See also

Deep-sea Ridges, Microbiology. Hydrothermal Vent Fluids, Chemistry of. Hydrothermal Vent Biota. Hydrothermal Vent Deposits. Hydrothermal Vent Ecology.

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HYDROTHERMAL VENT FLUIDS, CHEMISTRY OF

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Introduction

It was not until 1977 that we knew that fluids exit from the seafloor along the global midocean ridge system. With the first discovery of hydrothermal venting at the Galapagos Spreading Center, our ideas on how elements cycle through the oceans and lithosphere, and even how and where life on our planet may have originated were fundamentally and irrevocably changed. Although these fluids were only a few tens of degrees hotter than ambient sea water ($<30°C$ vs. $2°C$), on the basis of their chemical compositions it was immediately clear that these fluids were derived from reactions at much higher temperatures between sea water and the oceanic crust. Less than two years later, spectacular jets of hot ($\geqslant 350°C$) and black water were discovered several thousand kilometers away on the northern East Pacific Rise, and 'black smokers' and 'chimneys' (**Figure 1**) entered the oceanographic lexicon.

From a chemical oceanography perspective, hydrothermal venting and hydrothermal vent fluids provide both new source and sink mechanisms for elemental cycling in the ocean, and therefore possible resolutions to a number of the outstanding chemical flux imbalances. They therefore play a fundamental role in regulating the chemistry of the oceans through geological time. From a biological oceanography perspective, hydrothermal vents provide us with new ecosystems based on chemosynthetic, rather than photosynthetic energy. Of the >500 new species discovered at these sites, the archea and other microbiological components are attracting increasing interest for both biotechnological applications and 'origin of life' questions on our own and other planets. From a physical oceanographic perspective, hydrothermal vents provide an input of both heat and materials into the oceanic mid-depth circulation. From a geological oceanographic perspective they provide an efficient means of removing heat from newly formed oceanic crust, as well as a means of altering the elements recycled into the mantle when the oceanic crust formed at spreading centers is later subducted back into the Earth's interior.
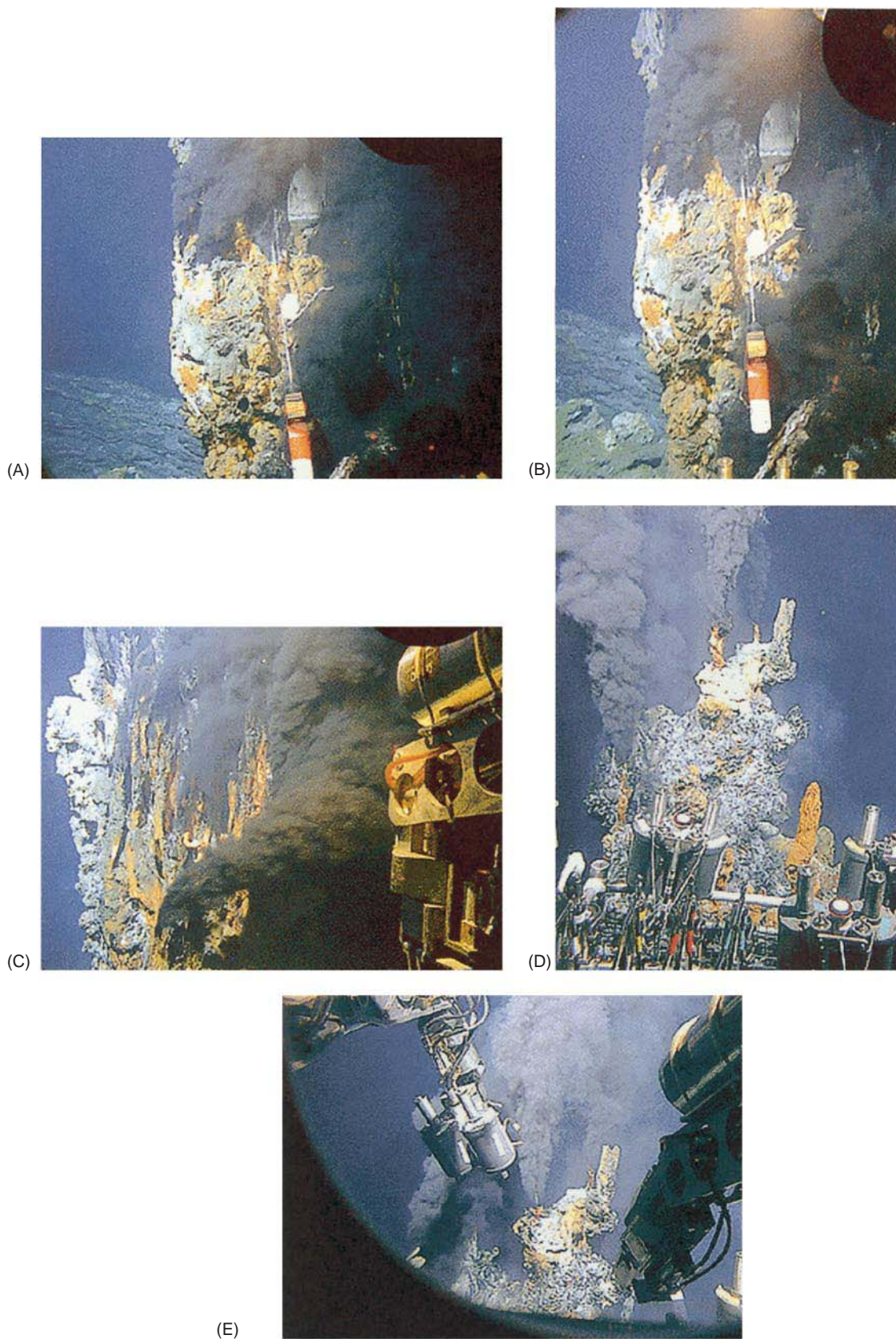
Figure 1 Pictures of black smokers. (A)–(C) Brandon Vent a black smoker with 405°C fluid temperatures on the Southern East Pacific Rise at 21°33′S at a depth of 2834 m; in (A) and (B), shown instrumented with a Hobo recording temperature probe and in (C) with one of *Alvin*'s manipulators. (D) Nadir vent at 17°26′S at a depth of 2562 m and fluid temperatures of 343°C shown prior to sampling in 1998. In the foreground is *Alvin*'s basket with water sampling equipment. (E) Water sampling of Nadir vent fluids.

Where Are Hydrothermal Vents Found?

Hydrothermal vents are now known to exist at approximately 30 locations on the global midocean ridge system (**Figure 2**). Initially some people had speculated that venting would only be found on intermediate- or faster-spreading ridges (i.e., ridges with full spreading rates of at least $60 \, \text{mm yr}^{-1}$); we now know of numerous locations on slow-spreading ridges (e.g., Mid-Atlantic Ridge) where they occur. Known sites occur at depths from 800 to $> 3600 \, \text{m}$, with spreading rates from < 20 to $> 150 \, \text{mm y}^{-1}$ (full rate), on both bare basalt and sedimented-covered ridges, as well as on seafloor where ultramafic rock types are known to outcrop,

and at temperatures up to $405 \, °\text{C}$. If one looks at the global distribution of known vent sites, it is obvious that many of the sites are in relatively close proximity to nations that operate submersibles, and are clustered disproportionately in the north Atlantic and eastern Pacific. Although not strictly part of the midocean ridge system, venting associated with back arc spreading centers is also known from a number of sites in the western Pacific. No sites have yet been discovered in the Indian Ocean, although cruises to this ocean are now planned. Similarly, no sites are known in the south Atlantic, or at high latitudes. This is an exploration issue, not a lack of their existence in these areas.

While initially vents were thought to occur at the mid-point of ridge segments, this was a largely
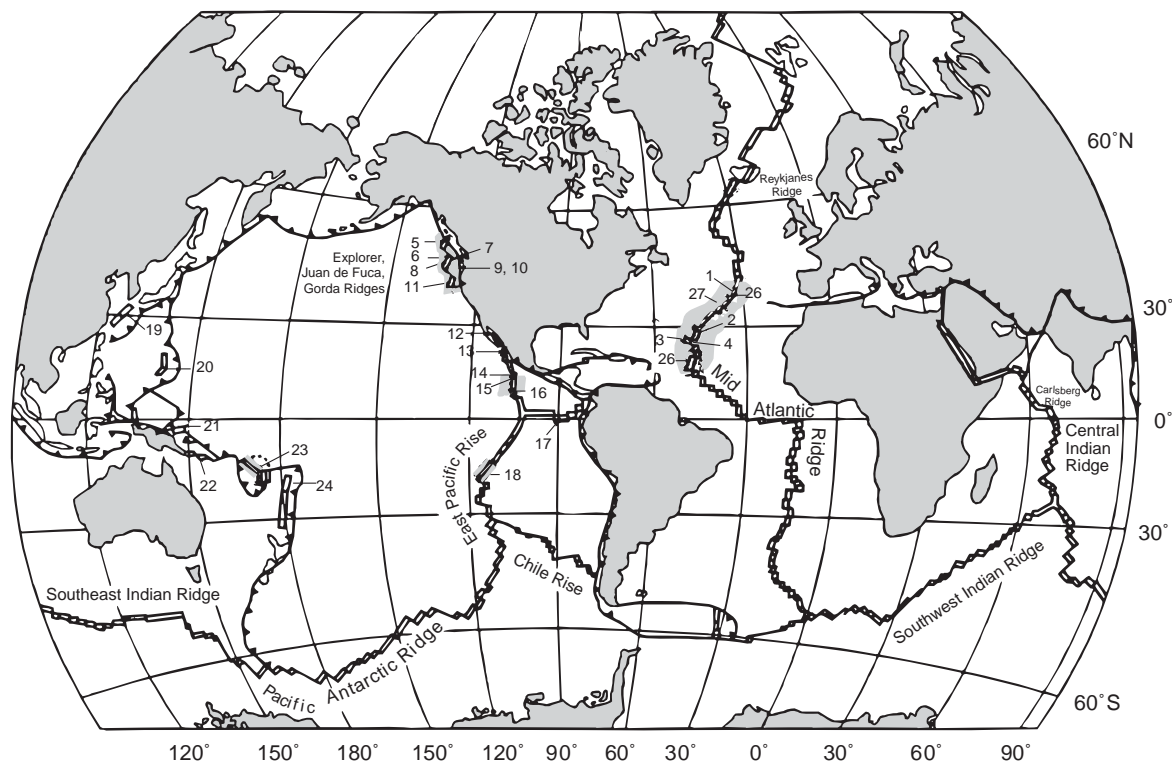
Figure 2 Global distribution of known (sampled) hydrothermal systems. (Modified from Baker *et al.* (1995).)

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1	Lucky Strike (37°17′N)		15	EPR (11°N)
2	Broken Spur (29°N)		16	EPR (10°N)
3	TAG (26°N)		17	Galapagos (86°W)
4	Snakepit/MARK (23°N)		18	EPR (17°–19°S)
5	Explorer Ridge (49°45′N)		19	Okinawa Trough (27°30′N)
6	Middle Valley		20	Mariana Trough
7	Endeavour (48°)		21	Manus Basin
8	Axial Volcano (46°N)		22	Woodlark Basin
9	Cleft—North (45°)		23	N. Fiji Basin (17°S)
10	Cleft—South (44°40′N)		24	Lau/Valu Fa (22°S)
11	Escanaba Trough		25	Logatchev (14°45′N)
12	Guaymas Basin (27°N)		26	Menez Gwen (37°50′N)
13	EPR (21°N)		27	Rainbow (36°16′N)
14	EPR (13°N)			

self-fulfilling prophesy, as this is where exploration for them was focused. There is increasing evidence that more venting occurs on the magmatically robust portions of the ridge, rather than on those areas that are deemed to be magma-starved, on the basis of their morphological characteristics.

How Are They Found?

Vent fields have been discovered in numerous ways, but surveys of the overlying water column and camera tows are the most common systematic approaches employed today. The venting of hot/warm water often forms a plume with unique temperature, salinity, reduced light transmittance, and other specific chemical signals several hundred meters above the ridge. The presence of such a plume is often the first indication that a given section of ridge is hydrothermally active. Cameras, or other deep-towed survey vehicles may also find visual evidence for communities of vent-specific organisms, sulfide structures (both active and extinct), and murky water. These surface ship surveys may then lead to the use of an ROV (remotely operated vehicle) or submersible, in what has been called a 'nested survey strategy.' Sites have also been found by the fortuitous dredging up of both pieces of hydrothermal chimneys and vent-specific animals.

Controls on Fluid Compositions

Hydrothermal vent fluids are primarily, if not entirely, sea water that has been altered due to reaction within the oceanic crust at high temperatures (at least 350°C, and more likely > 400°C) and elevated pressures (at least 80 bar, and more typically at least 250 bar). The two primary controls on vent fluid compositions are phase separation and water–rock reaction (**Figure 3**). Unlike pure water, sea water is a two-component system, containing both water and salt (primarily NaCl, especially for hydrothermal fluids from which the magnesium and sulfate have been essentially quantitatively removed). The critical point for sea water is higher than that for distilled water – 407°C and 298 bar rather than 374°C and 220 bar – and most importantly the two-phase curve therefore continues beyond the critical point (**Figure 4**). If fluids intersect the two-phase curve at pressure and temperature conditions less than the critical point, they will undergo subcritical phase separation or boiling. The vapor phase formed by this process will contain some salt, the exact amount and composition of which will depend on the pressure and temperature conditions at which the phase separation occurred,
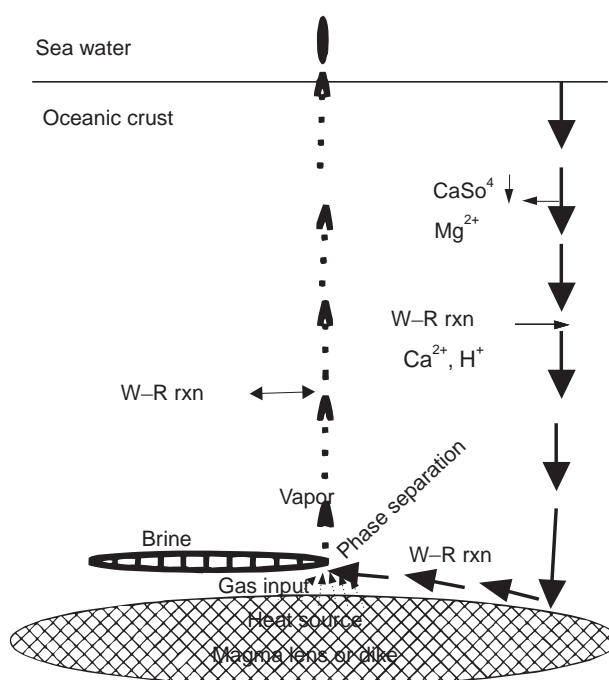
Figure 3 Schematic of a hydrothermal flow cell. W–R rxn = water–rock reaction. (Von Damm 1995 in Humphris *et al.*)

and will be enriched in dissolved gases. If the fluid intersects the two phase curve at pressure and temperature conditions higher than the critical point, supercritical phase separation or condensation will occur, and, rather than a low-salinity vapor being
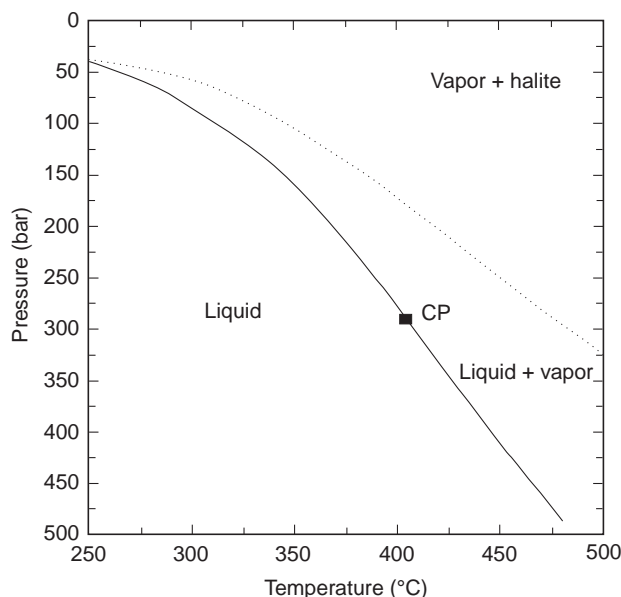
Figure 4 Two-phase curve for sea water, showing the location of the critical point (CP) for sea water (407°C, 298 bar), and the relative locations of the liquid, liquid + vapor, and vapor + halite stability fields. Note that, unlike for pure water, the two-phase curve continues beyond the critical point.

formed, a high-salinity brine or liquid phase will condense. In most, if not all, hydrothermal fluids that have been sampled, phase separation has occurred as evidenced by the chlorinities of these fluids, which can be from ~ 6% to 200% of those in sea water. While the change in the absolute chlorinity of seafloor hydrothermal fluids is primarily the result of phase separation, changes in the other dissolved ions in sea water also reflect substantial reaction of the fluids with the rock, mostly basalt, but also ultramafics and sometimes sediments. Seafloor hydrothermal fluids therefore do not show the 'constancy of composition' and elemental ratios known to characterize the major chemical species in sea water. The two primary mechanisms for determining the composition of hydrothermal fluids are therefore phase separation and water–rock interaction. This does not mean that other mechanisms may not be important. Two that have been identified but whose global importance is not yet known are magmatic degassing and biological uptake/removal. On the East Pacific Rise at 9°50′N latitude unusually high gas concentrations and gas/heat ratios have been observed in the hydrothermal fluids that suggest that we are seeing the degassing of a recently resupplied magma chamber. This has not yet been observed at any other sites, although it has been observed for ~ 7 years at this site. The potential biological effects on fluid compositions have long been speculated on, but there are few quantitative data at this time that can directly address this question. As the 'black smoker' fluids are at temperatures well beyond the known bounds of life on this planet, if biological effects are present they are most likely to be found in fluids with temperatures less than ~ 110°C.

The Division of Fluids by Temperature and Styles of Venting

Hydrothermal fluids are often subdivided into two categories: high-temperature or focused flow, and low-temperature or diffuse flow.. These terms are often poorly defined in the contexts in which they are used, and may mean different things to different authors. High-temperature fluids, generally > 200–250°C, are usually focused jets of water that are exiting from constructional features that either are precipitated from the hydrothermal fluids themselves when they encounter cold, alkaline sea water or are formed by precipitation due to the mixing of hydrothermal fluids with sea water, or, and more usually, both of these processes. Although these chimneys comprise metal sulfides and sulfates, other minerals are also present, usually in lesser quantities, although on sediment-covered ridges carbonates,

for example, may also be abundant in these chimney or mound structures. Low-temperature fluids, generally ⩽ 35°C, but sometimes approaching 100°C, have usually deposited (if they ever contained) much of their metal load below the seafloor and hence usually neither smoke nor have specific constructional features associated with their fluid flow. Because of this lack of specific structure, the fluid flow is often less organized, and hence is referred to as 'diffuse.' Some authors use this term to refer to fluids exiting directly from the basaltic substrate. These sites are usually well-colonized by various types of vent megafauna, making it difficult, if not impossible, to identify a specific orifice. Other authors use this same term to refer to fluids that are oozing out of large sulfide structures. At some sites, only high-temperature 'black smoker' vents are found, while at other sites only the lower-temperature diffuse venting is found (as at the Galapagos Spreading Center where venting was first discovered). At other sites, both focused and diffuse flow may occur right next to one another, and, at least at one site, we have now observed low-temperature diffuse flow evolving into high-temperature focused flow over several years. For all types of 'low temperature and/or diffuse flow,' all of the fluids that have been sampled to date appear to contain some fluid that has reacted at significantly greater temperatures than are measured directly in these fluids. Hence one could argue that, at least at the ridge axes, all fluids are ultimately high-temperature fluids and that some of them have undergone significant mixing with sea water at some depth, likely relatively shallow, within the oceanic crust. With the continued inability to drill these systems, our knowledge of their subsurface hydrology is rudimentary at best. One might note that fluids with temperatures in the ~ 100–200°C range have been left out of the above classification. This is because there are few fluids that have been sampled in this temperature range, which may reflect a true lack of abundance of fluids at such temperatures, or simply a sampling gap.

The Influence of Volcanic Events

In the late 1980s there was a real dichotomy in our understanding of the controls on seafloor hydrothermal systems. We knew of individual vents that were chemically stable for years at a time, yet each individual vent had a distinctive chemistry, and rapid changes in the hydrothermal plumes above these sites had been noted. In 1991 some of this puzzle was resolved with the first opportunity to sample a mid-ocean ridge hydrothermal site immediately following a volcanic eruption and to study the

evolution of this site on timescales now approaching decadal. The discovery of an eruption on the East Pacific Rise at 9°45–52′N was fortuitous, but it could be sampled and documented with the DSV *Alvin* within weeks of the volcanic event. Since that time using the US Navy's SOSUS system, it has been possible to determine real-time when some of these events are occurring on the Juan de Fuca and Gorda Ridges, but immediate response to these events have been limited to surface ship observations due to logistical constraints. The events studied so far have been characterized by a volcanic eruption at the seafloor, the intrusion of a dike, or both. The knowledge gained from responding to these events has revolutionized our understanding of these systems, especially their pronounced temporal variability on very short timescales (much less than days to weeks). Presumably we will be able to study more of these events and to gain a sense of their frequency, perhaps as a function of spreading rate, as we begin to instrument more of the ridge crest with hydrophones to detect the T-phase signals associated with these events.

The Influence of Tectonic/Cracking Events

Magmatic events have provided new insights into the processes that drive hydrothermal systems and their fluid compositions on intermediate- to fast-spreading ridges, but presumably tectonic events are more important (or at least more frequent than magmatic events) on slow-spreading ridges. As we have not yet been able to observe one of these events, we cannot assess their importance. In a relatively small cracking event on a fast-spreading ridge observed with a seismic array, changes in fluid temperatures were marked, and changes in fluid compositions were profound, leading to major changes in the biological communities existing at this site. Presumably the observation of one or more tectonic events on slow-spreading ridges will also provide critical new insights into how hydrothermal systems on these types of ridges function and evolve.

On-Axis versus Off-Axis

The discussion above has focused on the axial component of midocean ridge hydrothermal systems. Many debates have focused on the importance of these axial systems compared to hydrothermal systems on the ridge flanks. The net amount of heat transported and the total geographical extent of the flanks is much larger than that of the axial parts of the ridges, the division often being drawn at 1 My, resulting in a partitioning of 70%:30% relative heat loss. Hence, the relative chemical anomaly and volume of fluids expelled on the axis versus the flanks of the ridge will determine which of these parts of the midocean ridge hydrothermal system is most important for the cycles of individual chemical elements and species. It has been difficult to acquire quantitative data on the fluids exiting from the flanks, one of the reasons being that sites of flank fluid venting are difficult to identify because water column plumes are not present, nor are the distinctive animal communities (distinctive both for their animal types as well as their white color on the black basalt) found at the axial sites of venting. In the last several years drilling by the Ocean Drilling Program on the flanks of the Juan de Fuca Ridge has provided important new information on the chemistry and hydrology of these systems, as well as demonstrating a viable method for further approaching the flank question.

Observed Fluid Compositions

Compositions of hydrothermal fluids not only vary widely but also are almost always very different from those of sea water (**Table 1**). While some of the low temperature diffusely venting fluids may be close to sea water in their major element compositions, they will often have very different compositions of dissolved gases (e.g., H_2S, CO_2, CH_4, H_2, and He) and will usually be highly enriched in iron and manganese compared to local ambient sea water. Compared to sea water, hydrothermal fluids have lost essentially all of their magnesium and sulfate, and are highly enriched in H_2S, CH_4, H_2, He, Si, Li, Fe, and Mn. As hydrothermal fluids are very acid, they also have no alkalinity, and with the loss of sulfate, chloride becomes the major, and almost only anion (bromide is present in much lower concentrations). The behavior of the cations is more variable. As the amount of chloride present is a result of the phase separation history of the fluids, and the fluids must maintain electroneutrality, to determine whether a particular cation has been added to or removed from the fluid, not only the absolute concentration but also its ratio to chloride must be compared to the local ambient sea water value. Hydrothermal fluids are also very reducing, often containing large amounts of H_2S, H_2, and CH_4. In most, but not all hydrothermal fluids (fluids that are formed immediately after a volcanic eruption being a major exception), Li, K, Rb, Cs, Ca, Sr, Si, the transition metals in reduced forms, including Fe, Mn, Cu, and Zn, are enriched in hydrothermal fluids, the cause being water–rock interaction. Sodium may be either enriched or depleted with respect to the chloride content of the

Table 1 Range of physical parameters and chemical compositions for hydrothermal vent fluids[a]

Parameter	Units[b]	Vents	Seawater
Temperature	°C	> 2–405	~ 1–5 (bottom water)
Depth (pressure)	m (bars)	800–3600 (80–360)	
pH 25°C, 1 atm		2.5–7.8	7.8
Alkalinity$_{total}$	meq kg^{-1}	− 2.7–10.6	2.3
Cl	mmol kg^{-1}	31–1245	545
SO$_4^{2-}$	mmol kg^{-1}	0	28
H$_2$S	mmol kg^{-1}	0–110	0
Si	mmol kg^{-1}	2.7[b]–24.0	0.032–0.180
Li	mmol kg^{-1}	< 0.012–2.35	0.026
Na	mmol kg^{-1}	< 15–924	465
K	mmol kg^{-1}	< 1–58.7	10
Ca	mmol kg^{-1}	< 0.2–109	10
Mg	mmol kg^{-1}	0	53
Sr	μmol kg^{-1}	< 1–348	87
Fe	mmol kg^{-1}	0–18.7	< 0.001
Mn	mmol kg^{-1}	0–4.48	< 0.001
Cu	μmol kg^{-1}	0–310	0.007
Zn	μmol kg^{-1}	0–900	0.01
Cd	nmol kg^{-1}	< 10–1000	1
Co	nmol kg^{-1}	< 5–2570	0.03
Pb	nmol kg^{-1}	50–2200	0.01
B	μmol kg^{-1}	416–1630	416
Al	μmol kg^{-1}	0–20.0	0.02
Br	μmol kg^{-1}	29–1880	840
CO$_2$	mmol kg^{-1}	2.3–375	2.3
CH$_4$	μmol kg^{-1}	0.0003–6800	0.0003
H$_2$	mmol kg^{-1}	< 0.001–38	0.0000003

[a]Only includes mid-ocean ridge systems, both bare rock and sediment-covered.
[b]From high-temperature vents.

fluids, the loss being due to albitization, with a concomitant gain in the calcium-content of the fluids. It is the loss of magnesium to form magnesium hydroxy silicates that, along with other aluminosilicate reactions, generates and then maintains the acidity of the fluids. In the case of sulfate, some is lost as anhydrite (CaSO$_4$) in the downflow zone, while some is reduced to sulfide (as H$_2$S).

The compositions of fluids exiting from a single hydrothermal vent may vary widely over time. The cases in which this has been observed are increasing, and are usually associated with vents where a known magmatic event has occurred. The variation in the composition of a single vent can vary from vapor to brine, and may encompass almost the entire range of known compositions. In contrast, some sites of venting are known where the fluid compositions have been stable during the time interval over which they have been sampled. None of these vents with constant compositions have known 'magmatic' or 'tectonic' events associated with them, although several of these sites have now been sampled over times of ~ 15 years. Presumably, these vents are in a period of steady-state venting, although we do not have adequate constraints to

determine how long after an eruptive event, or at what spreading rates, this may occur. While our data has increased on the temperature and chemical characteristics of vents during their early histories, few data exist for their waning stage(s). Presumably all this variability – or lack thereof – and the timescale(s) on which it occurs can ultimately be tied to the nature of the heat source at a given site. Aside from the most general characteristics related to the presence or absence of a seismic low-velocity zone, and the depth at which it occurs, little is known about the specifics of the heat sources at sites that are hydrothermally active, especially in contrast to those that are not.

The composition of a hydrothermal fluid cannot be correlated to, or predicted by, such known physical parameters as the depth of the seafloor on which it occurs, the spreading rate of the ridge on which it occurs, and so on. As the fluid compositions in most cases are probably due to the achievement of steady-state, if not true thermodynamic equilibrium, of the fluids with the rock substrate, some of the measured compositions can be tied to either the measured exit temperature or the presumed *in situ* conditions within the hydrothermal

system itself. While there has been some success, especially recently, with understanding the chemical controls on these systems using thermodynamic modeling, a major limitation in many cases remains the proximity to the critical point of both pure water and sea water.

The Flux Question

One of the driving questions for the study of seafloor hydrothermal systems is to understand their net flux to the ocean in terms of energy (thermal and chemical) and mass. The thermal, or heat, energy they carry is believed to be relatively well constrained, as various independent ways of estimating this flux provide similar values. The mass of chemicals they add and/or remove remains problematic. In some cases whether hydrothermal activity is a net source or sink for particular elements remains unresolved as well. In addition to absolute concentrations, or concentrations normalized to the chloride content, the isotopic signature of various species can also be used to constrain the source and sink terms, as well as helping to identify the important processes occurring within the hydrothermal circulation cell.

Summary and Conclusions

Hydrothermal venting along the global midocean ridge system is a process that is widespread throughout the ocean basins and impacts all of the oceanographic disciplines. Our studies of these systems remain in their infancy, however, and we do not yet completely understand the controls on the chemistry of these systems, the controls on the locations of individual vent sites, their overall importance to ocean chemistry, productivity, and circulation, and their net effects on the structure and composition of the oceanic crust.

See also

Hydrothermal Vent Deposits. Mid-Ocean Ridge Tectonics, Volcanism and Geomorphology. Mid-ocean Ridge Geochemistry and Petrology. Mid-Ocean Ridge Seismic Structure. Seamounts and Off-ridge Volcanism.

Further Reading

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