6.07 Hydrothermal Processes

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6.07.1 INTRODUCTION
6.07.1.1 What is Hydrothermal Circulation?
6.07.1.2 Where Does Hydrothermal Circulation Occur?
6.07.1.3 Why Should Hydrothermal Fluxes Be Considered Important?

6.07.2 VENT-FLUID GEOCHEMISTRY
6.07.2.1 Why are Vent-fluid Compositions of Interest?
6.07.2.2 Processes Affecting Vent-fluid Compositions
6.07.2.3 Compositions of Hydrothermal Vent Fluids
   6.07.2.3.1 Major-element chemistry
   6.07.2.3.2 Trace-metal chemistry
   6.07.2.3.3 Gas chemistry of hydrothermal fluids
   6.07.2.3.4 Nutrient chemistry
   6.07.2.3.5 Organic geochemistry of hydrothermal vent fluids
6.07.2.4 Geographic Variations in Vent-fluid Compositions
   6.07.2.4.1 The role of the substrate
   6.07.2.4.2 The role of temperature and pressure
   6.07.2.4.3 The role of spreading rate
   6.07.2.4.4 The role of the plumbing system
6.07.2.5 Temporal Variability in Vent-fluid Compositions

6.07.3 THE NET IMPACT OF HYDROTHERMAL ACTIVITY

6.07.4 NEAR-VENT DEPOSITS
6.07.4.1 Alteration and Mineralization of the Upper Ocean Crust
6.07.4.2 Near-vent Hydrothermal Deposits

6.07.5 HYDROTHERMAL PLUME PROCESSES
6.07.5.1 Dynamics of Hydrothermal Plumes
6.07.5.2 Modification of Gross Geochemical Fluxes
   6.07.5.2.1 Dissolved noble gases
   6.07.5.2.2 Dissolved reduced gases (H₂S, H₂, CH₄)
   6.07.5.2.3 Iron and manganese geochemistry in hydrothermal plumes
   6.07.5.2.4 Co-precipitation and uptake with iron in buoyant and nonbuoyant plumes
6.07.5.2.5 Hydrothermal scavenging by Fe-oxhydroxides
6.07.5.3 Physical Controls on Dispersing Plumes
6.07.5.4 Biogeochemical Interactions in Dispersing Hydrothermal Plumes
6.07.5.5 Impact of Hydrothermal Plumes Upon Ocean Geochemical Cycles

6.07.6 HYDROTHERMAL SEDIMENTS
6.07.6.1 Near-vent Sediments
6.07.6.2 Deposition from Hydrothermal Plumes
6.07.6.3 Hydrothermal Sediments in Paleoceanography
6.07.6.4 Hydrothermal Sediments and Boundary Scavenging

6.07.7 CONCLUSION

REFERENCES
6.07.1 INTRODUCTION

6.07.1.1 What is Hydrothermal Circulation?

Hydrothermal circulation occurs when seawater percolates downward through fractured ocean crust along the volcanic mid-ocean ridge (MOR) system. The seawater is first heated and then undergoes chemical modification through reaction with the host rock as it continues downward, reaching maximum temperatures that can exceed 400 °C. At these temperatures the fluids become extremely 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 “MORs” to produce fresh ocean crust at a rate of ~20 km³ yr⁻¹, forming new seafloor at a rate of ~3.3 km² yr⁻¹ (Parsons, 1981; White et al., 1992). 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), i.e., through 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 (Degens and Ross, 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 MOR spreading centers. An analysis of core-top 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 (Boström et al., 1969). Another early indication of hydrothermal activity came from the detection of plumes of excess ³He in the Pacific Ocean Basin (Clarke et al., 1969)—notably the >2,000 km wide section in the South Pacific (Lupton and Craig, 1981)—because ³He 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 and Hobart, 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 ± 30 °C) vent fluids were found at 21°N on the East Pacific Rise (EPR) (Spiess 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 found at more than 40 locations throughout the Pacific, North Atlantic, and Indian Oceans (e.g., Van Dover et al., 2002) with further evidence—from characteristic chemical anomalies in the ocean water column—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) to the extremes of the ice-covered Arctic (Edmonds et al., 2003).

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

![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 (after C. A. Stein and S. Stein, 1994).](image-url)
Figure 2  Global map of the (Al + Fe + Mn):Al ratio for surficial marine sediments. Highest ratios mimic the trend of the global MOR axis (after Boström et al., 1969).

Figure 3  Schematic map of the global ridge crest showing the major ridge sections along which active hydrothermal vents have already been found (red circles) or are known to exist from the detection of characteristic chemical signals in the overlying water column (orange circles). Full details of all known hydrothermally active sites and plume signals are maintained at the InterRidge web-site: http://triton.ori.u-tokyo.ac.jp/~intridge/wg-gdha.htm.
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 fraction—perhaps as little as 10%—of the total hydrothermal heat flux close to ridge axes. A range of studies—most notably along the Juan de Fuca Ridge (JdFR) in the NE Pacific Ocean (Rona and Trivett, 1992; Schultz et al., 1992; Ginster et al., 1994) have suggested that, instead, axial hydrothermal circulation 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. The relative importance of high- and low-temperature hydrothermal circulation to overall ocean chemistry remains a topic of active debate.

While most studies of seafloor hydrothermal systems have focused on the currently active plate boundary (~0–1 Ma crust), 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 crust from 0–65 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).

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 high-temperature 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.

6.07.1.2 Where Does Hydrothermal Circulation Occur?

Hydrothermal circulation occurs predominantly along the global MOR crest, a near-continuous volcanic chain that extends over ~6 × 10^4 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 major transform faults that extend further 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 Rodrigues 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 as the incipient ocean basin that is the Red Sea (Section 6.07.1.1). The other branch of the global ridge crest branches south east from the Rodrigues 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 ≈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 ≈40° N, to form the Gorda, Juan de Fuca, and Explorer Ridges—all of which hug the NE Pacific/N. American margin up to ≈55° N. Submarine hydrothermal activity is also known to be associated with the back-arc spreading centers formed behind ocean–ocean subduction zones which 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. 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, Society Islands), but these sites are much less extensive, laterally, than ridge crests and back-arc spreading centers, combined. A continuously updated map of reported hydrothermal vent sites is maintained by the InterRidge community as a Vents Database (http://triton.ori.u-tokyo.ac.jp/~intridge/wg-gdha.htm).

As described earlier, the first sites of hydrothermal venting to be discovered were located along the intermediate to fast spreading Galapagos Spreading Center (6 cm yr\(^{-1}\)) and northern EPR (6–15 cm yr\(^{-1}\)). A hypothesis, not an unreasonable one, 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; Ishibashi et al., 1997) along the superfast spreading southern EPR (17–19° S), where ridge-spreading rate is among the fastest known (>44 cm yr\(^{-1}\)). Evidence for reasonably widespread venting has also been found most recently along some of the slowest-spreading sections of the global ridge crest, both in the SW Indian Ocean (German et al., 1998a; Bach et al., 2002) and in the Greenland/Arctic Basins (Connelly et al., 2002; Edmonds et al., 2003). Most explorations so far, however, have focused upon ridge crests 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, in the western Pacific back-arc basins and along the northern MAR (Figure 3), while other parts of the global MOR system remain largely unexplored (e.g., southern MAR, Central Indian Ridge, SE Indian Ridge, Pacific–Antarctic Ridge).

Reinforcing how little of the seafloor is well explored, as recently as December 2000 an entirely new form of seafloor hydrothermal activity, in a previously unexplored geologic setting was discovered (Kelley et al., 2001). Geologists diving at the Atlantis fracture zone, which offsets part of the MAR near 30° N, found moderate-temperature fluids (40–75 °C) exiting from tall (up to 20 m) chimneys, formed predominantly from calcite [CaCO\(_3\)], aragonite [CaCO\(_3\)], and brucite [Mg(OH)\(_2\)]. These compositions are quite unlike previously documented hydrothermal vent fluids (Section 6.07.2), yet their geologic setting is one that may recur frequently along slow and very slow spreading ridges (e.g., Gracia et al., 1999, 2000, Parson et al., 2000; Sauter et al., 2002). The Lost City vent site may, therefore, represent a new and important form of hydrothermal vent input to the oceans, which has hitherto been overlooked.
6.07.1.3 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 (Edmond et al., 1979, 1982; Staudigel and Hart, 1983; Von Damm et al., 1985a; C. A. Stein and S. Stein, 1994; Elderfield and Schultz, 1996; Schultz and Elderfield, 1997; Mottl, 2003). Of the total heat flux from the interior of the Earth (~32 TW) is associated with cooling through oceanic 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 (C. A. Stein and S. 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 (i) heat released from the crystallization of basaltic magma at emplacement temperatures (latent heat), and (ii) heat mined from the solidified crust during cooling from emplacement temperatures to hydrothermal temperatures, assumed by Mottl (2003) to be 1175 °C and 350 °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 yr$^{-1}$ and the maximum heat available from crystallization of this basaltic magma and cooling to hydrothermal temperatures is 2.8 ± 0.3 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 $10^{16}$ g yr$^{-1}$. 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 critical point is approached. Thus, for example, at 350 bar, a moderate increase in temperature near 400 °C could cause an increase in $c_p$ approaching an order of magnitude resulting in a concomitant drop in the water flux required to transport this much heat (Bischoff and Rosenbauer, 1985; Elderfield and Schultz, 1996).

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 $10^{16}$ g yr$^{-1}$). In those calculations, the remainder of the axial heat flux was assumed to be transported by a much larger volume flux of lower-temperature fluid (280–560 $10^{16}$ g yr$^{-1}$ at ~5 °C). But how might such diffuse flow manifest itself? Should diffuse 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 were only restricted to 0–0.1 Ma crust, the associated fluid flow might still extend over the range of kilometers from the axis on medium-fast ridges—i.e., out onto young ridge flanks. For slow and ultraslow spreading ridges (e.g., the MAR) by contrast, all 0–0.1 Ma and, indeed 0–1 Ma crustal circulation would occur within the confines of the axial rift valley (order 10 km wide). The partitioning of “axial” and “near-axial” hydrothermal flow, on fast and slow ridges and between “focused” and “diffuse” flow, remains very poorly constrained in the majority of MOR settings and is an area of active debate.

On older oceanic 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 ± 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 magnesium 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 $10^{19}$ g yr$^{-1}$ (Mottl, 2003).

To put these volume fluxes in context, the maximum flux of cool (<20 °C) hydrothermal fluids, calculated above is almost identical to the global riverine flux estimate of 3.7–4.2 $10^{19}$ g yr$^{-1}$ (Palmer and Edmond, 1989). The flux of high-temperature fluids close to the ridge axis, by contrast, is ~1,000-fold lower. Nevertheless, for an ocean volume of ~1.4 $10^{24}$ g, this still yields a (geologically short) oceanic residence time, with respect to high-temperature circulation, of ~20–30 Ma—and the hydrothermal fluxes will be important for those elements which exhibit high-temperature...
fluid concentrations more than 1,000-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 6.07.5) with typical dilution ratios of ~10^4:1 (e.g., Helfrich and Speer, 1995). If 50% of the fluids circulating at high temperature through young ocean crust are entrained into hydrothermal plumes then the total water flux through hydrothermal plumes would be approximately one order of magnitude greater than all other hydrothermal fluxes and 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 just 4–8 kyr, i.e., directly comparable to the mixing time of the global deep-ocean conveyor (~1.5 kyr; Broecker and Peng, 1982). From that perspective, therefore, we can anticipate that hydrothermal circulation should play an important role in the marine geochemistry of any tracer which exhibits a residence time greater than ~1–10 kyr in the open ocean (see Chapter 6.02).

The rest of the chapter is organized as follows. In Section 6.07.2 we discuss the chemical composition of hydrothermal fluids, why they are important, what factors control their compositions, and how these compositions vary, both in space, from one location to another, and in time. Next (Section 6.07.3) we identify that the fluxes established thus far represent gross fluxes into and out of the ocean crust associated with high-temperature venting. We then examine the other source and sink terms associated with hydrothermal circulation, including alteration of the oceanic 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 6.07.4 provides a detailed discussion of near-vent deposits, including the formation of polymetallic sulfides and other minerals, as well as near-vent sediments. In Section 6.07.5 we present a detailed description 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. Section 6.07.6 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. We conclude (Section 6.07.7) by identifying some of the unresolved questions associated with hydrothermal circulation that are most in need of further investigation.

6.07.2 VENT-FLUID GEOCHEMISTRY

6.07.2.1 Why are Vent-fluid Compositions of Interest?

The compositions of vent fluids found on the global MOR system are of interest for several reasons; how and why those compositions vary has important implications. The overarching question, as mentioned in Section 6.07.1.3, 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 6.07.1, 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 (e.g., Von Damm, 1995) and we now know that these compositions often vary profoundly on short

Table 1  Overview of hydrothermal fluxes: heat and water volume: data from Elderfield and Schultz (1996) and Mottl (2003).

| (I) Summary of global heat fluxes | Heat flux from the Earth’s interior | 43 TW |
| Heat flux associated with ocean crust | 32 TW |
| Seafloor hydrothermal heat flux | 11 TW |

| (II) Global hydrothermal fluxes: heat and water | Heat flux (TW) | Water flux (10^16 g yr⁻¹) |
| Axial flow (0–1 Ma) | 2.8 ± 0.3 | 5.6 ± 0.6 |
| All flow at 350 °C | 2.8 ± 0.3 | 420 ± 140 |
| 10%@350 °C/90%@5 °C Hydrothermal plumes (50%) | 28,000 ± 3,000 |
| Off-axis flow (1–65 Ma) | 7 ± 2 | 1,000–4,000 |
| Global riverine flux | 3,700–4,200 |
(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 oceanic 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 we can not yet drill young oceanic 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. 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 oceanic crust at certain temperatures. Because the dissolved chemicals in hydrothermal fluids provide energy sources for microbial communities living within the oceanic 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. Although the mineral deposits found are not economic themselves, they have provided 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.

6.07.2.2 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 oceanic crust. Four factors have been identified: the two most important are (i) phase separation and (ii) water–rock interaction; the importance of (iii) biological processes and (iv) magmatic degassing has yet to be established.

Water–rock interaction and phase separation are processes that are inextricably linked. As water passes through the hydrothermal system it will react with the rock and/or sediment substrate that is present (Figure 5). These reactions begin in the downflow zone, and continue throughout. When

![Figure 5](image)

(a) Schematic illustration of the three key stages of submarine hydrothermal circulation through young ocean crust (after Alt, 1995). Seawater enters the crust in widespread “recharge” zones and reacts under increasing conditions of temperature and pressure as it penetrates downward. Maximum temperatures and pressures are experienced in the “reaction zone,” close to the (magmatic or hot-rock) “heat source” before buoyant plumes rise rapidly back toward the seafloor—the “discharge” zone. (b) Schematic of processes controlling the composition of hydrothermal vent fluid, as it is modified from starting seawater (after Von Damm, 1995). During recharge, fluids are heated progressively. Above \(\sim 130\, ^\circ\text{C}\) anhydrite (\(\text{CaSO}_4\)) precipitates and, as a result of water–rock reaction, additional calcium (\(\text{Ca}^{2+}\)) is leached from the rock in order to precipitate most of the sulfate (\(\text{SO}_4^{2-}\)) derived from seawater. Magnesium (\(\text{Mg}^{2+}\)) is also lost to the rock and protons (\(\text{H}^+\)) are added. As the fluid continues downward and up the temperature gradient, water–rock interactions continue and phase separation may occur. At least two sites on the global MOR system, direct degassing of the magma must be occurring, because very high levels of gas (especially \(\text{CO}_2\), and helium) are observed in the hydrothermal fluids. The buoyant fluids then rise to the seafloor. In most cases the fluids have undergone phase separation, and in at least some cases storage of the liquid or brine phase has occurred which has been observed to vent in later years from the same sulfide structure (Von Damm et al., 1997).

See Figure 6 for additional discussion of phase separation.
vent fluids exit at the seafloor, what we observe represents the net result of all the reactions that have occurred along the entire hydrothermal flow path. Because the kinetics of most reactions are faster at higher temperatures, it is assumed that much of the reaction occurs in the “reaction zone.” 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 oceanic crust, back toward the seafloor. However, without a direct view into any of the active seafloor hydrothermal systems, for simplicity of discussion, and because we lack better constraints, we often view the system as one of: (i) water–rock reaction on the downflow leg; (ii) phase separation and water–rock reaction in the “reaction zone”; (iii) additional water–rock reaction after the phase separation “event” (Figure 5). Unless confronted with clear inconsistencies in the (chemical) data that invalidate this approach, we usually employ this simple “flow-through” as our working conceptual model. Even though we are unable 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 we employ.

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, magnesium and SO\(_4\) are lost, and the pH is lowered so substantially that all the alkalinity is titrated. The large quantities of silicon, iron, and manganese that are frequently gained may be sufficient for these to become “major elements” in hydrothermal fluids. For example, silicon and iron can exceed the concentrations of calcium and potassium, two major elements in seawater. Much of the dissolved SO\(_4\) in seawater is lost on the downflow leg of the hydrothermal system as CaSO\(_4\) (anhydrite) precipitates at temperatures of \(\sim 130^\circ C\)—just by heating seawater. Because there is more dissolved SO\(_4\) than calcium in seawater, on a molar basis, additional calcium 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. In fact, it is now recognized that at least some dissolved SO\(_4\) must persist down into the reaction zone, based on the inferred redox state at depth (see later discussion). Some seawater SO\(_4\) is also reduced to H\(_2\)S, substantial quantities of which may be precipitated in this way. This results in the generation of H\(^+\), which accounts for the low pH and titration of the alkalinity. Sodium can also be lost from the fluids due to Na–Ca replacement reactions in plagioclase feldspars, known as albitionization. Potassium (and the other alkalis) are also involved in similar types of reaction that can also generate acidity. Large quantities of iron, manganese, and silicon are also leached out of the rocks and into the fluids.

An element that is relatively conservative through water–rock reaction is chloride in the form of the anion chloride. Chloride is key in hydrothermal fluids, because with the precipitation and/or reduction of SO\(_4\) and the titration of HCO\(_3^–/CO_3^{2–}\), chloride becomes the overwhelming and almost only anion (Br is usually present in the seawater proportion to chloride). Chloride becomes a key component, therefore, because almost all of the cations in hydrothermal fluids are present as chloro-complexes; thus, the levels of chloride 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 (see Volume Editor’s Introduction). Because these constant proportions are not maintained in vent fluids and because chloride is the predominant anion, discussions of vent fluids are best discussed in terms of their chlorinity, not their salinity.

Although small variations in chloride may be caused by rock hydration/dehydration, there are almost no mineralogic sinks for chloride 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 process in seafloor hydrothermal systems. Essentially no hydrothermal fluids are found with chlorinities equal to the local ambient seawater value. To phase separate seawater at typical intermediate-to-fast spreading MOR depths of \(\sim 2,500\) m requires temperatures \(\geq 389^\circ C\) (Bischoff, 1991). This sets a minimum temperature that fluids must have reached, therefore, during their transit through the oceanic crust. The greater the depth, the higher the temperature required for phase separation to occur. Known vent systems occur at depths of \(800–3,600\) m, requiring maximum temperatures in the range 297–433 \(^\circ C\) to phase separate seawater. Seawater, being a two-component system, H\(_2\)O + NaCl (to a first approximation) exhibits different phase separation behavior from pure water. The critical point for seawater is 407 \(^\circ C\) and 298 bar (Bischoff and Rosenbauer, 1985) compared to 374 \(^\circ C\) and 220 bar for pure water. For the salt solution, the two-phase curve does not stop at the critical point but, instead, continues beyond it. As a solution crosses the two-phase curve, it will separate into two phases, one with chlorinities greater than starting seawater, and the other with chlorinities less than starting seawater. If the fluid reaches the two-phase curve at temperature and pressure
conditions less than the critical point, subcritical phase separation (also called boiling) will occur, with the generation of a low chlorinity “vapor” phase. This phase contains salt, the amount of which will vary depending on where the two-phase curve was intersected (Bischoff and Rosenbauer, 1987). 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 (or condensation). In this case a small amount of a relatively high chlorinity liquid phase is condensed out of the fluid. Both sub- and super-critical phase separation occur in seafloor hydrothermal systems. To complete the phase relations in this system, halite may also precipitate.
There is evidence that halite forms, and subsequently redissolves, in some seafloor hydrothermal systems (Oosting and Von Damm, 1996; Berndt and Seyfried, 1997; Butterfield et al., 1997; Von Damm, 2000). The $P$–$T$ conditions at which the fluid intersects the two-phase curve, will determine the relative compositions of the two phases, as well as their relative amounts. Throughout this discussion, we have assumed the starting fluid undergoing phase separation is seawater (or, rather, an NaCl equivalent, because the initial magnesium and SO$_4$ will already be lost by this stage). If the NaCl content is different, the phase relations in this system change, 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 also a function of the salt content, and hence is really a critical curve in $P$–$T$–$x$ ($x$ referring to composition) space.

As phase separation occurs, substantially changing the chloride content of vent fluids (values from $<6\%$ to $\sim200\%$ of the seawater concentration have been observed), other chemical species will change in concert. It has been shown, both experimentally as well as in the
field, that most of the cations (and usually bromide) maintain their element-to-Cl ratios during the phase separation process (Berndt and Seyfried, 1990; Von Damm, 2000; Von Damm et al., 2003), i.e., most elements are conservative with respect to chloride. Exceptions do occur, however—primarily for those chemical species not present as chlorocomplexes. Dissolved gases (e.g., CO$_2$, CH$_4$, He, H$_2$, H$_2$S) are preferentially retained in the low chlorinity or vapor phase, and boron, which is present as a hydroxyl complex, is relatively unaffected by phase separation (Bray and Von Damm, 2003a). Bromide, as viewed through the Br/Cl ratio, is sometimes seen to be fractionated from chloride; this occurs whenever halite is formed or dissolves because bromide is preferentially excluded from the halite structure (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 or expressed as ratios with respect to chloride, rather than as absolute concentrations. This normalization to chloride must be used when trying to evaluate net gains and losses of chemical species as seawater traverses the hydrothermal circulation cell, to correct for the fractionation caused by phase separation.

Aside from early eruptive fluids (discussed later), the chemical composition of most high-temperature fluids (Figure 7) appears to be controlled by equilibrium or steady state with the rock assemblage. (Equilibrium requires the assemblage to be at its lowest energy state, but the actual phases present may be metastable, in which case they are not at true thermodynamic equilibrium but, rather, have achieved a steady-state condition.) When vent-fluid data are modeled with geochemical modeling codes using modern thermodynamic databases, the results suggest equilibrium, or at least steady state, has been achieved. The models cannot be rigorously applied to many of the data, however, because the fluids are often close to the critical point and in that region the thermodynamic data are not as well constrained. Based on results from both geochemical modeling codes and elemental ratios, current data indicate that not only the major elements, but also many minor elements (e.g., rubidium, caesium, lithium, and strontium) are controlled by equilibrium, or steady-state, conditions between the fluids and their host-rocks (Bray and Von Damm, 2003b). The rare earth elements (REE) in vent fluids present one such example. REE distributions in hydrothermal fluids are light-REE enriched and exhibit strong positive europium anomalies, apparently quite unrelated to host-rock MORB compositions (Figure 8). However, 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

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**Figure 7** Compositional data for vent fluids. (a) Time series data from “A” vent for chloride and H$_2$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 becoming more common. The data plotted are referred to as the “end-member” data (data from Von Damm et al., 1995 and unpublished). 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 has increased and the fluids sampled more recently, in 2002, are the liquid (brine) phase. As is expected, the concentration of H$_2$S, a gas that will be partitioned preferentially into the vapor phase, is anticorrelated with the chloride content. The vertical axis has 10 divisions with the following ranges: T (°C) 200–405 (ambient seawater is 2 °C); Cl (mmol kg$^{-1}$) 0–800 (ambient is 540 mmol kg$^{-1}$); H$_2$S (mmol kg$^{-1}$) 0–120 (ambient is 0 mmol kg$^{-1}$). (b) Whenever vent fluids are sampled, varying amounts of ambient seawater are entrained into the sampling devices. Vent fluids contain 0 mmol kg$^{-1}$ while ambient seawater contains 52.2 mmol kg$^{-1}$. Therefore, if actual sample data are plotted as properties versus magnesium, least squares linear regression fits can be made to the data. The calculated “end-member” concentration for a given species, which represents the “pure” 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$^{-1}$). These plots versus magnesium are therefore mostly sampling artifacts and are referred to as “mixing” diagrams. While these types of plots were originally used to illustrate vent-fluid data, they have been largely superceded by figures such as (a) or (c). This figure (b) shows the data used to construct the time series represented in (a). 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 shape, the different colors within a year grouping 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 et al., 1995 and unpublished data). (c) As the chloride 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 chloride content. Variations in the chloride content are a result of phase separation. This shows the relationship between the potassium (K) and chloride content in vent fluids in the global database, as of 2000. The line is the ratio of K/Cl in ambient seawater. Closed circles are from 9–10° N EPR following the 1991 eruption, open circles are other 9–10° N data not affected by the eruptive events; triangles are from sites where vents occur 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 in Von Damm (2000).
REE concentrations may be intrinsically linked to the high-temperature alteration of this particular mineral.

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 two sites along the global MOR system—at 9° 50' N and at 32° S on the EPR (M. D. Lilley, personal communication; Lupton et al., 1999a). These sites have very high levels of CO₂, and very high He/heat ratios. The interpretation is that we are seeing areas with recent magma resupply within the crust and degassing of the lavas, resulting in very high gas levels in the hydrothermal fluids found at these sites. We do not know the spatial—temporal variation of this process, hence, we cannot yet evaluate its overall importance. Presumably, every site on the global MOR system undergoes similar processes episodically. What is not known, however, is the frequency of recurrence at any one site. Consequently, the importance of fluxes due to this degassing process, versus more “steady-state” venting, cannot currently be assessed. At 9° 50' N, high gas contents have now been observed for almost a decade; no signature of volatile-metal enrichment has been observed in conjunction with these high gas contents (Von Damm, 2003).

The fourth process influencing vent-fluid compositions is biological change, which can take the form of either consumption or production of various chemical species. As the current known limit to life on Earth is ~120°C (e.g., Holland and Baross, 2003) this process can only affect fluids at temperatures lower than this threshold. This implies that high-temperature vents should not be subject to these effects whereas they may occur in both lower-temperature axial diffuse flow and beneath ridge flanks. From observations at the times of seafloor eruptions and/or diking events, it is known that there are microbial communities living within the oceanic crust (e.g., 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 H₂, CH₄, and H₂S contents of those fluids (Von Damm and Lilley, 2003). Hence, biological influences have been observed; how widespread this is, which elements are affected, and what the overall impact on chemical fluxes may be all remain to be resolved.

6.07.2.3 Compositions of Hydrothermal Vent Fluids

6.07.2.3.1 Major-element Chemistry

The known compositional ranges of vent fluids are summarized in Figure 9 and Table 2. Because no two vents yet discovered have exactly the same composition, these ranges often change with each new site. As discussed in Section 6.07.2.2, vent fluids are modified seawater characterized by the loss of magnesium, SO₄, and alkalinity and the gain of many metals, especially on a chloride normalized basis.

Vent fluids are acidic, but not as acid as may first appear from pH values measured at 25°C and 1 atm (i.e., in shipboard laboratories). The cation H⁺ in vent fluids is also present as a chloro-complex with the extent of complexation increasing as P and T increase. At the higher in situ conditions of P and T experienced at the seafloor, therefore, much of the H⁺ is incorporated into the HCl–aqueous complex; hence, the activity of H⁺ is reduced and the in situ pH is substantially higher than what is measured at laboratory temperatures. The K_w for water also changes as a function of P and T such that neutral pH is not necessarily 7 at other P–T conditions. For most vent fluids, the in situ pH is 1–2 pH units more acid than neutral, not the ~4 units of acidity that the measured (25°C, 1 atm) data appear to imply. Most high-temperature vent fluids have (25°C measured) pH values of 3.3 ± 0.5 but a few are more acidic whilst several are less acid. If fluids are more acid than pH 3.3 ± 0.5, it is often an indicator that metal sulfides have precipitated below the seafloor because such reactions produce protons. Two mechanisms are known that can cause fluids to be less acidic than the norm: (i) cases where the rock substrate appears to be more highly altered—the rock cannot buffer the solutions to as low a pH; (ii) when organic matter is present, ammonium is often present and
the NH₃/NH₄⁺ couple serves to buffer the pH to a higher level.

Vent fluids are very reducing, as evidenced by the presence of H₂S rather than SO₄, as well as H₂, CH₄ and copious amounts of Fe²⁺ and Mn²⁺. In rare cases, there can be more H₂S and/or H₂ than chloride on a molar basis and it is the prevailing high acidity that dictates that H₂S rather than HS⁻ or S²⁻ is the predominant form in high-temperature vent fluids. Free H₂ is derived as a result of water–rock reaction and there is substantially more H₂ than O₂ in these fluids. Therefore, although redox calculations are typically given in terms of the log fO₂, the redox state is best calculated based on the H₂/H₂O couple for seafloor vent fluids. This can then be expressed in terms of the log fO₂. The K for the reaction:

\[
    \text{H}_2 + \frac{1}{2} \text{O}_2 = \text{H}_2\text{O}
\]

also changes as a function of temperature and pressure. Another way to determine how reducing vent fluids are is by comparing them to various mineralogic buffers such as pyrite–pyrrhotite–magnetite (PPM) or hematite–magnetite–pyrite (HMP). Most vent fluids lie between these two extremes, but there is some systematic variation (Seyfried and Ding, 1995). The observation that vent fluids are more oxic than would be expected based on the PPM buffer, provides one line of evidence that the reaction zone is not as reducing as initially predicted, consistent with at least some dissolved seawater SO₄ penetrating into the deeper parts of the system rather than being quantitatively removed by anhydrite precipitation within shallower levels of the downflow limb.

Lower-temperature (<100°C) vent fluids found right at the 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 “ground water,” with temperatures of ~150 °C within the oceanic crust. Evidence for the latter is found in some Ocean Drilling Program data (Magenheim et al., 1992), some high-temperature vent fluids from 9°50’N on the EPR (Ravizza et al., 2001), and some very unusual ~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 whilst lower-temperature fluids are typically a dilution of this same material with seawater. The few exceptions to this will be discussed below.

### 6.07.2.3.2 Trace-metal 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 ROV-deployed sampling bottles, they become supersaturated with respect to many solid phases and, thus, precipitate. Once this occurs, everything in the sampling apparatus must be treated as one sample: a budget can only be constructed by integrating these different fractions back together. In the difficult sampling environment found at high-temperature vent sites, pieces of chimney structure are also sometimes entrained into the sampling apparatus. It is necessary, therefore, to be able to discriminate between particles that have precipitated from solution in the sampling bottle and “contaminating” particles that are extraneous to the sample. In addition, water samples are often...
Table 2  Ranges in chemical composition for all known vent fluids.

<table>
<thead>
<tr>
<th>Chemical species</th>
<th>Units</th>
<th>Seawater overall range</th>
<th>Slow $^a$ (0–2.5 cm yr$^{-1}$)</th>
<th>Intermediate $^a$ &gt; 2.5–6</th>
<th>Fast $^a$ &gt; 6–12</th>
<th>Ultrafast $^a$ &gt; 12</th>
<th>Sediment covered$^b$</th>
<th>Ultramafic hosted$^c$</th>
<th>Arc, back-arc$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>25 °C, 1 atm</td>
<td>7.8</td>
<td>2.0–9.8</td>
<td>2.5–4.85</td>
<td>2.8–4.5</td>
<td>2.45–&gt; 6.63</td>
<td>2.96–5.53</td>
<td>5.1–5.9</td>
<td>2.7–9.8</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>meq kg$^{-1}$</td>
<td>2.4</td>
<td>-3.75–10.6</td>
<td>-3.4–0.31</td>
<td>-3.75–0.66</td>
<td>-2.69–&lt; 2.27</td>
<td>-0.915</td>
<td>1.45–10.6</td>
<td>-0.20–3.51</td>
</tr>
<tr>
<td>Cl</td>
<td>mmol kg$^{-1}$</td>
<td>540</td>
<td>30.5–1,245</td>
<td>357–675</td>
<td>176–1,245</td>
<td>30.5–902</td>
<td>113–1,090</td>
<td>412–668</td>
<td>515–756</td>
</tr>
<tr>
<td>SO$_4$</td>
<td>mmol kg$^{-1}$</td>
<td>28</td>
<td>&lt;0–&lt; 28</td>
<td>&lt;3.5–19</td>
<td>&lt;25–0.763</td>
<td>&gt;8.76</td>
<td>&lt;5.02–9.53</td>
<td>0</td>
<td>&lt;12.9</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>mmol kg$^{-1}$</td>
<td>0</td>
<td>0–110</td>
<td>0.5–5.9</td>
<td>0–19.5</td>
<td>0–110</td>
<td>0–35</td>
<td>1.10–5.98</td>
<td>0.064–1.0</td>
</tr>
<tr>
<td>Si</td>
<td>mmol kg$^{-1}$</td>
<td>0.03–0.18</td>
<td>&lt;24</td>
<td>7.7–22</td>
<td>11–24</td>
<td>2.73–22.0</td>
<td>8.69–21.3</td>
<td>5.60–13.8</td>
<td>6.4–8.2</td>
</tr>
<tr>
<td>Li</td>
<td>umol kg$^{-1}$</td>
<td>26</td>
<td>4.04–5,800</td>
<td>238–1,035</td>
<td>160–2,350</td>
<td>4,04–1,620</td>
<td>248–1,200</td>
<td>370–1,290</td>
<td>245–345</td>
</tr>
<tr>
<td>K</td>
<td>mmol kg$^{-1}$</td>
<td>10.1</td>
<td>-1.17–79.0</td>
<td>17–28.8</td>
<td>6.98–58.7</td>
<td>-1.17–51</td>
<td>2.2–44.8</td>
<td>13.5–49.2</td>
<td>20.2–22</td>
</tr>
<tr>
<td>Rb</td>
<td>umol kg$^{-1}$</td>
<td>1.3</td>
<td>0.156–360</td>
<td>9.4–40.4</td>
<td>22.9–59</td>
<td>0.156–31.1</td>
<td>0.39–6.8</td>
<td>22.5–105</td>
<td>28–37.1</td>
</tr>
<tr>
<td>Cs</td>
<td>mmol kg$^{-1}$</td>
<td>2</td>
<td>2.3–7,700</td>
<td>100–285</td>
<td>168–364</td>
<td>2.3–264</td>
<td>1,000–7,700</td>
<td>331–385</td>
<td></td>
</tr>
<tr>
<td>Be</td>
<td>mmol kg$^{-1}$</td>
<td>0</td>
<td>10–91</td>
<td>10–37</td>
<td>37–91</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>mmol kg$^{-1}$</td>
<td>52.2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>mmol kg$^{-1}$</td>
<td>10.2</td>
<td>-1.31–109</td>
<td>9.9–43</td>
<td>9.75–109</td>
<td>-1.31–106</td>
<td>4.02–65.5</td>
<td>26.6–81.0</td>
<td>21.0–67</td>
</tr>
<tr>
<td>Sr</td>
<td>umol kg$^{-1}$</td>
<td>87</td>
<td>-29–387</td>
<td>42.9–133</td>
<td>0.0–348</td>
<td>-29–387</td>
<td>10.7–190</td>
<td>160–257</td>
<td>138–203</td>
</tr>
<tr>
<td>Ba</td>
<td>umol kg$^{-1}$</td>
<td>0.14</td>
<td>1.64–100</td>
<td>&lt;52.2</td>
<td>&lt;8–&gt; 46</td>
<td>1.64–18.6</td>
<td>&gt;12</td>
<td>&gt;45–79</td>
<td>5.9–100</td>
</tr>
<tr>
<td>Mn</td>
<td>umol kg$^{-1}$</td>
<td>&lt;0.001</td>
<td>10–7,100</td>
<td>59–1,000</td>
<td>140–4,480</td>
<td>62.7–3,300</td>
<td>20.6–2,750</td>
<td>10–236</td>
<td>330–2,350</td>
</tr>
<tr>
<td>Fe</td>
<td>mmol kg$^{-1}$</td>
<td>&lt;0.001</td>
<td>0.007–25.0</td>
<td>0.0241–5.590</td>
<td>0.009–18.7</td>
<td>0.007–12.1</td>
<td>0.038–14.7</td>
<td>0–0.18</td>
<td>2.5–25.0</td>
</tr>
<tr>
<td>Cu</td>
<td>umol kg$^{-1}$</td>
<td>0.007</td>
<td>0–162</td>
<td>0–150</td>
<td>0.142</td>
<td>0.18–97.3</td>
<td>2.6–150</td>
<td></td>
<td>27–162</td>
</tr>
<tr>
<td>Zn</td>
<td>umol kg$^{-1}$</td>
<td>0.012</td>
<td>0–3,000</td>
<td>0–400</td>
<td>2.2–600</td>
<td>13–411</td>
<td>1.9–740</td>
<td>0.1–40.0</td>
<td>29–185</td>
</tr>
<tr>
<td>Co</td>
<td>umol kg$^{-1}$</td>
<td>0.00003</td>
<td>&lt;0.005–14.1</td>
<td>0.130–0.422</td>
<td>0.022–0.227</td>
<td></td>
<td></td>
<td>&lt;0.005</td>
<td>11.8–14.1</td>
</tr>
<tr>
<td>Ni</td>
<td>umol kg$^{-1}$</td>
<td>0.012</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>nmol kg$^{-1}$</td>
<td>0.02</td>
<td>&lt;1–230</td>
<td>&lt;1–38</td>
<td>&lt;1–230</td>
<td></td>
<td></td>
<td></td>
<td>11–47</td>
</tr>
<tr>
<td>Cd</td>
<td>nmol kg$^{-1}$</td>
<td>1.0</td>
<td>0–180</td>
<td>75–146</td>
<td>0–180</td>
<td>0–180</td>
<td></td>
<td>63–178</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>nmol kg$^{-1}$</td>
<td>0.01</td>
<td>&lt;20–3,900</td>
<td>221–376</td>
<td>183–360</td>
<td>&lt;20–652</td>
<td>86–169</td>
<td>36–3,900</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>umol kg$^{-1}$</td>
<td>0.02</td>
<td>0.1–18.7</td>
<td>1.03–13.9</td>
<td>4.0–5.2</td>
<td>0.1–18</td>
<td>9.3–18.7</td>
<td>0.9–7.9</td>
<td>1.9–4</td>
</tr>
<tr>
<td>Br</td>
<td>umol kg$^{-1}$</td>
<td>840</td>
<td>29.0–1,910</td>
<td>666–1,066</td>
<td>250–1,789</td>
<td>290–1,370</td>
<td>210–1910</td>
<td>770–1,180</td>
<td>306–1,045</td>
</tr>
<tr>
<td>F</td>
<td>umol kg$^{-1}$</td>
<td>68</td>
<td>&lt;38.8</td>
<td>16.1–38.8</td>
<td>“0”</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>CO$_2$</td>
<td>mmol kg$^{-1}$</td>
<td>3.56–39.9</td>
<td>&lt;5.7</td>
<td>&lt;200</td>
<td>8.4–22</td>
<td></td>
<td></td>
<td>14.4–200</td>
<td></td>
</tr>
<tr>
<td>CH$_4$</td>
<td>umol kg$^{-1}$</td>
<td>0.0003</td>
<td>&lt;15.6</td>
<td>&lt;15.6</td>
<td>&lt;15.6</td>
<td>&lt;15.6</td>
<td>&lt;15.6</td>
<td></td>
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<tr>
<td>NH$_3$</td>
<td>mmol kg$^{-1}$</td>
<td>0</td>
<td>&lt;15.6</td>
<td>&lt;15.6</td>
<td>&lt;15.6</td>
<td>&lt;15.6</td>
<td>&lt;15.6</td>
<td></td>
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</tr>
<tr>
<td>H$_2$</td>
<td>umol kg$^{-1}$</td>
<td>0.0003</td>
<td>&lt;38,000</td>
<td>1.1–727</td>
<td>&lt;0.45</td>
<td>&lt;0.45</td>
<td>&lt;0.45</td>
<td>&lt;0.45</td>
<td>&lt;0.45</td>
</tr>
</tbody>
</table>

$^a$ These omit sedimented covered and um hosted.  
$^b$ Includes: Guaymas, Escanaba, Middle Valley. 
$^c$ Includes Rainbow, Lost City, kvd unpublished data for Logatchev.  
$^d$ Compilation from Ishibashi and Urabe (1995).
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 co-precipitate 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 7–8 orders of magnitude (as is sometimes true for iron). At least some data exist demonstrating the enrichment of all of vanadium, cobalt, nickel, copper, zinc, arsenic, selenium, aluminium, silver, cadmium, antimony, caesium, barium, tungsten, gold, thallium, lead, and REE relative to seawater. Data also exist showing that molybdenum and uranium are often lower than their seawater concentrations. These trace-metal data have been shown to vary with substrate and the relative enrichments of many of these trace metals varies significantly between MOR 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 GSC fluids (Edmond et al., 1979) showed these fluids 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).

6.07.2.3.3 Gas chemistry of hydrothermal fluids

In general, concentrations of dissolved gases are highest in the lowest-chlorinity fluids, which represent the vapor phase. However, there are exceptions to this rule, and gas concentrations vary significantly between vents, even at a single location. In the lowest chlorinity and hottest fluids, H₂S may well be the dominant gas. However, because H₂S levels are controlled by metal-sulfide mineral solubility, this H₂S is often lost via precipitation. While the first vent sites discovered contained less than twice the CO₂ present in seawater (Welhan and Craig, 1983), more vents have higher levels of CO₂ than is commonly realized. Few MOR vent fluids have CO₂ levels less than or equal to the total CO₂ levels present in seawater (~2.5 mmol kg⁻¹). Instead, many fluids have concentrations approaching an order of magnitude more CO₂ than seawater; the highest approach two orders of magnitude more CO₂ than seawater, but these highest levels are uncommon (M. D. Lilley, personal communication). Back-arc systems more commonly have higher levels of CO₂ in their vent fluids, but concentrations two orders of magnitude greater than seawater are, again, close to the upper maximum of what has been sampled so far (Ishibashi and Urabe, 1995). CH₄ is much less abundant than CO₂ in most systems. Vent-fluid CH₄ concentrations are typically higher in sedimented systems and in systems hosted in ultramafic rocks, when compared to bare basaltic vent sites. CH₄ is also enriched in low-temperature vent fluids when compared to concentrations predicted from simple seawater/vent-fluid mixing (Von Damm and Lilley, 2003). Longer-chain organic molecules have also been reported from some sites, usually at even lower abundances than CO₂ and/or CH₄ (Evans et al., 1988). The concentrations of H₂ gas in vent fluids vary substantially, over two orders of magnitude (M. D. Lilley, personal communication). Again the highest levels are usually observed in vapor phase fluids, especially those sampled immediately after volcanic eruptions or diking events. Relatively high values (several mmol kg⁻¹) have also been reported from sites hosted by ultramafic rocks. Of the noble gases, helium, especially ³He, is most enriched in vent fluids. ³He 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 6.07.5). Radon, a product of radioactive decay in the uranium series, is also greatly enriched in vent fluids (e.g., Kadko and Moore, 1988; Rudnicki and Elderfield, 1992). 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).

6.07.2.3.4 Nutrient chemistry

The concentrations of nutrients available in seawater control biological productivity. Consequently, the dissolved nutrient concentrations in natural waters are always of great interest. Compared to deep-ocean seawater, the PO₄ contents of vent fluids are significantly lower, but are not zero. Much work remains to be done on the distribution of nitrogen species, and the nitrogen cycle in general, in vent fluids. Generally, in basalt-hosted systems, the nitrate + nitrite content is also lower than local deepwaters but, again, is not zero. Ammonium in these systems typically measures less than 10 μmol kg⁻¹ but, in some systems in which no sediment cover is present, values of 10s to even 100s of μmol kg⁻¹ are sometimes observed (cf. Von Damm, 1995). In Guaymas Basin, in contrast, ammonium concentrations as high as 15 mmol kg⁻¹ have been measured (Von Damm et al., 1985b). N₂ is also
6.07.2.3.5 Organic geochemistry of hydrothermal vent fluids

Studies of the organic chemistry of vent fluids are truly in their infancy and little field data exist (Holm and Charlou, 2001). There are predictions of what should be present based on experimental work (e.g., Berndt et al., 1996; Cruse and Seewald, 2001) and thermodynamic modeling (e.g., McCollom and Shock, 1997, 1998). These results await confirmation “in the field.” Significant data on the organic geochemistry are uniquely available for the Guaymas Basin hydrothermal system (e.g., Simoneit, 1991), which underlies a very highly productive area of the ocean, and is hosted in an organic-rich sediment-filled basin.

6.07.2.4 Geographic Variations in Vent-fluid Compositions

6.07.2.4.1 The role of the substrate

There are systematic reasons for some of the variations observed in vent-fluid compositions. One of the most profound is the involvement of sedimentary material in the hydrothermal circulation cell, as seen at sediment-covered ridges (Von Damm et al., 1985b; Campbell et al., 1994; Butterfield et al., 1994). The exact differences this imposes depend upon the nature of the sedimentary material involved: the source/nature of the aluminosilicate material, the proportions and type of organic matter it contains and the proportion and type of animal tests present, calcareous and/or siliceous. In the known sediment-hosted systems (Guaymas Basin, EPR; Escanaba Trough, Gorda Ridge; Middle Valley, JDFR; and perhaps the Red Sea) basalts are intercalated with the sediments or else underlie them. Hence, in these systems, reactions with basalt are overprinted by those with the sediments. In most cases, depending on the exact nature as well as thickness of the sedimentary cover, this causes a rise in the pH, which results in the precipitation of metal sulfides before the fluids reach the seafloor. The presence of carbonate and/or organic matter also buffers the pH to significantly higher levels (at least pH 5 at 25 °C and 1 atm).

The chemical composition of most seafloor vent fluids can be explained by reaction of unaltered basalt with seawater. However, in some cases the best explanation for the fluid chemistry is that the fluids have reacted with basalt that has already been highly altered (Von Damm et al., 1998). Two indicators for this are higher pH values (pH ~ 4 versus pH ~ 3.3 at 25 °C), as well as lower K/Na molar ratios and lower concentrations of the REEs. In the last several years, several vent sites have been sampled that cannot be explained by these mechanisms. At some locations, vent fluids must be generated by reaction of seawater with ultramafic rocks (Douville et al., 2002). These fluids can also have major variations from each other, depending on the temperature regime. In high-temperature fluids that have reacted with an ultramafic substrate, silicon contents are generally lower than in basalt-hosted fluids; H2, calcium, and iron contents are generally higher, but these fluids remain acidic (Douville et al., 2002). Not much is yet known about the seafloor fluids that are generated from lower-temperature ultramafic hydrothermal circulation. In the one example studied thus far (Lost City) the measured pH is greater than that in seawater, and fluid compositions are clearly controlled by a quite distinct set of serpentinization-related reactions (Kelley et al., 2001). An illustration of this fundamental difference is given by magnesium which is quantitatively stripped from “black smoker” hydrothermal fluids but exhibits ~20–40% of seawater concentrations (9–19 mM) in the Lost City vents, leading to the unusual magnesium-rich mineralization observed at this site (see later). The seafloor fluids from Lost City are remarkably similar to those found in continental hydrothermal systems hosted in ultramafic environments (Barnes et al., 1972). In back-arc spreading centers such as those found in the western Pacific, andesitic rock types are common and profound differences in vent-fluid compositions arise (Fouquet et al., 1991; Ishibashi and Úrabe, 1995, Gamo et al., 1997). These fluids can be both more acidic and more oxidizing than is typical and the relative enrichments of transition metals and volatile species in these fluids are quite distinct from what is observed in basalt-hosted systems.

Major differences in substrate are, therefore, reflected in the compositions of vent fluids. Insufficient trace-metal data for vent fluids exist, however, to discern more subtle substrate differences, e.g., between EMORB and N-MORB on non-hotspot influenced ridges. Where the ridge axis is influenced by hot-spot volcanism, some differences may be seen in the fluid compositions, as, for example, the high barium in the Lucky Strike vent fluids, but in this case most of the fluid characteristics (e.g., potassium concentrations) do not appear to be explained by substrate effects.
not show evidence for an enriched substrate (Langmuir et al., 1997; Von Damm et al., 1998).

### 6.07.2.4.2 The role of temperature and pressure

Temperature, of course, plays a major role in determining vent-fluid compositions. Pressure is often thought of as less important than temperature, but the relative importance of the two depends on the exact $P−T$ conditions of the fluids. Because of the controls that pressure and temperature conditions exert on the thermodynamics as well as the physical properties of the fluids, the two effects cannot be discussed completely independently from each other. Not only do $P−T$ conditions govern phase separation, as discussed above, they control transport in the fluids and mineral dissolution and precipitation reactions. Temperature, especially, plays a role in the quantities of elements that are leached from the host rocks. When temperature decreases, as it often does due to conductive cooling as fluids rise through the oceanic crust, most minerals become less soluble. Due to these decreasing mineral solubilities, transition metals and sulfide, in particular, may be lost from the ascending fluids. $P−T$ conditions in the fluids also control the strength of the aqueous complexes. In general, as $P$ and $T$ rise, aqueous species become more associated. Because of the properties of water at the critical point (the dielectric constant goes to zero), all the species must become associated, as there can be no charged species in solution at the critical point. Therefore, transport of species can increase markedly as the critical point is approached because there will be smaller amounts of the (charged) species present in solution which are needed if mineral solubility products are to be exceeded (Von Damm et al., 2003). It is in this critical point region that small changes in pressure can be particularly significant—for example, as a fluid is rising in the upflow (“discharge”) limb of a hydrothermal cell (Figure 5). Because most vent-fluid compositions are controlled by equilibrium or steady state, and because the equilibrium constants for these reactions change as a function of pressure and temperature, $P−T$ conditions will ultimately control all vent-fluid compositions. One problem associated with modeling vent fluids and trying to understand the controls on their compositions is that we really do not know the temperature in the “reaction zone.” Basaltic lavas are emplaced at temperatures of 1,100–1,200 °C, but rocks must be brittle to retain fractures that allow fluid flow, and this brittle–ductile transition lies in the range 500–600 °C. A commonplace statement is that the reaction zone temperature is ~450 °C, but we do not really know this value with any accuracy, nor how variable it may be from one location to another. At the seafloor, we have sampled fluids with exit temperatures as high as ~405 °C. Hence, in addition to the constraints provided by the recognition that at least subcritical phase separation is pervasive (see above) we can further determine that (i) reaction zone temperatures must exceed 405 °C, at least in some cases, and (ii) that in cases where evidence for supercritical phase separation has been determined (e.g., Butterfield et al., 1994; Von Damm et al., 1998) temperatures must exceed 407 °C within the oceanic crust.

The pressure conditions at any hydrothermal field are largely controlled by the depth of the overlying water column. Pressure is most critical in terms of phase separation and vent fluids are particularly sensitive to small changes in pressure when close to the critical point. It is in this region, close to the critical point, when fluids are very expanded (i.e., at very low density) that small changes in pressure can cause significant changes in vent-fluid composition.

### 6.07.2.4.3 The role of spreading rate

When one considers tables of vent-fluid chemical data, one cannot separate vents from ultrafast-versus slow-spreading ridges (Table 2); the range of chemical compositions from each of these two end-member types of spreading regime overlap. There has been much debate in the marine geological literature whether rates of magma supply, rather than spreading rate, should more correctly be applied when defining ridge types (e.g., “magma-starved” versus “magma-rich” sections of ridge crest). While any one individual segment of ridge crest undoubtedly passes through different stages of a volcanic–tectonic cycle, regardless of spreading rate (e.g., Parson et al., 1993; Haymon, 1996), it is generally the case that slow-spreading ridges are relatively magma-starved whilst fast spreading ridges are more typically magma-rich. Consequently, we continue to rely upon (readily quantified) spreading rate (De Mets et al., 1994) as a proxy for magma supply. To a first approximation, ridge systems in the Atlantic Ocean are slow-spreading, while fast-spreading ridges are only found in the Pacific. The Pacific contains ridges that spread at rates from ~15 cm yr$^{-1}$ full opening rate to a minimum of ~2.4 cm yr$^{-1}$ on parts of the Gorda Ridge (comparable to the northern MAR). In the Indian Ocean, ridge spreading varies between intermediate (~6 cm yr$^{-1}$, CIR and SEIR) and very slow rates (<2.0 cm yr$^{-1}$, SWIR). In the Arctic Ocean the spreading rate is the slowest known, decreasing to <1.0 cm yr$^{-1}$ from west to east as the Siberian shelf is approached. Discussion of vent-fluid compositions from different oceans,
therefore, often approximates closely to variations in vent-fluid chemistries at different spreading rates. Although tables of the ranges of vent-fluid chemistries do not show distinct differences between ocean basins, some important differences do become apparent when those data are modeled. (NB: Although there is now firm evidence for hydrothermal activity in the Arctic, those systems have not yet been sampled for vent fluids; similarly, in the Indian Ocean, only two sites have recently been discovered). Consequently, meaningful comparisons can only readily be made, at present, between Atlantic and Pacific vent-fluid compositions. In systems on the slow spreading MAR, the calculated $f_{O_2}$ of hydrothermal fluids is higher, suggesting that these systems are more oxidizing. Also, for example, both TAG and Lucky Strike vent fluids contain relatively little potassium compared to sodium (Edmond et al., 1995; Von Damm et al., 1998). Boron is also low in some of the Atlantic sites, especially at TAG and Logatchev (You et al., 1994; Bray and Von Damm, 2003a). The explanation for these observations is that on the slow-spreading MAR, hydrothermal activity is active for a much longer period of time at any given site (also reflected in the relative sizes of the hydrothermal deposits formed: Humphris et al., 1995; Fouquet et al., submitted). Consequently, MAR vent fluids become more oxic because more dissolved seawater SO$_4$ has penetrated as deep as the reaction zone; the rocks within the hydrothermal flow cell have been more completely leached and altered. Because of the more pronounced tectonic (rather than volcanic) activity that is associated with slow spreading ridges, rock types that are normally found at greater depths within the oceanic crust can be exposed at or near the surface. Thus, hydrothermal sites have been located along the MARs that are hosted in ultramafic rocks: the Rainbow, Logatchev, and Lost City sites. No ultramafic-hosted systems are expected to occur, by contrast, along the fast-spreading ridges of the EPR.

6.07.2.4.4 The role of the plumbing system

Another fundamental difference observed in the nature of hydrothermal systems at fast- and slow-spreading ridges concerns intra-field differences in vent-fluid compositions. (Note that the terms “vent field” and “vent area” are often used interchangeably, have no specific size classifications, and may be used differently by different authors. In our usage, “vent area” is smaller, referring to a cluster of vents within 100 m or so, while a “vent field” may stretch for a kilometer or more along the ridge axis—but this is by no means a standard definition.) On a slow spreading ridge, such as the MAR, all of the fluids venting, for example, at the TAG site, can be shown to have a common source fluid that may have undergone some change in composition due to near surface processes such as mixing and/or conductive cooling. Many of the fluids can also be related to each other at the Lucky Strike site. In contrast, on fast spreading ridges, vents that may be within a few tens of meters of each other, clearly have different source fluids. A plausible explanation for these differences would be that vents on slow spreading ridges are fed from greater depths than those on fast-spreading ridges, with emitted fluids channeled upward from the subsurface along fault planes or other major tectonic fractures. Hence, in at least some cases, hydrothermal activity found on slow spreading ridges may be located wherever fluids have been preferentially channeled. Active vent sites on slow spreading ridges also appear to achieve greater longevity, based on the size of the sulfide structures and mounds they have produced. Fluids on fast spreading ridges, by contrast, are fed by much shallower heat sources and the conduits for these fluids appear to be much more localized, resulting in the very pronounced chemical differences often observed between immediately adjacent vent structures. Clearly, the plumbing systems at fast and slow spreading ridges must be characterized by significant, fundamental differences.

6.07.2.5 Temporal Variability in Vent-fluid Compositions

The MOR is, in effect, one extremely long, continuous submarine volcano. While volcanoes are commonly held to be very dynamic features, however, little temporal variability was observed for more than the first decade of work on hydrothermal systems. Indeed, a tendency arose not to view the MOR as an active volcano, at least on the timescales that were being worked on. This perspective was 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 almost span 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, if not all of the heat that supports venting immediately following magmatic emplacement. Over timescales of as little as a year, however, an individual dike will have largely cooled and the heat source driving any continuing vent activity 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 oceanic crust. Vent-fluid compositions change, too, because the conditions of phase separation change; so, too, do the subsurface path length and residence time, such that the likelihood that circulating fluids reach equilibrium or steady state with the ocean crust also vary. Detailed time-series studies at sites perturbed by magmatic emplacements 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. In the best documented case study available, “brine” fluids were actively venting at a location some three years after the vapor phase had been expelled from the same individual hydrothermal chimney; at other event-affected vent sites, similar evolutions in vent-fluid composition have been observed over somewhat longer timescales.

The temporal variability that has now been observed has revolutionized our ideas about the functioning of hydrothermal systems and the timescales over which processes occur on the deep ocean floor. It is no exaggeration to state that processes we thought would take 100–1,000 yr, have been seen to occur in <10 yr. The majority of magmatic intrusions/eruptions that have been detected have been along the JdFR (Cleft Segment, Co-axial 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 at these sites, within days to weeks. We also have good evidence for two volcanic events on the ultrafast spreading southern EPR, but the best-studied eruption site, to date, has been at 9°45′–52′ N on the EPR. Serendipitously, submersible studies began at 9–10° N EPR less than one month after volcanic eruption at this site (Haymon et al., 1993; Rubin et al., 1994). Profound chemical changes (more than a factor of two in some cases) were noted at some of these vents during a period of less than a month (Von Damm et al., 1995; Von Damm, 2000). Subsequently, it has become clear that very rapid changes occur within an initial one-year period which are related to changes in the conditions of phase separation and water rock reaction. These, in turn, are presumed to reflect responses to the mining of heat from the dike-intrusion, including lengthening of the reaction path and increases in the residence time of the fluids within the crust. At none of the other eruptive sites has it been possible to complete comparable direct sampling of vent fluids within this earliest “post-event” time period. It is now clear that the first fluid to be expelled is the vapor phase (whether formed as a result of sub- or supercritical phase separation), probably because of its lower density. What happens next, however, 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 fluids; in other vents, the transition appears to occur more as a step function—although those observations may be aliased by the episodic nature of the sampling programs involved. What is most certainly the case at 9°N EPR, however, is that following initial vapor-phase expulsion, some vents have progressed to venting fluids with chlorinities greater than seawater much faster (≤3 yr), than others (∼10 yr), and several have never made the transition. Further, in some parts of the eruptive area, vapor phase fluids are still the predominant type of fluid being emitted more than a decade after the eruption event. Fluids exiting from several of the vents have begun to decrease in chlorinity again, without ever having reached seawater concentrations. Conversely, other systems (most notably those from the Cleft segment) have been emitting vent fluids with chlorinities approximately twice that of seawater for more than a decade. If one wanted to sustain an argument that hydrothermal systems followed a vapor-to-brine phase evolution as a system ages (e.g., Butterfield et al., 1997), it would be difficult to reconcile the observation that systems that are presumed to be relatively “older” (e.g., those on the northern Gorda Ridge) vent vapor-phase fluids, only (Von Damm et al., 2001). Finally, one vent on the southern EPR, in an area with no evidence for a recent magmatic event, is emitting fluids which are phase separating “real time,” with vapor exiting from the top of the structure, and brine from the bottom, simultaneously (Von Damm et al., 2003). Fundamentally, there is a chloride-mass balance problem at many known hydrothermal sites. For example, at 21° N EPR, where high-temperature venting was first discovered and an active system is now known to have persisted for at least 23 years (based on sampling expeditions from 1979 and 2002) only low-chlorinity fluids are now being emitted (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, at best, poor. What is clear is that pronounced temporal variability occurs at many vent sites, most notably...
at those that have been affected by magmatic events. There is also evidence for changes accompanying seismic events that are not related to magma-migration, but most likely related to cracking within the upper ocean crust (Sohn et al., 1998; Von Damm and Lilley, 2003).

In marked contrast to those sites where volcanic eruptions and/or intrusions (diking events) have been detected, there are several other sites that have been sampled repeatedly over timescales of about two decades where no magmatic activity is known to have occurred. At some of these sites, chemical variations observed over the entire sampling period fall within the analytical error of our measurement techniques. The longest such time-series is for hydrothermal venting at 21°N on the EPR, where black smokers were first discovered in 1979, and where there has been remarkably little change in the composition of at least some of the vent fluids. Similarly, the Guaymas Basin vent site was first sampled in January 1982 (Von Damm et al., 1985b), South Cleft on the JdF ridge in 1984 (Von Damm and Bischoff, 1987), and TAG on the MAR in 1986 (Campbell et al., 1988). All these sites have exhibited very stable vent-fluid chemistries, although only TAG would be considered as a “slow spreading” vent site. Nevertheless, it is the TAG vent site that has shown perhaps the most remarkable stability in its vent-fluid compositions; these have remained invariant for more than a decade, even after perturbation from the drilling of a series of 5 ODP holes direct into the top of the active sulfide mound (Humphris et al., 1995; Edmonds et al., 1996).

Accounting for temporal variability (or lack thereof) when calculating hydrothermal fluxes is, clearly, problematic. It is very difficult to calculate the volume of fluid exiting from a hydrothermal system accurately. Many of the differences from seawater are most pronounced in the early eruptive period (∼1 yr), which is also the time when fluid temperatures are hottest (Von Damm, 2000). Visual observations suggest that this is a time of voluminous fluid flow, which is not unexpected given that an enhanced heat source will have recently been emplaced directly at the seafloor in the case of an eruption, or, in the case of a dike intrusion, at shallow depths beneath. The upper oceanic crust exhibits high porosity, filled with ambient seawater. At eruption/intrusion, this seawater will be heated rapidly, its density will decrease, the resultant fluid will quickly rise, and large volumes of unreacted, cooler seawater will be drawn in and quickly expelled. It is not unreasonable to assume, therefore, that the water flux through a hydrothermal system may be at its largest during this initial period, just when chemical compositions are most extreme (Von Damm et al., 1995; Von Damm, 2000). The key to the problem, therefore, probably lies in determining how much time a hydrothermal system spends in its “waxing” (immediate post-eruptive) stage when compared to the time spent at “steady state” (e.g., as observed at 21° N EPR) and in a “waning” period, together with an evaluation of the relative heat, water, and chemical fluxes associated with each of these different stages. If fluid fluxes and chemical anomalies are greatest in the immediate post-eruptive period, for example, the initial 12 months of any vent-field 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 “lifecycle” can be completed. Alternately, the converse may hold true: early-stage eruptions may prove relatively insignificant over the full lifecycle of a prolonged, unperturbed hydrothermal site.

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

6.07.3 THE NET IMPACT OF HYDROTHERMAL ACTIVITY

It is important to remember that the gross chemical flux associated with expelled vent fluids (Section 6.07.2) is not identical to the net flux from hydrothermal systems. Subsurface hydrothermal circulation can have a net negative flux for some chemicals, the most obvious being magnesium which is almost quantitatively removed from the starting seawater and is added instead to the oceanic crust. Another example of such removal is uranium, which is also completely removed from seawater during hydrothermal circulation and then recycled into the upper mantle through subduction of altered oceanic crust. Even where, compared to starting seawater, there is no concentration gain or loss, an element may nevertheless undergo almost complete isotopic exchange within the oceanic crust indicating that none of the substance originally present in the starting seawater has passed conservatively through the hydrothermal system—the most obvious example being that of strontium. We present a brief summary of ocean crust mineralization in Section 6.07.4.1, but a more detailed treatment of ocean crust alteration is given elsewhere (see Chapter 3.15).
6.07.4 NEAR-VENT DEPOSITS

6.07.4.1 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 basement (Alt, 1995). The direction and extent of chemical and isotopic exchange between seawater and oceanic crust depends on variations in temperature and fluid penetration and, thus, 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 at, or close beneath, the sediment–water interface (Hannington et al., 1995, Herzig and Hannington, 2000). As we have seen (Section 6.07.2), hydrothermal circulation within the ocean crust can be subdivided into three major components—the recharge, reaction, and discharge zones (Figure 5).

Recharge zones, which are broad and diffuse, represent areas where seawater is heated and undergoes reactions with the crust as it penetrates, generally downwards. (It is important to remember, however, that except where hydrothermal systems are sediment covered, the location of the recharge zone has never been established; debate continues, for example, whether recharge occurs along or across axis.) Important reactions in the recharge zone, at progressively increasing temperatures, include: low-temperature oxidation, whereby iron oxyhydroxides replace olivines and primary sulfides; fixation of alkalis (potassium, rubidium, and caesium) in celadonite and nontronite (ferrimica and smectite, respectively) and fixation of magnesium, as smectite (<200 °C) and chloride (>200 °C). At temperatures exceeding ~130–150 °C, two other key reactions occur: formation of anhydrite (CaSO₄) and mobilization of the alkalis (potassium, rubidium, lithium) (Alt, 1995). Upon subduction, the altered mineralogy and composition of the ocean crust can lead to the development of chemical and isotopic heterogeneities, both in the mantle and in the composition of island arc volcanic rocks. This subject is discussed in greater detail by Staudigel (see Chapter 3.15).

The reaction zone represents the highest pressure and temperature (likely >400 °C) conditions reached by hydrothermal fluids during their subsurface circulation; it is here that hydrothermal vent fluids are believed to acquire much of their chemical signatures (Section 6.07.2). As they become buoyant, these fluids then rise rapidly back to the seafloor through discharge zones. The deep roots of hydrothermal discharge zones have only ever been observed at the base of ophiolite sequences (e.g., Nehlig et al., 1994). Here, fluid inclusions and losses of metals and sulfur from the rocks indicate alteration temperatures of 350–440 °C (Alt and Bach, 2003) in reasonable agreement with vent-fluid observations (Section 6.07.2). Submersible investigations and towed camera surveys of the modern seafloor have allowed surficial hydrothermal deposits to be observed in some detail (see next section). By contrast, the alteration pipes and “stockwork” zones that are believed to form the “roots” underlying all seafloor hydrothermal deposits (Figure 10) and which are considered to be quantitatively important in global geochemical...
cycles (e.g., Peucker-Ehrenbrink et al., 1994) remain relatively inaccessible. Direct sampling of the stockwork beneath active seafloor hydrothermal systems has only been achieved on very rare occasions, e.g., through direct sampling from ODP drilling (Humphris et al., 1995) or through fault-face exposure at the seabed (e.g., Fouquet et al., 2003). Because of their relative inaccessibility, even compared to all other aspects of deep-sea hydrothermal circulation, study of sub-seafloor crustal mineralization remains best studied in ancient sulfide deposits preserved in the geologic record on-land (Hannington et al., 1995).

6.07.4.2 Near-vent Hydrothermal Deposits

The first discoveries of hydrothermal vent fields (e.g., Galapagos; EPR, 21° N) revealed three distinctive types of mineralization: (i) massive sulfide mounds deposited from focused high-temperature fluid flow, (ii) accumulations of Fe–Mn oxyhydroxides and silicates from low-temperature diffuse discharge, and (iii) fine-grained particles precipitated from hydrothermal plumes. Subsequently, a wide range of mineral deposits have been identified that are the result of hydrothermal discharge, both along the global ridge crest and in other tectonic settings (Koski et al., 2003). Of course, massive sulfides only contain a fraction of the total dissolved load released from the seafloor. Much of this flux is delivered to ridge flanks via dispersion in buoyant and nonbuoyant hydrothermal plumes (Section 6.07.5). In addition, discoveries such as the carbonate-rich “Lost City” deposits (Kelley et al., 2001), silica-rich deposits formed in the Blanco Fracture Zone (Hein et al., 1999), and metal-bearing fluids on the flanks of the JdFR (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 black smoker chimney forms (Figure 11). The first step is the formation of an anhydrite (CaSO₄) framework due to the heating of seawater, and mixing of vent fluids with that seawater. The anhydrite walls then protect subsequent hydrothermal fluids from being mixed so extensively with seawater, as well as providing a template onto which sulfide minerals can precipitate as those 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 copper-rich phases being formed towards the interior, zinc-rich phases towards the exterior, and iron-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 (copper-rich) fluids interact with the sulfides within this carapace to precipitate chalcopyrite and mobilize more soluble, lower-temperature metals such as lead and zinc toward the outer, cooler parts of the deposit. Thus, it is the steep temperature and chemical gradients, caused by both mixing and diffusion, which account for the variations in wall mineralogy and Cu–Zn zonation observed in both chimneys and larger 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 Ocean Drilling Program Leg 158 revealed that similar internal variations can also occur on much larger scales—e.g., across the entire TAG mound (Humphris et al., 1995; Petersen et al., 2000). That work revealed the core of the mound to be dominated by chalcopyrite-bearing massive pyrite, pyrite–anhydrite and pyrite–silica breccias whilst the mound top and margins contained little or no chalcopyrite but more sphalerite and higher concentrations of metals soluble at lower temperatures (e.g., zinc, gold). The geochemical modeling results of Tivey (1995) point to a mechanism of entrainment of seawater into the

Figure 10 Schematic illustration of an idealized hydrothermal sulfide mound including: branching stockwork zone beneath the mound; emission of both high-temperature (350 °C) and lower-temperature (100–250 °C) fluids from the top of the mound together with more ephemeral diffuse flow; and deposition by mass-wasting of an apron of sulfidic sediments around the edges of the mound.
focused upflow zone within the mound which would, almost simultaneously: (i) induce the precipitation of anhydrite, chalcopyrite, pyrite, and quartz; (ii) decrease the pH of the fluid; and (iii) mobilize zinc and other metals. When combined, the processes outlined above—zone refining and the entrainment of seawater into active sulfide deposits—appear to credibly explain mineralogical and chemical features observed both in modern hydrothermal systems (e.g., the TAG mound) and in “Cyprus-type” deposits found in many ophiolites of orogenic belts (Hannington et al., 1998).

A quite different 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 away from the more recently erupted volcanic ridge axis. Instead, it is situated high up 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, extending 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 alteration both as flanges and peridotite mineralization, which is 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 a very high pH (9.0–9.8) and compositions which are rich in H₂S, CH₄, and H₂—consistent with serpentinization reactions (Section 6.07.2)—but low in dissolved silica and metal contents (Kelley et al., 2001). Consistent with this, the chimneys of the Lost City field are composed predominantly of magnesium and calcium-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-oxhydroxides and silicate minerals also occur at tectonically diverse rift zones, from MORs such as the Galapagos Spreading Center to back-arc systems such as the Woodlark Basin (Corliss et al., 1978; Binns et al., 1993). Unlike polymetallic sulfides, Fe–Mn oxide-rich, low-temperature deposits should be chemically stable on the ocean floor. Certainly, metalliferous sediments in ophiolites—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 Spreading Center (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 oxide facies deposits formed at modern hydrothermal sites also remains enigmatic. Fe–Mn–Si oxide deposits may simply represent “failed” massive sulfides. Alternately, it may well be that there are important aspects of, for example, axial versus off-axis plumbing systems (e.g., porosity, permeability, chemical variations caused by phase separation) or controls on the sulfur budget of hydrothermal systems that remain inadequately understood. What seems certain is that the three-dimensional problem of hydrothermal deposit formation (indeed, 4D if one includes temporal evolution) cannot be solved from seafloor observations alone. Instead, what is required is a continuing program of seafloor drilling coupled with analogue studies of hydrothermal deposits preserved on land.

6.07.5 HYDROTHERMAL PLUME PROCESSES

6.07.5.1 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 the gross fluxes from venting, significantly. Plumes are of further interest to geochemists because they can be exploited in the detection and location of 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., Mullineaux and France, 1995). In certain circumstances the heat and energy released into hydrothermal plumes could act as a driving force for mid-depth oceanic circulation (Helfrich and Speer, 1995).

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 high-temperature 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 and vortices or eddies which are readily visible in both still and video-imaging of active hydrothermal vents. These eddies or vortices act to 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, beyond which it cannot rise (Figure 12). The first, rising stage of hydrothermal plume evolution is termed the buoyant plume. The later stage, where plume rise has ceased and hydrothermal effluent begins to be dispersed laterally, is termed the nonbuoyant plume also referred to in earlier literature as the neutrally buoyant plume.

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

\[
\frac{z_{\text{max}}}{} = 3.76 F_0 N^{-3/4}
\]

where \( F_0 \) and \( N \) represent parameters termed the buoyancy flux and the Brunt–Väisälä frequency, respectively. The concept of the buoyancy flux, \( F_0 \) (units cm\(^4\) s\(^{-3}\)) can best be understood from an explanation that the product \( F_0 p_0 \) represents the total weight deficiency produced at the vent source per unit time (units g cm\(^{-3}\)). The Brunt–Väisälä frequency, also termed the buoyancy frequency, \( N \) (units s\(^{-1}\)) is defined as:

\[
N^2 = -(g/\rho_0) d\rho/dz
\]

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 \( z_{\text{max}} \), the plume retains some finite positive vertical velocity. This leads to “momentum overshoot” (Turner, 1973) and “doming” directly above the plume source before this (now negatively buoyant) dome collapses back to the level of zero buoyancy (Figure 12).

Note also the very weak dependence of emplacement height \( z_{\text{max}} \) upon the buoyancy flux or heat flux of any given vent source. A doubling of \( z_{\text{max}} \) 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 with which the buoyant plume becomes progressively more diluted exerts a significant influence because the volumes entrained are nontrivial. For a typical plume with \( F_0 = 10^{-2} \text{m}^4 \text{s}^{-3}, N = 10^{-3} \text{s}^{-1} \) the entrainment flux is of the order \( 10^2 \text{m}^3 \text{s}^{-1} \) (e.g., Helfrich and Speer, 1995) resulting in very rapid dilution of the primary vent fluid \( (10^2:10^4:1) \) within the first 5–10 m of plume rise and even greater dilution \((\sim 10^4:1)\) by the time of emplacement within the nonbuoyant, spreading hydrothermal plume (Feely et al., 1994). Similarly, the time of rise for a buoyant hydrothermal plume, is entirely dependent on the background buoyancy frequency, \( N \) (Middleton, 1979):

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

which, for a typical value of \( N = 10^{-3} \text{s}^{-1} \), yields a plume rise-time of \( \leq 1 \text{~h} \).
6.07.5.2 Modification of Gross Geochemical Fluxes

Hydrothermal plumes represent a significant dispersal mechanism for chemicals released from seafloor venting to the oceans. Consequently, it is important to understand the physical processes that control this dispersion (Section 6.07.5.1). It is also important to recognize that hydrothermal plumes represent non-steady-state fluids whose chemical compositions evolve with age (Figure 13). Processes active in hydrothermal plumes can lead to significant modification of gross hydrothermal fluxes (cf. 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).

6.07.5.2.1 Dissolved noble gases

For one group of tracers, however, inert marine geochemical behavior dictates that they do undergo conservative dilution and dispersion within hydrothermal plumes. Perhaps the simplest example of such behavior is primordial dissolved \(^3\)He, which is trapped in the Earth’s interior and only released to the deep ocean through processes linked to volcanic activity—notably, submarine hydrothermal vents. As we have seen, previously, end-member vent fluids typically undergo \(\sim 10,000\)-fold dilution prior to emplacement in a nonbuoyant hydrothermal plume. Nevertheless, because of the large enrichments of dissolved \(^3\)He in hydrothermal fluids when compared to the low background levels in seawater, pronounced

**Figure 13** Schematic representation of an MOR hydrothermal system and its effects on the overlying water column. Circulation of seawater occurs within the oceanic crust, and so far three types of fluids have been identified and are illustrated here: high-temperature vent fluids that have likely reacted at \(>400\,^\circ\mathrm{C}\); high-temperature fluids that have then mixed with seawater close to the seafloor; fluids that have reacted at “intermediate” temperatures, perhaps \(\sim 150\,^\circ\mathrm{C}\). 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, sorption of aqueous oxyanions may occur onto the vent-derived particles (e.g., phosphate, vanadium, arsenic) 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 the 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 (Von Damm, unpublished).
enrichments of dissolved $^3$He relative to $^4$He can be traced over great distances in the deep ocean. Perhaps the most famous example of such behavior is the pronounced $^3$He plume identified by Lupton and Craig (1981) dispersing over ~2,000 km across the southern Pacific Ocean, west of the southern EPR (Figure 14). A more recent example of the same phenomenon, however, is the large-scale $^3$He anomaly reported by Ru¨ th et al. (2000) providing the first firm evidence for high-temperature hydrothermal venting anywhere along the southern MAR. Rn-222, a radioactive isotope of the noble element radon, is also enriched in hydrothermal fluids; while it shares the advantages of being a conservative tracer with $^3$He, it also provides the additional advantage of acting as a “clock” for hydrothermal plume processes because it decays with a half-life of 3.83 d. Kadko et al. (1990) used the fractionation of $^{222}$Rn/$^3$He ratios in a dispersing nonbuoyant hydrothermal plume above the JdFR to estimate rates of dispersion or “ages” at different locations “down-plume” and, thus, deduce rates of uptake and/or removal of various nonconservative plume components (e.g., $^2$H$_2$, CH$_4$, manganese, particles). A complication to that approach arises, however, with the recognition that—in at least some localities—maximum plume-height $^{222}$Rn/$^3$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 $^{222}$Rn entering ascending hydrothermal plumes (Rudnicki and Elderfield, 1992).

6.07.5.2.2 Dissolved reduced gases ($H_2S$, $H_2$, CH$_4$)

The next group of tracers that are important in hydrothermal plumes are the reduced dissolved gases, $H_2S$, $H_2$, and CH$_4$. As we have already seen, dissolved $H_2S$ is commonly the most abundant dissolved reduced gas in high-temperature vent fluids (Section 6.07.2). Typically, however, any dissolved $H_2S$ released to the oceans undergoes rapid reaction, either through precipitation of polymetallic sulfide phases close to the seafloor and in buoyant plumes, or through oxidation in the water column. As of the early 2000s, there has only been one report of measurable dissolved $H_2S$ at nonbuoyant plume height anywhere in the deep ocean (Radford-Knöery et al., 2001). That study revealed maximum dissolved $H_2S$ concentrations of $\leq 2$ nM, representing a $5 \times 10^5$-fold decrease from vent-fluid concentrations (Douville et al., 2002) with complete oxidative removal occurring in just 4–5 h, within ~1–10 km of the vent site. Dissolved $H_2$, although not commonly abundant in such high concentrations in vent fluids (Section 6.07.2),
Hydrothermal Plume Processes

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 nM and 32 nM above the Main Endeavour vent site, JDfR and above the Steinhöll vent site, Reykjanes Ridge. From use of the ²²²Rn/³He “clock,” Kadko et al. (1990) estimated an apparent “oxidative-removal” half-life for dissolved H₂ of ~10 h.

The most abundant and widely reported dissolved 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). Vent-fluid concentrations are significantly enriched over seawater values (10–2,000 μmol kg⁻¹ versus <5 nmol kg⁻¹) but the behavior of dissolved methane, once released, appears variable from one location to another: e.g., rapid removal of dissolved CH₄ was observed in the Main Endeavour plume (half-life = 10 d; Kadko et al., 1990) yet near-conservative behavior for the same tracer has been reported for the Rainbow hydrothermal plume, MAR, over distances up to 50 km from the vent site (Charlou et al., 1998; German et al., 1998b). Possible reasons for these significant variations are discussed later (Section 6.07.5.4).

6.07.5.2.3 Iron and manganese geochemistry in hydrothermal plumes

The two metals most enriched in hydrothermal vent fluids are iron and manganese. These elements are present in a reduced dissolved form (Fe²⁺, Mn²⁺) in end-member vent fluids yet are most stable as oxidized Fe(III) and Mn(IV) precipitates in the open ocean. Consequently, the dissolved concentrations of iron and manganese in vent fluids are enriched ~10⁸:1 over open-ocean values (e.g., Landing and Bruland, 1987; Von Damm, 1995; Statham et al., 1998). When these metal-laden fluids first enter the ocean, two important processes occur. First, the fluids are instantaneously cooled from >350 °C to ≤30 °C. This quenching of a hot saturated solution leads to precipitation of a range of metal sulfide phases that are rich in iron but not manganese 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 iron oxyhydroxide particulate material. The dissolved manganese 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 iron and manganese are so enriched in primary vent fluids, nonbuoyant plumes typically exhibit total (dissolved and particulate) iron and manganese concentrations, which are ~100-fold higher than ambient water column values immediately following nonbuoyant plume emplacement. Consequently, iron and manganese, together with CH₄ and ³He (above), act as extremely powerful tracers with which to identify the presence of hydrothermal activity from water-column investigations. The fate of iron 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 (e.g., Lilley et al., 1995).

Because of their turbulent nature, buoyant hydrothermal plumes have continued to elude detailed geochemical investigations. One approach has been to conduct direct sampling using manned submersibles or ROVs (e.g., Rudnicki and Elderfield, 1993; Feely et al., 1994). An alternate, and 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., Cowen et al., 2001; German et al., 2002). From direct observations it is apparent that up to 50% of the total dissolved iron emitted from hydrothermal vents is precipitated rapidly from buoyant hydrothermal plumes (e.g., Mottl and McConachy, 1990; Rudnicki and Elderfield, 1993) forming polymetallic sulfide phases which dominate (>90%) the iron flux to the near-vent seabed (Cowen et al., 2001; German et al., 2002). The remaining dissolved iron within the buoyant and nonbuoyant hydrothermal plume undergoes oxidative precipitation. In the well-ventilated N. Atlantic Ocean, very rapid Fe(II) oxidation is observed with a half-life for oxidative removal from solution of just 2–3 min (Rudnicki and Elderfield, 1993). In the NE Pacific, by contrast, corresponding half-times of up to 32 h have been reported from JDfR hydrothermal plumes (Chin et al., 1994; Massoth et al., 1994). Field and Sherrell (2000) have predicted that the oxidation rate for dissolved Fe²⁺ 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):

\[-d[Fe(II)]/dt = k[OH^-][O_2][Fe(II)]\]  (4)

The first Fe(II) incubation experiments conducted within the Kairei hydrothermal plume, Central Indian Ridge, are consistent with that prediction, yielding an Fe(II) oxidation half-time of ~2 h (Statham et al., 2003, submitted).
6.07.5.2.4 Co-precipitation and uptake with iron in buoyant and nonbuoyant plumes

There is significant co-precipitation of other metals enriched in hydrothermal fluids, along with iron, to form buoyant plume polymetallic sulfides. Notable among these are copper, zinc, and lead. Common accompanying phases, which also sink rapidly from buoyant plumes, are barite and anhydrite (barium and calcium 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 iron concentrations and numerous other tracers. To a first approximation, three differing iron-related behaviors have been identified (German et al., 1991b; Rudnicki and Elderfield, 1993): (i) co-precipitation; (ii) fixed molar ratios to iron; and (iii) oxyhydroxide scavenging (Figure 15). The first is that already alluded to above and loosely termed “chalcopyrile” behavior—namely preferential co-precipitation with iron as sulfide phases followed by preferential settling from the nonbuoyant plume. Such elements exhibit a generally positive correlation with iron for plume particle concentrations but with highest $X/Fe$ ratios closest to the vent site ($X = Cu, Zn, Pb$) 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 dispersal distance “down-plume” (Figure 15). Elements that have been shown to exhibit such “linear” behavior include potassium, vanadium, arsenic, chromium, and uranium (e.g., Trocine and Trefry, 1988; Feely et al., 1990, 1991; German et al., 1991a,b). Hydrothermal vent fluids are not particularly enriched in any of these elements, which typically occur as rather stable “oxyanion” dissolved species in seawater. Consequently, this uptake must represent a significant removal flux, for at least some of these elements, from the deep ocean. 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 value 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, thus, may offer potential as a long-term tracer of past ocean circulation, if preserved faithfully in metalliferous marine sediments (Feely et al., 1998).

Figure 15 Plots of particulate copper, vanadium, and neodymium concentrations versus particulate iron for suspended particulate material filtered in situ from the TAG hydrothermal mound, MAR, 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.
6.07.5.2.5 Hydrothermal scavenging by Fe-oxhydroxides

A final group of elements identified from hydrothermal plume particle investigations are of particular importance: “particle-reactive” tracers. Perhaps the best examples are the REE although other tracers that show similar behavior include beryllium, yttrium, thorium, and protactinium (German et al., 1990, 1991a,b, 1993; Sherrell et al., 1999). These tracers, like the two preceding groups, exhibit generally positive correlations with particulate iron concentrations in hydrothermal plumes (Figure 15). Unlike the “oxyanion” group, however, these tracers do not show constant X:Fe ratios within the nonbuoyant plume. Instead, highest values (e.g., for REE:Fe) are observed at increasing distances away from the vent site, rather than immediately above the active source (German et al., 1990; Sherrell et al., 1999). One possible interpretation of this phenomenon is that the Fe-oxhydroxide particles within young nonbuoyant plumes are undersaturated with respect to surface adsorption and that continuous “scavenging” of dissolved, particle-reactive species occurs as the particles disperse through the water column (German et al., 1990, 1991a,b). An alternate hypothesis (Sherrell et al., 1999) argues, instead, for two-stage equilibration within a nonbuoyant hydrothermal plume: close to the vent source, a maximum in (e.g., particulate REE concentrations present and the finite dissolved tracer (e.g., REE) concentrations present in plume-water. As the plume disperses and undergoes dilution, however, particulate iron concentrations also decrease; re-equilibration between these particles and the diluting “pristine” ambient seawater, at the same fixed distribution constants between the high particulate iron concentrations present and the finite dissolved tracer (e.g., REE) concentrations present in plume-water. As the plume disperses and undergoes dilution, however, particulate iron concentrations also decrease; re-equilibration between these particles and the diluting “pristine” ambient seawater, at the same fixed distribution constants, would then account for the higher REE/Fe ratios observed at lower particulate iron concentrations. More work is required to resolve which of these interpretations (kinetic versus equilibrium) more accurately reflects the processes active within hydrothermal plumes. What is beyond dispute concerning these particle-reactive tracers is that their uptake fluxes, in association with hydrothermal Fe-oxhydroxide precipitates, far exceeds their dissolved fluxes 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 “particle-reactive” elements which are greatly enriched in vent fluids over seawater concentrations (e.g., REE), the processes active within hydrothermal plumes dictate that hydrothermal circulation causes a net removal of these tracers not just relative to the vent fluids themselves, but also from the oceanic water column (German et al., 1990; Rudnicki and Elderfield, 1993). In the extreme, these processes can be sufficient to cause geochemical fractionations as pronounced as those caused by “boundary scavenging” in high-productivity ocean margin environments (cf. Anderson et al., 1990; German et al., 1997).

Thus far, we have treated the processes active in hydrothermal plumes as inorganic geochemical processes. However we know this is not strictly the case: microbial processes are well known to mediate key chemical reactions in hydrothermal plumes (Winn et al., 1995; Cowen and German, 2003) 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 below (Section 6.07.5.4).

6.07.5.3 Physical Controls on Dispersing Plumes

Physical processes associated with hydrothermal plumes may affect their impact upon 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 more saline at the point of emplacement than that part of the water column into which they intrude (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, for example, the TAG nonbuoyant plume is anomalously cold and fresh when compared to the background waters 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, Central Indian Ridge) nonbuoyant plumes are typically emplaced within the confining bathymetry of the rift-valley walls (order 1,000 m). Along faster spreading ridges such as the EPR, by contrast, buoyant plumes typically rise clear of the confining topography (order 100 m, only). Within rift-valley “corridors” plume dispersion is highly dependent upon 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 (e.g., thorium isotopes) within the local water column (German and Sparks, 1993). At the Rainbow vent site (MAR 36°N) by contrast, much stronger prevailing currents (∼10 cm s⁻¹) are observed and a more unidirectional, topographically controlled flow is observed (German et al., 1998b). Failure to appreciate the potential complexities of such dispersion precludes the “informed” sampling required to resolve processes of geochemical evolution within a dispersing hydrothermal plume. Nor should it be assumed that such topographic steering is entirely a local effect confined to slow spreading ridges’ rift-valleys. In recent work, 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 yr integrated period. With few exceptions (e.g., major fracture zones) the net effect reported was that these dispersal trajectories tend to be constrained by the overall form of the ridge and flow parallel to the ridge axis over great distances (Speer et al., 2003).

The processes described above are relevant to established “chronic” hydrothermal plumes. Important exceptions (only identified rarely—so far) are Event (or “Mega-”) Plumes. One interpretation of these 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 fast ridges that are extending at rates in excess of ten centimeters per year. In circumstances where there is frequent recurrence, either of intrusions of magma close beneath the seafloor or dike-fed eruptions at the seabed, seafloor venting may commence with a rapid exhalation of a large volume of hydrothermal fluid to generate an “event” plume high up in the overlying water column (e.g., Baker et al., 1995; Lupton et al., 1999b). Alternately, Palmer and Ernst (1998, 2000) have argued that cooling of pillow basalts, erupted at ∼1,200 °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 eruption-related process causes their formation, an important question that follows is: how much hydrothermal flux is overlooked if we fail to intercept “event” plumes at the onset of venting at any given location? To address this problem, Baker et al. (1998) estimated that the event plume triggered by dike-intrusion at the co-axial vent field (JdFR) contributed less than 10% of the total flux of heat and chemicals released during the ∼3 yr life span of that vent. If widely applicable, those deliberations suggest 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 (e.g., Summit and Baross, 1998).

6.07.5.4 Biogeochemical Interactions in Dispersing Hydrothermal Plumes

Recognition of the predominantly along-axis flow of water masses above MORs as a result of topographic steering has renewed speculation that hydrothermal plumes may represent important vectors for gene-flow along the global ridge crest, transporting both chemicals and vent larvae alike, from one adjacent vent site to another (e.g., Van Dover et al., 2002). If such is the case, however, it is also to be expected that a range of biogeochemical processes should also be active within nonbuoyant hydrothermal plumes. One particularly good example of such a process is the microbial oxidation of dissolved manganese. In the restricted circulation regime of the Guaymas Basin, formation of particulate manganese is dominated by bacteria and the dissolved manganese residence time is less than a week (Campbell et al., 1988). Similarly, uptake of dissolved manganese in the Cleft Segment plume (JdFR) is bacterially dominated, albeit with much longer residence times, estimated at 0.5 yr to >2 yr (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 which vary widely for CH₄ (7–177 d) but are much shorter for dissolved H₂ (<1 d).

The release of dissolved H₂ and CH₄ 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 (Roth and Dymond, 1989; German et al., 2002) 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 5–10-fold greater than the photosynthetic-flux driven from the overlying upper ocean (Cowen and German, 2003). Although the detailed microbiology of hydrothermal plumes remains poorly studied, as of the early 2000s, bacterial counts from the Rainbow plume have identified both an increase in total cell concentrations at plume-height compared to background (Figure 16) and, further, that 50–75% of the microbial cells identified in that work were particle-attached compared to typical values of just 15% for the open ocean. Detailed molecular biological analysis of those particle-associated microbes have also revealed that the majority (66%) are archeal in nature rather than bacterial (German et al., 2003); in the open ocean, by contrast, it is the bacteria which typically dominate (Fuhrmann et al., 1993; Mullins et al., 1995). It is tempting to speculate that these preliminary data may provide testament to a long-established (even on geological timescales) chemical-microbial symbiosis at hydrothermal vents.

6.07.5.5 Impact of Hydrothermal Plumes Upon 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 effect of this dilution is such that 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 perhaps only manganese and calcium achieved a significant dissolved metal flux from hydrothermal venting to the oceans. (For comparison, the following 27 elements exhibited no evidence for a significant dissolved hydrothermal flux: iron, beryllium, aluminum, magnesium, chromium, vanadium, cobalt, copper, zinc, arsenic, yttrium, molybdenum, silver, cadmium, tin, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, holmium, erbium, lead, and uranium.) In addition to rapid co-precipitation and deposition of vent-sourced metals to the local sediments (e.g., Dymond and Roth, 1988; German et al., 2002), hydrothermal plumes are also the site of additional uptake of other dissolved tracers from the water column—most notably large dissolved “oxyanion” species (phosphorus, vanadium, chromium, arsenic, uranium) and particle-reactive species (beryllium, yttrium, REE, thorium, and protactinium). For many of these tracers, hydrothermal plume removal fluxes are as great as, or at least significant when compared to, riverine input fluxes to the oceans (Table 3). What remains less certain, however, is the extent to which these particle-associated species are subsequently retained within the hydrothermal sediment record.

6.07.6 HYDROTHERMAL SEDIMENTS

Deep-sea metalliferous sediments were first documented in the reports of the Challenger Expedition, 1873–1876 (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 (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 become recognized that hydrothermal sediments can be classified into two types: those derived
from plume fall-out (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).

### 6.07.6.1 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. Whilst there is ample evidence for extensive mass wasting in ancient volcanogenic sulfide deposits, only limited attention has been paid, to date, to this aspect of modern hydrothermal systems. Indeed, much of our understanding comes from a series of detailed investigations from a single site, the TAG hydrothermal field at $26^\circ$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 out, away from the flanks of the hydrothermal mound.

Similar ponds of metalliferous sediment are observed close to other inactive sulfide structures 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, ~2 km NNE of the active TAG mound. That 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 layers, 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 (see earlier) and high uranium contents attributed to uptake from seawater during oxidation of sulfides (German et al., 1993). Lead isotopic compositions in sulfidic 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 lead isotope, REE, and U–Th compositions which much more closely reflected input of Fe-oxyhydroxide particulate material from non-buoyant hydrothermal plumes (see below).

### 6.07.6.2 Deposition from Hydrothermal Plumes

Speer et al. (2003) have modeled deep-water circulation above the global ridge crest and concluded that this circulation is dominated by topographically steered flow along-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 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 (i) close to the equator ($-5^\circ$ N to $5^\circ$ S), (ii) where the ridge intersects boundary currents or regions...
of deep-water formation, and (iii) 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 already been well documented is on the southern EPR (Figure 14). There, metalliferous sediment enrichments underlie the pronounced dissolved 3He plume which extends westward across the southern Pacific Ocean at ~15°S (cf. Boström 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 this latitude (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 at this latitude (Lyle et al., 1987). A series of holes were drilled extending westward from the ridge axis into 5–28 Ma crust; the recovered cores comprised mixtures of biogenic carbonate and Fe–Mn oxyhydroxides. One important result of that work was the demonstration, based on lead isotopic analyses, that even the most distal sediments, collected at a range of >1,000 km from the ridge axis, contained 20–30% mantle-derived lead (Barrett et al., 1987). In contrast, analysis of the same samples indicated that REE distributions in the metalliferous sediments were dominated by a seawater source (Ruhlin and Owen, 1986). This is entirely consistent with what has subsequently been demonstrated for hydrothermal plumes (see Section 6.07.5, 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).

6.07.6.3 Hydrothermal Sediments in Paleooceanography

Phosphorus and vanadium, which are typically present in seawater as dissolved oxyanion species, have been shown to exhibit systematic plume-particle P : Fe and V : Fe variations which differ from one ocean basin to another (e.g., Trefry and Metz, 1989; Feely et al., 1990). This has led to the hypothesis (Feely et al., 1998) that (i) plume P : Fe and V : Fe ratios may be directly linked to local deep-ocean dissolved phosphate concentrations and (ii) ridge-flank metalliferous sediments, preserved under oxic diagenesis, might faithfully record temporal variations in plume-particle P : Fe and/or V : Fe ratios. Encouragingly, a study of slowly accumulating (~0.5 cm kyrr) sediments from the west flank of the JdFR has revealed that V : Fe ratios in the hydrothermal component from that core appear faithfully to record local plume-particle V : Fe ratios for the past ~200 kyr (German et al., 1997; Feely et al., 1998). More recently, however, Schaller et al. (2000) have shown that while cores from the flanks of the southern EPR (10°S) also exhibit V : Fe ratios that mimic modern plume-values, in sediments dating back to 60–70 kyr, the complementary P : Fe and As : Fe ratios in these samples are quite different from contemporaneous nonbuoyant plume values. These variations have been attributed to differences in the intensity of hydrothermal iron oxide formation between different hydrothermal plumes and/or significant uptake/release of phosphorus and arsenic, following deposition (Schaller et al., 2000).

Unlike vanadium, 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). Further, hydrothermal sediments’ REE/Fe ratios increase systematically with distance away from the paleo-ridge crest (Ruhlin and Owen, 1986; Olivarez and Owen, 1989). 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 deep-water REE patterns from preserved metalliferous sediment records remain 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, neodymium 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 also exhibits a similar behavior and seawater dominates the isotopic composition of metalliferous sediments even close to active vent sites (Ravizza et al., 1996). Consequently, analysis of preserved metalliferous carbonate sediments has proven extremely useful in determining the past osmium isotopic composition of the oceans, both from modern marine sediments (e.g., Ravizza, 1993; Peucker-Ehrenbrink et al., 1995) 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 osmium isotopic composition been observed (Cave et al., 2003, in press).
6.07.6.4 Hydrothermal Sediments and Boundary Scavenging

It has been known for sometime that sediments underlying areas of high particle settling flux exhibit pronounced fractionations between particle-reactive tracers. Both $^{231}$Pa and $^{10}$Be, for example, exhibit pronounced enrichments relative to $^{230}$Th, in ocean margin environments, when compared to sediments underlying mid-ocean gyres (e.g., Bacon, 1988; Anderson et al., 1990; Lao et al., 1992). Comparable fractionations between these three radiotracers ($^{230}$Th, $^{231}$Pa, and $^{10}$Be) have also been identified in sediments underlying hydrothermal plumes (German et al., 1993; Bourlès et al., 1994; German et al., 1997).

For example, a metalliferous sediment core raised from the flanks of the JdFR exhibited characteristic hydrothermal lead-isotopic and REE/Fe compositions, together with high $^{10}$Be/$^{230}$Th ratios indicative of net focusing relative to the open ocean (German et al., 1997). The degree of fractionation observed was high, even compared to high-productivity ocean-margin environments (Anderson et al., 1990; Lao et al., 1992), presumably due to intense scavenging onto hydrothermal Fe-oxyhydroxides. Of course, the observation that REE and thorium are scavenged into ridge-crest metalliferous sediments is not new; sediments from the EPR near 17° S, with mantle lead, excess $^{230}$Th and seawater-derived REE compositions were reported more than thirty 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., $^{230}$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 material 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.

6.07.7 CONCLUSION

The field of deep-sea hydrothermal research is young; it was only in the mid-1970s when it was first discovered, 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 surely remains to be learnt. There are three key questions that will continue to focus efforts within this vigorous research field:

(i) What are the geological processes that control submarine hydrothermal venting? How might these have varied during the course of Earth’s history?

(ii) To what extent do geochemical and biological processes interact to regulate hydrothermal fluxes to the ocean? How might past-ocean processes have differed from the present-day ones?

(iii) What are the timescales relevant to hydrothermal processes? Whilst some long-term proxies do exist (sulfide deposits, metalliferous sediments) for active processes, we do not have any time-series records longer than 25 years!

REFERENCES


References


Hydrothermal Processes


