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### 8.7 Hydrothermal Processes

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#### 8.7.1 Introduction

#### 8.7.1.1 What Is Hydrothermal Circulation?

Hydrothermal circulation occurs when seawater percolates downward through fractured ocean crust along the volcanic/ tectonic mid-ocean ridge system. The seawater is first heated and then undergoes chemical modification through reaction with the host rock as it continues downward, reaching maximum temperatures which can exceed 400 °C. At these temperatures, the fluids become buoyant and rise rapidly back to the seafloor where they are expelled into the overlying water column. Seafloor hydrothermal circulation plays a significant role in the cycling of energy and mass between the solid earth and the oceans; the first identification of submarine hydrothermal venting and their accompanying chemosynthetically based communities in the late 1970s remains one of the most exciting discoveries in modern science. The existence of some form of hydrothermal circulation had been predicted almost as soon as the significance of ridges themselves was first recognized, with the emergence of plate tectonic theory. Magma wells up from the Earth's interior along 'spreading centers' or 'mid-ocean ridges' to produce fresh ocean crust at a rate of  $\sim 20 \text{ km}^3 \text{ year}^{-1}$ , forming new seafloor at a rate of  $\sim$ 3.3 km<sup>2</sup> year<sup>-1</sup> (Parsons, 1981; White et al., 1992). Fast-spreading ridges are thought to have a broad region of upwelling mantle that focuses magma toward the axis (Forsyth et al., 1998) through decompression melting (Reynolds et al., 1992; Sparks and Parmentier, 1993), with recent evidence suggesting that magma might form and rise through the system in a matter of decades (Rubin et al., 2005). The young oceanic lithosphere formed in this way cools as it moves away from the ridge crest. Although much of this cooling occurs by upward conduction of heat through the lithosphere, early heat-flow studies quickly established that a significant proportion of the total heat flux must also occur via some additional convective process (Figure 1), that is, through



**Figure 1** Oceanic heat flow versus age of ocean crust. Data from the Pacific, Atlantic, and Indian oceans averaged over 2 Ma intervals (circles) depart from the theoretical cooling curve (solid line), indicating convective cooling of young ocean crust by circulating seawater. Reproduced from Stein CA and Stein S (1994) Constraints on hydrothermal heat flux through the oceanic lithosphere from global heat flow. *Journal of Geophysical Research* 99: 3081–3095.

circulation of cold seawater within the upper ocean crust (Anderson and Silbeck, 1981).

The first geochemical evidence for the existence of hydrothermal vents on the ocean floor came in the mid-1960s when investigations in the Red Sea revealed deep basins filled with hot, salty water (40-60 °C) and underlain by thick layers of metal-rich sediment (Bischoff, 1969). Because the Red Sea represents a young, rifting ocean basin, it was speculated that the phenomena observed there might also prevail along other young mid-ocean ridge spreading centers. An analysis of coretop sediments from throughout the world's oceans (Figure 2) revealed that such metalliferous sediments did, indeed, appear to be concentrated along the newly recognized global ridge crest (Bostrom et al., 1969). Another early indication of hydrothermal activity came from the detection of plumes of excess <sup>3</sup>He in the Pacific Ocean basin (Clarke et al., 1969) – notably the >2000-km-wide section in the South Pacific (Lupton and Craig, 1981) - because <sup>3</sup>He present in the deep ocean could only be sourced through some form of active degassing of the Earth's interior, at the seafloor.

One area where early heat-flow studies suggested hydrothermal activity was likely to occur was along the Galapagos spreading center in the eastern equatorial Pacific Ocean (Anderson et al., 1976). In 1977, scientists diving at this location found hydrothermal fluids discharging chemically altered seawater from young volcanic seafloor at elevated temperatures up to 17 °C (Edmond et al., 1979). Two years later, the first high-temperature  $(380\pm30$  °C) vent fluids were found at 21° N on the East Pacific Rise (EPR) (MacDonald et al., 1980) with fluid compositions remarkably close to those predicted from the lower temperature Galapagos findings (Edmond et al., 1979). Since that time, hydrothermal activity has been documented at numerous locations throughout the Pacific, central Atlantic, and Indian oceans (Baker and German, 2004; Baker et al., 2006, 2008; German et al., 2006, 2008a, 2010a; Pedersen et al., 2010; Tao et al., 2012), with evidence from characteristic chemical anomalies in the ocean water column and data from new deep-submergence technologies (German et al., 2008b) - of its occurrence in even the most remote and slowly spreading ocean basins (Figure 3), from the polar seas of the Southern Ocean (German et al., 2000; Klinkhammer et al., 2001; Rogers et al., 2012) to the extremes of the ice-covered Arctic (Edmonds et al., 2003; Pedersen et al., 2010).

The most spectacular manifestation of seafloor hydrothermal circulation is without doubt the high-temperature (>400 °C) 'black smokers' that expel fluids from the seafloor along all parts of the global ocean ridge crest. In addition to being visually compelling, vent fluids also exhibit important enrichments and depletions when compared to ambient seawater. Many of the dissolved chemicals released from the Earth's interior during venting precipitate upon mixing with the cold, overlying seawater, generating thick columns of black metal sulfide- and oxide mineral-rich smoke - hence the colloquial name for these vents: 'black smokers' (Figure 4). In spite of their common appearance, high-temperature hydrothermal vent fluids actually exhibit a wide range of temperatures and chemical compositions, which are determined by subsurface reaction conditions. Despite their spectacular appearance, however, high-temperature vents may only represent a small



**Figure 2** Global map of the (Fe+Mn+Al):Al ratio for surficial marine sediments. Highest ratios mimic the trend of the global mid-ocean ridge axis. Reproduced from Bostrom K, Peterson MNA, Joensuu O, Fisher DE (1969) Aluminum-poor ferromanganoan sediments on active ocean ridges. *Journal of Geophysical Research* 74: 3261–3270.



**Figure 3** Schematic map of the global ridge crest showing the major ridge sections along which active hydrothermal vents have already been found (red symbols) or are known to exist from the detection of characteristic chemical signals in the overlying water column (yellow symbols). A continuously updated database of known and detected hydrothermal vent sites, including an interactive version of this map, is maintained by the international InterRidge program at http://www.interridge.org/irvents/.



Figure 4 Photograph of a 'black smoker' hydrothermal vent emitting hot  $(>350 \,^{\circ}C)$  fluid at a depth of  $\sim 3000 \,$ m into the base of the oceanic water column at the Logatchev hydrothermal field, northern Mid-Atlantic Ridge. Photograph courtesy of MARUM, Bremen, DE.

fraction of the total hydrothermal heat flux close to ridge axes, which may be dominated by much lower temperature diffuse flow exiting the seafloor at temperatures comparable to those first observed at the Galapagos vent sites in 1977 (Elderfield and Schultz, 1996; Mottl, 2003). While the relative importance of high- and low-temperature axial hydrothermal venting remains a topic of active debate (Davis et al., 2003; German and Lin, 2004; Vance et al., 2009), a current preferred estimate would suggest that perhaps 20% of the heat available at midocean ridges is released via high-temperature black-smoker venting (Nielsen et al., 2006).

Most studies of seafloor hydrothermal systems to date have focused on the currently active plate boundary ( $\sim 0-1$  Ma crust), but pooled heat-flow data from throughout the world's ocean basins (Figure 1) indicate that convective heat loss from the oceanic lithosphere actually continues in the crust from 0 to 65 Ma in age (Stein et al., 1995). Indeed, most recent estimates would indicate that hydrothermal circulation through this older (1–65 Ma) section, termed 'flank fluxes,' may be responsible for some 70% or more of the total hydrothermal heat loss associated with spreading plate boundaries – either in the form of warm (20–65 °C), altered seawater or as cooler water which is only much more subtly chemically altered (Mottl, 2003; Nielsen et al., 2006).

When considering the impact of hydrothermal circulation upon the chemical composition of the oceans and their underlying sediments, however, attention returns – for many elements – to the high-temperature black-smoker systems. Only here do many species escape from the seafloor in high abundance. When they do, the buoyancy of the hightemperature fluids carries them hundreds of meters up into the overlying water column as they mix and eventually form nonbuoyant plumes containing a wide variety of both dissolved chemicals and freshly precipitated mineral phases. The processes active within these dispersing hydrothermal plumes play a major role in determining the net impact of hydrothermal circulation upon the oceans and marine geochemistry.

#### 8.7.1.2 Where Does Hydrothermal Circulation Occur?

Hydrothermal circulation occurs predominantly along the global mid-ocean ridge crest, a near-continuous volcanic chain that extends over  $\sim 60000$  km (Figure 3). Starting in the Arctic basin, this ridge system extends south through the Norwegian-Greenland Sea as far as Iceland and then continues southward as the Mid-Atlantic Ridge (MAR), passing through the Azores and onward into the far South Atlantic where it reaches the Bouvet Triple Junction, near 50° S. To the west, a major transform fault connects this triple junction to the Sandwich and Scotia plates that are separated by the East Scotia Ridge (an isolated back-arc spreading center). These plates are also bound, to north and south, by two further major transform faults that extend farther west between South America and the Antarctic Peninsula before connecting to the south Chile trench. To the east of the Bouvet Triple Junction lies the SW Indian Ridge, which runs east and north as far as the Rodriguez Triple Junction (~25° S, 70° E) where the ridge crest splits in two. One branch, the Central Indian Ridge, extends north through the western Indian Ocean and Gulf of Aden, ending at the incipient ocean basin that is the Red Sea (Section 8.7.1.1). The other branch of the global ridge crest branches southeast from the Rodriguez Triple Junction to form the SE Indian and Pacific-Antarctic ridges which extend across the entire southern Indian Ocean past Australasia and on across the southern Pacific Ocean as far as ~120°W, where the ridge again strikes north. The ridge here, the EPR, extends from  $\sim$  55° S to 30° N but is intersected near 30° S by the Chile Rise which connects to the south Chile trench. Further north, near the equator, the Galapagos spreading center meets the EPR at another triple junction. The EPR (and, hence, the truly continuous portion of the global ridge crest, extending back through the Indian and Atlantic oceans) finally ends where it runs 'on land' at the northern end of the Gulf of California. There, the ridge crest is offset to the NW by a transform zone more commonly known as the San Andreas Fault, which continues offshore once more, off northern California at  $\sim 40^{\circ}$  N, to form the Gorda, Juan de Fuca, and Explorer ridges - all of which hug the NE Pacific/North American margin up to  $\sim$ 55° N. Submarine hydrothermal activity is also known to be associated with the back-arc spreading centers formed behind ocean-ocean subduction zones. These occur predominantly around the northern and western margins of the Pacific Ocean, from the Aleutians via the Japanese archipelago and Indonesia all the way south to New Zealand but also arise in the Andaman Sea (eastern Indian Ocean), the East Scotia Rise and Bransfield Strait (Antarctica), and the Mid-Cayman Rise (western Caribbean Sea). In addition to ridge-crest hydrothermal venting, similar circulation also occurs associated with hot spot-related intraplate volcanism - most prominently in the central and western Pacific Ocean (e.g., Hawaii, Samoa, and Society Islands), but these sites are much less extensive, laterally, than ridge crests and back-arc spreading centers combined. A continuously updated database of hydrothermal vent sites (both those that have been investigated at the seafloor and those which have only been detected based on water-column chemical anomalies) is maintained by the international Inter-Ridge program in their Vents Database (http://www.interridge. org/irvents).

As described earlier, the first sites of hydrothermal venting to be discovered are located along the intermediate- to fastspreading Galapagos spreading center (6 cm year $^{-1}$ ) and northern EPR (6-15 cm year<sup>-1</sup>). A not unreasonable hypothesis influenced heavily by these early observations, but only formalized nearly 20 years later (Baker et al., 1996), proposed that the incidence of hydrothermal venting along any unit length of ridge crest should correlate positively with spreading rate because the latter is intrinsically linked to the magmatic heat flux at that location. Thus, the faster the spreading rate, the more abundant the hydrothermal activity, with the most abundant venting expected and found (Charlou et al., 1996; Feely et al., 1996; Gamo et al., 1997; Von Damm et al., 2003) along the superfast-spreading southern EPR (17-19°S) where the ridge spreading rate is among the fastest known  $(>14 \text{ cm year}^{-1}).$ 

Evidence for widespread and long-lived venting has also been found more recently, however, along some of the slowest-spreading sections of the global ridge crest in the SW Indian Ocean (Bach et al., 2002; German et al., 1998; Tao et al., 2012), in the Greenland/Arctic basins (Connelly et al., 2007; Edmonds et al., 2003; Petersen et al., 2011), and at the Mid-Cayman Rise (German et al., 2010a), providing support for models of hydrothermal activity involving more than just magmatic activity (German and Lin, 2004). Further, in December 2000, an entirely new form of seafloor hydrothermal activity, in a previously unexplored geologic setting, was discovered (Fruh-Green et al., 2003; Kelley et al., 2001, 2005). Geologists diving at the Atlantis fracture zone, which offsets part of the MAR near 30° N, found moderate-temperature fluids (40-90 °C) exiting from tall (up to 20 m) chimneys, formed predominantly from calcite (CaCO<sub>3</sub>), aragonite (CaCO<sub>3</sub>), and brucite (Mg(OH)<sub>2</sub>). These compositions are quite unlike previously documented hydrothermal vent fluids (Section 8.7.2), yet their geologic setting is one which recurs frequently along slow- and very slow-spreading ridges. To date, tectonically controlled settings appear to account for approximately 50% of all known vent sites along the slow-spreading MAR (German et al., 2010b) which coincides with the observation that asymmetric, amagmatic spreading may account for up to 50% of all plate separation, along axis and along slowand ultraslow-spreading ridges (Escartin et al., 2008). Hence, it is now clear that the influence of tectonic effects imposed by detachment-related faulting plays an important role, providing permeability that allows seawater-derived hydrothermal fluid to penetrate deeply and mine heat from the lower crust and upper mantle before venting at sites distant from the heat source, providing important distinctions between hydrothermal systems at slow- and fast-spreading ridges (Allen and Seyfried, 2004; McCaig et al., 2007).

However, most exploration in the recent past has focused upon the medium- and fast-spreading ridge crests that lie closest to nations with major oceanographic research fleets and in the low to mid-latitudes where weather conditions are most favorable toward use of key research tools such as submersibles and deep-tow vehicles. Consequently, numerous active vent sites are known along the NE Pacific ridge crests and in the western Pacific (Figure 3). While the northern MAR has received moderately comparable attention, this represents just one portion of the 50% of the global mid-ocean ridge system that is slow- or ultraslow-spreading (Sinha and Evans, 2004). Other parts of the global ridge crest (notably those in the southern Atlantic, Indian, and Pacific oceans) remain almost completely unexplored but are increasingly the focus for planned future international collaborations (German et al., 2011).

# 8.7.1.3 Why Should Hydrothermal Fluxes Be Considered Important?

Since hydrothermal systems were first discovered on the seafloor, determining the magnitude of their flux to the ocean and, hence, their importance in controlling ocean chemistry has been the overriding question that numerous authors have tried to assess (Davis et al., 2003; Edmond et al., 1979, 1982; Elderfield and Schultz, 1996; Jupp and Schultz, 2004; Mottl, 2003; Nielsen et al., 2006; Schultz and Elderfield, 1997; Staudigel and Hart, 1983; Stein and Stein, 1994; Vance et al., 2009; Von Damm et al., 1985a). Of the total heat flux from the interior of the Earth (~43 TW), approximately 32 TW is associated with cooling through ocean crust, and, of this, some 34% is estimated to occur in the form of hydrothermal circulation through ocean crust up to 65 Ma in age (Stein and Stein, 1994). The heat supply that drives this circulation is of two parts, magmatic heat, which is actively emplaced close to the ridge axis during crustal formation, and heat that is conducted into the crust from cooling lithospheric mantle, which extends out beneath the ridge flanks.

At the ridge axis, the magmatic heat available from crustal formation can be summarized as (1) heat released from the crystallization of basaltic magma at emplacement temperatures (latent heat) and (2) heat mined from the solidified crust during cooling from emplacement temperatures to hydrothermal temperatures, assumed by Mottl (2003) to be  $1175\pm25$ and  $350 \pm 25$  °C, respectively. For an average crustal thickness of ~6 km (White et al., 1992), the mass of magma emplaced per annum is estimated at  $6 \times 10^{16}$  g year<sup>-1</sup>, and the maximum heat available from crystallization of this basaltic magma and cooling to hydrothermal temperatures is  $2.8\pm0.3$  TW (Elderfield and Schultz, 1996; Mottl, 2003). If all this heat were transported as high-temperature hydrothermal fluids expelled from the seafloor at 350 °C and 350 bar, this heat flux would equate to a volume flux of  $5-7 \times 10^{16}$  g year<sup>-1</sup>. It should be noted, however, that the heat capacity  $(c_p)$  of a 3.2% NaCl solution becomes extremely sensitive to increasing temperature under hydrothermal conditions of temperature and pressure, as the two-phase boundary is approached. Thus, for example, at 350 bars, a moderate increase in temperature near 400 °C could cause an increase in c<sub>p</sub> approaching an order of magnitude, resulting in a concomitant drop in the water flux required to transport this much heat (Driesner, 2007; Jupp and Schultz, 2000).

Of course, high-temperature hydrothermal fluids may not be entirely responsible for the transport of all the axial hydrothermal heat flux. Elderfield and Schultz (1996) considered a uniform distribution, on the global scale, in which only 10% of the total axial hydrothermal flux occurred as 'focused' flow (heat flux = 0.2–0.4 TW; volume flux= $0.3-0.6 \times 10^{16}$ g year<sup>-1</sup>). For comparison, a more recent calculation of the high-temperature water flux based on the mass balance of TI in the oceans yields a value of  $0.17-2.93 \times 10^{16}$  g year<sup>-1</sup>, which is roughly equivalent to 5-80%, with a best estimate of 20%, of the thermal energy available at mid-ocean ridge axes (Nielsen et al., 2006). The remainder of the axial heat flux is likely transported by a much larger volume flux of lower temperature fluid (Elderfield and Schultz, 1996; Ginster et al., 1994; Nielsen et al., 2006). However, how might such lowtemperature flow manifest itself? On a more fundamental level, should diffuse (low-temperature) fluid be considered as diluted high-temperature vent fluid, conductively heated seawater, or some combination of the above? Where might such diffuse fluxes occur? Even if the axial hydrothermal heat flux was restricted to 0-0.1 Ma crust, the associated fluid flow might still extend over a range of kilometers from the axis on mediumfast ridges - that is, out onto young ridge flanks. For slow- and ultraslow-spreading ridges (e.g., the MAR), by contrast, all 0-0.1 Ma and, indeed, all 0-1 Ma crustal circulation would still be expected to occur within the confines of the axial rift valley (order 10 km wide). The partitioning of 'axial' and 'nearaxial' hydrothermal flow, on fast and slow ridges and between 'focused' and 'diffuse' flow, remains poorly constrained in the majority of mid-ocean ridge settings and is an area of active study and debate.

On older ocean crust (1-65 Ma), hydrothermal circulation is driven by upward conduction of heat from cooling of the underlying lithospheric mantle. Heat fluxes associated with this process are estimated at  $7 \pm 2$  TW (Mottl, 2003). These values are significantly greater than the total heat fluxes associated with axial and near-axis circulation combined and represent as much as 75-80% of Earth's total hydrothermal heat flux, >20% of the total oceanic heat flux, and >15% of the Earth's entire heat flux. Mottl and Wheat (1994) chose to subdivide the fluid circulation associated with this heat into two components, warm (>20 °C) and cool (<20 °C) fluids, which exhibit large and small changes in the composition of the circulating seawater, respectively. Constraints from the Mg mass balance of the oceans suggest that the cool (less altered) fluids carry some 88% of the total flank heat flux, representing a cool-fluid water flux (for 5-20 °C fluid temperatures) of  $1-4 \times 10^{19}$ g year<sup>-1</sup> (Mottl, 2003). A more recent estimate, derived from Tl-based calculations, indicates that lowtemperature hydrothermal volume fluxes at ridge flanks could be an order of magnitude greater, at  $0.2-5.4 \times 10^{20}$  $g year^{-1}$  (Nielsen et al., 2006). This, in turn, would imply that the circulating fluids might have an average temperature anomaly of only 0.1-3.6 °C, and at these low temperatures, both Mg and Sr would be expected to be largely unreactive. This could explain why ridge-flank hydrothermal fluxes appear insufficient to balance the modern marine budgets of 87Sr/86Sr and Mg; although, conversely, any such putative imbalance in global budgets could relate more to variably high Quaternary weathering fluxes (Nielsen et al., 2006; Vance et al., 2009).

To put hydrothermal volume fluxes in context, the maximum flux of cool (<20 °C) hydrothermal fluids calculated above (from, e.g., Tl mass balance) is comparable to or even greater than the global riverine water flux of  $3.7-4.2 \times 10^{19}$  g year<sup>-1</sup> (Palmer and Edmond, 1989). The flux of high-temperature fluids close to the ridge axis, by contrast, is ~1000-fold lower. Nevertheless, for an ocean volume of *c*.  $1.4 \times 10^{24}$  g, this still yields an (geologically short) oceanic residence time, with respect to high-temperature circulation, of ~20–30 My – and

 
 Table 1
 Heat and volume fluxes associated with seafloor hydrothermal circulation

(I) Summary of	global heat fluxes		
	Heat flux from the	43 TW	
	Earth's interior		
	Heat flux associated with ocean crust	32 TW	
	Seafloor hydrothermal heat flux	11 TW	
(II) Global hydro	thermal fluxes: heat and wa	ater	
		Heat flux (TW)	Water flux (10 <sup>16</sup> g year <sup>-1</sup> )
Axial flow (0-1	Ma)		, , , , , , , , , , , , , , , , , , ,
,	All flow at 350 °C	2.8	5.6
	20% @ 350 °C/80% @ 5 °C	2.8	375
	Hydrothermal plumes (20%)	-	$\sim\!11~000$
Off-axis flow	X ,	$7\pm2$	2000–10 000
(1–65 Ma)			
Global riverine flux		-	$\sim$ 4000

the hydrothermal fluxes will be important for those elements which exhibit changes in high-temperature fluid concentrations more than 1000-fold greater than river waters. Furthermore, high-temperature fluids emitted from black-smoker hydrothermal systems typically entrain large volumes of ambient seawater during the formation of buoyant and neutrally buoyant plumes (Section 8.7.5) with typical dilution ratios of  $\sim 10^4$ :1 (Lupton, 1995). If 20% of the fluids circulating at high temperature through young ocean crust are entrained into hydrothermal plumes, therefore, the total water flux through hydrothermal plumes should be comparable to or greater than all other hydrothermal fluxes as well as exceeding the global riverine flux to the oceans (Table 1). The associated residence time of the global ocean, with respect to cycling through hydrothermal plume entrainment, would be  $\sim 10$  ky and, hence, comparable to the mixing time of the global deep-ocean conveyor (Broecker and Peng, 1982). From that perspective, therefore, one can anticipate that hydrothermal circulation should play an important role in the marine geochemistry of any tracer that exhibits a residence time greater than c. 1–10 ky in the open ocean.

#### 8.7.1.4 Outline Structure for Rest of this Chapter

The following Section 8.7.2 discusses the chemical composition of hydrothermal fluids, why they are important, what factors control their composition, and how these compositions vary, both in space, from one location to another, and in time. Particular attention is focused on substrate controls intrinsic to crustal (host rock) composition on the chemical evolution of marine hydrothermal fluids. Next (Section 8.7.3), it is identified that the fluxes established thus far represent gross fluxes into and out of the ocean crust associated with high-temperature venting. The other sources and sink terms associated with hydrothermal circulation are then examined, including alteration of the ocean crust, formation of hydrothermal mineral deposits, interactions/uptake within hydrothermal plumes, and settling into deep-sea sediments. Each of these 'fates' for hydrothermal material is then considered in more detail. Section 8.7.4 provides new insights on hydrothermal alteration processes from constraints imposed from in situ studies of the ocean crust as well as a detailed discussion of near-vent deposits, including the formation of polymetallic sulfides and other minerals, as well as near-vent sediments. In Section 8.7.5, a detailed description is presented of the processes associated with hydrothermal plumes, including a brief explanation of basic plume dynamics, a discussion of how plume processes modify the gross flux from high-temperature venting, and further discussions of how plume chemistry can be both determined by, and influence, physical oceanographic and biological interactions. The following Section 8.7.6 discusses the fate of hydrothermal products and concentrates on ridge-flank metalliferous sediments, including their potential for paleoceanographic investigations and role in 'boundary scavenging' processes. The chapter concludes (Section 8.7.7) by identifying some of the unresolved questions associated with hydrothermal circulation which are most in need of further investigation.

#### 8.7.2 Vent-Fluid Geochemistry

#### 8.7.2.1 Why Are Vent-Fluid Compositions of Interest?

The compositions of hydrothermal vent fluids found on the global mid-ocean ridge system are of interest for several reasons; how and why those compositions vary has important implications. The overarching question, as mentioned in Section 8.7.1.3, is to determine how the fluids emitted from these systems influence and control ocean chemistry, on both short and long timescales. This question is very difficult to address in a quantitative manner because, in addition to all the heat flux and related water flux uncertainties discussed in Section 8.7.1, it also requires an understanding of the range of chemical variation in these systems and an understanding of the mechanisms and variables that control vent-fluid chemistries and temperatures. Essentially every hydrothermal vent that is discovered has a different composition (Von Damm, 1995), and it is now known that these compositions often vary profoundly on short (minutes to years) timescales. Hence, the flux question remains a difficult one to answer. Vent-fluid compositions also act as sensitive and unique indicators of processes occurring within young ocean crust, and, at present, this same information cannot be obtained from any other source. The 'window' that vent fluids provide into subsurface crustal processes is especially important because one cannot yet drill deeply into young ocean crust, due to its unconsolidated nature, unless it is sediment covered. The chemical compositions of the fluids exiting at the seafloor provide an integrated record of the reactions and the pressure and temperature (P-T) conditions these fluids have experienced during their transit through the crust. Thus, vent fluids can provide information on the depth of fluid circulation (hence, information on the depth to the heat source) as well as information on the residence time of fluids within the ocean crust at certain temperatures. Because the dissolved chemicals in hydrothermal fluids provide energy sources for microbial communities living within the ocean crust, vent-fluid chemistries can also provide information on whether such communities are active at a given location. Vent fluids may also lead to the formation

of metal-rich sulfide and sulfate deposits at the seafloor. These deposits provide important insights into how metals and sulfide can be transported in the same fluids and, thus, how economically viable mineral deposits are formed. Seafloor deposits also have the potential to provide an integrated history of hydrothermal activity at sites where actively venting fluids have ceased to flow.

#### 8.7.2.2 Processes Affecting Vent-Fluid Compositions

In all known cases, the starting fluid for a submarine hydrothermal system is predominantly, if not entirely, seawater, which is then modified by processes occurring within the ocean crust (see also Chapter 4.16). Four factors have been identified: (1) phase separation, (2) water-rock interaction and phase equilibria, (3) biological processes, and (4) magmatic degassing.

Water-rock interaction and phase separation are processes that are inextricably linked. As seawater passes through the hydrothermal system, it reacts with the rock and/or sediment substrate that is present and becomes compositionally modified (Figure 5). These reactions begin in the recharge zone and continue throughout. When vent fluids exit at the seafloor, what one observes represents the net result of all the reactions that have occurred along the entire hydrothermal flow path. Because the kinetics of most reactions involving minerals and fluids are faster at higher temperatures (Pester et al., 2011; Seewald and Seyfried, 1990; Seyfried and Shanks, 2004), it is assumed that much of the reaction occurs at or near the base of the sheeted dike complex, which can be envisaged as the 'root zone' of the hydrothermal system (Figure 5). Phase separation may also occur at more than one location during the fluid's passage through the crust and may continue as the P-T conditions acting on the fluid change as it rises through the ocean crust, back toward the seafloor. Unless confronted with clear inconsistencies in the chemical data that invalidate this approach, this simple 'flow-through' concept is usually employed as the working model. Even though it is not possible to rigorously constrain the complexities for any given system, it is always important to remember that the true system is likely far more complex than any model employed.

In water-rock reactions, chemical species are both gained and lost from the fluids. In terms of differences from the major element chemistry of seawater, Mg and sulfate are lost and pH is lowered so substantially that all the alkalinity is titrated. The large quantities of Si, Fe, and Mn that are frequently gained may be sufficient for these to become 'major elements' in hydrothermal fluids. For example, Si and Fe can exceed the concentrations of Ca and K, two major elements in seawater. Much of the dissolved sulfate in seawater is lost on the recharge limb of the hydrothermal system because anhydrite (empirical formula: CaSO<sub>4</sub>) precipitates at temperatures of ~130 °C - just by heating seawater (Bischoff and Seyfried, 1978). Exactly where this occurs along the subseafloor flow path, however, depends critically on the magnitude and mechanism of heat exchange between cold seawater and the ocean crust (Coogan, 2008). Because there is more dissolved sulfate than Ca in seawater, on a molar basis, additional Ca would have to be leached from the host rock if more than  $\sim$ 33% of all the available seawater sulfate were to be precipitated in this way.



**Figure 5** Schematic model for fluid–rock reaction and metamorphism within the upper crust at intermediate- to fast-spreading ridges. Fluid recharging the hydrothermal system cools the sheeted dike complex while ultimately being heated by the underlying magma, resulting in high-temperature fluid–rock reaction and phase separation. These reactions can continue throughout the discharge zone within the sheeted dike complex, facilitated by cracking induced by hydrothermal stresses, which maintains high permeability (Tolstoy et al., 2008). The upflow zone likely migrates with time to produce the alteration observed in the sheeted dike complex, as suggested by studies of in situ crustal sections (Alt et al., 2010; Heft et al., 2008) and vent fluids that often show continuously high concentrations of mobile trace elements (Seyfried and Shanks, 2004). Heat- and mass-transfer reactions occur along both recharge and discharge paths, which at the transition from one to the other can be thought of as the 'root zone' for seafloor hydrothermal systems. Reproduced from Coogan LA (2008) Reconciling temperatures of metamorphism, fluid fluxes, and heat transport in the upper crust at intermediate to fast spreading mid-ocean ridges. *Geochemistry, Geophysics, Geosystems* 9: Q02013.

In fact, it is now recognized that significant dissolved sulfate must persist down into the base of the sheeted dike complex, based on the reduction-oxidation (redox) state at depth inferred from high-temperature vent-fluid chemistry (see later discussion). Some seawater sulfate is reduced to H2S, substantial quantities of which may be found in hydrothermal fluids at any temperature, based on information from sulfur isotopes, including <sup>33</sup>S (Ono et al., 2007; Shanks, 2001), as described subsequently. Seawater Mg is lost by the formation of Mg-OH silicates (e.g., chlorite and tremolite). This results in the generation of H<sup>+</sup>, which accounts for the low pH and titration of the alkalinity (Seyfried and Shanks, 2004). Na can also be lost from the fluids due to Na-Ca replacement reactions in plagioclase feldspars, known as albitization. Na does not simply replace Ca in plagioclase but rather is buffered along with Ca by plagioclase-fluid equilibria (Berndt and Seyfried, 1993).

An element that is relatively conservative during water–rock reaction is Cl. Cl is key in hydrothermal fluids because, with the precipitation and/or reduction of sulfate and the titration of  $HCO_3^{-7}/CO_3^{2-}$ , Cl becomes the overwhelming and almost only anion (Br is usually present in the seawater in proportion to Cl). Cl becomes a key component, therefore, because almost all of the cations in hydrothermal fluids are present as chlorocomplexes; thus, the levels of Cl in a fluid effectively determine the total concentration of cationic species that can be present. A fundamental aspect of seawater is that the major ions are present in relatively constant ratios – this forms the basis of

the definition of salinity. Because these constant proportions are not maintained in vent fluids and because Cl is the predominant anion, vent fluids are best discussed in terms of their chlorinity, not their salinity.

Although small variations in Cl may be caused by rock hydration/dehydration, there are almost no mineralogic sinks for Cl in these systems. Therefore, the main process that effects changes in the chloride concentrations in the vent fluids is phase separation (Figure 6). Phase separation is a ubiquitous and dominant process in seafloor hydrothermal systems. To phase separate seawater at typical intermediate- to fast-spreading mid-ocean ridge depths of ~2500 m requires temperatures  $\geq$  389 °C (Bischoff, 1991). This sets a minimum temperature that fluids must have reached, therefore, during their transit through the ocean crust. The greater the depth, the higher the temperature required for phase separation to occur. Vent systems known to date occur at depths of 800-3600 m, requiring minimum temperatures in the range 297-433 °C to phase separate seawater. Seawater is a two-component system,  $H_2O + NaCl$ , to a first approximation and so exhibits different phase separation behavior from pure water. The critical point for seawater (3.2 % NaCl) is 407 °C and 298 bars (Bischoff and Rosenbauer, 1985; Driesner and Heinrich, 2007), compared with 374 °C and 220 bars for pure water. For the two-component system, the two-phase curve does not stop at the critical point but continues beyond it (Figure 6). As a solution crosses the two-phase curve, it will separate into two



**Figure 6** Phase diagram for the system  $H_2O$ –NaCl in pressure–temperature–salinity space. Phase boundaries are indicated by the *V+L* surface, *V+L+H* surface, halite liquidus, critical curve, and critical point of  $H_2O$  (solid black circle). The two-phase boundary of seawater (3.2% NaCl) is also displayed. At temperatures and pressures less than the critical temperature ( $T_c$ ) and pressure ( $P_c$ ) for 3.2% NaCl (~407 °C/30 MPa; Bischoff and Rosenbauer, 1984), seawater has a higher salinity than the conjugate fluid, intersects the limiting liquid–vapor two-phase surface on the liquid side of the critical curve, and the system starts to boil. At temperatures and pressures in excess of *T* c and *P*c, seawater has a lower salinity than the conjugate fluids, intersects the two-phase surface on the vapor side of the critical curve, and starts to condense. The term 'supercritical' to describe phase separation under these conditions should be avoided, especially since fluids of seawater salinity are not uniquely present in subseafloor hydrothermal systems (see text). The overwhelming majority of marine hydrothermal vent fluids have undergone phase separation along their flow path, as indicated by the ubiquitous departure from seawater salinity (Seyfried and Shanks, 2004; Von Damm, 2000, 2004). Reproduced from Driesner T and Heinrich CA (2007) The system  $H_2O$ -NaCl. Part I: Correlation formulae for phase relations in temperature-pressure-composition space from 0 to 1000 °C, 0 to 5000 bar, and 0 to 1 *X*NaCl. *Geochimica et Cosmochimica Acta* 71: 4880–4901.

phases, one with chlorinity greater than seawater and the other with chlorinity less than seawater. If the fluid reaches the twophase curve at temperature and pressure conditions lower than the critical point, boiling will occur, with the generation of a low-chlorinity 'vapor' phase. This phase contains some salt, the amount of which will vary depending on where the two-phase curve is intersected (Driesner and Heinrich, 2007). What is conceptually more difficult to grasp is that when a fluid intersects the two-phase curve at P-T conditions greater than the critical point, the process is called 'supercritical phase separation' and resembles condensation rather than boiling, as a small amount of a relatively high-chlorinity liquid separates out of the supercritical fluid. A seawater-derived solution altered at high temperature typically contains about 3.2 wt% NaCl, and this has often been used as a constraint in modeling supercritical phase separation in subseafloor hydrothermal systems. It is becoming increasingly clear, however, that both vapor and brine can form in these systems, and their subsequent water-rock reaction and mixing with nonphaseseparated seawater can produce a wide range of NaCl concentrations, which in turn may also undergo phase separation. To avoid misunderstanding, therefore, and to be consistent with the terminology used by the broader physical science community, it is recommended that the term 'supercritical phase separation' be avoided, since it cannot always be defined unambiguously, and the term 'condensation' be used instead.

To complete the phase relations in the NaCl-H<sub>2</sub>O system, halite may also precipitate (Figure 6). There is evidence that halite forms, and subsequently redissolves, in some seafloor hydrothermal systems, especially in the aftermath of subseafloor magmatic intrusions (Berndt and Seyfried, 1997; Butterfield et al., 1997; Oosting and Von Damm, 1996; Von Damm, 2000).

The *P*–*T* conditions at which the fluid intersects the twophase curve will determine the relative compositions of the fluid phases as well as their relative amounts (**Figure 6**). Note that the separating surface is not a phase boundary, but comprises instead the locus of all critical isochors, which are lines of constant fluid density emerging from all points along the critical curve of the systems. If the NaCl content is different from seawater, the phase relations in this system change (as noted above), forming a family of curves or surfaces that are a function of the NaCl content, as well as pressure and temperature. The critical point is thus also a function of the salt content and hence is really a critical curve in *P*–*T*–*x* space (where *x* refers to composition).

As phase separation substantially changes the Cl content of vent fluids (values from <6 to  $\sim$ 200% of the seawater concentration have been observed), other chemical species change in concert. It has been shown both experimentally and in the field that most of the cations as well as the anion bromide maintain their element-to-Cl ratios during phase separation (Berndt and Seyfried, 1990; Von Damm, 2000; Von Damm et al., 2003).



**Figure 7** Compositional data for vent fluids. Top panel: time-series data from 'A' vent for Cl and H<sub>2</sub>S concentrations and measured temperature (*T*). When time-series data are available, this type of figure, demonstrating the change in fluid composition in a single vent over time, is commonly used. The data plotted are referred to as 'end-member' data (data from Von Damm et al., 1995 and K.L.Von Damm, unpublished data). Points on the *y*-axis are values for ambient seawater. Note the low-chlorinity (vapor phase) fluids venting initially from A vent; over time, the chloride content increased, and the fluids sampled in 2002 represented the higher-chlorinity liquid (brine) phase. As expected, the concentration of H<sub>2</sub>S, a gas that should partition preferentially into the vapor phase, is anticorrelated with Cl concentration. The vertical axis has 10 divisions with the following ranges: T(°C) 200–405 (ambient seawater is 2 °C), Cl (mmol kg<sup>-1</sup>) 0–800 (ambient is 540 mmol kg<sup>-1</sup>), and H<sub>2</sub>S

Exceptions do occur, however, primarily for those chemical species not present in solution as chloro-complexes. Dissolved gases such as CO2, CH4, He, H2, and H2S are preferentially retained in the low chlorinity or vapor phase. B, too, which is typically present as a hydroxyl complex, shows a slight preference for the vapor phase in laboratory experiments, on a Clnormalized basis (Berndt and Seyfried, 1990). Br is sometimes fractionated from Cl, causing a change in the Br/Cl ratio; this occurs most clearly when halite precipitates or redissolves because Br is preferentially excluded from the halite structure (Berndt and Seyfried, 1990; Oosting and Von Damm, 1996; Von Damm, 2000). Fluids that have deposited halite, therefore, will have a high Br/Cl ratio, while fluids that have dissolved halite will have a low Br/Cl ratio relative to seawater. It is because of the ubiquity of phase separation that vent-fluid compositions are often now viewed as ratios-to-Cl rather than as absolute concentrations. This normalization to Cl must be used when trying to evaluate net gains and losses of chemical species as seawater traverses a hydrothermal system, to correct for the fractionation caused by phase separation. Recent experimental studies have measured the partitioning of numerous other elements in addition to Br and Cl during phase separation in the NaCl-H<sub>2</sub>O system, both in the two-phase (vapor-liquid) region and in the three-phase (vapor-liquid-halite) system, with important implications for subseafloor hydrothermal alteration processes (Foustoukos and Seyfried, 2007a,c; Pokrovski et al., 2005).

Aside from early eruptive fluids (discussed later), the chemical composition of most high-temperature fluids (Figure 7)

(mmol per kg) 0–120 (ambient is 0 mmol kg $^{-1}$ ). Middle panel: Whenever vent fluids are sampled, varying amounts of ambient seawater are entrained into the sampling device. Vent fluids contain nearly 0 mmol kg<sup>-1</sup> Mg, while ambient seawater contains 52.2 mmol kg<sup>-1</sup> Therefore, if actual sample data are plotted as properties versus Mg, leastsquares linear regression fits can be made to the data. The calculated end-member concentration for a given species, which represents the undiluted hydrothermal fluid, is then taken as the point where that line intercepts the y-axis (i.e., the calculated value at Mg = 0 mmol kg<sup>-1</sup>). The range in values exhibited is therefore mostly a result of sampling artifacts, and the resulting property versus Mg plots are referred to as 'mixing' diagrams. While these types of plots were originally used to illustrate vent-fluid data, they have been largely superseded by figures such as those in the upper and lower panels. This figure simply shows the data used to construct the time series represented in the upper panel. Note the different lines for the different years. In some years, samples were collected on more than one date. All samples for a given year are shown by the same symbol shape; the different colors within a year indicate different sample dates. In some years, the chemical composition varied from day to day, but for simplicity, a single line is shown for each year in which samples were collected (Von Damm, 1995, 2000). Lower panel: because the CI content of a vent fluid is a major control on the overall composition of the vent composition, most of the cations vary as a function of the CI content. Variations in the CI content are a result of phase separation. This plot shows the relationship between potassium (K) and CI concentrations in vent fluids in the global hydrothermal database, c.2000. The line represents the ratio for K/Cl in ambient seawater. Closed circles are from EPR 9-10° N following the 1991 eruption, open circles are other 9–10° N data not affected by the eruptive events, triangles are vents on enriched oceanic crust, diamonds are from bare-basalt (MORB) hosted sites, filled diamonds are other sites impacted by volcanic eruptions. Data sources and additional discussion are in Von Damm (2000).

appears to be controlled by equilibrium or steady state with the mineral assemblage in the host rock. Equilibrium requires the assemblage to be at its lowest energy state, but the actual phases present are often metastable and thus represent a steady state rather than true thermodynamic equilibrium. When ventfluid data are analyzed with geochemical modeling codes using current thermodynamic databases, the results typically suggest that equilibrium with appropriate mineral assemblages has been achieved or at least approached. The models cannot be applied rigorously to many of the datasets, however, because the fluids are often close to the critical region, where the thermodynamic data are not well constrained. Based on results from both thermodynamic modeling and elemental ratios, fluid compositional data indicate that not only the major elements but also many minor elements are controlled by equilibrium, or at least steady state, conditions between the fluids and their host rocks. One example is the rare earth elements (REE). REE distributions in hydrothermal fluids are light REE-enriched and exhibit strong positive Eu anomalies, apparently quite unrelated to host rock mid-ocean ridge basalt (MORB) compositions (Figure 8). Klinkhammer et al. (1994) have shown that when these same REE concentrations are plotted versus their ionic radii, the fluid trends not only become linear but also show the same fractionation trend exhibited by plagioclase during magma segregation, indicating that vent-fluid REE concentrations may be controlled by the high-temperature alteration of this particular mineral. More recently, Allen and Seyfried (2005) have confirmed experimentally the effect of dissolved chloride and redox conditions on the relative mobility of REEs during fluid-mineral equilibria at elevated temperatures and pressures.

Two other processes are known to influence the chemistry of seafloor vent fluids: biological processes and magmatic degassing. Evidence for magmatic degassing has been identified at several sites along the global mid-ocean ridge system (Lilley et al., 2003; Lupton et al., 1999). Its effects are typically indicated by high levels of CO<sub>2</sub> and very high He/heat ratios,



Figure 8 End-member REE concentrations in vent fluids from four different black smokers at the 21° N site, East Pacific Rise, normalized to chondrite (REE data from Klinkhammer et al., 1994). NGS, National Geographic Smoker; HG, Hanging Gardens; OBS, Ocean Bottom Seismometer; SW, South West vent.

interpreted to result from recent magma resupply within the crust and attendant degassing. It is not known how this process varies in space and time; hence, its overall importance cannot yet be evaluated. Presumably, every site on the global MOR system undergoes these processes episodically, with sites on fast-spreading and magmatically robust ridge segments more frequently affected, as documented at Axial Volcano (Juan de Fuca Ridge) and the EPR at 9°50′ N.

The fourth process influencing vent-fluid compositions is biological, in the form of either consumption or production of various chemical species. As the current known limit to life on Earth is ~120 °C (Holland and Baross, 2003; Kashefi and Lovley, 2003), this process can affect fluids only at temperatures below this threshold. High-temperature vents should therefore not be subject to these effects, but they may occur in both lower temperature axial diffuse flow and beneath ridge flanks. From observations of seafloor eruptions and intrusion (e.g., diking events), it is known that there are microbial communities living within the ocean crust (Haymon et al., 1993). Their signatures can be seen clearly in at least some low temperature fluids, as noted in particular by changes in the  $H_{2'}$  CH<sub>4'</sub> and  $H_2$ S contents of these fluids (Von Damm and Lilley, 2004). Questions remain as to how widespread such activity may be, which elements are affected, and what the overall impact is on global biogeochemical fluxes.

#### 8.7.2.3 Compositions of Hydrothermal Vent Fluids

#### 8.7.2.3.1 Major element chemistry

The known compositional range of vent fluids is summarized in **Figure 9**. Because no two vents yet discovered have exactly the same composition, these ranges often change with each new site. As discussed in **Section 8.7.2.2**, vent fluids are seawater modified by the loss of Mg, sulfate, and alkalinity and by the gain of many metals, especially relative to chloride.

Vent fluids are acidic, but not as acid as may first appear from pH values measured at 25 °C and 1 atm. The cation H<sup>+</sup> in vent fluids is also present as a chloro-complex, and the extent of complexation increases as P and T rise. At the higher in situ conditions of P and T experienced at the seafloor, therefore, much of the H<sup>+</sup> is incorporated into the HCl-aqueous complex; hence, the activity of H<sup>+</sup> is reduced and the in situ pH is substantially higher than that measured at laboratory temperatures. The  $K_w$  for water also changes as a function of P and T, as does the value of pH at neutrality. For most vent fluids, the in situ pH is 1–2 pH units more acid than neutral, not the  $\sim$ 4 units of acidity that the measured (25 °C, 1 atm) data appear to imply (Ding and Seyfried, 2007; Ding et al., 2005). Most hightemperature vent fluids have (25 °C measured) pH values of  $3.3\pm0.5$ , but a few are more acidic, while some are less acid. If fluids are more acid than pH  $3.3 \pm 0.5$ , it is often an indicator that metal sulfides have precipitated below the seafloor (because such reactions produce protons) or that the solutions have been affected by SO2 and/or HF degassed from magma, as observed for back-arc basins (see below and Mottl et al., 2011). Two mechanisms are known that can cause fluids to be less acidic than the norm: (1) the rock substrate may be so highly altered that it cannot buffer the solutions to as low a pH; (2) organic matter may be present, contributing ammonium, so





Enriched with respect to seawater on a CI-normalized basis Depleted with respect to seawater on a CI-normalized basis Enriched and depleted

Figure 9 Periodic table showing those elements that are enriched in hydrothermal vent fluids relative to seawater (red), depleted (blue), and those that have been shown to exhibit both depletions and enrichments in different hydrothermal fluids (yellow) relative to seawater. All data are normalized to the CI concentration of seawater in order to evaluate true gains and losses relative to the starting seawater concentrations.

that the  $NH_3/NH_4^+$  couple buffers the pH at a higher value (Tivey et al., 1999).

Vent fluids are moderately reducing, as evidenced by the presence of  $H_2S$  rather than sulfate, as well as  $H_2$ ,  $CH_4$ , and significant amounts of Fe<sup>2+</sup> and Mn<sup>2+</sup>. In the immediate aftermath of seafloor eruptions associated with basalt-hosted hydrothermal systems, there can be more  $H_2S$  and/or  $H_2$  than Cl on a molar basis, and it is the prevailing high acidity that dictates that  $H_2S$  rather than  $HS^-$  or  $S^{2-}$  is the predominant form in high-temperature vent fluids (Von Damm, 2000). Free  $H_2$  is derived from water–rock reactions, and there is substantially more  $H_2$  than  $O_2$  in these fluids. Therefore, although redox calculations are typically given in terms of log  $fO_2$ , the redox state is best estimated from the  $H_2/H_2O$  couple. This can then be expressed in terms of log  $fO_2$ . The equilibrium constant for the reaction

$$H_2 + 0.5O_2 = H_2O$$
 [1]

also changes as a function of temperature and pressure. Another way to determine how reducing vent fluids are is to compare them to various mineralogic buffers such as pyritepyrrhotite-magnetite (PPM) or hematite-magnetite-pyrite (HMP). Most vent fluids lie between these two extremes, but there is some systematic variation (Seyfried and Ding, 1993, 1995). The observation that vent fluids are less reducing than the PPM buffer provides one line of evidence that redox reactions contributing to vent-fluid chemistry are buffered by dissolved seawater sulfate penetrating into deeper parts of the system, rather than being quantitatively precipitated as anhydrite within shallower levels of the downwelling limb. Sulfur isotope data are consistent with this observation (see Section 8.7.2.3.2).

Lower-temperature (<100 °C) vent fluids found along the ridge axis are in most known cases a dilution of some amount of high-temperature fluids with seawater, or a low-temperature fluid with a composition close to seawater. There is some evidence for an 'intermediate' fluid, perhaps most analogous to a crustal 'groundwater,' with temperatures of ~150 °C within the ocean crust. Evidence for the latter is found in some Ocean Drilling Program (ODP) data (Magenheim et al., 1992; these are from 6 million-year-old crust, not from the

ridge axis), some high-temperature vent fluids from  $9^{\circ}50'$  N on the EPR (Ravizza et al., 2001), and some very unusual  $\sim 90 °C$  fluids from the southern EPR (O'Grady, 2001). To conclude, the major element composition of high-temperature vent fluids can be described as acidic, reducing, metal-rich NaCl solutions, while lower temperature fluids are typically a dilution of this same material with seawater.

#### 8.7.2.3.2 Trace element and isotope chemistry

Compared to the number of vent fluids sampled and analyzed for their major element data, relatively little trace metal data exist. This is because when hot, acidic vent fluids mix with seawater or even just cool within submersible or ROVdeployed sampling bottles, they become supersaturated with respect to many solid phases which can precipitate. Once this occurs, everything in the sampling apparatus must be treated as one sample: a budget can only be constructed by combining these different fractions. In the difficult sampling environment found at high-temperature vent sites, pieces of chimney are also sometimes entrained into the samplers. It is necessary, therefore, to be able to discriminate between particles that have precipitated from solution in the sampling bottle and contaminant particles that are extraneous to the sample. In addition, water samples are often subdivided into different fractions aboard ship, making accurate budget reconstructions difficult if not impossible to complete. It is because of these difficulties that there are few robust analyses of many trace metals, especially those that precipitate as, or coprecipitate with, metal sulfide phases. Some general statements can, however, be made. In high-temperature vent fluids, most metals are enriched relative to seawater, sometimes by seven to eight orders of magnitude (as is sometimes true for Fe). At least some data exist demonstrating the enrichment relative to seawater of V, Co, Ni, Cu, Zn, As, Se, Al, Ag, Cd, Sb, Cs, Ba, W, Au, Tl, Pb, and the REE. Data also show that Mo and U are often lower than their seawater concentrations. Trace metal concentrations have been shown to vary with substrate, and the relative enrichments of many of these trace metals vary significantly among mid-ocean ridge hydrothermal systems, those located in back-arcs, and those with a significant sedimentary component. Even fewer trace metal data exist

for low-temperature 'diffuse' fluids. The original work on the <20 °C Galapagos spreading center fluids (Edmond et al., 1979) showed these samples to be a mix of high-temperature fluids with seawater, with many of the transition metals present at less than their seawater concentrations due to precipitation and removal below the seafloor. Essentially, the same results were obtained by James and Elderfield (1996) using the MEDUSA system to sample diffuse-flow fluids at TAG (26° N, MAR).

Owing to recent advances in analytical and isotope geochemistry, especially involving multicollector-inductively coupled plasma-mass spectrometry (MC-ICP-MS), nontraditional stable isotopes of some elements have proven enormously useful as tracers in seafloor hydrothermal systems. Such elements include Cu, Fe, and Zn, and metalloids such as Se (Dauphas and Rouxel, 2006; Rouxel et al., 2002, 2003a,b; Zhu et al., 2002), as well as sulfur isotopes <sup>33</sup>S and <sup>36</sup>S (Ono et al., 2006). In the case of the sulfur system, multiple-stable isotope analytical capabilities have shown that various mass-dependent fractionation processes, including diffusion, biological metabolism, and high-temperature equilibrium reactions, can follow slightly different mass-dependent fractionation laws (Farguhar and Wing, 2003; Ono et al., 2006; Young et al., 2002), and may, therefore, be useful, especially coupled with the other nontraditional isotope systems, in resolving fundamental problems involving marine hydrothermal systems.

Rouxel et al. (2008) reported on coupled Fe and S isotope systematics of hydrothermal fluids from the EPR at 9-10° N. Their study confirms results from earlier studies that Fe isotopes in hydrothermal fluids and vent sulfides generally exhibit negative  $\delta^{56}$ Fe values relative to the bulk silicate earth (Figure 10). Variations in Fe isotopic ratios are significant:  $\delta^{56}$ Fe values as low as -0.67‰ and as high as -0.09‰ have been observed in hydrothermal fluids along the MAR and EPR (Dauphas and Rouxel, 2006; Rouxel et al., 2004a, 2008). Processes that may control Fe isotope variability in hydrothermal fluids include: (1) phase separation in the NaCl-H<sub>2</sub>O system where changes in Fe-bearing speciation between vapor and brine might induce Fe isotope fractionation; (2) hightemperature basalt alteration resulting in the transfer and oxidation of Fe between coexisting solid phases, such as olivine and chlorite; and (3) secondary processes associated with the mixing and cooling of end-member vent fluids by seawater within or immediately below seafloor chimney structures (Rouxel et al., 2008), resulting in kinetic isotope effects. Available data from EPR 9-10° N suggest that this latter process may dominate, especially for pyrite/marcasite. The opposite may be true for chalcopyrite, the precipitation of which on chimney walls produces slightly positive (apparent) Fe isotope fractionation factors  $(0.14 \pm 0.09\%)$ , suggesting that fluid-mineral equilibrium may have been achieved or closely approached (Rouxel et al., 2008). Similar processes can be inferred from nontraditional mineral-fluid isotope data for hydrothermal vent systems in the Atlantic (Rouxel et al., 2004a,b).

The recent application of nontraditional sulfur isotope data ( $\Delta^{33}$ S) has similarly provided new insights into processes controlling the origin and chemical evolution of hydrothermal vent fluids at mid-ocean ridges (Ono et al., 2007). These data have allowed us to distinguish unambiguously between



**Figure 10** Diagram showing the distribution of  $\delta^{56}$ Fe in vent fluids and sulfides (chalcopyrite, pyrite, marcasite, and sphalerite) at EPR 9–10° N compared with literature and unpublished data for other vent fields along the Mid-Atlantic Ridge. Data sources: (a) Beard et al. (2003b); (b) Rouxel et al. (2011); (c) Adams et al. (2011); (d) Severmann et al. (2004); (e) Rouxel, unpublished data (samples from Rouxel et al., 2004a. Light gray bar represents the bulk Earth isotopic composition estimated from the composition of igneous rocks (Beard et al., 2003a; Dauphas and Rouxel, 2006). Reproduced from Rouxel 0, Shanks WC, Bach W, and Edwards KJ (2008) Integrated Fe- and S-isotope study of seafloor hydrothermal vents at East Pacific rise 9–10° N. *Chemical Geology* 252: 214–227.

basalt-derived H<sub>2</sub>S ( $\sim$ 73–89%) and reduced seawater sulfate (11–27%) that together account for the total inventory of dissolved H<sub>2</sub>S in hydrothermal vent fluids issuing from chimney structures on the EPR and MAR. Conventional sulfur isotope studies have been inconclusive because the <sup>34</sup>S/<sup>32</sup>S ratios of vent-fluid H<sub>2</sub>S and chimney sulfide minerals may reflect not only the mixing ratio of sulfur sources at depth, but also isotope exchange between sulfate and sulfide in the near-chimney environment. Seafloor vent sulfides have lower  $\Delta$ <sup>33</sup>S values than biogenic sulfides, suggesting little contribution of sulfide from microbial sulfate reduction to hydrothermal sulfides at sediment-free mid-ocean ridges.

Although what has been emphasized here is the application of nontraditional transition metal and sulfur isotopes to constrain mass-transfer reactions contributing to the chemistry of hydrothermal fluids, analytical protocols have also been developed for nontraditional Ca (Amini et al., 2008; Caro et al., 2010) and Mg (Tipper, 2006) isotopes, which will further enhance our understanding of processes controlling the origin and evolution of seafloor hydrothermal systems.

#### 8.7.2.3.3 Gas chemistry of hydrothermal fluids

In general, concentrations of dissolved gases tend to be highest in the lowest chlorinity fluids, which represent the vapor phase, although alteration substrate effects (see below) can also influence this. Moreover, gas concentrations vary significantly between vents, even at a single location. In the lowest chlorinity and hottest fluids,  $H_2S$  may well be the dominant gas. However, because  $H_2S$  levels are controlled by metal-sulfide mineral solubility, this  $H_2S$  is often lost via precipitation. While the first vents discovered contained less than twice the  $CO_2$  present in seawater (Welhan and Craig, 1983), these vents have not proved typical. Few mid-ocean ridge vent fluids have  $CO_2$  levels less than or equal to the total  $CO_2$  levels present in seawater (approximately 2.5 mmol kg<sup>-1</sup>), and many have concentrations an order of magnitude more; the highest approach two orders of magnitude, but these levels are uncommon. In the immediate aftermath of an eruption such as at EPR 9–10° N in 1991, very high dissolved gas concentrations in vent fluids were observed (see below).

Back-arc systems commonly have higher levels of CO<sub>2</sub> in their vent fluids, but concentrations two orders of magnitude greater than seawater are, again, close to the maximum of what has been sampled to date (Ishibashi and Urabe, 1995; Mottl et al., 2011).  $CH_4$  is much less abundant than  $CO_2$  in most systems. Vent-fluid CH<sub>4</sub> concentrations are typically higher in sedimented systems and in systems hosted in ultramafic rocks (see below). CH<sub>4</sub> is also enriched in low-temperature vent fluids when compared to concentrations predicted from simple seawater/vent-fluid mixing (Von Damm and Lilley, 2004). The concentrations of H<sub>2</sub> gas in vent fluids vary over two orders of magnitude. Again, the highest levels are usually observed in vapor-phase fluids, especially those sampled immediately after volcanic eruptions or diking events (Lilley et al., 2003). High values (10-20 mmol kg<sup>-1</sup>) have also been reported from sites hosted by ultramafic rocks (Charlou et al., 2002, 2010; see below). Of the noble gases, He, especially <sup>3</sup>He, is most enriched in vent fluids. <sup>3</sup>He can be used as a conservative tracer in vent fluids because its entire source in vent fluids is primordial from within the Earth (see Section 8.7.5). Radon, a product of radioactive decay in the uranium series, is also greatly enriched in vent fluids (Kadko and Moore, 1988; Rudnicki and Elderfield, 1993). Less data are available for the other noble gases, at least some of which appear to be relatively conservative compared to their concentration in starting seawater (Kennedy, 1988; Kennedy et al., 1988).

#### 8.7.2.3.4 Organic geochemistry of hydrothermal vent fluids Studies of the organic chemistry of vent fluids represent an exciting and important area of research that has only emerged in recent years. The justification for this is derived not only from the clues these data can provide on the nature of masstransfer processes during hydrothermal alteration, but also because dissolved organics in subseafloor hydrothermal fluids can serve as a metabolic energy source for biological communities at the seafloor and in the overlying water column (Karl, 1995; Kelley et al., 2002; McCollom, 2000; McCollom and Shock, 1997). Moreover, some current theories propose that life originated on Earth in submarine hydrothermal systems, and abiotic synthesis may have provided the prebiotic organic compounds essential for this to occur (Reysenbach and Shock, 2002; Russell and Hall, 1997; Shock, 1992, 1994; Shock and Schulte, 1998).

The first discovery of abundant and diverse dissolved organics in high-temperature ( $\sim$ 360 °C) hydrothermal fluids on an unsedimented mid-ocean ridge was reported by Holm and Charlou (2001) and confirmed by Konn et al. (2009) at the ultramafic-hosted Rainbow field, 36° N, MAR. Compared with deep seawater, these investigators reported a diverse spectrum of organic molecules, with a dominance of aliphatic hydrocarbons  $(C_9-C_{14})$ , aromatic compounds  $(C_6-C_{16})$ , and carboxylic acids (C8-C18). Dissolved methane and other alkanes, however, represent the overwhelming abundance of the reported organic compounds, in keeping with observations of vent-fluid chemistry from other hydrothermal systems along the slowspreading MAR, where ultramafic affinities are implicated (Charlou et al., 1988, 2010; Keir et al., 2008; Melchert et al., 2008; Schmidt et al., 2007, 2011). Even the low-temperature Lost City hydrothermal system at 30° N, which is offset from the MAR by about 15 km but similarly hosted in peridotite (Kelley et al., 2001, 2005), reveals high concentrations of dissolved alkanes and organic acids (Lang et al., 2010; Proskurowski et al., 2006, 2008). The putative origin of these hydrocarbon-rich hydrothermal fluids involves abiotic synthesis made possible in part by the high dissolved hydrogen concentrations that also characterize these fluids. In contrast, hydrocarbons in hydrothermal fluids from sediment-covered or unsedimented ridges where seawater recharge may still involve high-temperature interaction with sedimentary components (Cruse and Seewald, 2006; Lang et al., 2006; Lilley et al., 1993; Seewald et al., 2003; Simoneit et al., 1992) are interpreted to form from microbial methanogenesis and thermal maturation of sedimentary organic matter, based on carbon and hydrogen isotope systematics (McCollom and Seewald, 2007).

In addition to the critical role of dissolved hydrogen in the abiotic synthesis of hydrocarbons in some hydrothermal vent fluids, a mineral catalyst is often needed to serve as a substrate for electron transfer and polymerization, as indicated by results of an impressive body of experimental data (Berndt et al., 1996; Horita and Berndt, 1999; McCollom and Seewald, 2001, 2006). The results of Horita and Berndt (1999) indicate that mineral catalysis can have a dramatic effect on hydrocarbon formation, albeit selectively. The Ni-bearing Fe alloy awaruite was shown to convert significant quantities of dissolved bicarbonate to methane, in amounts proportional to awaruite abundance. In natural systems, Ni-Fe alloys are typically formed under strongly reducing conditions, and such conditions are sometimes attained in subseafloor environments during hydrothermal alteration of ultramafic rocks (Alt and Shanks, 2003; Frost, 1985). The experiments by McCollom and Seewald (2001), which used novel carbon isotope tracer techniques, demonstrated that other potential mineral catalysts typical of serpentinization, such as magnetite and serpentine, could generate only small amounts of methane while also failing to yield the diversity of hydrocarbons observed for many natural hydrothermal systems. Foustoukos and Seyfried (2004), however, using similar isotopic doping techniques to quantify carbon sources and sinks, showed that abiotic synthesis of ethane (C<sub>2</sub>H<sub>6</sub>) and propane (C<sub>3</sub>H<sub>8</sub>) could in fact proceed under hydrothermal conditions when the mineral chromite was present. Thus, existing experimental data support the notion that the mineral catalyst present can qualitatively influence hydrocarbon formation in hydrothermal fluids. How this relates quantitatively to similar processes in

open natural hydrothermal systems, where there may exist sharp gradients in temperature, compositional variability, redox buffering, and the residence time of fluids in association with specific minerals, is uncertain and in need of additional investigation.

Mineral catalysts, of course, can only enhance the progress of reactions that are thermodynamically favorable. The thermodynamic basis for organic synthesis in deep-sea hydrothermal systems has been clearly elucidated by Shock and colleagues (Shock, 1992, 1994; Shock and Schulte, 1998), as illustrated in Figure 11. In the figure, the solid curves represent redox buffer assemblages in typical geologic systems that span the range of oxidation states that exist in many subsurface environments. At temperatures in excess of ~500 °C, thermodynamic equilibrium according to the reaction

$$CO_2 + 4H_2 = CH_4 + 2H_2O$$
 [2]

favors  $CO_2$  at oxidation states buffered by appropriate mineral assemblages (Figure 11). Thus, hydrothermal fluids that have equilibrated at high temperatures should be dominated by  $CO_2$ with trace quantities of  $CH_4$ , as is often the case with magmatic degassing at mid-ocean ridges. As temperatures decrease, however,  $CH_4$  stability increases, creating a strong thermodynamic drive for the reduction of  $CO_2$  in fluids that have cooled following equilibration at high temperatures. Formation of other organic compounds is similarly favored thermodynamically as temperatures decrease in hydrothermal environments, provided



Figure 11 Diagram illustrating mineral-buffered oxidation states, expressed as the fugacity of  $H_2(g)$  and carbon speciation as a function of temperature. Curves labeled FMQ (fayalite-magnetite-quartz), PPM (pyrite-pyrrhotite-magnetite), and HMP (hematite-magnetite-pyrite) correspond to the oxidation state that would be attained at thermodynamic equilibrium in geologic systems buffered by these mineral assemblages. Dotted lines reflect equilibrium ratios of CO<sub>2</sub> to CH<sub>4</sub> according to the following reaction:  $CO_2 + 4H_2 = CH_4 + 2H_2O$ . Stippled area corresponds to the region where synthesis of aqueous organic compounds in metastable states may be most easily detected. Dotted vertical line at 500 °C separates range of temperatures where stable equilibrium in the C-H-O system is attained in submarine hydrothermal systems ( $T > 500 \,^{\circ}$ C), from that at which CO<sub>2</sub> reduction to CH<sub>4</sub> is kinetically inhibited, and where metastable equilibrium states between CO (g) and aqueous organic compounds may prevail. Reproduced from Shock EL (1992) Chapter 5 Chemical environments of submarine hydrothermal systems. Origins of Life and Evolution of Biospheres 22: 67-107.

CH<sub>4</sub> formation is inhibited. Experimental and observational studies indicate that this is typically the case, so that organic compounds other than methane may form and persist in nonequilibrium abundances within hydrothermal environments as depicted by the shaded region in Figure 11. Thus, a broad range of environments intrinsic to marine hydrothermal systems may possess the pertinent combinations of chemical and physical attributes that allow abiotic synthesis. In comparison with what is presently known about the controls on inorganic species in hydrothermal systems at mid-ocean ridges, however, the organic geochemistry of vent fluids is clearly in its infancy, obfuscating cause and effect. Accordingly, there is great need to investigate the dissolved organic composition of hydrothermal vent fluids in much greater detail than has yet been achieved. Although noteworthy progress has been made in recent years (Charlou et al., 2010; Konn et al., 2009; Lang et al., 2006, 2010; McCollom and Seewald, 2007; Proskurowski et al., 2006, 2008), there remains an urgent need to deploy new generations of samplers and sensors that can sequester and analyze these species in time and space to avoid ambiguities caused by seawater mixing and other changes in physiochemical conditions induced by sample processing.

#### 8.7.2.4 Geographic Variations in Vent-Fluid Compositions

#### 8.7.2.4.1 Basalt-hosted hydrothermal systems

There are systematic reasons for some of the variations observed in vent-fluid compositions. One of the most important is the involvement of the lithospheric substrate with which hydrothermal fluids interact - chemically and physically. Discovery was made more than 30 years ago of the existence of high-temperature hydrothermal fluids issuing from chimney structures on fast- to intermediate-spreading ridge segments on the EPR, first at 21° N (Von Damm et al., 1985a) and then at numerous other localities such as 9-11° N (Haymon et al., 1991) and on the Juan de Fuca Ridge (Butterfield and Massoth, 1994; Butterfield et al., 1994, 2003; Delaney et al., 1992, 1997). There can be no question that the lithospheric basaltic composition (E and N-MORB) and the existence of a relatively shallow axial magma chamber (AMC) that characterize most basalt-hosted hydrothermal systems in the eastern Pacific ocean have a dominating effect on the composition and temporal evolution of coexisting hydrothermal fluids (Seyfried et al., 2003; Von Damm, 1995, 2000, 2004). As emphasized earlier (Section 8.7.2.2; Figure 5), the formation of hydrothermal vents in such systems involves discharge by focused upflow and recharge by ambient seawater, each with a unique potential for compositional modification of the seawater source fluid. For example, at EPR 9°50' N, earthquakes forming a pipelike pattern near a small ridge axis offset are interpreted as a zone of hydrothermal recharge where cold seawater is entering the crust with fluid pathways kept open by cracking from the tectonic stress associated with the axial discontinuity (Figure 12; Tolstoy et al., 2008). The inferred recharge pipe feeds into a ~500-m-thick zone of cracking above the AMC (Tolstoy et al., 2008), reflecting hydrothermal stresses where fluids and basalt are interacting (Sohn et al., 1998). Ongoing fracturing indicated by these earthquakes maintains the permeability essential for sustained hydrothermal circulation. Temperatures in excess of 400 °C occur at the base of this



**Figure 12** Cartoon illustrating proposed hydrothermal cell structure. This model shows downflow at fourth-order ridge-segment discontinuities, with the northern vents fed by a downflow zone near the  $9^{\circ}52.0'$  N discontinuity and the southern vents fed by the  $\sim 9^{\circ}49.3'$  N offset. The features of the best-defined hydrothermal cell are shown with black arrows, and the features inferred in adjacent cells are shown with gray arrows. Light blue dots illustrate the area where tectonic stresses are likely to dominate earthquake generation, creating a zone of permeability. Light gray dots illustrate where hydrothermal stresses probably dominate. The exact location of this transition is not well constrained. Changes in source from the northern and southern cells may occur between the Io/Ty and the P/Bio 9 (B9) vents. TWP and Biovent, the closest vents to the inferred downflow zones, both show decreases in temperature with time, whereas the central vents have been steadily increasing in temperature since about 1994 (Scheirer et al., 2006). Prolonged cooling close to the inferred downflow zones may lead to a decreasing percentage melt in the AMC. The seismicity gap at  $\sim 9^{\circ}50.4'$  N may represent a break or transition zone (such as melt to mush) within the AMC. Reproduced from Tolstoy M, Waldhauser F, Bohnenstiehl DR, Weekly RT, and Kim WY (2008) Seismic identification of along-axis hydrothermal flow on the East Pacific Rise. *Nature* 451: 181–187.

hydrothermal cell near the top of the AMC, enhancing the potential for phase separation and fluid–mineral equilibria (Driesner and Heinrich, 2007; Fontaine et al., 2009; Foustoukos and Seyfried, 2007b; Von Damm, 2004). Accordingly, vaporrich fluids that are redox and pH buffered by basalt– fluid interaction dominate the geochemical evolution of hydrothermal fluids at the base of the axial convection cell. Ridge-parallel circulation enhances heat transfer from the underlying magma consistent with recent geodynamical models (Coogan, 2008), seismic observations (Tolstoy et al., 2008), and regional tectonic fabric (Haymon et al., 1991). Cracking, in particular, illuminated by the sustained microearthquakes (Figure 12), is essential for maximizing heat and mass-transfer reactions.

Basalt-hosted hydrothermal systems associated with ridge segments formed at fast- to intermediate-spreading rates are often characterized by high thermal gradients consistent with the existence of shallow AMCs, while variability of chloride in vent fluids indicates active phase separation, as previously described. Taking explicit account of constraints imposed by phase equilibria in the SiO2-H2O-NaCl (Foustoukos and Seyfried, 2007b) and H<sub>2</sub>O-NaCl systems at elevated temperatures and pressures, Fontaine et al. (2009) proposed minimal variation in peak hydrothermal temperatures (ranging from 415 to 445 °C) at pressures consistent with the inferred location of the AMC for a number of basalt-hosted hydrothermal systems. The likely presence of quartz as an alteration phase not only provides a valuable constraint temperature and pressure, but also plays an important role in controlling pH by affecting the stability and solubility of hydrous alteration phases.

The formation of sufficient dissolved silica for quartz formation in basalt-hosted hydrothermal systems is fundamentally linked to incipient reactions between basalt and seawater, as follows:

Anorthite + 2Diopside + 
$$4H_2O + 3Mg^{2+}$$
  
=  $3Ca^{2+}$  + Clinochlore +  $3SiO_2(aq)$  [3]

where anorthite and clinochlore stand for components of plagioclase and chlorite solid solution, respectively. Not only does this reaction depict the release of dissolved silica to solution, but it also provides a reasonable explanation for the wellknown exchange of Mg from seawater for Ca from basalt that has long been recognized for hydrothermal fluids at mid-ocean ridges. If one conserves Mg between tremolite and chlorite to account for the near-quantitative removal of Mg from solution while fixing dissolved silica as quartz, the following reaction is derived:

Anorthite + 
$$6H^+$$
 + Tremolite  
=  $3Ca^{2+}$  + Clinochlore + 7Quartz [4]

This reaction shows that the complete exchange of Mg for Ca requires the existence of a Ca-bearing secondary mineral to control pH at the relatively low value measured in hydrothermal vent fluids. In effect, it is the high Ca from dissolution of plagioclase and diopside that buffers pH and thus plays an important role in rock–water reactions and mass transfer in basalt-hosted hydrothermal systems (Berndt and Seyfried, 1993; Ding and Seyfried, 1996; Ding et al., 2005; Seyfried and Ding, 1995).

Redox conditions must also be buffered to account for concentrations of transition metals and dissolved sulfur species in the hydrothermal fluids that form black-smoker chimneys (Tivey, 1995, 2007). Based on the measured hydrogen and hydrogen sulfide concentrations (Ding and Seyfried, 2007; Seyfried and Ding, 1995; Seyfried et al., 2003), redox appears to be controlled by the PPM assemblage when more reducing conditions prevail, to anhydrite-pyrite-magnetite under more oxidizing conditions. These two buffer assemblages may be linked to different stages of alteration, with the former typical of incipient reaction with abundant fresh basalt and the latter of an evolved system with small concentrations of dissolved sulfate  $(0.05-0.1 \text{ mmol kg}^{-1})$  in equilibrium with anhydrite. That significant amounts of seawater sulfate penetrate the sharply increasing metamorphic grade characteristic of mid-ocean ridge hydrothermal systems is indicated by vent-fluid strontium and sulfur isotopic systematics (Shanks, 2001). In spite of these observations, the role of anhydrite as a redox buffer for high-temperature hydrothermal fluids is still controversial, based largely on its occurrence in sections of ocean crust formed at fast- to intermediate-spreading rates, such as were sampled at Integrated Ocean Drilling Program (IODP) Site 1256 (Alt et al., 2010).

The above conclusions apply to basalt-hosted systems at fast- to intermediate-spreading ridges. Basalt-hosted systems, of course, are also associated with slow-spreading mid-ocean ridges, as indicated by the well-studied vent systems on the MAR. While some of these sites, such as the Turtle Pits, Red Lion, and Two Sisters vents near 5° S, are hosted in recent lava flows similar in extent to those at the EPR 9°50' N vent sites (German et al., 2008a; Soule et al., 2007), others, including the TAG and Lucky Strike sites at 26°10' and 37°18' N, respectively, are notable for the complex crustal structure of their geologic setting and the existence of deep-seated heat sources. Recent geophysical studies at TAG, for example, have revealed the hydrothermal field is underlain by rocks with high seismic velocities typical of lower-crustal gabbros, with no evidence of low seismic velocities associated with mid-crustal magma bodies (Canales et al., 2007; deMartin et al., 2007). Moreover, the TAG hydrothermal field is located on the hanging wall of a detachment fault, which seems not to have been active long enough to expose mantle rocks. Furthermore, based on energy flux calculations, these investigators conclude that the magmatic heat source for at TAG is located 4-7 km beneath the surface. In spite of the complex geological structures at TAG and its unusually deep heat source, the chemistry of the vent fluids is similar in many ways to the basalt-hosted systems in the eastern Pacific. These include relatively low dissolved hydrogen concentrations, indicating moderately oxidizing conditions, slightly acidic pH at elevated temperatures and pressures, and moderate levels of dissolved transition metals and metal ratios (Foustoukos and Seyfried, 2005). On the other hand, dissolved chloride is elevated at TAG ( $\sim$ 640 mmol kg<sup>-1</sup>), suggesting phase separation at depth, and the venting of high salinity fluids there at ~360 °C with virtually no variation for more than 20 years also reveals an unusual degree of stability. There can be no question that these interesting chemical and physical phenomena at TAG provide important clues on subseafloor hydrothermal circulation that is distinct from other basalt-hosted hydrothermal systems (Campbell et al., 1988; Foustoukos and Seyfried, 2005; Von Damm, 1990, 1995).

Unlike TAG, seismic data for the Lucky Strike system (37°18′ N) indicate the presence of a steady-state magma lens or AMC at approximately 3-3.2 km below the summit where current hydrothermal activity is focused (Crawford et al., 2010; Singh et al., 2006). These data also indicate large faults within the axial valley and east and west bounding faults between the edge of the median valley and the summit graben that penetrate to depths consistent with the dike-gabbro interface, in close proximity to the AMC. A model proposed by Humphris et al. (2002) suggests alternating periods of magmatic and tectonic extension, where the tectonic phase creates highly permeable pathways for fluid circulation, while the magmatic phase provides heat-to-fuel convection of seawater-derived hydrothermal fluids. Indeed, the contemporary lava lake appears to serve as an impermeable cap with respect to fluid flow, as hydrothermal venting has not been observed in its center. Maximum vent-fluid temperatures have persistently been ~300 °C at Lucky Strike (Charlou et al., 2000; Von Damm et al., 1998), which is lower than most other basalthosted hydrothermal systems.

Lucky Strike vent-fluid chemistry had previously provided evidence for compositional stability (Charlou et al., 2000; Von Damm et al., 1998), characterized by moderate dissolved CO<sub>2</sub> concentrations, dissolved chloride concentrations slightly below seawater, and Na and Ca systematics and transition metal ratios that led Von Damm et al. (1998) to conclude the existence of an oxidizing alteration substrate depleted in Ca and Fe. More recent sampling of Lucky Strike vent fluids (2008), however, reveals similar characteristics but with CO<sub>2</sub> concentrations higher by a factor of 3-4 suggesting magmatic resurgence (Pester et al., 2012). These more recent data also provide the first evidence for dissolved chloride concentrations at Lucky Strike that are greater than in seawater. Geochemical modeling of the 2008 data using constraints imposed by fluidfluid and mineral-fluid equilibria (Pester et al., 2012) suggests the presence of high-temperature fluids that have reacted with relatively fresh basalt before rising to the seafloor along paths of high permeability. Thus, although the TAG and Lucky Strike hydrothermal systems are linked by substrate composition, the chemistry of the respective hydrothermal fluids is very different owing to the nature and location of the heat source and the volcano-tectonic processes unique to each system.

#### 8.7.2.4.2 Ultramafic-hosted systems

Over the past two decades, there have been discoveries of hydrothermal fluids venting from ultramafic lithologies on the MAR (Charlou and Donval, 1993; Charlou et al., 1998, 2002; Douville et al., 2002; Escartin et al., 2008; German and Parson, 1998; German et al., 1996, 2010b; Schmidt et al., 2007, 2011). Where it was once thought that the limited magma supply intrinsic to slow- and ultraslow-spreading ridges would inhibit or preclude significant hydrothermal activity, it is now recognized that a combination of magmatism and tectonism can provide highly efficient circulation pathways with the potential for robust hydrothermal venting at the seafloor (Baker and German, 2004; Baker et al., 2004; German and Lin, 2004; German and Parson, 1998; German et al., 2010a).

One of the first well-studied examples of the association of ultramafic lithologies and venting of high-temperature hydrothermal fluids is the Rainbow system at 36° N on the MAR (Charlou et al., 2002; Douville et al., 2002; German et al., 2010b; Seyfried et al., 2011). Vent fluids issuing from chimney structures at Rainbow indicate temperatures in excess of 360 °C and compositions that contrast sharply with similarly hightemperature vent fluids from basalt-hosted systems (Douville et al., 2002). These fluids are characterized by unusually high concentrations of methane and other dissolved organics, as noted earlier, while dissolved H<sub>2</sub> and silica concentrations are significantly higher and lower, respectively, than in basaltic hydrothermal systems (Charlou et al., 2002; Lilley et al., 2003; Seyfried et al., 2003; Von Damm, 1995). In addition to high concentrations of dissolved hydrocarbons and H<sub>2</sub>, these fluids also contain surprisingly high transition metal concentrations (Douville et al., 2002; Schmidt et al., 2007). In fact, Rainbow vent fluids contain the highest dissolved Fe concentrations of any MOR vent fluid yet studied. The relatively high dissolved H<sub>2</sub> concentrations undoubtedly contribute to the high Fe, although other physical and chemical factors may be important as well (Allen and Seyfried, 2003; Douville et al., 2002), such as low pH and moderately high dissolved chloride, which enhance the solubility of Fe-bearing alteration phases (e.g., magnetite). To account for the redox and pH control of vent-fluid compositions at Rainbow, Seyfried et al. (2011) proposed a model that entails fluid equilibria with an alteration assemblage represented by chlorite solid solution, tremolite, and talc  $\pm$  plagioclase at 400 °C and 500 bars. Model results predict an inverse correlation between dissolved silica and H<sub>2</sub>, in good agreement with Rainbow data and geochemical data from other ultramafic-hosted hydrothermal systems. The presence of gabbroic bodies at depth would provide plagioclase for chlorite formation while also providing chemical components for redox and pH control and a source of heat-to-drive convection.

The emplacement of gabbroic bodies at depth as a source of heat and chemicals is but one explanation that could account for the chemistry of black-smoker fluids in ultramafic-hosted hydrothermal systems. Deep circulation of seawater-derived hydrothermal fluids along faults may allow residual heat to be 'mined' from the lithosphere. The direct interaction between these fluids and peridotite-dominated lithologies would result in replacement of olivine and pyroxene components that could contribute to the formation of hydrous secondary minerals and pH buffering:

$$\begin{array}{l} \mbox{6Tremolite} + 2 H_2 O + 24 H^+ = 10 \mbox{Chrysotile} \\ + 28 \mbox{SiO}_{2(aq)} + 12 \mbox{Ca}^{2+} \end{array} \end{tabular} \end{tabular} \end{tabular}$$

Reaction [5] illustrates the important role of both dissolved Ca and SiO<sub>2(aq)</sub> in lowering pH. This reaction provides an alternative explanation for the low pH and high dissolved metal concentrations of the Rainbow vent fluid. The coexistence of tremolite and serpentine  $\pm$  talc is a typical association for marine ultramafic rocks altered by seawater at elevated temperatures and pressures (Boschi et al., 2008; Frost and Beard, 2007; Mevel, 2003).

Although Rainbow was one of the first recognized ultramafic-hosted hydrothermal systems on the slowspreading MAR, more recent investigations have discovered systems at other MAR sites with similar geochemical, geological, and geophysical characteristics. The association of these systems with ridge segment ends and large normal faults (Escartin et al., 2008; Fontaine et al., 2008; German and Lin, 2004; German et al., 1996; McCaig et al., 2007; Melchert et al., 2008; Schmidt et al., 2007) is telling and underscores the important role of the interplay of crustal thickness and tectonic controls on the formation and evolution of robust hydrothermal systems even when magma supply is limited.

The linkage between detachment faulting and hydrothermal activity is particularly clear for the Lost City Hydrothermal Field (LCHF), which is situated near the summit of the Atlantis Massif, ~15 km west of the MAR axis (Kelley et al., 2001, 2005). Unlike the high-temperature Rainbow system, this vent field is characterized by towering carbonate chimneys up to 60 m tall that diffusely vent high pH (9-11), moderatetemperature (28-90 °C) fluids, produced by reaction of seawater with rocks originating from the mantle (Kelley et al., 2001). The relatively low vent temperatures notwithstanding, the LCHF is enriched in H<sub>2</sub>, CH<sub>4</sub>, and low molecular weight volatile hydrocarbons but is highly depleted in CO<sub>2</sub> and dissolved metals (Proskurowski et al., 2008). The basement directly beneath this system consists of highly serpentinized peridotites dominated by depleted mantle harzburgites, with lesser talc schists and metagabbros exposed by the long-lived detachment faulting (Fruh-Green et al., 2003, 2004). Geochemical models indicate that fluid circulation is driven by cooling of the underlying rocks and strongly implicate higher temperatures than are manifested at the site of venting (Allen and Seyfried, 2003, 2004), consistent with the metamorphic grade recognized in the basement rocks.

#### 8.7.2.4.3 Back-arc systems

Seafloor spreading in back-arc basins contrasts significantly with that along mid-ocean ridges, characterized by very distinct manifestations of hydrothermal activity imposed by a unique combination of mantle dynamics and crustal structure and composition (Baker et al., 2006; Ferrini et al., 2008; Martinez et al., 2006). Thus, it is not surprising that the composition of hydrothermal fluids in the vicinity of the well-studied Lau Basin offers an amazing degree of diversity of trace and major elements from one location to another. Mottl et al. (2011) reported on the composition of vent fluids from six hydrothermal fields along the Eastern Lau Spreading Center (ELSC). The chemistry of the waters reveals enormous variability both within and between fields in response to the wide range of chemical and physical factors that affect the origin and evolution of the fluids, not the least of which is the substrate composition that varies along axis as a function of magmatic processes and input of subducted sediment. Hot spring temperatures range from 229 to 363 °C and show temporal variability where comparisons can be made. Chloride variability, which is likely caused by phase separation effects, has a significant influence on vent chemistry as it does in virtually all other submarine hydrothermal systems due to the effect of chloride complexing on mass-transfer reactions. Although pH for most ELSC hot springs falls in the range observed for all other high-temperature systems, suggesting pH buffering by silicate assemblages at depth, magmatic degassing in back-arc systems is evidenced by unusually low pH for the Mariner and

Vai Lili fields when sampled in 2004 and 1989, respectively, much lower than the value of 5.2 at Vai Lili when sampled in 2005 (Figure 13). The combination of low pH and briny fluids at Mariner gives rise to some of the highest heavy metal concentrations (Figure 13). Dissolved  $H_2S$  concentrations tend to correlate with dissolved Fe, suggesting phase equilibria control by pyrite in the subsurface, although this would need to be confirmed by a study of redox effects, particularly the determination of dissolved  $H_2$  concentrations.

A striking feature of the chemical composition of ELSC vent fluids is the strong correlation of mobile trace elements with substrate composition. The dissolved concentrations of K, Rb, Cs, and B in vent fluids increase systematically from north to south, consistent with the higher abundance of these species in more slab-influenced felsic rocks as the ridge-arc separation diminishes. Although complex variations in substrate composition and magmatic degassing that are intrinsic to back-arc spreading systems contribute to the systematic variations observed in vent-fluid chemistry, pH buffering by silicate mineral hydrolysis reactions and phase separation are common to mid-ocean ridge hydrothermal systems in general, underscoring some degree of commonality in process in spite of the well-recognized compositional variability.

The chemical and isotopic composition of hydrothermal fluids sampled from vents along the Manus Spreading Center (MSC) and Pual Ridge (PR) in the Manus back-arc basin also reveal unusual diversity owing to the complex interplay of substrate variability, geographical location relative to the New Britain subduction zone, phase separation, conductive cooling, subsurface entrainment of seawater along the fluid flow path, and inputs of acidic magmatic vapor (Craddock and Bach, 2010; Craddock et al., 2010; Reeves et al., 2011). Substrate variability (mafic at the Vienna Woods site on the MSC and felsic for vents at PR) is clearly reflected by the absolute abundances and differing ratios of soluble alkali elements and boron (Reeves et al., 2011), similar to the vent-fluid



**Figure 13** Plots showing pH measured at 25 °C and zero-Mg end-member concentrations of Fe, Mn, and H<sub>2</sub>S for 40 vents from six vent fields along the ELSC sampled in 2005 (arranged from north to south). Also shown are equivalent data for samples collected from the Mariner vent field in 2004 and Vai Lilli in 1989 (stars). For the 2005 samples, symbols denote the Mg concentration (mmol kg<sup>-1</sup>) measured in each sample: solid squares, 0.7–9 mM; open squares, 12–38 mM; plusses 45–49.5 mM. Bottom seawater at the six vent fields ranged in pH from 7.50 to 7.64. Reproduced from Mottl MJ, Seewald JS, Wheat CG, et al. (2011) Chemistry of hot springs along the Eastern Lau Spreading Center. *Geochimica et Cosmochimica Acta* 75: 1013–1038.

chemistry-substrate linkage recognized for the ELSC discussed above. Moreover, the Manus Basin study unambiguously demonstrated the profound effect of magmatic acid volatiles on hydrothermal alteration for most or all of the vent fluids in this back-arc system. Evidence of this effect can be found in the relatively high transition metal concentrations and unusually low pH<sub>(25°C)</sub> values, as well as the ubiquitous negative  $\delta D_{H_2O_2}$ especially for vent fluids at PR. Although magmatic SO<sub>2</sub> likely plays a key role in lowering pH, addition of other acid volatiles such as HF contributes as well. Craddock et al. (2010) showed that REE can be used as an indicator of the type of magmatic acid volatile (HCl, HF, and SO<sub>2</sub>) degassing into the Manus Basin hydrothermal systems, providing a new tool to unravel the sources and sinks of components involved in the temporal and spatial evolution of magmatically and tectonically complex back-arc hydrothermal systems. Vent fluids from magmatic-hydrothermal systems hosted in felsic crust have historically been underrepresented, accentuating the importance of the chemical and isotopic data recently obtained for hydrothermal systems in the western Pacific.

#### 8.7.2.5 Temporal Variability in Vent-Fluid Compositions

#### 8.7.2.5.1 Temporal variability

The mid-ocean ridge is, in effect, one extremely long, continuous submarine volcano. While volcanoes are commonly held to be very dynamic features, little temporal variability was observed for more than the first decade of work on hydrothermal systems. Indeed, a tendency arose not to view the midocean ridge as an active volcano, at least on the timescales that had been observed. This perspective changed dramatically in the early 1990s. Together with evidence for recent volcanic eruptions at several sites, profound temporal variability in vent-fluid chemistries, temperatures, and styles of venting were also observed (Figure 7). In one case, the changes observed at a single vent nearly spanned the full range of known compositions reported from throughout the globe. These temporal variations in hydrothermal venting reflect changes in the nature of the underlying heat source. The intrusion of a basaltic dike into the upper ocean crust, which may or may not be accompanied by volcanic extrusion at the seafloor, has been colloquially termed 'the quantum unit of ocean accretion.' These dikes are of the order 1 m wide, 10 km long, and can extend hundreds of meters upward through the upper crust toward the ocean floor. These shallow-emplaced and relatively small, transient heat sources provide most of the heat that drives hydrothermal circulation immediately following magma emplacement. Over timescales of as little as a year, however, an individual dike will have largely cooled, and the heat source deepens. An immediate result is a decrease in measured exit temperatures for the vent fluids because more heat is now lost, conductively, as the fluids rise from deeper within the ocean crust. Vent-fluid compositions change too because the conditions of phase separation change; so too do the subsurface path length and residence time and consequently the likelihood that circulating fluids reach equilibrium or steady state within the ocean crust. Time-series studies at sites perturbed by magma emplacement have shown that it is the vapor phase which vents first in the earliest stages after a magmatic/volcanic event, while the high-chlorinity liquid

phase is expelled somewhat later. At EPR  $9^{\circ}50'$  N, the bestdocumented site, brine was venting at one location 3 years after vapor had exited from the same chimney (Figure 7); at other eruption sites, a similar evolution in vent-fluid composition has been observed over somewhat longer timescales.

The observed temporal variability has revolutionized our ideas about the functioning of hydrothermal systems and the timescales over which processes occur on the deep-ocean floor. Most magmatic intrusions/eruptions detected to date have been along the Juan de Fuca Ridge, on Cleft Segment, Coaxial Segment, and Axial Volcano, where acoustic monitoring of the T-phase signal that accompanies magma migration in the upper crust has provided real-time data for events in progress and allowed 'rapid response' cruises to be organized within days to weeks. There is also good evidence for two volcanic events on the ultrafast-spreading southern EPR, but the beststudied eruption site to date is the Ridge 2000 integrated studies site at 9°45-52' N on the EPR. Serendipitously, submersible dives began at EPR 9-10° N less than 1 month after a volcanic eruption there in 1991 (Haymon et al., 1993; Smith and Rubin, 1994). Profound chemical changes (more than a factor of 2) were noted at some of the vents during a period of less than a month (Von Damm, 1995, 2000). Subsequently, it became clear that rapid change can occur within a single year, related to changes in phase separation and water-rock reaction. These changes are presumed to be responses to mining of heat from the dike intrusion, including lengthening of the reaction path and increasing the residence time of the fluids within the crust. At none of the other eruptive sites has it been possible directly to sample vent fluids within this earliest postevent time period. It is now clear that the first fluid to be expelled is vapor, probably because of its lower density. What happens next is less clear. In several cases, the brine (liquid) phase has been emitted next. In some vents, this has occurred as a gradual progression to higher chlorinity; in others, the transition appears to occur more as a step function – although those observations may be aliased by the episodic nature of the sampling. What is certain at EPR 9° N, however, is that following initial vapor-phase expulsion, some vents have progressed to chlorinity greater than seawater much faster ( $\leq$ 3 years) than others ( $\sim$ 10 years), and several have never made the transition. In some parts of the eruptive area, moreover, vapor was still the dominant fluid more than a decade after the eruption and immediately prior to the next eruption at the same site. Conversely, other systems, most notably those from the Cleft Segment, have been venting fluids with chlorinities approximately twice that of seawater for more than a decade. Finally, one vent on the southern EPR, in an area with no evidence for recent magmatism, emitted fluid that was phase separating in 'real time,' with vapor exiting from the top of the structure and brine from the bottom simultaneously (Von Damm et al., 2003).

The above discussion emphasizes changes at EPR  $9-10^{\circ}$  N in the aftermath of the 1991 magmatic event. Similar observations were made at this same location following a seafloor eruption in 2005–06 (Escartin et al., 2007; Tolstoy et al., 2006). Although the complete composition of vent fluids affected by this more recent event is not yet available, dissolved volatile concentrations have been reported and reveal trends from several vents that are similar to those following the 1991

eruption. They also resemble changes following a somewhat analogous event at the Main Endeavour Field on the Juan de Fuca Ridge in 1999 (Lilley and Von Damm, 2008; Lilley et al., 2003; Seyfried et al., 2003). The 1991 dataset is very complete for A-vent at EPR 9°46.5' N, which shows large increases in dissolved CO2 and H2. These gases reached maximum concentrations 2 weeks after the onset of diking/eruption and had returned to preevent levels when next sampled a year later (Figure 14). As CO<sub>2</sub> increased, the <sup>3</sup>He/heat ratio decreased rapidly, indicating that CO<sub>2</sub> and He were differentially released during the magmatic event - a phenomenon observed previously at the Main Endevour Field (Lilley et al., 2003). CO2 and H<sub>2</sub> also increased greatly at EPR 9°50' N in 2006, especially for vents that were situated closest to the eruption (Lilley and Von Damm, 2008). These high CO<sub>2</sub> concentrations persisted long after the magmatic event, unlike in 1991 (Figure 14). Elevated CO2 in all of these magmatically perturbed systems reflects degassing, whereas high H<sub>2</sub> reflects rock-water interaction at unusually high temperatures, consistent with the vapordominated fluids (Cl <50 mmol kg<sup>-1</sup>) emitted immediately after the eruption (Lilley et al., 2003; Seyfried et al., 2003; Von Damm, 2000).

There is a Cl mass balance problem at many known hydrothermal sites. At EPR 21° N, where high-temperature venting was first discovered in 1979 and an active system has persisted for at least 23 years, only low-chlorinity fluids were still being emitted at the most recent sampling in 2002 (Von Damm et al., 2002). Clearly, there must be some additional storage and/or transport of higher-chlorinity fluids within the underlying crust. Our understanding of such systems is poor, at best. Results of recent models suggest that only by cooling the heat source can the brine be vented, so it is likely to be stored temporarily (Fontaine and Wilcock, 2006) and flushed from the system only in the waning stages of hydrothermal activity (Coumou et al., 2009). This sequence must contribute to the observed temporal variability at many vent sites, especially those that have been disturbed by magmatic events. Changes also accompany seismic events that are not related to magma migration, but rather to cracking within the upper ocean crust (Sohn et al., 1998, 1999; Tolstoy et al., 2008).

In marked contrast to those sites where volcanic eruptions and/or dike intrusions have been detected, several other sites have been sampled repeatedly over two decades where no magmatic activity is known to have occurred. At some of these sites, chemical variation over the entire sampling period is smaller than the analytical error of the measurements. The longest such time series is at 21°N on the EPR, where black smokers were first discovered in 1979. Others include Guaymas Basin (first sampled in January 1982) (Von Damm et al., 1985b), South Cleft on the Juan de Fuca Ridge (1984) (Von Damm and Bischoff, 1987), TAG on the MAR (1988) (Campbell et al., 1988; Edmonds et al., 1996; Foustoukos and Seyfried, 2005), Manus Basin (mid-1990s) (Gamo et al., 1993), and Rainbow on the MAR (1997) (Charlou et al., 2002, 2010). All these sites have exhibited stable vent-fluid chemistries, although only TAG and Rainbow are on slowspreading ridges. Indeed, it is the TAG site that has shown perhaps the most remarkable stability in its vent-fluid compositions; these have remained invariant for more than two decades, even after perturbation from drilling of five holes on ODP Leg 158 in 1994, directly into the active sulfide mound (Humphris et al., 1995).

#### 8.7.2.5.2 Effect on flux estimates

Accounting for temporal variability (or lack thereof) when calculating hydrothermal fluxes remains problematic. It is difficult to estimate the volume of fluid exiting from a hydrothermal system accurately. Many chemical differences from seawater are most pronounced within a year of a magmatic event, which is also the time when fluid temperatures are hottest (Von Damm, 2000). Visual observations suggest this is a time of voluminous flow, which is not unexpected given



**Figure 14** Time-series volatile element data for 'A' vent at  $9^{\circ}50'$  N on the EPR in the aftermath of the 1991 magmatic event (**Figure 7**). Shown are concentrations of He, CO<sub>2</sub>, H<sub>2</sub>, and CH<sub>4</sub>, and the <sup>3</sup>He/heat ratio. Samples were collected with DSV Alvin on 10, 17, and 24 April 1991; 10 March 1992; and 26 March 1994. Reproduced from Lilley MD, Lupton JE, Butterfield DA, Olson E (2003) Magmatic events produce rapid changes in hydrothermal vent chemistry. *Nature* 422: 878–881.

the role of magma as a heat source for driving circulation. The upper ocean crust is highly porous, and these pores are filled with ambient seawater. In a magmatic event, this seawater will be heated rapidly, its density will decrease, it will quickly react and rise, and large volumes of unreacted, cooler seawater will be drawn in and quickly expelled. It is not unreasonable to assume, therefore, that the seawater flux through a hydrothermal system is at its largest during this initial period, just when chemical compositions are most extreme and changeable (Von Damm, 1995, 2000). The key to the problem, therefore, lies in determining how long a hydrothermal system spends in its waxing (immediate posteruptive) stage versus the decadelong period at steady state (as at 21° N EPR), together with an evaluation of the relative heat, water, and chemical fluxes associated with each of these stages (Figure 15). If fluid fluxes and chemical anomalies are greatest in the immediate posteruptive period, for example, the initial 12 months following any eruption may be geochemically more significant than a further 20 years of steady-state emission. At fast-spreading ridges, new eruptions might even occur faster than such a vent



Figure 15 Graphical representation of a conceptual model for how hydrothermal heat flux (red curve) and cumulative heat release (blue curve) may evolve as a function of time following a volcano-magmatic event at a medium/fast-spreading ridge. During the 'event' period (daysweeks), event plumes form, releasing large quantities of heat and chemicals into the water column. The 'evolving' period (months-years) is characterized by vigorous hydrothermal venting which evolves, compositionally, over a period of one or more years up to a decade. This is followed by a 'quiescent' period (more than one decade), during which sustained stable-composition venting may dominate the cumulative efflux of heat and chemical species from the system from one eruptive event to the next. Reproduced from German CR and Lin J (2004) The thermal structure of the ocean crust, ridge spreading and hydrothermal circulation: How well do we understand their inter-connections. In: German CR, Lin J, and Parsons LM (eds.) Mid-Ocean Ridges: Hydrothermal Interactions between the Lithosphere and Ocean, Geophysical Monograph Series, vol. 148, pp. 1–19. Washington, DC: American Geophysical Union.

'life cycle' can be completed. Alternatively, the converse may be true: early-stage eruptions may prove relatively insignificant over the full life cycle of a prolonged, unperturbed hydrothermal site.

To advance our understanding of the chemical variability of vent fluids, it will be important to find new sites which may be at evolutionary stages not previously observed and to continue studies of temporal variability at known sites, both those that have varied in the past and those that have been stable. Understanding the mechanisms and physical processes that control vent-fluid compositions is key to calculating hydrothermal fluxes.

#### 8.7.3 The Net Impact of Hydrothermal Activity

It is important to remember that the gross chemical flux associated with venting fluids (see Section 8.7.2) is not identical to the net flux from hydrothermal systems to the oceans, because some chemical species have higher concentrations in seawater than in vent fluids and so are transported in net from the oceans to the crust. Two of these elements are Mg and U, which are almost quantitatively removed from circulating seawater into the ocean crust (see also Chapter 4.16). Even for elements which show no net elemental exchange, such as Sr, there can be almost complete isotopic exchange with the crust, indicating that none of the substance originally present in the circulating seawater has passed through the hydrothermal system. Section 8.7.4.1 below presents a brief summary of ocean crust mineralization.

For the remainder of this chapter the focus is on the fate of hydrothermal discharge once it reaches the seafloor. Much of this material, transported in dissolved or gaseous form in warm or hot fluids, does not remain in solution but forms solid phases as fluids cool and/or mix with colder, more alkaline seawater. These products, whose formation may be mediated as well as modified by a range of biogeochemical processes, occur from the ridge axis out into the deep-ocean basins. Massive sulfides as well as silicates, oxides, and carbonates deposited from high-temperature fluids are progressively altered by high-temperature metasomatism, as well as low-temperature oxidation and mass wasting, much of which again may be biologically mediated. Various low-temperature deposits may also form, with or without accompanying biological activity. In addition to these near-vent hydrothermal products, abundant fine-grained particles are formed in hydrothermal plumes, which subsequently settle to the seafloor to form metalliferous sediments, both close to vent sites and across ridge flanks into adjacent ocean basins. The postdepositional fates of these nearand far-field deposits remain poorly understood. Sulfide deposits, for example, may undergo extensive diagenesis and dissolution, leading to further release of dissolved chemicals into the deep ocean. Conversely, oxidized hydrothermal products may remain well preserved in the sedimentary record and only be recycled via subduction back into the Earth's interior. On ridges where volcanic eruptions are frequent, both relatively fresh and more oxidized deposits may be covered over by subsequent lava flows on timescales of a decade, and thus become assimilated into the ocean crust, isolated from the overlying water and sediment columns. In the following sections, the fates of various hydrothermal products are

discussed, in order of their distance from the vent source: near-vent deposits (Section 8.7.4), hydrothermal plumes (Section 8.7.5), and hydrothermal sediments (Section 8.7.6).

#### 8.7.4 Near-Vent Deposits

#### 8.7.4.1 Alteration and Mineralization of the Upper Ocean Crust

Hydrothermal circulation causes extensive alteration of the upper ocean crust, reflected both in mineralization of the crust and in changes to physical properties of the basaltic basement (Alt, 1995, 1999, 2003). The direction and extent of chemical and isotopic exchange between seawater and ocean crust depend on variations in temperature and permeability, which vary strongly as a function of depth. Extensive mineralization of the upper ocean crust can occur where metals leached from large volumes of altered crust become concentrated (Hannington et al., 1995; Petersen et al., 2000) and even deeper in the system where ingress of cold seawater is made possible by local variations in permeability, especially at the lava–dike contact (Alt, 1995; Alt et al., 2010).

In situ sections of ocean crust recovered by ODP/IODP drilling (Alt, 1995; Alt et al., 2010), together with studies of rocks collected by submersible from exposed cross sections through the crust, such as at Pito Deep at the northeast corner of the Easter microplate (Barker et al., 2008; Heft et al., 2008), provide important insight into hydrothermal alteration processes that ultimately link the rock record to the chemistry and temperature of hydrothermal fluids. Conceptual models for water-rock reaction and metamorphism within the upper crust at intermediate- to fast-spreading ridges based on these data emphasize the importance of a recharge zone and a discharge zone (Figure 5). The recharge zone represents regions where downwelling seawater undergoes incipient reaction with the crust. Although debate on the exact nature of recharge continues, recent models note the cooling effects of cold seawater recharge while emphasizing its relatively abrupt heating at the base of the sheeted dike complex due to conduction of heat from the underlying magma body and along axis circulation (Coogan, 2008; Tolstoy et al., 2008). Ultimately, seawater is transformed into the fluid observed at vents with the coexisting dikes variably altered to an assemblage containing chlorite+amphibole+secondary plagioclase + quartz  $\pm$  epidote  $\pm$  anhydrite (see earlier).

The recharge flow can be inferred to feed into a zone of cracking several hundred meters thick above the AMC, reflecting the thermally and tectonically induced hydrothermal stresses where fluids and rocks interact (Tolstoy et al., 2008). Thus, relatively high-temperature reactions are envisaged for the base of the recharge zone, which transitions into the discharge zone where regions of high permeability are encountered. Recent modeling of tidal pressure-wave diffusion at EPR 9°50' N indicates high in situ permeability (>10<sup>-10</sup> m<sup>2</sup>) near upflow (active venting) regions and lower permeability (<10<sup>-13</sup> m<sup>2</sup>) away from these regions (Crone and Wilcock, 2005). This supports the hypothesis that permeability largely determines the location of local discharge.

It has long been recognized that the temperature and chemistry of hydrothermal vent fluids reflect relatively low water/ rock mass ratios consistent with the mining of heat from a relatively large reservoir of fresh basalt and gabbro (Chan et al., 2002; Elderfield and Schultz, 1996; Mottl, 2003). Although this process has typically been viewed as a downward propagation of fluid by cracking into previously unaltered crust, more recent models (Barker et al., 2008; Coogan, 2008; Heft et al., 2008) emphasize the upward migration of fluid heated from below and the reaction between this fluid and dike rocks. Hydrothermal stresses associated with fluid-rock interaction throughout the sheeted dike complex would not only maintain permeability (Tolstoy et al., 2008) but would also provide a mechanism for supplying chemicals to hydrothermal fluids, especially highly mobile elements such as Li, B, Cs, and K, which are used to estimate water/rock ratios and which suggest constancy in source composition (Berndt et al., 1988; Seyfried and Shanks, 2004).

Thermal and chemical buffering throughout the lower portion of the sheeted dike complex characterizes the so-called reaction zone which, with the recharge and discharge zones, has long constituted the standard conceptual model of hydrothermal circulation at mid-ocean ridges based on the rock record (Alt, 1995; Coogan, 2008). Phase separation in the NaCl-H2O system likely occurs relatively deep, near the conductive boundary layer of the AMC. It would be here, in response to constraints imposed by temperature, pressure, and salinity of the bulk fluid, that the composition of vapor and coexisting brine would be established (Coumou et al., 2009; Fontaine and Wilcock, 2006; Lowell and Germanovich, 1997). Upward movement of the more mobile and buoyant vapor phase would provide heat to the sheeted dike rocks, as described above, while also facilitating hydrothermal alteration and formation of upper greenschist facies minerals (tremolite/actinolite, chlorite). Recent data suggest that quartz saturation and phase separation (NaCl-H2O) occur at approximately the same P-T-x condition (Fontaine et al., 2009), but this is not always the case (Pester et al., 2011). Transition metals and dissolved H<sub>2</sub>S concentrations in hydrothermal fluids, on the other hand, are particularly sensitive to temperature (Ding and Seyfried, 1992; Seewald and Seyfried, 1990; Seyfried and Ding, 1995), so even small changes in temperature from conditions at depth, where the solubility of these species is buffered at high concentrations, may result in some loss, especially if mixing with seawater is involved. In the absence of mixing, though, the unusually high permeability of upflow zones will provide an effective means of transporting metals and sulfur, along with less temperature-sensitive species such as Ca, Si, and Cl, to the seafloor from the 'root zone' of the hydrothermal system at depth, where the transitional effects of recharge and discharge contribute most to the chemical modification of seawater.

#### 8.7.4.2 Near-Vent Hydrothermal Deposits

The first discoveries of hydrothermal vent fields (e.g., Galapagos; EPR 21°N) revealed three distinct types of mineralization: (1) massive sulfide mounds deposited from focused high-temperature flow, (2) accumulations of Fe–Mn oxyhydroxides and silicates from low-temperature diffuse discharge, and (3) fine-grained particles precipitated from hydrothermal plumes. Subsequently, a wide range of mineral deposits have been identified that result from hydrothermal discharge, both

along the global ridge crest and in other tectonic settings (Hannington et al., 2011; Koski et al., 2003). Of course, massive sulfide deposits contain only a fraction of the total dissolved load delivered to the seafloor. Much of this flux is delivered to ridge flanks via dispersion in buoyant and nonbuoyant hydrothermal plumes (Section 8.7.5). In addition, discoveries such as the carbonate deposits at Lost City on the MAR (Kelley et al., 2001), the silica-rich deposits in the Blanco Fracture Zone (Hein et al., 1999), and metal-bearing fluids on the flanks of the Juan de Fuca Ridge (Mottl et al., 1998) remind us that there is still much to learn about the formation of hydrothermal mineral deposits.

Haymon (1983) proposed the first model for how a blacksmoker chimney forms (Figure 16). The first step is the formation of an anhydrite (CaSO<sub>4</sub>) framework due to the heating of seawater, which supplies sulfate, and its mixing with vent fluids, which provides most of the Ca. Anhydrite walls protect subsequent venting fluids from being mixed so extensively with seawater and provide a template onto which sulfide minerals can precipitate as these fluids cool within the anhydrite structure. As the temperature and chemical compositions within the chimney walls evolve, a zonation of metal-sulfide minerals develops, with more Cu-rich phases toward the interior, Zn-rich phases toward the exterior, and Fe-rich phases ubiquitous. This model is directly analogous to the concept of an intensifying hydrothermal system developed by Eldridge et al. (1983), in which initial deposition of a fine-grained mineral carapace restricts mixing of hydrothermal fluid and seawater at the site of discharge. Subsequently, less dilute, higher-temperature (Cu-rich) fluids interact with the sulfides within this carapace to precipitate chalcopyrite and mobilize more soluble, lower temperature metals such as Pb and Zn toward the outer, cooler parts of the deposit. Thus, it is the steep temperature and chemical gradients caused by both mixing and diffusion that account for variations in wall mineralogy and Cu-Zn zonation observed in both chimneys and larger massive sulfide deposits. These processes, initially

proposed as part of a conceptual model, have subsequently been demonstrated more rigorously by quantitative geochemical modeling of hydrothermal fluids and deposits (Tivey, 1995).

Drilling during ODP Leg 158 revealed that similar internal variations can also occur on large scales, in this case across the entire TAG mound (Humphris et al., 1995; Petersen et al., 2000). Drilling revealed the core of the mound to be dominated by chalcopyrite-bearing massive pyrite and pyriteanhydrite and pyrite-silica breccias, while the mound top and margins contained little or no chalcopyrite but more sphalerite and higher concentrations of metals such as Zn and Ag that are soluble at lower temperatures. The geochemical modeling of Tivey (1995) points to entrainment of seawater into a focused upflow zone within the mound, which would, almost simultaneously (1) induce the precipitation of anhydrite, chalcopyrite, pyrite, and quartz; (2) decrease the pH of the fluid; and (3) mobilize Zn and other metals. When combined, these processes of zone refining and entrainment of seawater into active sulfide deposits can credibly explain mineralogical and chemical features observed both in modern hydrothermal systems such as the TAG mound and in Cyprus-type massive sulfide deposits found in many ophiolites of orogenic belts (Hannington et al., 1998).

A growing database on the occurrence of seafloor massive sulfide (SMS) deposits is providing insight into the likely distribution, size, and ore grades of these various deposits. Multiple abundant but small deposits are found along fast-spreading ridges, whereas fewer but larger deposits occur along slow and ultraslow ridges, where structural controls on hydrothermal upflow are increasingly important (Hannington et al., 2011). Deposits found in subduction zones are generally similar to those on mid-ocean ridges, though differences in crustal thickness, heat-flow regime, and host-rock lithology can impart important differences (Hannington et al., 2005). One commercial company has already been granted a license to exploit back-arc SMS deposits in the SW Pacific, stimulating urgent



**Figure 16** Schematic diagram showing mineral zonation in cross section and in plan view for a typical black-smoker chimney (after Haymon, 1983). Arrows indicate direction of inferred fluid flow.

debate about deep-sea mining (Hoagland et al., 2010; Van Dover, 2011). Key attractions for SMS mining in the SW Pacific include (1) high gold and base metal grades, (2) sites located close to land and within the national waters of a coastal state. and (3) water depths shallower than  $\sim$ 2000 m (Petersen et al., 2011). By contrast, the majority of the world's SMS deposits lie within The Area, defined by the United Nations Law of the Sea as that part of the seafloor outside any national exclusive economic zone and administered by the International Seabed Authority. Here, it is the large deposits found at slow and ultraslow ridges that are attracting national interests (Scott, 2011). Along the slow-spreading MAR between 10 and 20° N, for example, ongoing systematic exploration by Russian scientists has revealed multiple active and inactive hydrothermal fields of large size and tonnage. A subset of these hydrothermal deposits is associated with long-lived oceanic core complexes (John and Cheadle, 2010), including the Ashadze (12°58' N) and Semyenov (13°31' N) hydrothermal fields. These deposits exhibit high concentrations of gold and base metals that appear comparable to those receiving the most attention in the SW Pacific (Cherkashev et al., 2010).

A quite different low temperature form of hydrothermal deposit has also been located on the slow-spreading MAR. The Lost City vent site (Kelley et al., 2001) occurs near 30° N on the MAR, 15 km away from the most recently erupted volcanic ridge axis. It is situated high on a tectonic massif where faulting has exposed variably altered peridotite and gabbro (Blackman et al., 1998). The Lost City field hosts at least 30 active and inactive spires of up to 60 m in height, on a terrace that is underlain by diverse mafic and ultramafic lithologies. Cliffs adjacent to this terrace also host abundant white hydrothermal deposits as flanges, and alteration as peridotite mineralization, which are directly akin to deposits reported from Alpine ophiolites (Früh-Green et al., 1990). The Lost City chimneys emit fluids up to 75 °C which have very high pH (9.0-9.8) and compositions rich in H<sub>2</sub>S, CH<sub>4</sub>, and H<sub>2</sub>, consistent with serpentinization reactions (Section 8.7.2.4.2), but low in dissolved Si and metals (Kelley et al., 2001). Consistent with this, chimneys of the Lost City field are composed predominantly of Mg- and Ca-rich carbonate and hydroxide minerals, notably calcite, brucite, and aragonite.

In addition to the sulfide- and carbonate-dominated deposits described above, mounds and chimneys composed of Fe- and Mn-oxyhydroxides and silicate minerals also occur at tectonically diverse rift zones, from mid-ocean ridges such as the Galapagos Rift to back-arc settings such as the Woodlark Basin (Binns et al., 1993; Corliss et al., 1978). Unlike polymetallic sulfides, Fe-Mn oxide-rich low-temperature deposits should be chemically stable on the ocean floor. Certainly, Mn-rich metalliferous sediments in ophiolites - draped over pillow basalts and often referred to as 'umbers' - have long been identified as submarine hydrothermal deposits formed in ancient ocean ridge settings. These types of ophiolite deposit may be intimately linked to the Fe-Mn-Si oxide 'mound' deposits formed on pelagic ooze near the Galapagos Rift (Maris and Bender, 1982). It has proven difficult, however, to determine the precise temporal and genetic relationship of umbers to massive sulfides, not least because no gradation of Fe-Mn-Si oxide to sulfide mineralization has yet been reported from ophiolitic terranes. The genetic relationship

between sulfide and Fe–Mn–Si oxide facies deposits formed at modern hydrothermal sites also remains enigmatic. Fe–Mn–Si oxide deposits may simply represent 'failed' massive sulfides. Alternatively, there may be important aspects of axial versus off-axis plumbing systems, including porosity, permeability, chemical variations caused by phase separation, and controls on the sulfur budget, that remain inadequately understood. What seems certain is that the three-dimensional problem of hydrothermal deposition (indeed, 4D if one includes temporal evolution) cannot be solved from seafloor observations alone. What is required is a continuing program of seafloor drilling coupled with analog studies of hydrothermal deposits preserved on land.

#### 8.7.5 Hydrothermal Plume Processes

#### 8.7.5.1 Dynamics of Hydrothermal Plumes

Hydrothermal plumes form wherever buoyant hydrothermal fluids enter the ocean. They represent an important dispersal mechanism for the thermal and chemical fluxes delivered to the oceans, while the processes active within these plumes serve to modify significantly the gross fluxes from venting. Plumes are of further interest to geochemists because they can be exploited to detect and locate new hydrothermal fields and for the calculation of total integrated fluxes from any particular vent field. To biologists, hydrothermal plumes represent an effective transport mechanism for dispersing vent fauna, aiding gene flow between adjacent vent sites along the global ridge crest (e.g., Adams et al., 2011; Mullineaux and France, 1995). In certain circumstances, the heat and energy released into hydrothermal plumes could act as a driving force for mid-depth ocean circulation (Helfrich and Speer, 1995; Stommel, 1982).

Present day understanding of the dynamics of hydrothermal plumes is heavily influenced by the theoretical work of Morton et al. (1956) and Turner (1973). When hightemperature vent fluids are expelled into the base of the much colder, stratified oceanic water column, they are buoyant and begin to rise. Shear flow between the rising fluid and the ambient water column produces turbulence, producing vortices or eddies that are readily visible in both still and video imaging of active hydrothermal vents. These eddies or vortices entrain material from the ambient water column, resulting in a continuous dilution of the original vent fluid as the plume rises. Because the oceans exhibit stable density stratification, this mixing causes progressive dilution of the buoyant plume with water which is denser than both the initial vent fluid and the overlying water column into which the plume is rising. Thus, the plume becomes progressively less buoyant as it rises, and it eventually reaches some finite maximum height above the seafloor at which it is neutrally buoyant, beyond which it cannot rise (Figure 17). The first rising stage of hydrothermal plume evolution is termed the buoyant plume. The later stage, where plume rise has ceased and hydrothermal effluent disperses laterally, is termed the nonbuoyant plume, also sometimes called the neutrally buoyant plume.

The exact height reached by any hydrothermal plume is a complex function involving key properties of both the vent fluids and the water column into which they are



**Figure 17** Sketch of the hydrothermal plume rising above an active hydrothermal vent (after Helfrich and Speer, 1995) illustrating entrainment of ambient seawater into the buoyant hydrothermal plume, establishment of a nonbuoyant plume at height  $z_{max}$  (deeper than the maximum height of rise actually attained due to momentum overshoot), and particle settling from beneath the dispersing nonbuoyant plume.

injected – notably the initial buoyancy of the former and the degree of stratification of the latter. A theoretical approach to calculating the maximum height of rise that can be attained by any hydrothermal plume is given by Turner (1973) with the equation:

$$z_{\rm max} = 3.76 F_0^{1/4} N^{-3/4}$$
 [6]

where  $F_0$  and N represent parameters termed the buoyancy flux and the Brunt–Väisälä frequency, respectively. The concept of buoyancy flux,  $F_0$  (units: cm<sup>4</sup> s<sup>-3</sup>), can be explained in terms of the product  $F_0 \rho_0$ , which represents the total weight deficiency produced at the vent per unit time (units: g cm s<sup>-3</sup>). The Brunt–Väisälä frequency, also termed the buoyancy frequency, N (units: s<sup>-1</sup>) is defined as:

$$N^2 = -(g/\rho_0) \times d\rho/dz$$
<sup>[7]</sup>

where *g* is the acceleration due to gravity,  $\rho_0$  is the background density at the seafloor, and  $d\rho/dz$  is the ambient vertical density gradient. In practice, buoyant hydrothermal plumes always exceed this theoretical maximum because, as they reach the level  $z_{max}$ , the plume retains some finite positive vertical velocity. This leads to 'momentum overshoot' (Turner, 1973) and 'doming' directly above the plume source before this dome, now negatively buoyant, collapses back to the level of zero buoyancy (Figure 17).

Note the weak dependence of emplacement height ( $z_{max}$ ) upon the buoyancy flux or heat flux of any given vent source. A doubling of  $z_{max}$  for any plume, for example, could only be achieved by a 16-fold increase in the heat flux provided by its vent source. By contrast, the ambient water column into which the buoyant plume becomes progressively diluted is more significant because the volumes entrained are nontrivial. For a typical plume with  $F_0 = 10^{-2}$  m<sup>4</sup> s<sup>-3</sup> and  $N = 10^{-3}$  s<sup>-1</sup>, the entrainment flux is of the order  $10^2$  m<sup>3</sup> s<sup>-1</sup> (e.g., Helfrich and Speer, 1995), resulting in very rapid dilution of the primary vent fluid ( $10^2-10^3$ :1) within the first 5–10 m of plume rise

and even greater dilution ( $\sim 10^4$ :1) at the height of neutral buoyancy (Feely et al., 1994). Similarly, the time of rise for a buoyant hydrothermal plume is dependent entirely on the background buoyancy frequency, *N* (Middleton, 1979):

$$\tau = \pi N^{-1}$$
 [8]

which, for a typical value of  $N = 10^{-3} \text{ s}^{-1}$ , yields a plume rise time of  $\leq 1$  h.

#### 8.7.5.2 Modification of Gross Geochemical Fluxes

Hydrothermal plumes represent a significant dispersal mechanism for chemicals released from seafloor venting to the oceans (see also Chapter 8.2). Consequently, it is important to understand the physical processes that control this dispersion (Section 8.7.5.1). It is also important to recognize that hydrothermal plumes represent nonsteady-state fluids whose chemical compositions evolve with age (Figure 18). Processes active in hydrothermal plumes can lead to significant modification of gross hydrothermal fluxes (Edmond et al., 1979; German et al., 1991b) and, in the extreme, can even reverse the sign of net flux to/from the ocean (e.g., German et al., 1990, 1991a).

#### 8.7.5.2.1 Dissolved noble gases

For one group of tracers, their inert behavior in the oceans dictates that they do undergo conservative dilution and dispersion within hydrothermal plumes. Perhaps, the simplest example of such behavior is primordial dissolved <sup>3</sup>He, which is trapped in the Earth's interior and released to the deep ocean only through processes linked to volcanic activity, most notably submarine hydrothermal venting. As has been seen, endmember vent fluids undergo  $\sim 10000$ -fold dilution prior to emplacement in a nonbuoyant hydrothermal plume. Nevertheless, because of the large enrichments of dissolved <sup>3</sup>He in hydrothermal fluids relative to low background levels in seawater, pronounced enrichments of dissolved <sup>3</sup>He relative to <sup>4</sup>He can be traced over great distances in the deep ocean. Perhaps, the most famous example of such behavior is the pronounced <sup>3</sup>He plume, first identified by Lupton and Craig (1981), dispersing over >2000 km across the southern Pacific Ocean, west of the EPR (Figure 19). <sup>222</sup>Rn, a radioactive isotope of the noble element Rn, is also enriched in hydrothermal fluids; while it shares with <sup>3</sup>He the advantages of being a conservative tracer, it also acts as a 'clock' for plume processes because it decays with a half-life of 3.83 days. Kadko et al. (1990) used the fractionation of <sup>222</sup>Rn/<sup>3</sup>He ratios in a dispersing nonbuoyant hydrothermal plume above the Juan de Fuca Ridge to estimate rates of dispersion or plume 'ages' at different downstream locations and thus deduce rates of uptake and/or removal of various nonconservative plume components, including H<sub>2</sub>, CH<sub>4</sub>, Mn, and particles. This approach is complicated, however, by the recognition that, in at least some localities, maximum plume height <sup>222</sup>Rn/<sup>3</sup>He ratios exceed pristine high-temperature vent-fluid values; clearly, entrainment from near-vent diffuse flow can act as an important additional source of dissolved <sup>222</sup>Rn entering ascending hydrothermal plumes (Rudnicki and Elderfield, 1992).

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**Figure 18** Schematic representation of a mid-ocean ridge hydrothermal system and its effects on the overlying water column. Circulation of seawater occurs within the oceanic crust, and to date, three types of fluids have been identified and are illustrated here: high-temperature vent fluids that have likely reacted at >400 °C; high-temperature fluids that have then mixed with seawater close to the seafloor; fluids that have reacted at 'intermediate' temperatures, perhaps ~150 °C. When the fluids exit the seafloor, either as diffuse flow (where animal communities may live) or as 'black smokers,' the water they emit rises, and the hydrothermal plume then spreads out at its appropriate density level. Within the plume, aqueous oxyanions (e.g., phosphate, vanadium, and arsenic) may sorb onto the vent-derived particles, making the plumes a sink for these elements; biogeochemical transformations also occur. These particles eventually rain out, forming metalliferous sediments on the seafloor. While hydrothermal circulation is known to occur far out onto the flanks of ridges, little is known about the depth to which it extends or its overall chemical composition because few sites of active ridge-flank venting have yet been identified and sampled.

#### 8.7.5.2.2 Dissolved reduced gases (H<sub>2</sub>S, H<sub>2</sub>, and CH<sub>4</sub>)

The next group of tracers which are important in hydrothermal plumes are the reduced dissolved gases, H2S, H2, and CH4. As has already been seen, dissolved H<sub>2</sub>S is commonly the most abundant reduced gas in high-temperature vent fluids (Section 8.7.2). Typically, however, any dissolved H<sub>2</sub>S released to the oceans undergoes rapid reaction, either through precipitation of polymetallic sulfide minerals close to the seafloor (chimneys) and in buoyant plumes (black smoke) or through oxidation in the water column. To date, there has been only one report of measurable H<sub>2</sub>S at nonbuoyant plume height anywhere in the deep ocean (Radford-Knoery et al., 2001). That study revealed maximum dissolved H<sub>2</sub>S concentrations of  $\leq 2$  nM, representing a 5  $\times$  10<sup>5</sup>-fold decrease from vent-fluid concentrations (Douville et al., 2002) with complete oxidative removal occurring in just 4-5 h, within c.1-10 km of the vent site. Dissolved H<sub>2</sub>, although not commonly present in such high concentrations in vent fluids (Section 8.7.2), exhibits similarly short-lived behavior within hydrothermal plumes. Kadko et al. (1990) and German et al. (1994) have reported maximum plume height dissolved H2 concentrations of 12 and 32 nM above the Main Endeavour vent field on the Juan de Fuca Ridge and above the Steinahóll vent site on the Reykjanes Ridge. From use of the <sup>222</sup>Rn/<sup>3</sup>He 'clock,' Kadko et al. (1990) estimated an apparent half-life for dissolved  $\rm H_2$  of  ${\sim}10\,h$  for oxidative removal.

The most abundant and widely reported reduced gas in hydrothermal plumes is methane, which is released into the oceans from both high- and low-temperature venting and the serpentinization of ultramafic rocks (e.g., Charlou et al., 1998, 2010; Lilley et al., 1995; Love et al., 2008). Vent-fluid concentrations are significantly enriched over seawater concentrations (10–2000 µmol kg<sup>-1</sup> vs. <5 nmol kg<sup>-1</sup>), but the behavior of dissolved methane, once released, appears variable from one location to another. Rapid removal of dissolved CH<sub>4</sub> was observed in the Main Endeavour plume (half-life=10 days; Kadko et al., 1990) yet near-conservative behavior was reported for the Rainbow hydrothermal plume, MAR, over distances up to 50 km from the vent site (German et al., 2010b). Possible reasons for these significant variations are discussed later (Section 8.7.5.4).

**8.7.5.2.3** Fe and Mn geochemistry in hydrothermal plumes The two metals most enriched in hydrothermal vent fluids are Fe and Mn. These metals have traditionally been considered to be present in a reduced dissolved form ( $Fe^{2+}$  and  $Mn^{2+}$ ) in end-member vent fluids, yet are most stable as oxidized Fe(III)and Mn(IV) oxyhydroxide precipitates in the open ocean.



**Figure 19** Plan view of  $\delta^3$ He anomalies at 2500 m depth in the Pacific Ocean, as compiled by J.Lupton (NOAA-PMEL) from GEOSECS, Helios, and WOCE program data. A major hydrothermal plume sourced close to 15° S on the superfast-spreading East Pacific Rise extends westward across much of the South Pacific Basin to at least 150° W, due north of Tahiti.

Consequently, the dissolved concentrations of Fe and Mn in vent fluids are enriched approximately 106:1 over open-ocean concentrations (e.g., Landing and Bruland, 1987; Statham et al., 1998; Von Damm, 1995). When these metal-rich fluids first enter the ocean, two important processes occur. First, the fluids are instantaneously cooled from >350 to  $\leq$ 30 °C. This quenching of a hot saturated solution leads to precipitation of a range of metal sulfide phases which are rich in Fe but not Mn because the latter does not readily form sulfide minerals. In addition, turbulent mixing between the sulfide-bearing vent fluid and the entrained, oxidizing water column leads to a range of redox reactions resulting in the rapid precipitation of high concentrations of suspended Fe oxyhydroxide particles. The dissolved Mn within the hydrothermal plume, by contrast, typically exhibits much more sluggish oxidation kinetics and remains predominantly in dissolved form at the time of emplacement in the nonbuoyant plume. Because Fe and Mn are so enriched in primary vent fluids, nonbuoyant plumes typically exhibit total (dissolved plus particulate) Fe and Mn concentrations that are c.100-fold higher than ambient water column values immediately following nonbuoyant plume emplacement. Consequently, Fe and Mn, together with CH<sub>4</sub> and <sup>3</sup>He (above), act as extremely powerful tracers with which to identify the presence of hydrothermal activity from watercolumn sampling. The fate of Fe in hydrothermal plumes is of particular interest because it is the geochemical cycling of this element, more than any other, which controls the fate of much of the hydrothermal flux from seafloor venting to the oceans.

Because of their turbulent nature, buoyant hydrothermal plumes have continued to elude detailed geochemical investigation. One approach has been to conduct direct sampling using manned submersibles or ROVs (e.g., Breier et al., 2009; Feely et al., 1994; Mottl and McConachy, 1990; Rudnicki and Elderfield, 1993). An alternate, indirect method is to investigate the geochemistry of precipitates collected both rising in, and sinking from, buoyant hydrothermal plumes using near-vent sediment traps (e.g., Adams et al., 2011; Cowen et al., 2001; German et al., 2002; Toner et al., 2009). From direct observations, it is apparent that up to 50% of the total dissolved Fe emitted from hydrothermal vents may be precipitated rapidly from buoyant hydrothermal plumes (e.g., Mottl and McConachy, 1990; Rudnicki and Elderfield, 1993), forming polymetallic sulfide phases, which can dominate (>90%) the Fe flux to the near-vent seabed (Cowen et al., 2001; German et al., 2002). Until recently, it had been considered that the remaining dissolved Fe within the buoyant and nonbuoyant hydrothermal plume undergoes quantitative oxidative precipitation. In the well-ventilated N. Atlantic Ocean, very rapid Fe(II) oxidation is observed with a half-life for oxidative removal of just 2-3 min (Rudnicki and Elderfield, 1993). In the NE Pacific, by contrast, corresponding half-lives of up to 32 h have been reported from Juan de Fuca Ridge hydrothermal plumes (Chin et al., 1994; Massoth et al., 1994). Field and Sherrell (2000) have predicted that the oxidation rate for dissolved Fe<sup>2+</sup> in hydrothermal plumes should decrease along the path of the thermohaline circulation, reflecting the

progressively decreasing pH and dissolved oxygen content of the deep ocean (Millero et al., 1987):

$$-d[Fe(II)]/dt = k[OH^{-}]^{2}[O_{2}][Fe(II)]$$
[9]

Reassuringly, Fe( $\pi$ ) incubation experiments conducted within the Kairei hydrothermal plume, Central Indian Ridge, are consistent with that prediction, yielding an Fe( $\pi$ ) oxidation half-life of ~2 h. (Statham et al., 2005).

Most recently, much attention has been paid to whether or not hydrothermal plumes might release a significant flux of organically complexed and hence stabilized Fe to the deep oceans that is not removed through oxidative precipitation and particle settling. In a study of Fe isotope distributions in ferromanganese crusts, Chu et al. (2006) noted that crusts from close to the Izu-Bonin arc showed significant departures from background open-ocean values to more negative values in the range  $\delta^{56}$ Fe = -0.6 to -1.0, consistent with episodes of intense hydrothermal Fe input. Tellingly, however, the same study revealed a ~10 My record for a central Pacific crust that was invariant at  $\delta^{56}$ Fe  $\sim -0.45$ , indicating a significant offset from the bulk earth value (Figure 10). In the limit, these data suggest that up to 50% of the dissolved Fe incorporated into this authigenic crust, and hence of the dissolved Fe of the deep Pacific Basin, might be hydrothermally sourced. Building on this, Chu et al. (2006) calculated that such a level of hydrothermally sourced Fe could be maintained at steady state in the deep ocean if just 0.5-2.0% of the dissolved Fe released via high-temperature venting at the ridge axis could be stabilized at nonbuoyant plume height. However, how might such Fe stabilization be achieved?

Bennett et al. (2008) employed competitive ligand exchange-cathodic stripping voltammetry to investigate Fe speciation in a southern MAR hydrothermal plume and identified high dissolved Fe concentrations of ~20 nM that were inconsistent with simple plume dilution and Fe oxidation but would be consistent with development of organic Fe complexes and Fe colloids. Stabilized dissolved Fe complexes were also observed as part of this study, and dissolved ligand concentrations were sufficiently high to stabilize up to 4% of the total Fe flux from the underlying vent field. In a parallel development, however, Yucel et al. (2011) have shown that a further mechanism may account for the export of 'dissolved' Fe from hydrothermal vents to the deep-ocean interior. In their study, up to 10% of the total Fe present in hydrothermal fluids was found to be in the form of nanoparticles (<200 nM size fraction) in vent fluids collected from the EPR and ELSC. These authors argue that such nanoparticles may be preformed in vent fluids prior to their eruption from the seabed and then be resilient both to oxidation and particle settling, allowing them to persist in dispersing, nonbuoyant hydrothermal plumes.

That such processes can occur has been confirmed through grain-by-grain mineral analysis of settling hydrothermal particles collected in sediment traps at EPR 9°50' N (Section 8.7.5.4). Wu et al. (2011) recently provided basin-scale evidence that stabilized 'dissolved' Fe can be exported significant distances off-axis (Figure 20), while Tagliabue et al. (2010) noted that reconciling global models with observed dissolved Fe distributions, particularly in the Southern Ocean, requires a significant hydrothermal flux to the deep ocean. While stabilized dissolved (or colloidal) Fe released from hydrothermal vents may contribute significantly to dissolved Fe budgets in the open ocean, it is important to remember that the vast majority of hydrothermal Fe released at ridge axes is converted into particles. The fate of these particles is considered next.



**Figure 20** Cross section of dissolved Fe concentrations in the North Pacific near 135° W showing high dissolved Fe at ~1500 m, consistent with longrange down-plume transport from Loihi Seamount, Hawaii. Inset red circles show sampling locations along 158° W superposed on the  $\delta^3$ He map presented in **Figure 19**. Reproduced from Wu J, Wells ML, and Rember R (2011) Dissolved iron anomaly in the deep tropical-subtropical Pacific: Evidence for long-range transport of hydrothermal iron. *Geochimica et Cosmochimica Acta* 75: 460–468.

#### 8.7.5.2.4 Coprecipitation and uptake with Fe in buoyant and nonbuoyant plumes

In buoyant plumes, in particular, there is significant coprecipitation of other metals enriched in hydrothermal fluids, along with Fe, to form polymetallic sulfides. Notable among these are Cu, Zn, and Pb. Common accompanying phases, which also sink rapidly from buoyant plumes, are barite and anhydrite (Ba and Ca sulfates) and amorphous silica (e.g., Lilley et al., 1995). In nonbuoyant hydrothermal plumes, where Fe- and to a lesser extent Mn-oxyhydroxides predominate, even closer relationships are observed between particulate Fe concentrations and numerous other tracers. To a first approximation, three differing Fe-related behaviors have been identified (German et al., 1991b; Rudnicki and Elderfield, 1993): (1) coprecipitation, (2) fixed molar ratios to Fe, and (3) oxyhydroxide scavenging (Figure 21). The first was already alluded to above and is loosely termed 'chalcophile' behavior namely, preferential coprecipitation with Fe as sulfide phases followed by preferential settling from the nonbuoyant plume. Such elements exhibit a generally positive correlation with Fe for plume-particle concentrations but with highest X:Fe ratios closest to the vent site (X=Cu, Zn, and Pb) and much lower values farther afield.

The second group are particularly interesting. These are elements that establish fixed X:Fe ratios in nonbuoyant hydrothermal plumes which do not vary with dilution or downstream dispersal distance (Figure 21). Elements that exhibit such 'linear' behavior include P, V, As, Cr, and U (e.g., Feely et al., 1990, 1991; German et al., 1991a,b; Trocine and Trefry, 1988). Hydrothermal vent fluids are not particularly enriched in any of these elements, which typically occur in seawater as rather stable dissolved oxyanion species. These elements are thus taken up from seawater onto hydrothermal particles, and this uptake represents a significant removal flux from the deep ocean for at least some of these elements. The P:Fe ratios observed throughout all Pacific hydrothermal plumes are rather similar (P:Fe=0.17-0.21; Feely et al., 1998) and distinctly higher than the ratios observed in Atlantic hydrothermal plumes (P:Fe=0.06-0.12). This has led to speculation that plume P:Fe ratios may reflect the ambient dissolved  $PO_4^{3-}$  concentration of the host water column and may thus offer potential as a long-term tracer of past ocean circulation, if preserved faithfully in metalliferous marine sediments (Feely et al., 1998).

#### 8.7.5.2.5 Hydrothermal scavenging by Fe oxyhydroxides

A final group of elements identified from investigations of hydrothermal plume particles are the particle-reactive tracers, including the REE and Be, Y, Th, and Pa (German et al., 1990, 1991a,b, 1993; Sherrell et al., 1999). These tracers, like the two preceding groups, correlate positively with particulate Fe in hydrothermal plumes (Figure 21). Unlike the oxyanion group, however, these tracers do not show constant X:Fe ratios within the nonbuoyant plume; instead, the highest ratios (e.g., for REE:Fe) are found distant from the vent site (German et al., 1990; Sherrell et al., 1999). One possible interpretation of this phenomenon is that Fe oxyhydroxide particles within young nonbuoyant plumes are undersaturated with respect to surface adsorption and so continuously scavenge dissolved,



**Figure 21** Plots of particulate Cu, V, and Nd concentrations versus particulate Fe for suspended particulate material filtered in situ from the TAG hydrothermal mound, Mid-Atlantic Ridge, 26° N (data from German et al., 1990, 1991b). Note generally positive correlations with particulate Fe concentration for all three tracers but with additional negative (Cu) or positive (Nd) departure for sulfide-forming and scavenged elements, respectively.

particle-reactive species as the particles disperse through the water column (German et al., 1990, 1991a,b). An alternative hypothesis (Sherrell et al., 1999) argues instead for two-stage equilibration within a nonbuoyant hydrothermal plume: close to the vent source, a maximum in, for example, particulate REE concentrations is reached, limited by equilibration at fixed distribution constants between the high particulate Fe concentrations present, and the finite dissolved tracer (e.g., REE) concentrations present in plume water. As the plume disperses and undergoes dilution, however, particulate Fe concentrations also decrease; reequilibration between these particles and the diluting pristine ambient seawater, at the same fixed distribution constants, would then produce the higher REE/Fe ratios observed at lower particulate Fe concentrations. More work is required to resolve which of these interpretations (kinetic vs. equilibrium) more accurately reflect the processes active within hydrothermal plumes. What is beyond dispute is that the uptake fluxes of these particle-reactive tracers, in association with hydrothermal Fe oxyhydroxide precipitates, far exceed their dissolved flux entering the oceans from hydrothermal vents. Thus, hydrothermal plumes act as sinks rather than sources for these elements, even causing local depletions relative to the ambient water column concentrations (e.g., Klinkhammer et al., 1983). Thus, even for those particlereactive elements which are greatly enriched in vent fluids over seawater (e.g., REE), the processes active within hydrothermal plumes cause a net removal of these tracers, not just relative to the vent fluids but from the oceanic water column itself (German et al., 1990; Rudnicki and Elderfield, 1993). In the extreme, these processes can cause geochemical fractionations as pronounced as those caused by boundary scavenging in high-productivity ocean-margin environments (Anderson et al., 1990; German et al., 1997).

Thus far, the processes active in hydrothermal plumes have been treated as inorganic geochemical processes. It is known, however, that this is not strictly the case: microbial processes are well known to mediate key chemical reactions in hydrothermal plumes (Cowen and German, 2003; Cowen and Li, 1991; Winn et al., 1995), and more recently, the role of larger organisms such as zooplankton has also been noted (e.g., Burd et al., 1992; Herring and Dixon, 1998). The biological modification of plume processes is discussed more fully in Section 8.7.5.4 below.

#### 8.7.5.3 Physical Controls on Dispersing Plumes

Physical processes associated with hydrothermal plumes may influence their impact on ocean geochemistry. Because of the fundamentally different hydrographic controls in the Pacific versus Atlantic oceans, plume dispersion varies between these two oceans. In the Pacific Ocean, where deep waters are warmer and saltier than overlying water masses, nonbuoyant hydrothermal plumes which have entrained local deep water are typically warmer and saltier at the point of emplacement than the surrounding seawater (e.g., Lupton et al., 1985). The opposite has been observed in the Atlantic Ocean, where deep waters tend to be colder and less saline than the overlying water column. Consequently, the TAG nonbuoyant plume, for example, is colder and fresher than the surrounding water into which it intrudes, 300–400 m above the seafloor (Speer and Rona, 1989).

Of perhaps more significance geochemically are the physical processes which affect plume dispersion after emplacement at nonbuoyant plume height. Here, topography at the ridge crest exerts particular influence. Along slow- and ultraslow-spreading ridges (e.g., MAR, SW Indian Ridge, and Central Indian Ridge), nonbuoyant plumes are typically emplaced within the confining bathymetry of the rift valley walls on the order of 1000 m high. Along faster-spreading ridges such as the EPR, by contrast, buoyant plumes typically rise clear of the confining topography on the order of only  $\sim 100$  m high. Within rift valley 'corridors,' plume dispersion is highly dependent on along-axis current flow. At the TAG hydrothermal field (MAR 26° N), for example, residual currents are dominated by tidal excursions (Rudnicki et al., 1994). A net effect of these relatively stagnant conditions is that plume material trapped within the vicinity of the vent site appears to be recycled multiple times through the TAG buoyant and nonbuoyant plume, enhancing the scavenging effect upon particle-reactive tracers such as the Th isotopes within the local water column (German and Sparks, 1993). At the Rainbow vent site (MAR 36° N), by contrast, much stronger prevailing currents  $(\sim 10 \text{ cm s}^{-1})$  are observed, and a more unidirectional, topographically controlled flow is observed and can be exploited (German et al., 1998, 2010b). Adequate sampling of a dispersing hydrothermal plume to resolve geochemical processes requires knowledge of the potential complexities of its dispersion. Nor should it be assumed that such topographic steering is entirely a local effect confined to the rift valleys of slowspreading ridges. Speer et al. (2003) used a numerical simulation of ocean circulation to estimate dispersion along and away from the global ridge crest. A series of starting points were considered along the entire ridge system, 200 m above the seafloor, and at spacings of 30-100 km along axis; trajectories were then calculated over a 10 years integration period. With a few exceptions such as major fracture zones, the net effect was that dispersal trajectories tend to be constrained by the overall form of the ridge, such that plumes flow parallel to the ridge axis over great distances (Speer et al., 2003). While that work assumed that hydrothermal plume dispersion might be dominated in the deep ocean by relatively sluggish thermohaline circulation, Adams et al. (2011) have shown that in certain circumstances, for example, along the EPR, surface-generated mesoscale eddies can propagate all the way to ridge-crest depths, transporting chemicals and propagules hundreds of kilometers off-axis and involving previously unanticipated mechanisms that can introduce temporal variability on seasonal and/or interannual timescales at the deep-ocean floor.

While the processes described above are all relevant to established hydrothermal plumes from steady or 'chronic' venting, important exceptions identified only rarely to date are the event (or 'mega-') plumes. One interpretation of these transient features is as follows: however a hydrothermal system may evolve, it must first displace a large volume of cold seawater from pore spaces within the upper ocean crust. Initial flushing of this system must be rapid, especially on ridges that are opening at fast rates, in excess of 10 cm year<sup>-1</sup>. In circumstances where there is frequent recurrence of either magma intrusion close beneath the seafloor or dike-fed eruption at the seafloor, venting may commence with rapid expulsion of a large volume of hydrothermal fluid to generate an event plume high up in the water column (e.g., Baker et al., 1995;

Lupton et al., 1999). Alternately, Palmer and Ernst (1998, 2000) have argued that cooling of pillow basalts, erupted at  $\sim$ 1200 °C on the seafloor and the most common form of submarine volcanic extrusion, is responsible for the formation of these same event plume features. Whichever eruptionrelated process causes their formation, an important question is, "what fraction of the total hydrothermal flux is associated with event plumes (Figure 15)?" Baker et al. (1998) estimated that the event plume triggered by dike intrusion at the coaxial vent field on the Juan de Fuca Ridge contributed less than 10% of the total flux of heat and chemicals released during the  $\sim$ 3 years lifespan of that vent. If widely applicable, this estimate suggests that event plumes can safely be ignored when calculating global geochemical fluxes (Hein et al., 2003). They remain of great interest to microbiologists, however, as a potential 'window' into the deep, hot biosphere (Edwards et al., 2011).

#### 8.7.5.4 Biogeochemical Cycling in Hydrothermal Plumes

The recent debate over the potential for organic complexation of hydrothermal Fe (Section 8.7.5.2.3) and other metals (Sander and Koschinsky, 2011) has revealed a paucity of supporting data on organic carbon in these complex systems. Since typical basalt-hosted hydrothermal fluids are essentially devoid of organic carbon (Lang et al., 2006; Von Damm, 1995), it had previously been inferred that any elevated levels of Corg in hydrothermal plumes must be due to either entrainment or in situ production within the plume itself (Lang et al., 2006; McCollom, 2000; Roth and Dymond, 1989). To test this hypothesis, Bennett et al. (2011a) tracked the fate of both dissolved and particulate organic carbons (DOC and POC) from the seafloor to the distal nonbuoyant plume at EPR 9°50' N. They found that buoyant plume samples contained high levels of both DOC and POC, which could only be sustained through entrainment from chimney walls and adjacent areas of biologically rich diffuse flow. Within the dispersing nonbuoyant plume, there was evidence for further potential Corg fixation but, importantly, all evidence for Corg enrichment at plume height was as POC, with no persistent DOC anomaly apparent. Further, in sediment trap samples collected from this dispersing plume, POC uptake was coupled closely to Fe oxyhydroxide fluxes. Pursuing this line of research, Toner et al. (2009) conducted spectroscopic measurements of iron and carbon in subsets of these same hydrothermal plume particles. They could not find any discrete iron(II) particles but found instead pervasive organic carbon-rich matrices containing evenly dispersed iron(II)-rich materials, attesting to the intimate association of Corg and metal cycling in hydrothermal plumes (Figure 22).



**Figure 22** Iron spectromicroscopy of an EPR hydrothermal plume aggregate showing Fe speciation and its association with C: (a) STXM image recorded at the Fe 2p3/2 edge (707.6 eV) showing three areas of interest outlined in white; (b) Iron NEXAFS spectra extracted from the three areas of interest presented with Fe(III) (pyrrhotite) and Fe(III) (ferrihydrite). Spectra from areas of interest 1 and 2 are multiplied by 4 and 2, respectively, for display purposes; (c-e) Fe(III), Fe(III), and C distribution maps; (f) STXM image at the C 1s edge (300 eV). Scale bars are all 1  $\mu$ m. Reproduced from Toner BM, Fakra SC, Manganini SJ, et al. (2009) Preservation of iron(II) by carbon-rich matrices in a hydrothermal plume. *Nature Geosciences* 3: 197–201.

While the coupling of hydrothermal systems with the Corg cycle in the deep ocean remains an active area of research (Scientific Committee on Oceanic Research (SCOR) Working Group 135), it has long been recognized that elevated concentrations of hydrogen, methane, ammonium, reduced sulfur, iron, and manganese in redox disequilibria in hydrothermal plumes might provide energy for substantial microbial primary productivity (Bennett et al., 2011b; Cowen et al., 2002; Dick et al., 2009; German et al., 2010a; Lam et al., 2004; McCollom, 2000). A good example is the microbial oxidation of dissolved Mn. In the restricted circulation regime of Guaymas Basin in the Gulf of California, formation of particulate Mn is dominated by bacteria, and the dissolved Mn residence time is <1 week (Campbell et al., 1988). Uptake of dissolved Mn in the Cleft Segment plume on the Juan de Fuca Ridge is likewise bacterially dominated, albeit with much longer residence times, estimated at 0.5 to >2 years (Winn et al., 1995). Distributions of dissolved CH4 and H2 in hydrothermal plumes have also been shown to be controlled by bacterially mediated oxidation (de Angelis et al., 1993), with apparent residence times that vary widely for CH4 (7-177 days) but are much shorter for dissolved  $H_2$  (<1 day). While the role of Fe-cycling microorganisms had previously been overlooked because of the low energy yield from Fe oxidation (Edwards et al., 2003), it is now recognized that in certain Fe-rich systems (e.g., Rainbow hydrothermal field, MAR; Loihi Seamount, Hawaii), the uniquely Fe-rich, sulfide-poor nature of the vent fluids results in a significant role for Fe-oxidizing bacteria as a basis for chemosynthesis (Bennett et al., 2011b; Edwards et al., 2004; Schmidt et al., 2009).

The release of dissolved  $H_2$  and  $CH_4$  into hydrothermal plumes provides suitable substrates for both primary (chemolithoautotrophic) and secondary (heterotrophic) production within dispersing nonbuoyant hydrothermal plumes. Although the sinking organic carbon flux from hydrothermal plumes (German et al., 2002; Roth and Dymond, 1989) may be less than 1% of the total oceanic photosynthetic production (Winn et al., 1995), hydrothermal production of organic carbon is probably restricted to a corridor extending no more than ~10 km to either side of the ridge axis. Consequently, microbial activity within hydrothermal plumes may have a pronounced local effect, perhaps five to tenfold greater than the photosynthetic flux driven from the overlying upper ocean (Cowen and German, 2003).

#### 8.7.5.5 Impact of Hydrothermal Plumes on Ocean Geochemical Cycles

Hydrothermal plumes form by the entrainment of large volumes of ambient ocean water into rising buoyant plumes driven by the release of vent fluids at the seafloor. The entire volume of the oceans is cycled through buoyant and nonbuoyant hydrothermal plumes, on average, every few thousand years – a timescale comparable to that for mixing of the entire deep ocean.

Close to the vent source, rapid precipitation of a range of polymetallic sulfide, sulfate, and oxide phases leads to a strong modification of the gross dissolved metal flux from the seafloor. Independent estimates by Mottl and McConachy (1990) and German et al. (1991b) from buoyant and nonbuoyant plume investigations in the Pacific and Atlantic oceans, respectively, concluded that a significant proportion of the total hydrothermal flux of only Mn and Ca remains in dissolved form within hydrothermal plumes. By contrast, the following 27 elements exhibited no evidence for a significant dissolved hydrothermal flux: Fe, Be, Al, Mg, Cr, V, Co, Cu, Zn, As, Y, Mo, Ag, Cd, Sn, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Ho, Er, Pb, and U. At the Rainbow hydrothermal field (36° N MAR), German et al. (2010b) found that the particulate Fe:dissolved Mn ratio in a dispersing hydrothermal plume passing a sill ~4 km downstream from the active vent field was identical to that in the source hydrothermal fluids, as were the corresponding Mn:<sup>3</sup>He and CH<sub>4</sub>:<sup>3</sup>He ratios. In this particular setting, evidently, lateral advection of the plume was sufficiently rapid (Thurnherr et al., 2002) that the plume was transporting all dissolved and particulate matter as far as this narrow gate within the confining rift valley. Exploiting these favorable dynamics and integrating across the rift valley using in situ sensors and physical oceanographic moorings, these workers established a first comprehensive record of export fluxes from a single hydrothermal field to the surrounding ocean (Table 2). By coupling that flux to known concentrations in the end-member vent fluids (Charlou et al., 2002; Douville et al., 2002), they were able to estimate a volume flux for high-temperature vent fluids at this site of  $\sim$  500 ls<sup>-1</sup>. While the Rainbow hydrothermal field most certainly cannot be taken as representative of all hydrothermal

 Table 2
 Export fluxes from the Rainbow vent site (estimated accurate to within a factor of 2)

	Export flux	Units
Heat	0.5	(GW)
Vent-fluid flux (CH <sub>4</sub> )	450	(l s <sup>-</sup> ])
Vent-fluid flux (Mn)	400	(l s <sup>-1</sup> )
<sup>3</sup> He	$7.6  imes 10^{-9}$	$(mol s^{-1})$
CH <sub>4</sub>	1.0	$(mol \ s^{-1})$
Mn	0.9	$(mol \ s^{-1})$
Fe	9.6	$(mol \ s^{-1})$
Cu	0.11	$(mol s^{-1})$
Zn	0.05	$(mol \ s^{-1})$
Cd	$5.2  imes 10^{-4}$	$(mol s^{-1})$
Ag	$1.1  imes 10^{-4}$	$(mol \ s^{-1})$
Pb	$4.5  imes 10^{-4}$	$(mol s^{-1})$
Р	0.94	(mol s <sup>-1</sup> )
V	0.036	$(mol s^{-1})$
Со	$2.5  imes 10^{-3}$	$(mol s^{-1})$
U	$4.9  imes 10^{-6}$	$(mol s^{-1})$
Y	$2.6 imes10^{-4}$	$(mol s^{-1})$
La	$1.2 \times 10^{-4}$	$(mol s^{-1})$
Се	$4.9 imes10^{-5}$	$(mol s^{-1})$
Pr	$2.4 imes10^{-5}$	$(mol s^{-1})$
Nd	$9.6 imes10^{-5}$	$(mol s^{-1})$
Sm	$1.8  imes 10^{-5}$	$(mol s^{-1})$
Eu	$1.1  imes 10^{-5}$	$(mol s^{-1})$
Gd	$1.9 imes10^{-5}$	$(mol s^{-1})$
Tb	$3.3 \times 10^{-6}$	$(mol s^{-1})$
Dy	$2.0 imes10^{-5}$	$(mol s^{-1})$
Но	$4.3 imes10^{-6}$	$(mol s^{-1})$
Er	$1.2 \times 10^{-5}$	$(mol s^{-1})$
Tm	$1.5  imes 10^{-6}$	$(mol s^{-1})$
Yb	$9.5  imes 10^{-6}$	$(mol s^{-1})$
Lu	$1.3  imes 10^{-6}$	$(mol s^{-1})$
		· · · /

fields (Section 8.7.2), this study is valuable because it shows how similar hydrothermal flux estimates could be attempted in future.

#### 8.7.6 Hydrothermal Sediments

Deep-sea metalliferous sediments were first documented in the reports of the Challenger expedition of 1873-76 (Murray and Renard, 1891), but it took almost a century to recognize that such metalliferous material was concentrated along all the world's ridge crests (Figure 2). Bostrom et al. (1969) attributed these distributions to some form of 'volcanic emanations'; the accuracy of those predictions was confirmed some 10 years later with the discovery of ridge-crest venting (Corliss et al., 1978; Spiess et al., 1980), although metalliferous sediments had already been found in association with hot brine pools in the Red Sea (Degens and Ross, 1969). Following the discovery of active venting, it has been recognized that hydrothermal sediments can be classified into two types: those derived from plume fallout (including the majority of metalliferous sediments reported from ridge flanks) and those derived from mass wasting close to active vent sites (see, e.g., Mills and Elderfield, 1995).

#### 8.7.6.1 Near-Vent Sediments

Near-vent metalliferous sediments form from the physical degradation of hydrothermal deposits themselves, a process which begins as soon as deposition has occurred. While there is ample evidence for extensive mass wasting in ancient volcanogenic massive sulfide deposits, only limited attention has been paid to this aspect of modern hydrothermal systems. Much of our understanding comes from detailed investigations at a single site, the TAG hydrothermal field at 26° N on the MAR. It has been shown, for example, that at least some of the weathered sulfide debris at TAG is produced from collapse of the mound itself. This collapse is believed to arise from waxing and waning of hydrothermal circulation which, in turn, leads to episodic dissolution of large volumes of anhydrite within the mound (e.g., Humphris et al., 1995; James and Elderfield, 1996). The mass-wasting process at TAG generates an apron of hydrothermal detritus with oxidized sulfides deposited up to 60 m away from the flanks of the hydrothermal mound.

Similar ponds of metalliferous sediment are observed close to inactive sulfide mounds throughout the TAG area (Rona et al., 1993). Metz et al. (1988) characterized the metalliferous sediment in a core raised from a sediment pond close to one such deposit, c.2 km NNE of the active TAG mound. The core consisted of alternating dark red-brown layers of weathered sulfide debris and lighter calcareous ooze. Traces of pyrite, chalcopyrite, and sphalerite, together with elevated transition metal concentrations, were found in the dark red-brown lavers, confirming the presence of clastic sulfide debris. Subsequently, German et al. (1993) investigated a short core raised from the outer limit of the apron of 'stained' hydrothermal sediment surrounding the TAG mound itself. That core penetrated through 7 cm of metal-rich degraded sulfide material into pelagic carbonate ooze. The upper mass-wasting layer was characterized by high transition metal contents, just as observed by Metz et al. (1988), but also exhibited REE patterns similar to vent fluids and high U contents attributed to uptake from seawater during oxidation of sulfides (German et al., 1993). Pb isotopic compositions in sulfide sediments from both sites were indistinguishable from local MORB, vent fluids, and chimneys (German et al., 1993; Mills et al., 1993). By contrast, the underlying/intercalated carbonate/calcareous ooze layers from each core exhibited Pb isotopic, REE, and U–Th compositions which much more closely reflected input of Fe oxyhydroxide particles from nonbuoyant hydrothermal plumes (see below).

#### 8.7.6.2 Deposition from Hydrothermal Plumes

Speer et al. (2003) modeled deepwater circulation above the global ridge crest and concluded that this circulation is dominated by topographically steered flow along the axis. Escape of dispersed material into adjacent deep basins is predicted to be minimal, except in key areas where pronounced across-axis circulation occurs. If this model proves to be generally valid, the majority of hydrothermal material released into nonbuoyant hydrothermal plumes should not be dispersed more than ~100 km off-axis. Instead, most hydrothermal material should settle out in a near-continuous rain of metalliferous sediment along the length of the global ridge crest. Significant off-axis dispersion is only predicted (1) close to the equator  $(\sim 5^{\circ} \text{ N to } 5^{\circ} \text{ S})$ , (2) where the ridge intersects boundary currents or regions of deepwater formation, and (3) in the Antarctic Circumpolar Current (Speer et al., 2003). One good example of strong across-axis flow is at the equatorial MAR, where pronounced eastward flow of both Antarctic Bottom Water and lower North Atlantic Deep Water has been reported, passing through the Romanche and Chain Fracture zones (Mercier and Speer, 1998).

Another location where the large-scale off-axis dispersion modeled by Speer et al. (2003) has been documented is on the southern EPR (Figures 2 and 19). Metalliferous sediment enrichments there underlie the pronounced dissolved <sup>3</sup>He plume which extends westward across the southern Pacific Ocean at approximately 15°S (Bostrom et al., 1969; Lupton and Craig, 1981). Much of our understanding of ridge-flank metalliferous sediments comes from a large-scale study carried out at 19° S by Leg 92 of the Deep Sea Drilling Project (DSDP). That work targeted sediments underlying the westward-trending plume to investigate both temporal and spatial variability in hydrothermal output (Lyle et al., 1987). A series of holes was drilled extending westward from the ridge axis out to 5-28 Ma crust; the recovered cores comprise mixtures of biogenic carbonate and Fe-Mn oxyhydroxides. This work demonstrated from Pb isotopic analyses that even the most distal sediments, collected >1000 km from the ridge axis, contained 20-30% mantle-derived Pb (Barrett et al., 1987). In contrast, analysis of the same samples showed that REE distributions in the metalliferous sediments were dominated by a seawater source (Ruhlin and Owen, 1986). This is consistent with what has subsequently been demonstrated for hydrothermal plumes (Section 8.7.5, above), with the caveat that REE/Fe ratios in DSDP Leg 92 sediments are everywhere higher than the highest REE/Fe ratios yet measured in modern nonbuoyant hydrothermal plume particles (German et al., 1990; Sherrell et al., 1999).

#### 8.7.6.3 Hydrothermal Sediments in Paleoceanography

Because numerous trace elements are removed from the oceans in association with iron oxide hydrothermal particles (Section 8.7.5), an opportunity arises to exploit the sedimentary record of this plume fallout for paleocanographic reconstruction of past ocean conditions. The sedimentary record of any given trace element, however, also depends on the nature and extent of postdepositional reactions (Mills and Dunk, 2010; Poulton and Canfield, 2006; Schaller et al., 2000).

P and V, which are typically present in seawater as dissolved oxyanion species, exhibit systematic plume-particle P:Fe and V:Fe variations which differ from one ocean basin to another (e.g., Feely et al., 1990; Trefry and Metz, 1989). This has led to the hypothesis (Feely et al., 1998) that (1) plume P:Fe and V:Fe ratios may be directly linked to local deep-ocean dissolved phosphate concentrations and (2) ridge-flank metalliferous sediments preserved under oxic conditions might faithfully record temporal variations in plume-particle P:Fe and/or V:Fe ratios. A study of slowly accumulating ( $\sim 0.5 \text{ cm ky}^{-1}$ ) sediments from the west flank of the Juan de Fuca Ridge found that V:Fe ratios in the hydrothermal component appear to record local plume-particle V:Fe ratios faithfully for the past  $\sim$ 200 ky (Feely et al., 1998; German et al., 1997). Sediments from the flanks of the southern EPR (10° S), dating back to 60-70 ka, also exhibit V:Fe ratios that mimic modern plume values, but the complementary P:Fe and As:Fe ratios in these samples are quite different from contemporaneous nonbuoyant plume values (Schaller et al., 2000). Poulton and Canfield (2006) pursued this line of research further and argued that molar P:Fe ratios in oxic Fe-rich sediments might serve as proxies of relative changes in paleoseawater phosphate concentrations but only if Fe sulfide minerals did not form an important component during transport and deposition of those sediments.

Unlike V, REE/Fe ratios recorded in even the most recent metalliferous sediments are much higher than those in suspended hydrothermal plume particles (German et al., 1990, 1997; Sherrell et al., 1999). Moreover, the REE/Fe ratios of hydrothermal sediments increase systematically with distance from the paleoridge crest (Olivarez and Owen, 1989; Ruhlin and Owen, 1986). This indicates that the REE may continue to be taken up from seawater, at and near the sediment-water interface, long after the particles settle from the plume to the seabed. Because increased uptake of dissolved REE from seawater should also be accompanied by continuing fractionation across the REE series (e.g., Rudnicki and Elderfield, 1993), reconstruction of deepwater REE patterns from preserved metalliferous sediment records remains problematic. Much more tractable, however, is the exploitation of these same sample types for isotopic reconstructions.

Because seawater uptake dominates the REE content of metalliferous sediment, Nd isotopic analysis of metalliferous carbonate can provide a reliable proxy for contemporaneous seawater, away from input of near-vent sulfide detritus (Mills et al., 1993). Osmium exhibits similar behavior, and seawater dominates its isotopic composition in metalliferous sediments even close to active vent sites (Ravizza et al., 1996). Analysis of preserved metalliferous carbonate sediments has thus proven useful in determining the past Os isotopic composition of the oceans, both from modern marine sediments (e.g., Peucker-Ehrenbrink et al., 1995; Ravizza, 1993) and those preserved in ophiolites (e.g., Ravizza et al., 2001). Only in sediments close to an ultramafic-hosted hydrothermal system have perturbations from a purely seawater Os isotopic composition been observed (Cave et al., 2003).

Owing to recent advances in analytical and isotope geochemistry, especially involving MC-ICP-MS, the past decade has seen a rapid increase in our ability to measure novel trace elements and isotopes in the marine environment (SCOR Working Group, 2007). With the advent of the international GEO-TRACES program, it is anticipated that the decade ahead will spawn new understanding of the present day cycling of trace elements and isotopes, which will augment our ability to investigate past records of ocean behavior. As just one illustration of the power of that approach, Mills et al. (2010) investigated variations downcore in  $\delta^{13}C$ ,  $\delta^{18}O$ , major and trace element concentrations, and various element: Fe ratios in sediment cores from the Southern EPR to deconvolve basin-wide changes in ventilation extending back over ~740 ky.

#### 8.7.6.4 Hydrothermal Sediments and Boundary Scavenging

It has been known for some time that sediments underlying areas of high particle settling flux exhibit pronounced fractionations between particle-reactive tracers. Both <sup>231</sup>Pa and <sup>10</sup>Be, for example, exhibit larger enrichments relative to <sup>230</sup>Th in ocean-margin sediments than in sediments underlying midocean gyres (e.g., Anderson et al., 1990; Bacon, 1988; Lao et al., 1992). Comparable fractionations between these three radiotracers have also been identified in sediments underlying hydrothermal plumes (Bourlès et al., 1994; German et al., 1993, 1997). A metalliferous sediment core raised from the flanks of the Juan de Fuca Ridge, for example, exhibited characteristic hydrothermal Pb isotopic and REE/Fe compositions together with high <sup>10</sup>Be/<sup>230</sup>Th ratios, indicative of net focusing relative to the open ocean (German et al., 1997). The degree of fractionation was high even when compared with highproductivity ocean-margin environments (Anderson et al., 1990; Lao et al., 1992), presumably because of intense scavenging onto hydrothermal Fe oxyhydroxides. The observation that REE and Th are scavenged onto ridge-crest metalliferous sediments is not new; sediments from the EPR near 17° S, with mantle Pb, excess <sup>230</sup>Th, and seawater-derived REE compositions were described more than 30 years ago by Bender et al. (1971). More recently, however, examination of ridge-crest sediments and near-vent sediment traps has revealed that the settling flux of scavenged tracers (e.g., <sup>230</sup>Th) from hydrothermal plumes is higher than can be sustained by in situ production in the overlying water column alone (German et al., 2002). Thus, uptake onto Fe oxyhydroxide particles in hydrothermal plumes and sediments may act as a special form of deep-ocean 'boundary scavenging,' leading to the net focusing and deposition of these dissolved tracers in ridge-flank metalliferous sediments.

#### 8.7.7 Conclusion

The field of deep-sea hydrothermal research remains both young and vibrant; little more than 30 years has passed since

its first discovery anywhere in the oceans. To synthesize current understanding of its impact on marine geochemistry, therefore, could be considered akin to explaining the significance of rivers to ocean chemistry in the early part of the last century. This chapter has aimed to provide a brief synopsis of the current state of the art, but much more remains to be learned. In particular, three key questions are likely to continue to focus efforts within this vigorous research field in the immediate future:

#### 8.7.7.1 What Are the Integrated Fluxes of Hydrothermal Heat and Mass from a Single Vent System to the Surrounding Ocean?

While recent work (German et al., 2010b) has captured export fluxes associated exclusively with the high-temperature discharge through a nonbuoyant plume from a single vent site, much remains to be learned. The Ridge 2000 program has revealed a wealth of previously unrecognized processes in the past decade, but what is now urgently required is a comprehensive and integrated study of the partitioning of high- and low-temperature heat, fluid, and biogeochemical fluxes from a single basalt-hosted site, ideally at a fast- or medium-spreading section of ridge crest, over a complete 10-25 years cycle from one eruption event to the next. In recent years, the effect of subseafloor magmatic (±tectonic) events on the chemical and physical properties of hydrothermal fluids has become better recognized. The chemistry of volatile species in vent fluids, for example, has proven to be a powerful tool in distinguishing magmatic events from tectonic ones, while changes in halogens and metal/chloride ratios indicate extreme phase separation effects, suggesting high temperatures (430-450 °C) and low to moderate pressures. These inferences have been strengthened by recent advances in the collection of experimental and theoretical data for the NaCl-H2O and SiO2(c)-NaCl-H2O systems. Time-series changes in vent-fluid chemistry in the aftermath of magmatism at the EPR and the Juan de Fuca Ridge indicate similar changes as the respective hydrothermal systems reform and reestablish steady-state conditions. A major limitation in our understanding of the response of hydrothermal fluid chemistry to magmatic events, however, remains the difficulty in anticipating such events and the delay in responding to them when such events occur. It is for this reason that observatory-based initiatives such as Neptune Canada and the Ocean Observatories Initiative in the United States offer unusual potential for discovery and learning of high-resolution feedbacks between magmatic and hydrothermal systems in space and time.

## 8.7.7.2 What Role Does Protolith Composition Play in Hydrothermal Vent-Fluid Chemistry?

Owing largely to the success of the NSF Ridge and Ridge 2000 programs and to discoveries of hydrothermal systems associated with slow-spreading ridges, the effect of protolith on the composition of hydrothermal fluids is becoming clearer. Although constraints imposed by basalt composition on hydrothermal alteration at elevated temperatures and pressures are reasonably well known from field and laboratory studies over the past few decades, the same is not true for back-arc systems and ultramafic-hosted hydrothermal systems, where sourcerock composition and the inherent structure of these systems can be complex and variable. The diversity of protolith composition in back-arc systems produces an unusually diverse range of vent-fluid compositions, while tectonic controls on fluid circulation paths at slow-spreading ridges produce unique expressions of hydrothermal activity and uncertain controls on heat and mass transport. There can be no question that as these systems are explored further in coming years, the cause and effect that exists between protolith and ventfluid chemistry will become clearer. Field studies will have to take full advantage of ever-increasing advances in deepsubmergence technology while using integrated, interdisciplinary approaches of the type that have proven so successful for advancing our understanding of heat and mass transport in magmatically robust basalt-hosted hydrothermal systems.

### 8.7.7.3 What is the Impact of Seafloor Hydrothermal Venting on Global Ocean Biogeochemical Budgets?

One of the most exciting developments in hydrothermal research in the past decade has been the recognition that, contrary to received wisdom when the first edition of this chapter was published, hydrothermal discharge may play an important role in global biogeochemical cycles throughout the deep ocean. This is a rapidly emerging field, with strong cases already made for hydrothermal impacts upon both the Fe and Corg cycle throughout the deep ocean. Under the auspices of the international GEOTRACES program, a new study of detailed biogeochemical cycling has recently been approved to revisit and conduct the most detailed investigations to date of dissolved-particulate relationships in the hydrothermal plume that is advecting westward away from the southern EPR (Figure 19) - the world's largest single hydrothermal plume. That study, focusing on the behavior of trace elements and isotopes, coupled with the ongoing deliberations of SCOR Working Group 135 (Hydrothermal Energy Transfer and Its Impact on the Ocean Carbon Cycles), ensures that this field will continue to evolve and no doubt continue to spring surprises throughout the decade ahead.

#### Remembrance

The spectacular progress that has been made in our understanding of submarine hydrothermal systems would not have been possible without the pioneering efforts of Karen L. Von Damm (Figure 23(a)), who coauthored this chapter (with CRG) for the first edition. From the earliest discoveries of high-temperature vents at mid-ocean ridges, Karen played a monumental role in helping to identify the complex linkages between the geochemical, geological, and biological processes that characterize these systems. Indeed, her research has made a lasting contribution to the evolution of the field of marine and hydrothermal geochemistry that will benefit generations to come. Her untimely passing in 2008 was a great loss, and it is entirely appropriate that a recently discovered vent field on the Mid-Cayman Rise, which extends the known range of all vent-fluid chemical compositions, now carries her name (Figure 23(b)).

![](_page_37_Picture_2.jpeg)

(a) Karen L. Von Damm, 1955–2008.

![](_page_37_Picture_4.jpeg)

(b) Von Damm vent site on the Mid-Cayman Rise. Photo courtesy of NOAA's Ocean Exploration Program.

Figure 23 (a) Karen L. Von Damm, 1955–2008. (b) Von Damm vent site on the Mid-Cayman Rise. Photo courtesy of NOAA's Ocean Exploration program.

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