent fluids, 9–10°N East Pacific Rise: water–rock interaction and phase separation, *EOS Trans. AGU 72, Fall Meet. Suppl.* (1991) 481.
- [14] M.D. Lilley, E.J. Olson, E. McLaughlin, K.L. Von Damm, Methane, hydrogen and carbon dioxide in vent fluids from the 9°N hydrothermal system, *EOS Trans. AGU 72, Fall Meet. Suppl.* (1991) 481.
- [15] J.A. Welhan, H. Craig, Methane, hydrogen and helium in hydrothermal fluids at 21°N on the East Pacific Rise, in: P.A. Rona et al. (Eds.), *Hydrothermal Processes at Seafloor Spreading Centers*, Plenum Press, NY, 1983, pp. 391–409.
- [16] G.J. Massoth, H.B. Milburn, S.R. Hammond, D.A. Butterfield, R.E. McDuff, J.E. Lupton, The geochemistry of submarine venting fluids at Axial Volcano, Juan de Fuca Ridge: New sampling methods and a VENTS program rationale, in: M.P. DeLuca, I. Babb (Eds.), *Global Venting, Midwater, and Benthic Ecological Processes*, NURP Res. Rep., 88-4, 1988, pp. 29–59.
- [17] K.L. Von Damm, Chemistry of hydrothermal vent fluids from 9–10°N, East Pacific Rise: I. “Time zero” the immediate post-eruptive period, in prep.
- [18] J.L. Bischoff, Densities of liquids and vapors in boiling NaCl–H₂O solutions: a PVTX summary from 300° to 500°C, *Am. J. Sci.* 291 (1991) 309–338.
- [19] J.-L. Charlou, Y. Fouquet, J.M. Auzende, P. Jean-Baptiste, M. Stievenard, S. Michel, Mineral and gas chemistry of hydrothermal fluids on an ultrafast spreading ridge: East Pacific Rise, 17°–19°S (Naudur cruise, 1993) phase separation processes controlled by volcanic and tectonic activity, *J. Geophys. Res.* 101 (1996) 15889–15919.
- [20] S.E. Oosting, K.L. Von Damm, Bromide/chloride fractionation in seafloor hydrothermal fluids from 9–10°N East Pacific Rise, *Earth Planet. Sci. Lett.* 144 (1996) 133–145.
- [21] W.E. Seyfried Jr., K. Ding, The effect of redox on the relative solubilities of copper and iron in Cl-bearing aqueous fluids at elevated temperatures and pressures: an experimental study with application to seafloor hydrothermal systems, *Geochim. Cosmochim. Acta* 57 (1994) 1905–1917.
- [22] M.E. Berndt, W.E. Seyfried Jr., W.J. Beck, Hydrothermal alteration processes at mid-ocean ridge: experimental and theoretical constraints from Ca and Sr exchange reactions and Sr isotopic ratios, *J. Geophys. Res.* 93 (1988) 4573–4584.
- [23] T.S. Bowers, A.C. Campbell, C.I. Measures, A. Spivack, M. Khadem, 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 (1988) 4522–4536.
- [24] A.C. Campbell, T.S. Bowers, C.I. Measures, K.K. Faulkner, M. Khadem, 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 (1988) 4551–4561.
- [25] M.E. Berndt, W.E. Seyfried, Jr., Br/Cl fractionation during subcritical phase separation of seawater: evidence for halite in seafloor hydrothermal systems at 9–10°N, East Pacific Rise, *Geochim. Cosmochim. Acta*, 1997, in press.
- [26] W.C. Shanks, III, J.K. Böhlke, R.R. Seal II, Stable isotopes in mid-ocean ridge hydrothermal systems: interactions between fluids, minerals, and organisms, in: J. Lupton, L. Mullineaux and R. Zierenberg (Eds.), *Physical, Chemical, Biological and Geological Interactions Within Hydrothermal Systems*, AGU Monogr. 91 (1995) 194–221.
- [27] M.E. Berndt, R.R. Seal II, W.C. Shanks III, W.E. Seyfried Jr., Hydrogen isotope systematics of phase separation in submarine hydrothermal systems: Experimental calibration and theoretical models, *Geochim. Cosmochim. Acta* 60 (1996) 1595–1604.
- [28] J.L. Bischoff, R.J. Rosenbauer, Phase separation in seafloor geothermal systems: an experimental study of the effects of metal transport, *Am. J. Sci.* 287 (1987) 953–978.
- [29] H. Craig, J.A. Welhan, K.R. Kim, R. Poreda, J.E. Lupton, Geochemical studies of the 21°N EPR hydrothermal fluids, *Trans. Am. Geophys. Union* 61 (1980) 992.