

CHAPTER 7

Sulphur Emission and Transformations at Deep Sea Hydrothermal Vents

HOLGER W. JANNASCH

7.1 INTRODUCTION

The search for submarine volcanism, based on the newly emerging concept of plate tectonics, led in 1977 to the discovery of sulphide-containing warm and hot springs or vents at ocean floor spreading zones. These areas of hydrothermal water circulation through the Earth's crust greatly affect the chemistry of seawater. Estimation of fluxes has been based on the present composition of seawater. The estimated rate of sulphide emission as compared to the seawater (sulphate) entrainment, as well as the various chemical and biological sulphur transformations determining its deposition as polymetal sulphides and anhydrites, are significant with respect to the global sulphur cycle. This report briefly presents the information so far available on deep sea hydrothermal conversions of sulphur.

7.2 CHARACTERISTICS OF DEEP SEA VENTS

After considerable theoretical work and exploratory studies with surface-deployed instrumentation, warm vents (<20°C) were first located by the research submersible ALVIN in 1977 at the Galapagos Rift spreading zone at a depth of 2550 m (Ballard, 1977; Lonsdale, 1977; Corliss *et al.*, 1979; Edmond *et al.*, 1979). The presence of hydrogen sulphide in the collected hydrothermal fluid and the observations of copious animal populations in the immediate vicinity of the vents led to studies on the primary production of organic carbon by sulphur-oxidizing bacteria (Jannasch and Wirsén, 1979, 1981; Karl *et al.*, 1980). The fact that the emitted vent water contained between 10^5 and 10^8 bacterial cells per ml, and aerobic thiobacilli-type organisms could be isolated from greatly diluted samples, meant it could be concluded that subsurface mixing with oxygenated seawater had taken place prior to emission. This observation was corroborated by chemical analyses.

In 1979 hot vents, the so-called black smokers, were discovered at an active spreading zone of the East Pacific Rise at 21°N where hydrothermal fluid of about 350°C reaches the sea floor unmixed (Spiess *et al.*, 1980). The heavy precipitation of polymetal sulphides in particulate form produces the smoke-like plume and part of the chimney-like structures. These chimneys may be up to 20 m high, and consist, in addition to metal sulphides, of calcium sulphate (as anhydrite). When a vent dies (see below) the anhydrite dissolves as a corollary of cooling, and the chimneys collapse forming mounds of varied mineral composition, largely polymetal sulphides covered by iron-manganese oxides and hydroxides. Life forms are less abundant in the vicinity of hot vents than at warm vents and appear to be clustered around warm water leakages near the bases of chimneys.

These deep sea vents and the entire cycling of seawater through the upper 3 km of the Earth's crust are powered by the consecutive cooling-contraction and warming-expansion processes. In comparison to the weathering cycle and mineral dispersion by runoff from the continents, the hydrothermal cycle is only about 0.5% of the total river flow but about 200 times higher in mineral content (Edmond and Von Damm, 1983).

Since basalt and seawater are the only two reactants, the chemistry of deep sea vents is simpler than that of terrestrial hot springs. Within the crust the penetrating seawater attains temperatures of more than 350°C (Figure 7.1). On reacting with basalt, the resulting hydrothermal fluid is enriched in hydrogen sulphide stemming both from the reduction of sulphate and additional sulphur leached from the rocks. Carbon occurs in its most oxidized and most reduced form. While magnesium is depleted, heavy metals and calcium are also enriched (Edmond *et al.*, 1982).

The location and the rate at which the mixing of hydrothermal fluid with ambient seawater takes place has a strong effect on the dispersion of sulphur. In warm vents the mixing is estimated to occur in the extremely porous lava a few to 100 m below the sea floor. Subsurface precipitations may clog the flow of hydrothermal fluid, resulting in the formation of new conduits and contributing to the fact that individual vents have a relatively short life time. Hot vents are often surrounded by smaller warm leakages.

While the hot vents with flow rates of up to 2 m/s raise their plume several hundred metres above the sea floor, the plumes of warm vents (emission rates of 1 to 2 cm/s) can only be observed a few metres above the sea floor. The abundance of visible life forms (large clams (*Calyptogena magnifica*, Boss and Turner, 1980), vestimentiferan tube worms of the phylum Pogonophora (*Riftia pachyptila*, Jones, 1981), and clusters of a yet unnamed mussel) appears to correspond to the concentration of hydrogen sulphide.

A 'dead' vent results from the stop of flow or its diversion to a new outlet. The non-motile animals die rather quickly in the absence of hydrogen sulphide, and the soft parts are rapidly removed by scavengers. The rarity

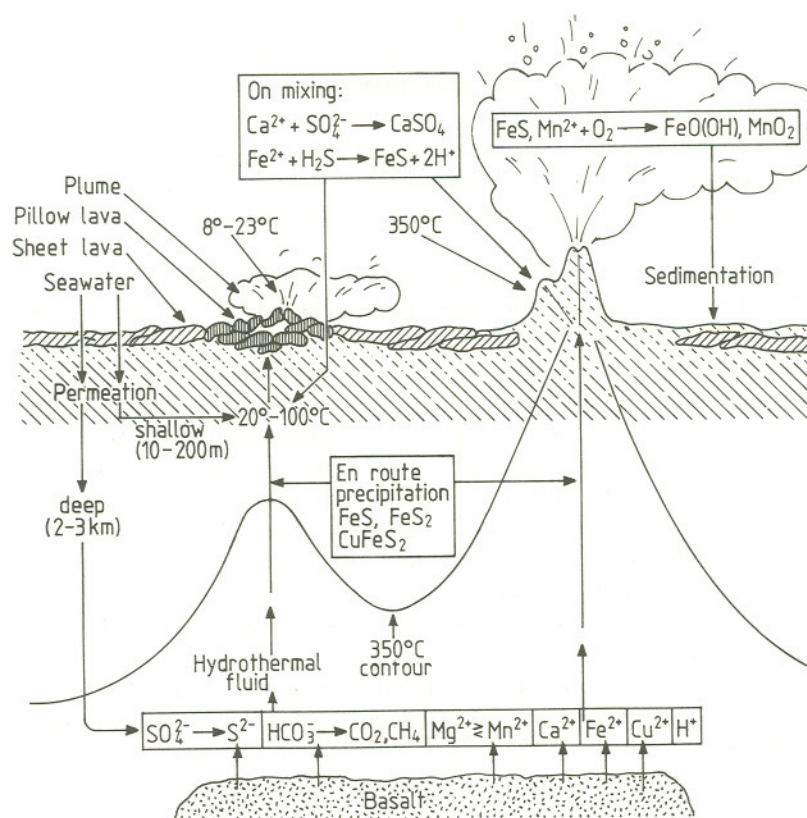


Figure 7.1 The major geochemical reactions occurring during the hydrothermal cycling of seawater through the Earth's crust at ocean floor spreading zones, indicating the two commonly observed types of vents (redrawn from Jannasch and Taylor, 1984)

of fossilized life forms in the metal-rich deposits of ancient spreading centres and presently mined ophiolites (Haymon *et al.*, 1984) may be a result of the fast and efficient scavenging of such organic-rich 'islands' in an otherwise oligotrophic environment. The complete dissolution of clam shells has been estimated to last 20 to 23 years (R. A. Lutz, personal communication) and serves as an excellent indicator of short-term vent histories.

7.3 EMISSIONS OF SULPHUR

The unmixed hydrothermal fluid of the deep sea hot vents near the 21°N East Pacific Rise area contains 6.75 to 8.37 mM hydrogen sulphide at

temperatures between 275 and 350°C (Von Damm, 1983). In several newly found hot vents of the 10°N to 13°N area, the concentrations range more widely between 0.5 and 10.0 mM hydrogen sulphide with pH values approximating 3.5 (J.M. Edmond, personal communication). The differences of the hydrogen sulphide concentrations in the various hot vents are assumed to be caused by the different quantities of metal sulphides and gypsum deposited prior to emission, and most likely relate to the age of individual vent systems.

Sulphur isotope analyses of dissolved hydrogen sulphide (Kerridge *et al.*, 1983) and of various sulphide minerals precipitated at the vents (Styrt *et al.*, 1981) indicate that the emitted sulphur derives largely (up to 90%) from leaching as primary sulphide from basalts (Arnold and Sheppard, 1981) and the smaller portion from the geothermal reduction of seawater sulphate. The latter is largely removed by deposition as anhydrite during the downward permeation into the crust and only the rest is reduced to sulphide. It has been suggested that the anhydrite subsequently redissolves in cooler waters when the crust moves off-axis (Wolery and Sleep, 1976; Humphris and Thompson, 1978; Mottl *et al.*, 1979; Mottl, 1983). In laboratory experiments the inorganic reduction of seawater sulphate coupled with the oxidation of Fe²⁺ from basalt has been demonstrated at 300°C and above (Mottl *et al.*, 1979; Shanks *et al.*, 1981).

An estimate of the quantity of sulphur emission from an individual hot vent can be based on the following average values: (1) a hydrogen sulphide concentration of 5.0 mM, (2) a flow rate of 1 m/sec, and (3) a chimney orifice diameter of 4 cm (own observation). The calculation results in a value of 0.7 kg sulphur per hour or 6 tons per year emitted from an average-size black smoker.

Estimates on the global sulphur emission from deep sea vents can be made from calculations by Edmond *et al.* (1979, 1982) and McDuff and Edmond (1982). Based on the concentrations of several key minerals in seawater, they arrived at a figure of 7–8 million years for a total hydrothermal seawater cycling through the Earth's crust. Such estimates result in an upper limit of sulphate entrainment at 4×10^{12} mol per year, and an upper limit of hydrogen sulphide emission into the ocean of 1×10^{12} mol per year. In other words, there is a net loss of sulphur from seawater during hydrothermal cycling in the form of polymetal sulphide deposits.

The annual emission of 10^{12} moles or 32×10^6 tons of hydrogen sulphide corresponds to 5×10^6 average-size smokers as defined above. However, this total or global number of smokers must certainly be lower because the observed occurrence of extensive chemosynthetically supported animal populations (see below) at the spreading centres suggests that a considerable portion of the hydrogen sulphide is emitted via warm rather than hot vents (see also Mottl, 1983).

7.4 TRANSFORMATIONS OF SULPHUR

The conditions for the reaction of emitted hydrothermal fluid with oxygenated seawater are distinctly different for the hot and warm vents. The forceful dispersion of hydrothermal fluid from black smokers distributes particulate polymetal sulphides over a wide area. Most of the particles are in the μm -size range (M. Mottl, personal communication) and only a small fraction of this material is sedimented. The larger portion becomes part of deep- and midwater circulation. The sulphides will oxidize to elemental sulphur and ultimately to sulphate.

In the immediate surrounding of the warm vents little abiological or spontaneous-chemical oxidation of emitted hydrogen sulphide is evident from deposits. If Kevex X-ray spectra of microbial mats sampled from an active vent plume (*ca* 20°C) are compared with those of a mat further removed from the vent orifice (*ca* 2°C), a change in the iron/manganese ratio becomes apparent (Figure 7.2). It results from the different dissolution products of the two metal compounds leading to a successively changing deposition during the outward flow of vent water. In contrast, the amount of sulphur within the mat deposits is hardly affected by the distance from the vent orifice. The relatively low and non-toxic concentrations of hydrogen sulphide in the warm vent plumes are, in contrast to hot vents, caused by the higher subsurface metal sulphide depositions (Figure 7.1).

A subsurface biological oxidation of hydrogen sulphide is evident in some vents where a turbidity and whitish-bluish iridescence of the emitted fluid was microscopically and biochemically resolved to represent dense bacterial cell suspensions (Jannasch and Wirsén, 1979; Karl *et al.*, 1980; Jannasch, 1984a). A high physiological activity was indicated by considerable adenosine 5'-triphosphate (ATP) concentrations and guanosine 5'-triphosphate/ATP ratios (Karl *et al.*, 1980). Measurements of CO₂ uptake rates conducted *in situ* with the appropriate controls (at 1 atm, 2°C, 23°C, and in the presence of a thiosulphate enrichment) indicated that the microbial chemosynthetic activity was (a) highly barotolerant, (b) not psychrophilic (low temperature adapted), and (c) readily stimulated by an additional source of reduced sulphur (Jannasch, 1984b).

Although there are a number of non-sulphur energy sources for autochemolithotrophic bacteria present in vent water (Table 7.1), the relative abundance of sulphur compounds is assumed to lead to the predominance of sulphur-oxidizing bacteria (Jannasch, 1984a). In turn, by far the largest part of the chemosynthetic production of organic carbon proceeds via sulphur oxidation. The existence of whole ecosystems dependent on terrestrial (geothermal) rather than solar (light) energy is unique for the warm deep sea vents. It represents the biologically most remarkable finding of their discovery.

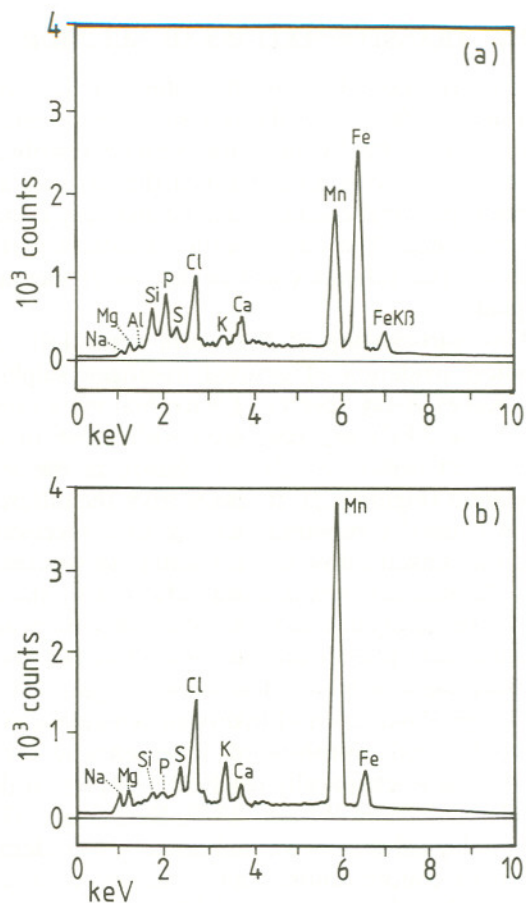


Figure 7.2 Spectra taken with a KeveX non-dispersive X-ray detector:
 (a) from a microbial mat grown on a glass slide incubated for 10.5 months in an active vent fissure;
 (b) from a microbial mat covering a mussel shell collected several metres away from the vent orifice (from Jannasch and Wirsen, 1981)

The biochemical versatility observed within the sulphur-oxidizing bacteria appears to be the key for the extraordinary efficiency of this process at the warm vents (Jannasch and Wirsen, 1985). The two most prominent characteristics are (1) the diversity of metabolic types, including the mixotrophic and facultative chemoautotrophic sulphur bacteria, and (2) the most unexpected symbiotic associations between certain invertebrates and chemolithoautotrophic bacteria. This symbiosis may account for up to 90% of the organic carbon production at the vents (Jannasch and Nelson, 1984).

Table 7.1 Types of bacterial chemotrophy*

	Electron donor	Electron acceptor	Carbon source	Organisms
Autolithotrophic	H ₂	O ₂	CO ₂	Hydrogen-oxidizing bacteria
	S ⁻² , S ⁰ , S ₂ O ₃ ²⁻	O ₂	CO ₂	Sulphur-oxidizing bacteria
	Fe ²⁺ (Mn ²⁺)	O ₂	CO ₂	Iron and manganese-oxidizing bacteria
	NH ₄ ⁺ , NO ₂ ⁻	O ₂	CO ₂	Nitrifying bacteria
	S ²⁻ , S ⁰ , S ₂ O ₃ ²⁻	NO ₃ ⁻	CO ₂	Denitrifying/sulphur-oxidizing bacteria
	H ₂	S ⁰ , SO ₄ ²⁻	CO ₂	Sulphur- and sulphate-reducing bacteria
Hetero-organotrophic	H ₂	CO ₂	CO ₂	Methanogenic and acetogenic bacteria
	Organic substrate	O ₂	Organic substrate	Aerobic heterotrophic bacteria
	Organic substrate	NO ₃ ⁻	Organic substrate	Denitrifying bacteria
	Organic substrate	S ⁰ , SO ₄ ²⁻	Organic substrate	Sulphur- and sulphate-reducing bacteria
	Organic substrate	Organic substrate	Organic substrate	Anaerobic heterotrophic and fermenting bacteria

*Modified after Jannasch and Wirsen (1985).

The discovery of symbioses between vent invertebrates and sulphur bacteria has subsequently led to similar findings with certain bivalves in shallow marine waters (Cavanaugh *et al.*, 1981; Felbeck, 1981; Cavanaugh, 1983). In this environment, however, the generation of hydrogen sulphide is a result of bacterial sulphate reduction dependent on organic energy sources. The comparison between primary and secondary production of organic carbon with reduced sulphur functioning as the source of energy has been discussed at an earlier SCOPE Workshop (Jannasch, 1983).

Recently similar deep sea animal communities were discovered in the absence of hydrothermal seawater cycling (Paull *et al.*, 1984). Saline seepages occur at the bottom of the escarpment of the western Florida continental platform at a depth of 3000 m. The extruding waters contain hydrogen sulphide and produce an invertebrate-dominated ecosystem of less spectacular productivity than that at the vents, but possibly stretched along the entire escarpment area. The source of sulphur might be the nearby sulphur domes, and its reduction is presently hypothesized to depend on the microbial oxidation of fossilized organic materials. For the discussion of global sulphur

cycling, too little information is available on this new type of natural sulphur containing deep water vents at this time.

The role of high temperatures in the biological transformations of sulphur at deep sea vents is not yet understood. The isolation of a highly thermophilic methanogenic bacterium from the base of a black smoker (Jones *et al.*, 1983) implies the possibility of reduction of elemental sulphur or possibly sulphate at high temperatures and pressures. Like many methanogenic bacteria (Stetter and Gaag, 1983), the above isolate is capable of reducing elemental sulphur anaerobically in the presence of hydrogen (W.J. Jones, personal communication). This chemolithoautotrophic sulphur and possibly sulphate reduction (included in Table 7.1) may be found to be an important process in deep sea vent sulphur transformations. The recent claim of bacterial growth at temperatures of 250°C (Baross *et al.*, 1984) has not yet been substantiated by cultural or physiological studies.

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ADDENDUM IN PROOF

Since this paper was submitted in December 1984, the 'unnamed' vent mussel has been described as *Bathymodiolus thermophilus* (Kenk, D.M. and Wilson, B.R. 1985. A new mussel (Bivalvia, Mytilidae) from hydrothermal vents in the Galapagos Rift zone. *Malacologia*, **26**, 253-71). Furthermore, the new observations on cold and slightly saline seepages in the deep sea have also been published (Paull, C.K., Hecker, B., Commeau, R., Freeman-Lynde, R.P., Neumann, C., Golubic, W.P., Hook, J.E., Sikes, E., and Curray, J., 1984. Biological communities at the Florida Escarpment resemble hydrothermal vent taxa. *Science* (Washington), **226**, 911-33). It appears that the growth of mussels at this particular deep sea site is based on the symbiotic microbial oxidation of methane rather than sulphide.

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