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SEAFLOOR HYDROTHERMAL ACTIVITY: BLACK SMOKER CHEMISTRY AND CHIMNEYS[1]

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INTRODUCTION

Venting of hydrothermal solutions on the seafloor, first discovered in 1977 at the Galapagos spreading center (GSC) (Figure 1), has now been shown to be a relatively common phenomenon on the world ridge-crest system. It is a consequence of the emplacement of hot rock at divergent plate boundaries and the accompanying circulation of seawater through the oceanic crust. This mechanism for convective cooling of the crust was first suggested based on the deficiency of conductive heat loss extending from the ridge axes (zero crustal age) to several thousand kilometers away on the ridge flanks (crustal ages of several million years) (Anderson et al 1977). Although relatively little of the 55,000-km length of the world ridge-crest system has been explored, at least 10 hydrothermally active sites have been visited and their fluids sampled by submersible. Photographic evidence from camera tows and dredging of hydrothermally precipitated or altered minerals and rocks suggest past or present hydrothermal activity at numerous other sites. The modes of occurrence of these seafloor hot springs differ widely; they are found over a wide range of spreading rates, at sediment-covered and sediment-starved ridge axes, and at temperatures ranging from just a few degrees above that of the ambient seawater (2–4°C) to ≥350°C. Table 1 summarizes some of the physical properties of the areas that have had vent fluid sampled by submersible. Where the measured exit temperature and the inferred temperature of reaction within the hydrothermal system differ significantly, both values are given. Although the fluids have certain common characteristics to their chemistry,

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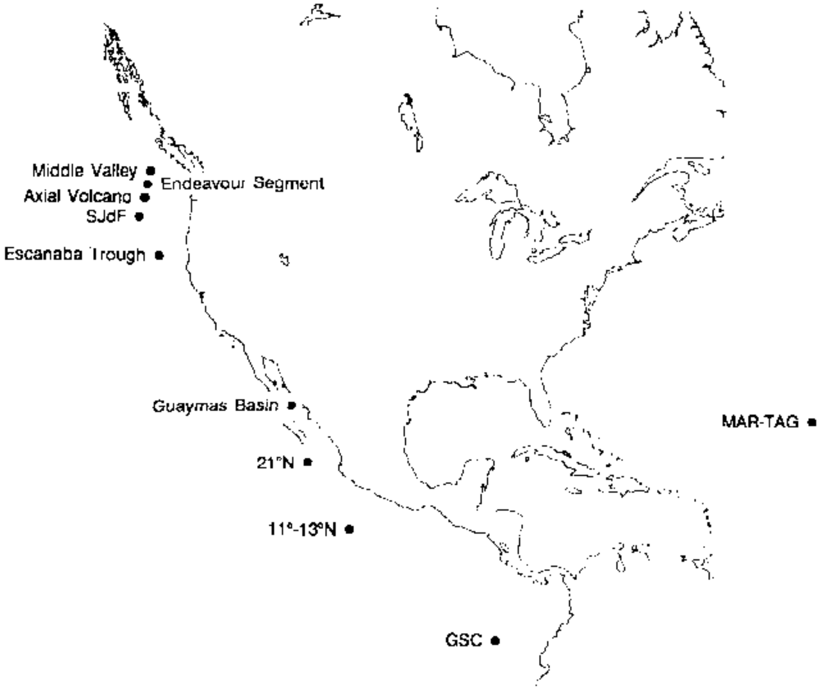

Figure 1 Map of sampled (except Middle Valley) seafloor hydrothermal systems. Not shown are the Red Sea (21°24′N, 38°03′E) and the Mariana Trough (18°13′N, 144°41′E). See Table 1 for explanation of abbreviations used in this figure.

in general each sampling of new vents has expanded our range of known compositional diversity.

CHEMISTRY OF THE FLUIDS

The chemistry of the vent fluids is the result of the interaction of seawater with basalt; and in some cases sediment, at elevated temperatures ($\geq 350°C$ in most cases). Most sampling to date has concentrated on the high-temperature fluids exiting from sulfide chimneys. Many chimneys are surrounded by diffuse flow of presumed lower temperature. The temperatures and the compositions of these diffuse flows remain largely unknown. All of the fluid samples have been obtained using submersibles. Sampling is often a difficult procedure, requiring the pilot to hold the submersible in one position while a sampling device is inserted into the chimney orifice, which is often only a few centimeters in diameter. When the hydrothermal fluids are sampled, some variable amount of seawater is usually entrained in the sample (Figure 2). Experimental work on basalt-

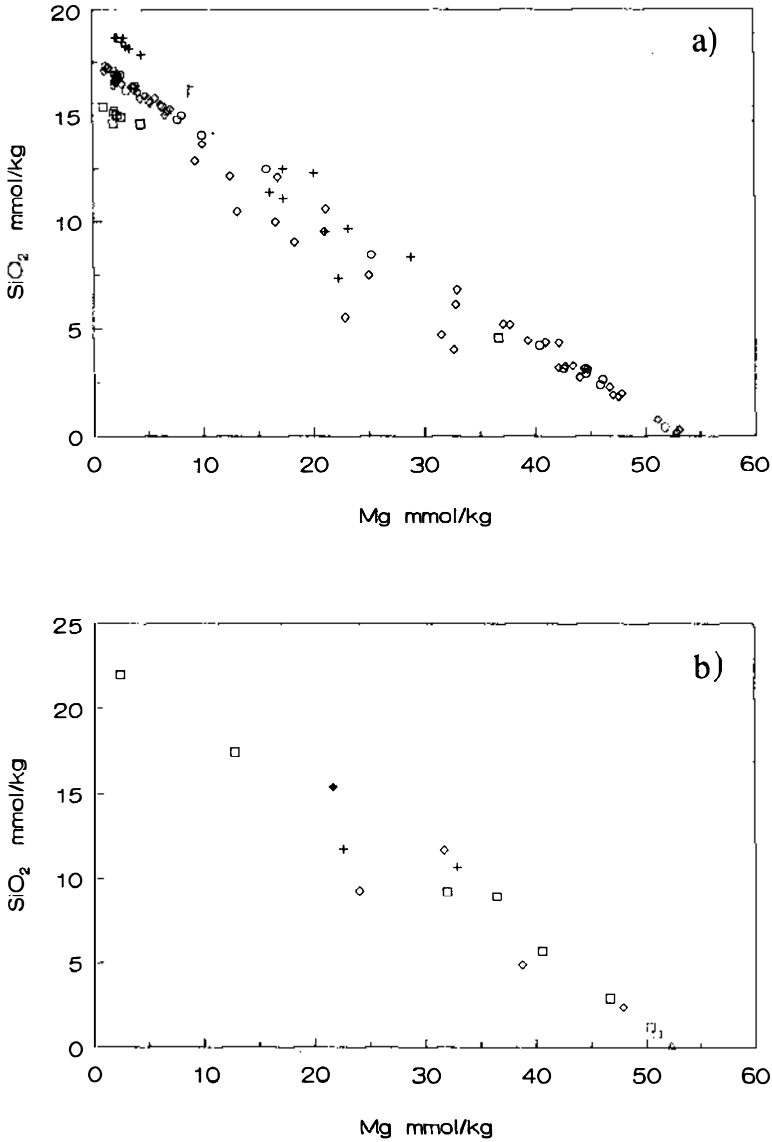

Figure 2 Graph of SiO$_2$ versus Mg for samples collected from (*a*) 21°N East Pacific Rise (EPR) in 1981 and (*b*) the southern Juan de Fuca Ridge (SJdF) in 1984, demonstrating the density of sample coverage and the amount of mixing occurring with seawater (Mg = 53 mmol kg^{-1}) during sampling. Different symbols designate different vent fields (see Table 1 for explanation of abbreviations). For (*a*), + = NGS, ○ = OBS, ◇ = SW, and □ = HG; for (*b*), □ = Plume, ◇ = Vent 1, and + = Vent 3. While values for 21°N EPR vents are well defined, those for Vent 3 of the SJdF are poorly defined owing to the collection of only two samples containing large amounts of admixed seawater from this site.

Table 1 Summary of physical characteristics of discovered seafloor hydrothermal areas

Vent area	Measured (inferred) temperature (°C)	Water depth (m)	Spreading rate (whole) (cm yr^{-1})	Sediment cover (m)	Years sampled	Other comments
Galapagos spreading center (GSC)		2450	7	None	1977, 1979	Low exit temperatures are result of subsurface mixing with cool seawater
Clambake (CB)	< 13(350)					
Garden of Eden (GE)	< 13(350)					
Dandelions (DL)	< 13(350)					
Oyster Beds (OB)	< 13(350)					
21°N East Pacific Rise (EPR)		2600	6	None	1979, 1981, 1985	
National Geographic Society (NGS)	273					
Ocean Bottom Seismograph (OBS)	350					
Southwest (SW)	355					
Hanging Gardens (HG)	351					
Guaymas Basin		2000	6	~ 500	1982, 1985, 1988	Sediment cover very organic- and carbonate rich
1	291					
2	291					
3	285					
4	315					
[redacted]	287					
6	264					
7	300					
9	100					
Southern Juan de Fuca Ridge (SJdF)		2300	[redacted]	None	1984, 1987	
Plume	224(> 340)					
Vent 1	285(> 340)					
Vent 3	(> 340)					
11–13°N EPR		2600	12	None	1982, 1984, 1985	

N & S–13°N	317					
1–13°N						
2–13°N	354					
3–13°N	380?					
4–11°N	347					
5–11°N						
6–11°N						
Mid-Atlantic Ridge (MAR)		3600	2.6	None	1986	
TAG	290, 321					
MARK-1	350					
MARK-2	335					
Axial Volcano, Juan de Fuca Ridge		1542		None	1986, 1987, 1988	Shallowest system sampled
Hell, Hillock & Mushroom (HE, HI, MR)	136–323					
Inferno	149–328					
Virgin Mound (VM), Crack	5–299					
Escanaba Trough, Gorda Ridge	18–220	3200	2.3	≤500	1987	
Middle Valley, Juan de Fuca Ridge		2500	6	~300–≥1500	—	Black smokers, but not yet sampled. Sediment is mostly terrigenous
Endeavour segment, Juan de Fuca Ridge	>400	2200	6	None	1984	
Mariana Trough	285–287	3650	6		1987	Back-arc spreading center
Red Sea, Atlantis II Deep	62.3(>250)	2000	1.5	10–30	Since mid-1960s	Fluids form brine pools; direct venting not observed. Fluids react with Miocene evaporites and basalt

seawater interaction under hydrothermal conditions representative of the seafloor systems has shown that Mg is close to being quantitatively removed from the solutions at temperatures ≥150°C (e.g. Bischoff & Dickson 1975, Seyfried & Bischoff 1979). In order to compare all of the sampled fluids from different locations on the same basis, it is assumed that any Mg present is due to the entrainment of ambient seawater, and all fluid compositions are extrapolated to Mg = 0 mmol kg^{-1}. For some samples, the extrapolated value is within the experimental error of the analytical data, whereas in other cases the extrapolation is considerably larger. All data in the subsequent tables and discussion are for the extrapolated end-member (Mg = 0 mmol kg^{-1}) values. This approach may not be valid for lower temperature solutions, from which all the Mg may not have been removed by rock-water interaction, and may obfuscate evidence related to mixing of higher and lower temperature solutions. It remains, however, the best means of correcting for seawater entrainment during sampling.

Table 2 presents a compendium of data for most of the seafloor hydrothermal fluids sampled to date; also listed for purposes of comparison is the composition of seawater. Each vent area normally consists of a number of isolated vent fields, which may be separated by a few kilometers. These vent fields contain individual vents that may have subtle or even large differences in chemistry over very short (e.g. 10 m) geographical distances. While the 21°N East Pacific Rise (EPR), 11–13°N EPR, southern Juan de Fuca Ridge (SJdF), Galapagos spreading center (GSC), Mid-Atlantic Ridge (MAR), and Axial Volcano fluids have reacted only with basalt, the Guaymas Basin fluids have also reacted with an organic- and carbonate-rich sediment cover. The sediment covers in Escanaba Trough of the Gorda Ridge and Middle Valley of the Juan de Fuca Ridge are more terrigenous and contain less organic matter and carbonate. The Red Sea remains a unique example of an area where hydrothermal fluids form brine pools on the seafloor owing to their high salinity, gained through reaction with Miocene evaporites. The GSC fluids have mixed below the seafloor with cool seawater, and the Axial Volcano and SJdF fluids have probably been affected by phase separation.

In the remainder of this section, I briefly summarize the results found in Table 2.

The alkalis and ammonium The elements Li, K, Rb, and Cs are variably enriched with respect to the initial seawater value, whereas sodium exhibits both enrichments and depletions with respect to initial seawater. As Na is the predominant cation in these fluids, its behavior is closely tied to that of chloride, the predominant anion. Although the sediments at Guaymas

Basin provide an additional, more enriched source of the alkali elements than does the basalt alone at the other sites, Guaymas Basin fluids do not contain the largest enrichments of all of these elements. The SJdF fluids are in many cases the most enriched in the alkalis, probably as a result of the higher chloride content of these fluids, which in turn complexes these metals and permits higher levels to be maintained in solution. Although small amounts of ammonium have been found in other vents (M. D. Lilley, personal communication, 1988), only the Guaymas Basin fluids contain substantial amounts of this compound. The ammonium is produced as a consequence of the decomposition of organic matter in the sediment column.

Alkaline earths Magnesium is assumed to be zero in the pure hydrothermal fluid, and samples with less than 1 mmol kg^{-1} Mg have been collected from a number of vents. The elements Be and Ca are both variably enriched in all the vent areas, whereas strontium is one of the few elements that displays both enrichments and depletions relative to the seawater value. Calcium varies by almost an order of magnitude, and in some vents it is essentially identical to the seawater value. Although the carbonate-rich sediments in Guaymas Basin provide an additional source of both Ca and Sr, these elements reach their highest concentration in the SJdF solutions, again presumably as a result of enhanced chloride complexing. The Sr isotopes suggest a predominantly basaltic source for the Sr present in the hydrothermal solutions, with a variable (but small) component of seawater Sr. The Guaymas Basin fluids are significantly more radiogenic, which may reflect reaction with sedimentary carbonates or the admixture of additional seawater Sr. Barium forms the very insoluble sulfate mineral barite. As some sulfate is always present owing to the entrainment of seawater during sampling, only a lower limit can be given for the barium dissolved in the hydrothermal solutions. Radium-226 and its daughters (radon-222 and lead-210) are also enriched (Krishnaswami & Turekian 1982, Dymond et al 1983, Kadko 1988), although radium enrichments are undoubtedly also affected by the precipitation of sulfate minerals.

Silica The silica contents of all the measured vent solutions vary less than many of the other chemical parameters. This relative lack of variation is believed to be due to the control of dissolved silica by equilibrium with quartz in these systems (Von Damm et al 1985a). A possible exception is the Guaymas Basin fluids, where the presence of other phases controlling the activity of silica cannot be ignored owing to both the lower temperatures (favoring amorphous silica) and authigenic aluminosilicates found in the sediment cover.

Table 2a Summary of chemical data for seafloor hydrothermal solutions. Alkali and alkaline earth metals, ammonium, and silica[a]

Vent	Temp. (°C)	Li (μmol kg^{-1})	Na (mmol kg^{-1})	K (mmol kg^{-1})	Rb (μmol kg^{-1})	Cs (nmol kg^{-1})	NH_4 (mmol kg^{-1})	Be (nmol kg^{-1})	Mg (mmol kg^{-1})	Ca (mmol kg^{-1})	Sr (μmol kg^{-1})	$^{87}Sr/^{86}Sr$	Ba (μmol kg^{-1})	SiO_2 (mmol kg^{-1})
Galapagos spreading center								11–37						
CB	<13	1142	487	18.7	20.3				0	40.2	87		>42.6	21.9
GE	<13	1142	451	18.8	21.2				0	34.3	87		>17.2	21.9
DL	<13	1142	313	18.8	17.3				0	34.3	87		>17.2	21.9
OB	<13	689	259	18.8	13.4				0	24.6	87		>17.2	21.9
21°N EPR														
NGS	273	1033	510	25.8	31.0		<0.01	37	0	20.8	97	0.7030	>16	19.5
OBS	350	891	432	23.2	28.0	202	<0.01	15	0	15.6	81	0.7031	>8	17.6
SW	355	899	439	23.2	27.0		<0.01	10	0	16.6	83	0.7033	>10	17.3
HG	351	1322	443	23.9	33.0		<0.01	13	0	11.7	65	0.7030	>11	15.6
Guaymas Basin														
1	291	1054	489	48.5	85.0		15.6	12	0	29.0	202		>12	12.9
2	291	954	478	46.3	77.0		15.3	18	0	28.7	184		>20	12.5
3	285	720	513	37.1	57.0		10.3	42	0	41.5	253	0.7052	>15	13.5
4	315	873	485	40.1	66.0		12.9	29	0	34.0	226	0.7052	>54	13.8
5	287	933	488	43.1	74.0		14.5	29	0	30.9	211		>13	12.4
6	264	896	475	45.1	74.0		14.5	60	0	26.6	172	0.7059	>16	10.8
7	300	1076	490	49.2	86.0		15.2	17	0	29.5	212		>24	12.8
9	100	630	480	32.5	57.0		10.7	91	0	30.2	160			9.3

Southern Juan de Fuca												0.7034		
Plume	224	1718	796	51.6	37.0			95	0	96.4	312			23.3
Vent 1	285	1108	661	37.3	28.0			150	0	84.7	230			22.8
Vent 3		1808	784	45.6	32.0			150	0	77.3	267			22.7
11–13°N EPR														
N & S–13°N	317	688	560	29.6	14.1				0	55.0	175	0.7041		22.0
1–13°N		614	587	29.8	18.0				0	44.6	171			21.9
2–13°N	354	592	551	27.5	19.0				0	53.7	182			19.4
3–13°N	(380)	591	596	28.8	20.0				0	54.8	168			17.9
4–11°N	347	884	472	32.0	24.0				0	22.5	80			18.8
5–11°N		623	577	32.9	25.0				0	35.2	135			20.6
6–11°N		484	290	18.7	15.0				0	10.6	38			14.3
Mid-Atlantic Ridge														
TAG	290, 321	411	584	17.0	10.0	100			0	26.0	99	0.7029		22.0
MARK-1	350	843	510	23.6	10.5	177		38.5	0	9.9	50	0.7028		18.2
MARK-2	335	849	509	23.9	10.8	181		38.0	0	10.5	51	0.7028		18.3
Axial Volcano														
HE, HI, MR	136–323	512	415	22.0					0	37.3				15.1
Inferno	149–328	637	500	27.5					0	46.8				15.1
VM, Crack	5–299	204	159	7.6					0	10.2				13.5
Seawater	2	26	464	9.8	1.3	2.0	< 0.01	0.0	52.7	10.2	87	0.7090	0.14	0.16

[a] Data references listed at end of Table 2*c*.

Table 2b Summary of chemical data for seafloor hydrothermal solutions. pH, carbon and sulfur systems, halogens, boron, aluminum, and water isotopes[a]

Vent	pH	Alk$_T$ (meq kg^{-1})	Total CO$_2$ (mmol kg^{-1})	SO$_4$ (mmol kg^{-1})	H$_2$S (mmol kg^{-1})	δ^{34}S	As (nmol kg^{-1})	Se (nmol kg^{-1})	Cl (mmol kg^{-1})	Br (μmol kg^{-1})	B (μmol kg^{-1})	δ^{11}B	Al (μmol kg^{-1})	δ^{18}O	δD
Galapagos spreading center			9.3–11.3							832–835					
CB	–	<0		0	+				595						
GE	–	<0		0	+				543						
DL	–	<0		0	+				395						
OB	–	<0		0	+				322						
21°N EPR			5.72											1.6–2.0	2.5
NGS	3.8	−0.19		0.00	6.6	3.4	30	<0.6	579	929	507	32.7	4.0		
OBS	3.4	−0.40		0.50	7.3	1.3–1.5	247	72	489	802	505	32.2	5.2		
SW	3.6	−0.30		0.60	7.5	2.7–5.5	214	70	496	877	500	31.5	4.7		
HG	3.3	−0.50		0.40	8.4	2.3–3.2	452	61	496	855	548	30.0	4.5		
Guaymas Basin															
1	5.9	10.60		−0.15	5.8		283	82	601	1054–1117			0.9		
2	5.9	9.60		−0.09	4.0		732	87	589		1630	17.4	1.2		
3	5.9	6.50		−0.34	5.2		1071	38	637				6.7		
4	5.9	8.10		0.06	4.8		1074	103	599	1063	1570	23.2	3.7		
5	5.9	9.70		−0.07	4.1		516		599				3.0		
6	5.9	7.30		−0.32	3.8		669	49	582				3.9		
7	5.9	10.50		−0.06	6.0		711	92	606	1054–1117	1730	19.6	1.0		
9	5.9	2.80		−4.20	4.6		577		581				7.9		

Southern Juan de Fuca			3.92–4.46												−2.5–+0.5
Plume	3.2			−0.50	3.5	4.2–7.3		<1	1087	1832	496	34.2		0.65	
Vent 1	3.2			−1.30	(3.0)	4.0–6.4		<1	896	1580				0.60	
Vent 3	3.2			−1.70	(4.4)	7.2–7.4		<1	951	1422				0.80	
11–13°N EPR															
N & S–13°N	3.2		10.8–16.7	0.00					740	1163				0.39–0.69	0.62–1.49
1–13°N	3.2	−0.64			2.9				718	1131			13.3		
2–13°N	3.1	−0.74			8.2	4.7			712	1158	467	34.9	19.8		
3–13°N	3.3	−0.40			4.5	2.3–3.5			760	1242			20.0		
4–11°N	3.1	−1.02			8.0	4.6			563	940			12.9		
5–11°N	3.7	−0.28			4.4	4.7–4.9			686	1105	451	36.8	13.5		
6–11°N	3.1	−0.88			12.2	4.1–5.2			338	533	493	31.5	13.6		
Mid-Atlantic Ridge															
TAG									659						
MARK-1	3.9	−0.06			5.9	4.9			559	847	518	26.8	5.3	2.37	
MARK-2	3.7	−0.24			5.9	5.0			559	847	530	26.5	5.0	2.37	
Axial Volcano											476	34.7			
HE, HI, MR	3.5	−0.52			8.1				515	760	565			0.8–1.1	
Inferno	3.5	−0.45			7.0				625	950	565			0.8–1.1	
VM, Crack	4.4	0.58	150–170		(19.5)				188	240	503			0.7–0.9	
Seawater	7.8	2.3	2.3	27.9	0.0		27	2.5	541	840	416	39.5	0.020	0.0	0.0

[a] Data references listed at end of Table 2c.

Table 2c Summary of chemical data for seafloor hydrothermal solutions. Trace metals[a]

Vent	Mn (μmol kg^{-1})	Fe (μmol kg^{-1})	Co (nmol kg^{-1})	Cu (μmol kg^{-1})	Zn (μmol kg^{-1})	Ag (nmol kg^{-1})	Cd (nmol kg^{-1})	Pb (nmol kg^{-1})
Galapagos spreading center								
CB	1140	+		0			0	
GE	390	+		0			0	
DL	480	+		0			0	
OB	360	+		0			0	
21°N EPR								
NGS	1002	871	22	<0.02	40	<1	17	183
OBS	960	1664	213	35.00	106	38	155	308
SW	699	750	66	9.70	89	26	144	194
HG	878	2429	227	44.00	104	37	180	359
Guaymas Basin								
1	139	56	<5	<0.02	4.2	230	<10	265
2	222	49	<5	<0.02	1.8	<1	<10	304
3	236	180	<5	<0.02	40.0	24	46	652
4	139	77	<5	1.10	19.0	2	27	230
5	128	33	<5	0.10	2.2	<1	<10	<20
6	148	17	<5	<0.02	0.1	<1	<10	<20
7	139	37	<5	<0.02	2.2	<1	<10	<20
9	132	83	<5	<0.02	21.0	<1	<10	<20
Southern Juan de Fuca								
Plume	3585	18,739		<2	900			900
Vent 1	2611	10,349		<2	<600			
Vent 3	4480	17,770		<2				

11–13°N EPR								
N&S–13°N	1000	1450						
1–13°N	1689	3980			102.0		55	135
2–13°N	2932	10,370			5.0		70	27
3–13°N	2035	10,760			2.0		65	14
4–11°N	766	6470			105.0		30	50
5–11°N	742	1640			73.0		43	270
6–11°N	925	2640			44.0		1	9
Mid-Atlantic Ridge								
TAG	1000	1640						
MARK-1	491	2180		17.0	50.0			
MARK-2	493	1832		10.0	47.0			
Axial Volcano								
HE, HI, MR	1081	1006		12.0	113.0			302
Inferno	1081	1006		12.0	113.0			302
VM, Crack	162	9		0.70	2.3			101
Seawater	<0.001	<0.001	0.03	0.007	0.01	0.02	1.0	0.0100

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[a] Data from following references:
Galapagos: Edmond et al 1979a,b, Welhan 1981.
21°N EPR: Craig et al 1980, Welhan 1981, Von Damm et al 1985a, Spivack & Edmond 1987, Woodruff & Shanks 1988, Campbell & Edmond 1989.
Guaymas: Von Damm et al 1985b, Spivack et al 1987, Campbell & Edmond 1989.
Juan de Fuca: Von Damm & Bischoff 1987, Shanks & Seyfried 1987, Hinkley & Tatsumoto 1987, Evans et al 1988, Campbell & Edmond 1989.
11–13°N EPR: Michard et al 1984, Merlivat et al 1987, Bowers et al 1988, Bluth & Ohmoto 1988, Campbell & Edmond 1989.
Mid-Atlantic Ridge: Campbell et al 1988b, Campbell & Edmond 1989.
Axial: Butterfield et al 1988, Massoth et al 1989.
( ) denotes large uncertainty in value.

pH The 25°C, 1 atm pH is quite acid for all of the vent fluids with the exception of the Guaymas Basin fluids. The calculation of an in situ pH requires a good knowledge of all the aqueous complexes. The original estimates of Bowers et al (1985) of values just a few tenths of a pH unit higher than the 25°C value have been superseded by values suggesting an in situ pH closer to 4.5 (Bowers et al 1988). The calculation of an in situ pH for the Guaymas Basin solutions is more problematic still, owing to the presence of unknown organic ligands. Best estimates suggest values close to neutrality.

Carbon system At the acid pHs observed for most of these fluids, zero, or even a slightly negative, total alkalinity has been measured. The exception is again the Guaymas Basin fluids, which have alkalinities significantly higher than seawater. The most abundant carbon species present in these solutions is dissolved CO_2. Carbon dioxide is also the most abundant gas in the vent fluids. Hence, measurements of the total condensable gases are primarily of the CO_2. Small amounts of CH_4 are also present, as are lesser amounts of short-chain hydrocarbons (Evans et al 1988). Measurements of the total CO_2 and other gases in Guaymas Basin fluids have been hindered by the extremely high gas content of these fluids, which tend to degas after sampling as the pressure decreases during the return of the submersible and samples to the surface. Gas-tight samples have shown the levels of total condensable gases to be very high, but the individual gases remain to be determined (J. Lupton, personal communication, 1989). Carbon isotopic measurements suggest that most of the carbon at GSC and 21°N EPR has a "mantle" signature, with $\delta^{13}C = -7.00‰$ vs. the PDB carbon standard at 21°N EPR (Welhan 1981).

Sulfur system Essentially all of the seawater sulfate is removed from the fluids, and variable amounts of sulfide are present. There is a net loss of sulfur from the solutions compared with the initial seawater concentration. The sulfur isotope systematics suggests that the sulfide present in the vent fluids is primarily from a basaltic source, with variable amounts of reduced-seawater sulfate being present as well. The majority of the seawater sulfate is probably being removed by the precipitation of anhydrite ($CaSO_4$) during the heating of cool seawater in the hydrothermal downflow zone. Several authors (Woodruff & Shanks 1988, Bluth & Ohmoto 1988) have suggested that the reduced-seawater sulfur is added within the upflow zone, either deep in the system or perhaps very close to the seafloor. Arsenic and selenium, which under certain conditions behave similarly to sulfur, are also enriched in most of the fluids compared with their initial seawater concentrations. The sediment cover in Guaymas Basin and Escanaba Trough provides an additional source for these two elements.

Halogens Fluoride has only been measured in a few of the hydrothermal fluids, and available evidence suggests that it is completely removed during the hydrothermal circulation (Edmond et al 1979a, Von Damm et al 1985a). Chloride is variably enriched and depleted in the hydrothermal solutions, with many of the sampled fluids having concentrations relatively close to that of seawater. The chloride concentration is important in controlling the concentration of other species, as it is the dominant anion in the fluids. For this reason its cycle is closely tied to that of sodium. The Na/chloride molar ratio (Table 3) suggests that in all vents except at 21°N EPR and MAR, there is a net loss of Na with respect to chlorides, regardless of whether chloride is enriched or depleted relative to the seawater concentration. The relative Na loss probably results from its uptake by the rock during albitization. The reasons for the variability in chloride concentrations remain open to speculation and are discussed in detail in a later section. Campbell & Edmond (1989) have recently shown that bromide appears to maintain a bromide/chloride ratio that is almost constant and close to the seawater value in the basaltic systems. They have also noted an input of Br and I to the fluids in sedimented systems from the decomposition of organic matter.

Boron The concentration of boron in seawater is relatively high, and only a relatively small addition is made to the hydrothermal fluids, with the exception of those in the Guaymas Basin. The boron isotope systematics confirms this additional sedimentary source (Spivack & Edmond 1987, Spivack et al 1987).

Aluminum Aluminum is significantly enriched in the vent fluids in all of these systems, although the amount added to the water is relatively small compared with the amount available from the rock. The 11–13°N EPR vent fluids contain the largest enrichments.

Table 3 Molar ratio of Na/Cl in vent fluids

Vent	Na/Cl
GSC	0.79–0.83
21°N EPR	0.88–0.89
Guaymas Basin	0.81–0.83
SJdF	0.73–0.82
11°–13°N EPR	0.76–0.86
MAR	0.89–0.91
Axial Volcano	0.80–0.85
Seawater	0.86

Water isotopes The oxygen and hydrogen isotopic contents of the vent fluids have been determined for a limited number of samples. Although most of the observed values differ from initial seawater, a systematic variation is not observed.

Trace metals Several difficulties are encountered in obtaining good trace-metal data for the vent fluids. At many vent areas, the fluids are clear as they exit from the sulfide chimneys and then rapidly begin to precipitate the characteristic black smoke of metal sulfides and sulfates as they mix with seawater. At other vents this mixing appears to begin within or below the chimney itself, as the fluids already appear to contain particles when they reach the chimney orifice. In some cases, chimney particles are also introduced into the fluid samples during the sampling procedure. The metals from particles precipitated during the sampling need to be incorporated into the metal content of the fluids, while chimney particles need to be excluded. It is sometimes possible for fluid samples containing very small amounts of admixed seawater to find essentially no particles, as is the case for some of the samples from 21°N EPR. Often, samples that were difficult to obtain suffer from the multiple problems of containing a large proportion of seawater, which results in an increased pH and hence in their having precipitated a large amount of their metal content, and of containing small pieces of chimney material. A consistent trace-metal concentration versus Mg concentration (e.g. the mixing line as shown in Figure 2) or several samples of similar Mg concentration with similar metal contents provide the best check on the accuracy of the trace-metal data. These difficulties are part of the reason that more comprehensive trace-metal data are not given for many of the vent areas (Table 2). Metals that are sulfide formers suffer from the largest uncertainties. Iron and manganese are extremely enriched in all of these fluids compared with the seawater value, although the enrichment is less so in the Guaymas Basin fluids. The enrichment of copper is also variable and appears to be related to temperature, with only those vents with exit temperatures $\geq 350°C$ containing substantial copper. Zinc is also quite enriched with respect to seawater in the hydrothermal solutions, especially in the high-chloride and $<300°C$ SJdF solutions. Cadmium, cobalt, silver, and lead are variably enriched in the hydrothermal fluids. The higher lead concentrations in the Guaymas Basin fluids reflect the additional sedimentary input of this element, and this conclusion is confirmed by the isotopic composition (Chen et al 1986).

Gases In addition to the enrichments in CO_2, CH_4, and H_2S noted above, the fluids are significantly enriched in ^3He, ^4He, and hydrogen (Craig et al 1980, Welhan 1981,

Controls on the Composition of the Solutions

As we cannot at present see below the seafloor into an active seafloor hydrothermal system, we must infer the subsurface processes that are occurring either from the solution chemistry alone or by analogy with ophiolites or the rocks found within Deep Sea Drilling Project (DSDP) Hole 504B (Leinen, Rea et al 1986). Some of the parameters that influence solution chemistry and hence the chemistry of the chimney deposits include the following: (*a*) temperature, both in the subsurface and at the seafloor; (*b*) pressure, which is related to the water depth; (*c*) rock composition, which is relatively constant; (*d*) at some locations, sediment compositions, which can be highly variable; (*e*) whether the rock is fresh or has been previously altered; (*f*) whether the fluids have reached equilibrium with the rocks or, alternatively, whether kinetics is controlling the observed fluid compositions and hence placing importance on the residence time of the fluid in the system; (*g*) whether the fluids have undergone, or are presently undergoing phase separation; and (*h*) whether subsurface mixing of different fluids has occurred.

Bowers et al (1988), based on results from the geochemical modeling code EQ3/6 (Wolery 1983), have recently suggested that the fluids are in equilibrium with a mineral assemblage that is similar to a greenschist facies assemblage (Table 4). It should be noted that many of the needed thermodynamic constants are poorly known at the pressure and temperature conditions of interest. Fluids with salinities significantly higher than seawater or temperatures much above 350°C are also outside the range of available data and models, which limits the applicability of this approach to solutions with higher ionic strengths. Many elemental ratios

Table 4 Proposed equilibrium mineral assemblage based on observed fluid chemistry and EQ3/6 modeling results of Bowers et al (1988)

Mineral	Chemical formula
Quartz	SiO_2
K-feldspar	$KAlSi_3O_8$
Albite	$NaAlSi_3O_8$
Anorthite	$CaAl_2Si_2O_8$
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$
Paragonite	$NaAl_2(AlSi_3O_{10})(OH)_2$
Ca-beidellite	$Ca_{0.165}Al_2(Al_{0.33}Si_{3.67}O_{10})(OH)_2$
Epidote	$Ca_2FeAl_2Si_3O_{12}(OH)$
Daphnite	$Fe_5Al(AlSi_3O_{10})(OH)_8$
Pyrrhotite (pyrite)	$FeS(FeS_2)$

and products and chemical geothermometers give similar results for all of the fluids (with the exception of Guaymas Basin), which also suggests an equilibrium or steady-state control (rather than kinetic) on the fluid chemistry (Von Damm 1988). The similarity between the model results and the more empirical elemental ratios for the areas examined also suggests that the conditions at depth within these hydrothermal systems are quite similar. Additional evidence bearing on the mineralogy of the subsurface alteration that is occurring in these hydrothermal systems comes from DSDP Hole 504B (Table 5), which penetrated over a kilometer of the oceanic crust. This drill hole cored through the sediments and pillow lavas into a sheeted dike section and intersected an area of hydrothermal alteration (Alt et al 1984). The mineralogy observed in the 504B core section is, with few exceptions, quite similar to that proposed by Bowers et al (1988). Studies of ophiolites are also providing insight into the subsurface behavior of the fluids, including flow paths and alteration processes (Haymon et al 1989, and references therein).

Mixing of hydrothermal fluids in the subsurface may occur more commonly than previously thought. Fluids from the GSC display clear chemical evidence for mixing between high-temperature hydrothermal fluids and cold seawater below the seafloor (Edmond et al 1979a,b). At SJdF, the chemistry of the fluids suggests that subsurface mixing of a brine with a hydrothermal solution having a chlorinity close to that of seawater has occurred (Von Damm & Bischoff 1987). Butterfield et al (1989) have also invoked subsurface mixing of hydrothermal fluids with differing compositions to explain the observed fluid chemistries at Axial Volcano. Mixing of a high-temperature fluid with a small amount of a low-temperature fluid may also explain the chemistry and temperature of the NGS vent at 21°N EPR, at which the best-sampled fluids appear to contain slightly more magnesium than is contained in other fluids from this location. The

Table 5 Observed mineral phases and potential elemental sinks in DSDP Hole 504B[a]

Element	Mineral phase(s)
Na	Albite
K	Orthoclase found in albite
Ca	Actinolite, epidote, sphene, chlorite-clay mixture
Fe	Sulfides, etc
Mn	Chlorite-clay mixture (actinolite, albite, epidote, sphene)
Si	Quartz
S	Sulfides

[a] Reference: Alt et al (1984).

concentrations of various elements (especially silica) in these solutions, which are interpreted to have mixed, suggest that the fluids are equilibrated with the same mineral assemblage as are the other vent fluids. This suggests in turn that the fluids have reequilibrated with the rock after mixing has occurred (Von Damm 1988, Butterfield et al 1989). These authors favor a model in which this observed composition of the hydrothermal fluids is explained as a mixture between a gas-depleted high-chlorinity fluid (brine), a gas-enriched low-chlorinity fluid (vapor), and a gas-containing fluid having a chlorinity close to that of seawater.

Whichever models are invoked to explain the chemistries of the vent fluids, they must account for several surprising observations. One of these is the time constancy of the chemistry of the vent solutions. Given the high heat output and the dynamic nature of these systems, it was initially thought that vents would rapidly come and go and that the chemistry of the fluids would reflect this instability on a time scale of years. Most observations to date, however, suggest that these vents, including the water chemistry, are stable on longer time scales. Repeated samplings of vent fluids at 21°N EPR in 1979, 1981, and 1985 (Campbell et al 1988a), the Guaymas Basin in 1982, 1985, and 1988 (Campbell et al 1988a, Gieskes et al 1988), the SJdF in 1984 and 1987 (Von Damm & Bischoff 1987, Massoth et al 1988), and the ASHES vent field on Axial Volcano in 1986, 1987, and 1988 (Massoth et al 1989) show very little change in fluid chemistries or temperatures. These observations support an equilibrium or steady-state model and also suggest that the at-depth hydrologic systems are very stable. This constancy provides a striking dichotomy to the episodicity of the two "megaplume" events observed on the Juan de Fuca Ridge (Baker et al 1987), in which large amounts of hydrothermal fluids and particles, and therefore heat, were released to the water column over a brief period of time, as evidenced by the presence of two large, particle-rich water column plumes. It remains an open question as to how common this type of event is on the world ridge-crest system. Evidence of changing fluid compositions also comes from the chimney deposits themselves. How these seemingly contradictory observations relate to the life cycle of an individual vent or vent field and to their relative input of heat and solutes to seawater remains unresolved.

Chloride Variability—Possible Explanations

The observed variability in the chloride content of vent solutions ranges from approximately one third to twice the normal seawater concentration. As chloride is by far the dominant anion in these solutions, its concentration plays a major role in their metal-carrying capacities, as well as in their physical and chemical properties, such as density and critical point. Several mechanisms that could significantly affect the chloride content of the solutions are available: (*a*) Although flow through evaporites has been invoked as a source of increased chlorinity for the Red Sea brines, it is unlikely for most of these other solutions, which occur on unsedimented, open ocean-ridge axes. (*b*) Although direct input of volatiles, such as water and HCl from magma degassing, cannot be ruled out, at present no evidence exists to suggest that this process is an important contributor to the chemistry of the hydrothermal fluids. (*c*) Small amounts of water can be lost from a solution as a result of rock hydration and could potentially be re-released at a later time owing to changes in the conditions in the hydrothermal system (e.g. a later thermal pulse, with resulting higher temperatures). (*d*) Not only water but also chloride could occupy sites in hydrous minerals that may serve as sources or sinks, depending on changing conditions. (*e*) Precipitation or dissolution of an unidentified chloride-rich phase with possible retrograde solubility has been suggested as a cause of the observed chloride anomalies. (*f*) Phase separation could result in the formation of low- and high-salinity fluids and may even result in the formation of halite, which could later redissolve. The high-salinity fluids, given their higher densities and lower buoyancies, may be stored in the oceanic crust between thermal pulses. Figure 3 shows the phase relation-

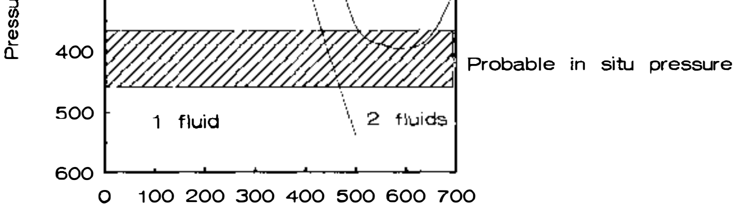

Figure 3 A pressure-temperature diagram applicable to seafloor hydrothermal systems. The critical point (c.p.) of seawater is shown (Bischoff & Rosenbauer 1988) along the two-phase boundary. The halite saturation curve is based on data from Sourirajan & Kennedy (1962). Also shown is a range of pressures typical of conditions at the seafloor for many of the sampled hydrothermal systems, as well as a range of inferred pressures occurring at depth within the hydrothermal systems.

ships that apply to a seawater hydrothermal system. In a seawater system, crossing the two-phase boundary below the critical point (i.e. boiling) will result in the formation of a small amount of a low-salinity "vapor," while crossing the two-phase boundary above the critical point (i.e. condensation) will result in the formation of a small amount of high-salinity "brine."

In addition to the sampled hydrothermal fluids, other evidence suggests that high-salinity fluids exist with the oceanic crust. In fact, the other evidence suggests that fluids of much higher salinities exist than have been sampled from vents. Table 6 summarizes the results from several fluid inclusion studies. In several of these studies (e.g. Cowan & Cann 1988) both high- and low-salinity inclusions were found, providing evidence consistent with phase separation as the cause. Although the data are limited, there is some evidence to suggest that these very high salinity fluids occur at greater depths in the oceanic crust than those depths at which axial hot springs are currently believed to circulate (Vanko 1988). This is one reason why Bischoff & Rosenbauer (1989) have recently suggested that two stacked hydrothermal circulation cells exist within the oceanic crust, with the deeper one being very saline and primarily responsible for the albitization of the oceanic crust and for transferring heat and some salt to the shallower, less saline cell. Several authors have also reported finding chloride-rich minerals within the oceanic crust. For example, Vanko (1986) and Stakes & Vanko (1986) found amphiboles containing up to 4.0 wt% chloride, compared with usual values of ≤ 0.05 wt%. They have inferred that these phases could only have formed in the presence of

Table 6 Summary of fluid inclusion evidence for the existence of high- and low-salinity fluids within the oceanic crust and critical point (C_p) data

Location	NaCl (wt%)	Inferred temperature, pressure (°C, bars)	Reference
Mathematician Ridge	58	600–>700, 600–1000	Vanko 1988
Kane Fracture Zone	10	>407, >298.5	Delaney et al 1987
	50	700, 1000–1200	Kelley & Delaney 1987
	1–2	400, 1000–1200	
Troodos Ophiolite	48(57)	500–525, 350–400	Cowan & Cann 1988
	0–2		
Seawater	3.2	$C_p = 407, 298.5$	Bischoff & Rosenbauer 1988
Distilled water	0	$C_p = 374.1, 220.4$	

fluids significantly more saline than seawater. Brett et al (1987) have reported finding lizardite [$Mg_3Si_2O_5(OH)_4$] containing up to 1.2 wt% chloride and a zinc-hydroxychlorosulfate [$Zn_{12}(OH)_{15}(SO_4)_3Cl_3 \cdot 5H_2O$] containing up to 7.0 wt% chloride. It should be noted that these phases are all relatively rare and could not provide the chloride source or sink needed to sustain the depletions and enrichments in chloride observed in a number of the hot springs. Edmond et al (1979a) first suggested a metal-hydroxycloride mineral found in altered ultrabasic rocks (Kohls & Rodda 1967, Ricklidge & Patterson 1977) as a possible source or sink for the chloride variations observed in the GSC hot springs. Seyfried et al (1986) were able to replicate the chloride depletions in an experimental study and suggested that the mineral phase involved was $Fe_2(OH)_3Cl$, although it was never identified as a run product. This phase has also yet to be identified from the seafloor. At the concentrations of chloride observed in the SJdF vents, which have been stable for at least three years, a very large amount of this phase would need to have formed and be redissolving, creating additional problems for the elemental cycles of Na and H^+ (Von Damm & Bischoff 1987). It has been suggested, as a test of the chloride-rich mineral hypothesis, that if a chloride-rich phase is forming it would discriminate against bromide, and hence that if high salinities in the fluids are the result of dissolution of a mineral phase, these same fluids should have a lowered bromide/chloride ratio compared with seawater. Conversely, low-salinity fluids formed by the precipitation of such phases should have elevated Br/Cl ratios. Campbell & Edmond (1989) have recently reported data on the bromide/chloride ratio for several of the high- and low-salinity vent fluids. They find that, with the exception of vents from sedimented systems where organic matter provides a significant additional source of bromide, the ratio is close to that of seawater. These results argue against the formation and dissolution of a chloride-rich phase having a significant influence on the chemistry of the vent fluids.

Von Damm & Bischoff (1987) and Von Damm (1988) have discussed the evidence for phase separation in the twice-seawater-chlorinity solutions found in the SJdF fluids. They have suggested, primarily on the basis of the gas data (Kennedy 1988, Evans et al 1988), that a fluid with approximately six times the chlorinity of seawater exists at depth within this system. Massoth et al (1989) have discussed the evidence for phase separation at Axial Volcano, where both high- and low-salinity fluids are found. The evidence is quite compelling that active phase separation of seawater is occurring at this site. Massoth et al (1988), in a revisit to the SJdF site, also found that the high chlorinity of the solutions had been maintained for three years. In addition, based on the heat and chemical balance between the SJdF vents and the overlying water column plume, they suggested that the high-temperature, high-salinity fluids were not representative of the vent field as a whole, because a heat and mass balance could not be made. Analysis of a sample of a diffuse water flow from the Plume site at SJdF has shown it to have a chlorinity below that of seawater (K. L. Von Damm, unpublished data). Contrary to the suggestion that phase separation had occurred at some unknown time in the past, resulting in the storage of brine within the oceanic crust at the SJdF site (Von Damm & Bischoff 1987), this finding suggests that phase separation may be an ongoing process at the site. Actively occurring phase separation could resolve the difficulties inherent in storing a three-year supply of brine within the crust, as well as the inconsistencies between the water column plume and vent chemistry data.

If brines (and vapors) exist within the oceanic crust, as suggested by fluid inclusion and other evidence described above, why do most of the hot springs that have been sampled fall within a relatively small compositional range close to seawater chlorinity? One problem relates to the segregation of the two phases from each other. Goldfarb & Delaney (1988) and Fox (1989) have recently discussed mechanisms related to this process, and although both agree that segregation can occur, their models give contrasting results. The model of Fox (1989) suggests that the low-salinity phase should form the diffuse flow, whereas that of Goldfarb & Delaney (1988) suggests that the brines will be the diffuse flow. A second problem relates to the sampling emphasis on "black smokers," which has resulted in an unrepresentative low sampling of the diffuse flows. Since it is the density of the fluids that is primarily responsible for their buoyancy, black smokers may, owing to the necessity to maintain rapid flow rates in order to build chimneys, be of a limited density and hence a limited compositional and temperature range. It is the density difference between the hydrothermal fluid and the overlying seawater that ultimately determines the hydrothermal fluid's buoyancy. McDuff (1988) has pointed out that the density of the hydrothermal fluid will affect the structure of the water column plume it forms. Density may, however, have a more primary control and affect which fluids exit from the seafloor and whether they exist as a diffuse flow. Table 7 gives the density of several different NaCl solutions at conditions representative of those at the seafloor (350°C, 200 bars) and at the higher temperature and pressure conditions (375°C, 400 bars) inferred to occur within the hydrothermal systems. With increasing salinity the density increases markedly, and even with larger increases in temperature (e.g. 450°C) it does not cause a large decrease in density and therefore does not result in a large increase in the density difference from seawater. High-salinity fluids, which have less of a density difference from bottom seawater, will also have less buoyancy, and this may result in lower

Table 7 Comparison of the densities of NaCl solutions similar to known or inferred hydrothermal solution chemistries at conditions representative of the seafloor (350°C, 200 bars) and within the hydrothermal system (375°C, 400 bars)[a]

Fluid	Molality NaCl	T (°C)	P (bars)	ρ (g cm^{-3})
Seawater	0.5	2	200	1.03
"Normal" hydrothermal	0.5	350	200	0.68
		375	400	0.66
Southern Juan de Fuca	1.0	350	200	0.71
		375	400	0.70
SJdF brine	3.0	350	200	—
		375	400	0.81
Brine	6.0	350	200	0.95
		375	400	0.94
		450	400	0.85
Distilled water	0	350	200	0.59
		375	400	0.61

[a] Data from Burnham et al (1969), Potter & Brown (1977) and Rogers & Pitzer (1982).

exit velocities on the seafloor. This lower velocity may also provide a longer transit time for the fluids to reach the seafloor, which may result in conductive cooling. The net effect of these processes may be that the highest salinity fluids have not been sampled because they appear as the diffuse flows, which are primarily identified by their "shimmering" (caused by their density differences with seawater). Similarly, in addition to the reasons given by Fox (1989) for the low-salinity phases to be diffuse flows, these solutions, although having the needed buoyancy to rise to the seafloor, will contain low metal and silica contents. Consequently, they cannot seal their channels by precipitation of metal sulfide and silica minerals and hence are more likely to entrain cold seawater "groundwater" during their passage through the crust to the seafloor. This entrainment may result in their cooling and hence a lowering of their velocity, with the result that they appear at the seafloor primarily as diffuse flows. An anhydrite chimney that is being formed as low-salinity and metal-poor fluids debouch from the seafloor at Axial Volcano (Massoth et al 1989) may result from an unusually tight "plumbing system" below the seafloor, since no other anhydrite chimneys have been observed.

While invoking phase separation as the primary mechanism to create high- and low-salinity seafloor hydrothermal fluids can explain many of the observations, it is not without its own problems. The concentrations of many of the dissolved species cannot be definitively used to determine if phase separation has occurred. In general, the metals should be concentrated in the high-salinity phase and the gases in the low-salinity phase. A specific example is the relationship between Fe, chloride, and H_2S. The higher chlorinity fluids appear to have $Fe/H_2S > 1$, while the inverse is true for the lower chlorinity fluids. In general, Fe content correlates with chloride content and is anticorrelated with H_2S content, but whether this is the result of Fe being primarily controlled by chloride-complexing or the solubility of Fe-sulfide minerals (or even some other factor) cannot be uniquely determined. The gas and isotopic data, which are of more limited availability for many of the vent fluids, in many cases do not neccssitate phase separation and may even appear to argue against it. Welhan & Craig (1979) first addressed this issue with respect to the 21°N EPR fluids, most of which have chlorinities close to seawater. If phase separation were the primary mechanism responsible for chloride variability, one would expect to see the highest gas contents in the lowest chlorinity fluids, and vice versa. Similarly, for the species with more than one isotope, the heavy isotope would be expected to be enriched in the high-chlorinity phase. Both of these simple statements are complicated by the ongoing water-rock reactions. An example is the case of sulfur, whose cycle appears to be strongly influenced by additional reduction of heavy-seawater sulfate in the hydrothermal upflow zone (Woodruff & Shanks 1988). The oxygen isotopic data for the SJdF fluids are at least internally consistent, with the heavier solutions being the ones of highest chlorinity. These fluids are, however, lighter than lower chlorinity fluids found at other areas, such as at 21°N EPR. The reasons may be attributable to the extent and specific conditions of alteration occurring in the subsurface, as these isotopes are influenced by rock-water interactions in addition to phase separation. Cathles (1983) has demonstrated how the oxygen isotopic composition of the fluid and rock in a hydrothermal system can evolve with time. It may be that the isotopic data and chlorinities are not consistent from hydrothermal system to hydrothermal system because of differences between the evolutionary state of these systems, but that the data should be consistent within a single system.

MINERALOGY OF THE CHIMNEYS

Just as the fluid compositions retain certain common characteristics among all the vent areas studied despite individual differences, so too are there similarities and yet differences in the mineralogy of the chimneys. The iron sulfides (pyrite and pyrrhotite) are the most commonly observed minerals, followed by zinc sulfides (sphalerite and wurtzite) and variable amounts of copper sulfides (primarily isocubanite, bornite, and chalcopyrite). Lesser amounts of the lead sulfide galena have also been described from some areas. Several authors have presented models of chimney growth (Haymon 1983, Goldfarb et al 1983, Tivey & Delaney 1986, Graham et al 1988, Koski et al 1988), and there is a consensus that the growth of a chimney begins with an anhydrite ($CaSO_4$) shell. Anhydrite will form when seawater is heated to temperatures greater than ~130°C. It is commonly found in active chimneys but is absent from most extinct chimneys, presumably owing to its higher solubility under cool, seafloor conditions. Lesser amounts of barite are also found in some chimneys. Magnesium silicates and silica (as either amorphous silica or quartz) have also been described from a number of sites. Unusual or new minerals that have been described from one or more sites include caminite (a Mg-hydroxide-sulfate-hydrate) at 21°N EPR and other sites (Haymon & Kastner 1986); and a hydrated Zn, Fe-hydroxychlorosulfate, a (Mn, Mg, Fe)-hydroxide or hydroxy-hydrate, lizardite ($Mg_3Si_2O_5(OH)_4$), starkeyite ($MgSO_4 \cdot 4H_2O$), and anastase (TiO_2) at SJdF (Brett et al 1987). Aragonite ($CaCO_3$) has only been found in MAR samples (Thompson et al 1988). Chimneys on sedimented ridge crests, of which the Guaymas Basin is the best described, in general contain the same minerals but in quite different abundances from those on unsedimented ridges. Carbonate (primarily calcite) is much more abundant, as are galena and the sulfate minerals anhydrite and barite (Peter & Scott 1988). Organic matter also forms a major constituent of the chimneys at both Guaymas Basin and the Escanaba Trough. Escanaba Trough sulfides are also unusual for the amounts of arsenic, antimony, and silver that they contain (Koski et al 1988).

The general model of chimney growth includes the formation of an anhydrite shell due to the rapid mixing of the calcium-rich vent water and the sulfate-rich seawater. The building of the anhydrite shell occurs quite rapidly: Several observations from submersibles have noted growth rates on the order of centimeters to tens of centimeters per day. The deposition of metal sulfides then commences, and as the chimney walls thicken, so too does their isolation and insulation from seawater, which results in decreased mixing, a rise in temperature, and a progressive change in the mineral assemblage deposited. Owing to the temperature gradient through the wall, a "zone refining" occurs as previously deposited minerals are transformed to other mineral phases. In many cases, concentric mineral banding becomes well developed within the chimney walls.

In some cases the relationship of the chimney mineralogy to the fluid composition is quite clear. Some fluids that are zinc rich and copper poor appear to issue primarily from zinc-rich chimneys, and the alkalinity- and relatively lead-rich fluids at Guaymas Basin deposit chimneys containing abundant calcite and more galena. In other cases the relationship is less clear. Peter & Scott (1988) have described fluid inclusions from the Guaymas Basin chimneys that are much more saline than any fluids presently found in this area. Woodruff & Shanks (1988) and Bluth & Ohmoto (1988) have found substantial differences between the sulfur isotopic content of the vent fluids and that of the sulfide minerals of the chimneys. Several other authors (e.g. Marchig et al 1988) have noted other changes within the chimneys that lead them to suggest that the composition of the vent fluids has evolved through time.

In addition to the classic chimney shape, which narrows toward the top and may consist of multiple spires, several other morphologies have been noted. These include pagoda-shaped chimneys at Guaymas Basin, asparagus-shaped chimneys at SJdF, and onion-shaped chimneys at TAG, in addition to the flanges noted on Endeavour segment (Goldfarb 1988). Sizes vary from the tiny "fairy castles" on SJdF (on a scale of centimeters) to chimneys several tens of meters in height. The chimneys are unstable, and it is often possible to see collapsed chimneys being incorporated into sulfide mounds. Our understanding of the process of sulfide deposition on the seafloor is limited by our ability to sample only the uppermost, rather spindly chimneys that a submersible can most easily break off. Knowledge of the interior of these mounds is inferred from onland analogues. Similarly, the subsurface extent of these mounds is poorly known. Many hydrothermally active areas contain extensive lava drain-back features, and presumably a fair amount of void space exists below a thin lava skin. These voids may provide trapping areas for sulfide that would otherwise be dispersed as particles of smoke. It is currently thought that the sediment-hosted systems may contain larger deposits owing to higher trapping efficiencies. To date, the largest sulfide deposits on unsedimented ridges appear to be those at the Galapagos spreading center (Embley et al 1988), the Endeavour segment (Tivey & Delaney 1986), and the TAG area (Thompson et al 1988).

FLUXES

Several key questions related to seafloor hydrothermal activity remain: What is the net flux of these solutions to the ocean? What is their present influence on seawater chemistry? What has this influence been throughout geologic time? With the discovery of the GSC vents, Jenkins et al (1978) tied the flux to the global ^{3}He and heat fluxes to arrive at global hydrothermal fluxes. Subsequent authors challenged these values (Hart & Staudigel 1982, Mottl 1983), partly on the basis that they required more K to be input than was present in the amount of new crust generated each year. The issue has gotten more complicated with the realization that the

^{3}He/heat ratio varies between vent areas (Lupton et al 1989); with the continued debate over how much of the conductive heat flow anomaly at spreading centers to ascribe to convection of high-temperature axial hot springs; and, as additional hot springs have been sampled, with the realization that their chemistry is not uniform. Sampling of hydrothermal fluids at the ridge axis has concentrated on the highest temperature "black smokers," and the chemistry, as well as the relative importance in transporting heat, of the ubiquitous diffuse flows remains to be defined. Based on the conductive heat flow anomaly, convection of fluids through the oceanic crust should extend over a large area on the ridge flanks to crust millions of years old. Very few observations of these fluids have been made (e.g. Maris et al 1984, Leinen et al 1987), and their chemistry and average temperature remain poorly known, although their volumetric input to the ocean may be much larger than that from the axial springs (COSOD II 1987). Additional complications arise from events such as the megaplumes, which added the annual heat equivalent of an estimated 200–2000 high-temperature vents (Baker et al 1987), and the unknown importance of megaplume-type events on a global scale. Although the influence of hydrothermal activity is evaluated primarily on the basis of the chemistry of the solutions themselves, recent work has shown that the particles in the hydrothermal plumes may actually scavenge a significant proportion of certain dissolved species (e.g. P, As, V, rare earth elements) from seawater (Feely et al 1988, Olivares & Owen 1988, Metz & Trefry 1988). The river fluxes are also not well known for many trace elements, which makes it difficult to evaluate the relative importance of the river fluxes versus the hydrothermal fluxes. Palmer & Edmond (1989) have recently suggested the use of strontium isotopes to constrain the relative importance of river and hydrothermal fluxes. They favor an even higher axial flux than previously suggested, based on the average strontium concentrations and isotopic signatures in rivers and in high-temperature hydrothermal fluids. The discrepancy in the alkali metal fluxes may result from the reaction of the hydrothermal fluids with previously altered, and hence alkali-enriched, crust.

The importance of the flux of hydrothermal fluids to the ocean will continue to be debated with respect to the river flux and to the sink in low-temperature alteration of the oceanic crust, e.g. weathering of rocks on the seafloor. Hydrothermal alteration is probably the main source of iron, manganese, and several of the alkali metals to the ocean, but as a result of the low-temperature weathering-type reactions, the oceanic crust is probably a net sink for the alkalis (Thompson 1983). The relative importance of these various sources and sinks remains unclear for most of the other elements.

SUMMARY

Seafloor hydrothermal activity, often manifested as "black smokers," occurs in a variety of locations and geologic settings. Chlorinities range from approximately one third to twice the seawater value, with other dissolved constituents varying in concert. All of the fluids and chimneys show a certain consistency, although individual differences occur between different vent areas as well as between individual vents separated by only a few tens of meters. Although much progress has been made in understanding the controls on the fluids and chimneys in individual areas, extension to a global context remains difficult. High-salinity fluids occur within the oceanic crust, but phase separation is not the only mechanism to create them. These mechanisms have not yet been unequivocally identified. Uncertainty remains in quantifying the hydrothermal fluxes and in evaluating their overall influence on oceanic chemistry due to unknown compositional and geographic variabilities.

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