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GEOCHEMISTRY OF HYDROTHERMAL VENT FLUIDS FROM THE NORTHERN JUAN DE FUCA RIDGE

by
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B.S., University of Missouri-Columbia, 1994
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Submitted in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

at the

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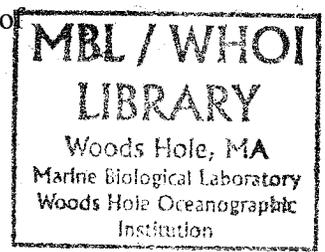
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WOODS HOLE OCEANOGRAPHIC INSTITUTION

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GEOCHEMISTRY OF HYDROTHERMAL VENT FLUIDS FROM THE NORTHERN JUAN DE FUCA RIDGE

by

Anna M. Cruse

Submitted on November 12, 2002, in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Massachusetts Institute of Technology and the Woods Hole Oceanographic Institution

ABSTRACT

The presence of aqueous organic compounds derived from sedimentary organic matter has the potential to influence a range of chemical processes in hydrothermal vent environments. For example, hydrothermal alteration experiments indicate that alteration of organic-rich sediments leads to up to an order of magnitude more metals in solution than alteration of organic-poor basalt. This result is in contrast to traditional models for the evolution of vent fluids at sediment-covered mid-ocean ridge axis environments, and indicates the fundamental importance of including the effects of organic compounds in models of crustal alteration processes. However, in order to rigorously constrain their role in crustal alteration processes, quantitative information on the abundances and distributions of organic compounds in hydrothermal vent fluids is required. This thesis was undertaken to provide quantitative information on the distributions and stable carbon isotopic compositions of several low-molecular weight organic compounds (C_1 - C_4 alkanes, C_2 - C_3 alkenes, benzene and toluene) in fluids collected in July, 2000, at three sites on the northern Juan de Fuca Ridge: the Dead Dog and ODP Mound fields, which are located at Middle Valley, and the Main Endeavour Field, located on the Endeavour segment.

At Middle Valley, the ridge axis is covered by up to 1.5 km of hemipelagic sediment containing up to 0.5 wt. % organic carbon. The Main Endeavour Field (MEF) is located approximately 70 km south of Middle Valley in a sediment-free ridge-crest environment, but previously measured high concentrations of NH_3 and isotopically light CH_4 relative to other bare-rock sites suggest that the chemical composition of these fluids is affected by sub-seafloor alteration of sedimentary material (LILLEY et al., 1993). Differences in the absolute and relative concentrations of NH_3 and organic compounds and the stable carbon isotopic compositions of the C_1 - C_3 organic compounds suggest that the three fields represent a continuum in terms of the extent of secondary alteration of the aqueous organic compounds, with the Dead Dog fluids the least altered, the MEF fluids the most altered and ODP Mound fluids in an intermediate state. At the two Middle Valley sites, the greater extent of alteration in the ODP Mound fluids as compared to the Dead Dog fluids is due either to higher temperatures in the subsurface reaction zone, or a greater residence time of the fluids at high temperatures. Higher reaction zone

temperatures at the ODP Mound field than at the Dead Dog field are consistent with differences in endmember Cl concentrations between the two fields. The greater extent of alteration in the MEF fluids is caused by relatively oxidizing conditions in the subsurface reaction zone that promote faster reaction kinetics.

Temperatures in the subsurface reaction zones calculated by assuming equilibrium among aqueous alkanes, alkenes and hydrogen are consistent with other inorganic indicators (Cl and Si concentrations) of temperature, indicating that metastable equilibrium among these compounds may be attained in natural systems. Isotopic equilibration among CH₄ and CO₂ appears to have been attained in ODP Mound fluids due to the high temperatures in the subsurface reaction zone and the approach to chemical equilibrium from excess methane. However, isotopic equilibrium between CH₄ and CO₂ was not attained in the MEF fluids, due to a short residence time of the fluids in the crust following late-stage addition of magmatic-derived CO₂ to the fluids.

Time series analysis indicate that Middle Valley fluid compositions are generally characterized by stable concentrations over the last decade. However, decreases in Br concentrations in Dead Dog fluids from 1990 to 2000 suggest that either a greater proportion of the fluids interact with basalt rather than sediments or that the sediment with which hydrothermal fluids interact is becoming exhausted. In contrast, the concentrations of H₂ and H₂S and the $\delta^{34}\text{S}$ of H₂S are quite different in fluids sampled from vents of differing ages at the ODP Mound field, despite their close spatial proximity. The observed variations are caused by the reaction of hydrogen-rich fluids within the ODP Mound massive sulfide to reduce pyrite to pyrrhotite during upflow. The replacement of pyrite by pyrrhotite is opposite to the reaction predicted during the weathering of sulfide minerals weather on the seafloor and reflects the real-time equilibration of the reduced fluids with mound mineralogy due to the very young age (< 2 years) venting from Spire vent. The presence of aqueous organic compounds therefore affects not only the inorganic chemical speciation in vent fluids, but can also control the mineralogy of associated sulfide deposits. These results also indicate that vent fluid compositions do not necessarily reflect conditions in the deep subsurface, but can be altered by reactions occurring in the shallow subsurface

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CHAPTER 1. INTRODUCTION

Convective circulation of seawater through the oceanic crust at mid-ocean ridges is a major mechanism by which heat and material is transferred from the interior of the Earth. During convection at mid-ocean ridges, seawater is heated and reacts with basaltic rocks and overlying sediments, if present, resulting in a fluid that is hot, acidic, reducing, enriched in the alkali and alkaline earth metals and transition metals, depleted in SO_4 and Mg, and either enriched or depleted in Cl, compared to the original seawater (EDMOND et al., 1979; VON DAMM, 1995). In the twenty-five years since the first report of the chemical composition of hydrothermal vent fluids sampled at the Galapagos Ridge (CORLISS et al., 1979), the concentrations of over 30 different chemical species have been analyzed in fluids from over 40 locations around the globe have been measured (e.g., BOTZ et al., 1999; BUTTERFIELD, 2000; KELLEY et al., 2001; VON DAMM, 1995). In comparison to the inorganic compounds, measurements of aqueous low molecular weight aqueous hydrocarbons has been very few, and predominantly confined to methane (Table 1-1). Other efforts at the quantitation of aqueous organic compounds, many of which are volatile or semi-volatile, have been hampered by the use of non-gas tight fluid samplers (e.g., WELHAN and LUPTON, 1987). Also, investigations of the altered sediments from environments such as Middle Valley and Guaymas Basin, Gulf of California, indicate that thermal maturation of organic matter results in the generation of number organic compounds such as C_{6+} *n*-alkanes, alkenones, aromatic and polyaromatic hydrocarbons, biomarker compounds and organic acids that may be transported in solution (KAWKA and SIMONEIT, 1990; KVENVOLDEN et al., 1990; KVENVOLDEN et al., 1986; RUSHDI and SIMONEIT, 2002; SIMONEIT, 1984, 1993; SIMONEIT, 1994; SIMONEIT et al., 1990; SIMONEIT and GALIMOV, 1984; SIMONEIT et al., 1992; SIMONEIT et al., 1988; SIMONEIT and KVENVOLDEN, 1994; SIMONEIT et al., 1994; WHELAN et al., 1988).

Organic compounds can play a key role in subsurface processes. For example, Crossy et al. (1984) have demonstrated that the generation of organic acids is key in the development of secondary porosity in aquifers. The presence of organic compounds in

hot fluids may play a key role in the formation of some economic-grade ore deposits (DISNAR and SUREAU, 1990, and references therein). Organic compounds present in hydrothermal vent fluids represent important energy sources for both the surface-dwelling vent fauna as well as for any subsurface microbial communities that might exist (SUMMIT and BAROSS, 2001).

An underlying goal in the study of hydrothermal vent fluids is to understand the conditions under which crustal alteration processes occur in subsurface environments that cannot be directly observed. Inorganic compounds such as Cl or Si have often been utilized as geochemical indicators of subsurface reaction conditions. Aqueous organic species also respond systematically to environmental variables and key reactions that can control their abundances have been identified in laboratory experiments. However, the lack of fundamental data on the abundance of many organic compounds in hydrothermal vent fluids precludes the assessment of the mechanisms that control their abundances in nature, and therefore, the role that they may play in crustal alteration processes, transport of transition metals, ore deposit formation, and the maintenance of subsurface microbial populations.

In this thesis, the first step toward addressing such issues has been taken by quantifying the concentration and isotopic composition of several organic compounds in vent fluids collected from two vent sites on the northern Juan de Fuca Ridge: Middle Valley and the Main Endeavour field (MEF; Fig. 1-1). At Middle Valley, the ridge axis is covered by up to 1.5 kilometers of hemipelagic and turbiditic sediment (GOODFELLOW and BLAISE, 1988) that represents a source of organic compounds to the vent fluids. In contrast, the MEF is located on sediment-free basaltic rocks (DELANEY et al., 1992). However, previous measurements of methane and ammonia concentrations, and the stable carbon and nitrogen compositions of these compounds, suggest that fluids at the MEF do interact with a sediment source that as yet remains unconstrained in terms of both its location and composition (LILLEY et al., 1993). These two sites vary in terms of physical conditions such as temperature and pressure, as well as the relative amounts of basalt versus sediment interaction with circulating hydrothermal fluids, providing an

ideal setting to compare and contrast different mechanisms by which organic compounds react in mid-ocean ridge settings.

1.1. HYDROTHERMAL CIRCULATION PROCESSES

Hydrothermal vents are a pervasive phenomenon associated with the generation of new oceanic crust at mid-ocean ridges. After formation, the crust cools as it moves away from the ridge axis. Cracks that form during cooling allow seawater to percolate into the crust resulting in the development of hydrothermal circulation systems. Hydrothermal circulation can be divided into three zones: recharge, reaction zone and discharge (ALT, 1995; Fig. 1-2), during which different characteristic chemical reactions occur. The following discussion has been taken largely from Alt (1995).

During recharge, large volumes of seawater percolate downward through the porous and permeable volcanic upper section, with only a small portion entering the underlying sheeted dikes. During the initial stages of circulation, low-temperature oxidation and fixation of the alkali metals from result in the formation of various alteration minerals such as celadonite, smectite, and Fe-oxyhydroxides. Reaction of seawater with the crust at temperatures as low as 50° causes the near quantitative removal of Mg from seawater, which, together with OH⁻, precipitates as smectite and chlorite (BISCHOFF and DICKSON, 1975; MOTTLE and HOLLAND, 1978; SEYFRIED and BISCHOFF, 1981b). This results in the dramatic pH shift of the fluid from ~8 in seawater to values typically between 3 and 5.5 (as measured at 25°C) in hydrothermal fluids. Fixation of Mg in the crust also releases Ca to solution (SEYFRIED and BISCHOFF, 1979, 1981a). Increased concentrations of Ca, combined with the retrograde solubility of anhydrite, results in the removal of virtually all of the sulfate from seawater as anhydrite precipitates from heated fluids during recharge (SEYFRIED, 1987). At this point, the initially cool, alkaline and oxidizing seawater has become a hot, acidic and reduced fluid.

In subsurface “reaction zones”, which are traditionally envisioned as the hottest portions of the hydrothermal system, the acidic, reducing fluids interact with basalt at temperatures above ~350°C (Fig. 1-2). This results in the leaching of transition metals, sulfur and a host of other elements (alkali metals, alkaline earths, Si) from the basalt.

Volatile compounds such as CO₂, and ³He can also be gained by the fluid from magma degassing in the deepest portion of the hydrothermal circulation cell. Precipitation of the leached metals and sulfur as sulfide minerals in response to the large contrast in temperature and acidity between hydrothermal fluids and seawater forms the smoke observed at high-temperature vents.

As the hydrothermal fluid is heated, it undergoes dramatic changes in its physical properties: the dielectric constant and density decrease, the coefficient of thermal expansion and heat capacity reach maxima and viscosity reaches a minimum as the temperature and pressure conditions approach the critical point for seawater (NORTON, 1984). These combine to provide maximum buoyancy forces, and the hydrothermal fluid rises to the seafloor. During upflow, quartz and epidote minerals may be deposited, resulting in a loss of Si and Ca from the fluid. The hydrothermal fluids can also entrain cooler seawater in the upper portions of the crust, which cools the hydrothermal fluid and results in the deposition of metal sulfides in the subsurface rather than at the seafloor.

1.2. PROCESSES OF ORGANIC MATTER ALTERATION

In traditional models for organic matter maturation in sedimentary basins, the generation of organic species and their resulting isotopic composition are controlled entirely by kinetic factors such as the composition of the initial products, residence time of products in the source region, and relative rates of competing production and consumption reactions (ABBOTT et al., 1985; BERNER et al., 1995; HUNT, 1996; LEWAN, 1983; LORANT et al., 1998; TISSOT and WELTE, 1984). In these models, geologic time and temperature can be regarded as interchangeable variables (CONNAN, 1974; HUNT, 1996; TISSOT and WELTE, 1984), although others have challenged this assumption (PRICE, 1983, 1985, 1993). In traditional models for the alteration of longer-chained hydrocarbons, degradation is hypothesized to occur via thermal cracking (HUNT, 1996; TISSOT and WELTE, 1984; WAPLES, 1984). Thermal cracking refers to the homolytic cleavage of C-C bonds caused by greater bond vibration frequencies in response to increasing temperature. A greater extent of alteration of organic compounds by this

mechanism will also be favored by longer reaction times at a given temperature since longer times will increase the possibility of bond cleavage.

Recent theoretical work suggests that metastable thermodynamic equilibrium among organic compounds, inorganic minerals and water may regulate the abundances of compounds such as carbon dioxide, hydrocarbons and organic acids (HELGESON et al., 1993; SHOCK, 1988, 1990). Of the myriad laboratory experiments that have attempted to constrain the stability of organic compounds at elevated temperatures and pressures, many have not been conducted in such a way that key variables such as pH or redox conditions have been measured or buffered, or under geologically realistic conditions (ELLIOT et al., 1994; KATRITZKY et al., 1990; SISKIN and KATRITZKY, 1991). In experiments conducted with water and inorganic minerals at temperatures and pressures that are attained within the crust, Seewald (1994; 1997) demonstrated that alkanes and alkenes rapidly reacted readily so as to attain concentrations in equilibrium with dissolved H₂ at the temperature and pressure of the system. Similarly, McCollom et al. (2001) demonstrated the attainment of thermodynamic equilibrium among species where the reactions involved the breaking of C-C bonds in an experimental investigation of the thermal stability of monocyclic aromatic compounds. In these studies, the rate at which equilibrium was attained was a function of the redox state within the system, which was controlled by the mineral buffers that were used. As an alternative to thermal cracking reactions, Seewald (2001) has developed a model whereby the distributions of aqueous low molecular weight hydrocarbons are controlled by a stepwise oxidation reaction mechanism in which alkanes undergo oxidation and hydration reactions with alkenes, alcohols, ketones and organic acids produced as reaction intermediaries. The participation of H₂O and mineral-derived H₂ as reactants within this scheme point to the likely pervasive interactions between organic and inorganic constituents that should not be neglected in models of crustal alteration in hydrothermal environments.

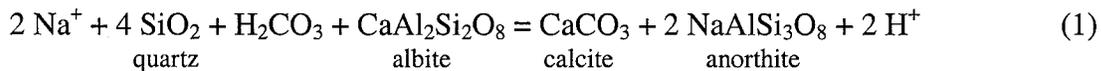
1.3. ORGANIZATION OF THIS THESIS

The results from this thesis are organized into four chapters that describe the effects of organic carbon on the mobilization of metals into high-temperature fluids,

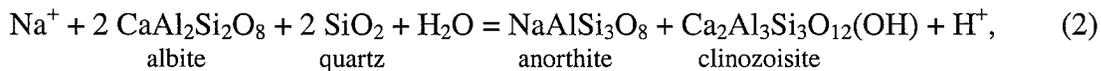
compare and contrast the organic geochemistry of vent fluids from Middle Valley and the Main Endeavour field, and investigate the temporal variability of vent fluid compositions at Middle Valley.

Chapter 2. The role of organic matter in the mobilization of metals in high-temperature fluids.

Fluids from sediment-covered mid-ocean ridge hydrothermal systems are characterized by metal concentrations that are lower than those determined in fluids from bare-rock hydrothermal systems (Table 2-1). In early models of crustal alteration processes, this difference was attributed to the buffering of pH by different reactions during basalt versus sediment alteration (BOWERS et al., 1985; SCOTT, 1985; VON DAMM et al., 1985b). Chapter 2 presents experimental work comparing the results of hydrothermal alteration experiments utilizing basalt, organic-rich sediment from Guaymas Basin and organic-lean sediment from Middle Valley. These experiments demonstrated a trend opposite to that predicted from these early models: at a given temperature and pressure, alteration of organic-rich sediments released greater concentrations of metals to fluids as compared to organic-free basaltic rocks. Thermodynamic modeling indicated that this is due to the generation of acidity from calcite precipitation, which is caused by the release of CO₂ from organic matter and release of Ca from the formation of anorthite from albite. The overall reaction mechanism is:



In contrast, the alteration of organic-free basaltic rocks Ca is fixed in hydrous alteration minerals such as epidote:



a reaction which results in higher fluid pH at a given temperature and pressure than Reaction 1. Consequently, the lower metal abundances observed in natural fluids from sedimented systems is a function of their lower temperature as compared to bare-rock systems, not to the reaction mechanism by which organic carbon-bearing sediments are

altered. The results from this chapter provide evidence that organic compounds can be powerful controls on the potential composition of vent fluid chemistry, and need to be considered in chemical models of ridge crest systems. To do this, the organic compounds in hydrothermal vent fluids need to be identified and quantified, which was a main objective of this thesis.

Chapter 3. Organic geochemistry of Middle Valley vent fluids.

Middle Valley is a sedimented ridge crest environment, where circulating hydrothermal fluids interact with a large source of sediment-derived organic compounds as well as basaltic rocks. In Chapter 3, the aqueous abundances of several low-molecular weight organic compounds and their stable carbon isotopic composition are reported from two areas of venting at Middle Valley, the Dead Dog and ODP Mound fields (Fig. 1-3), and utilized to provide insight into subsurface reaction zone conditions at the vent fields. At the Dead Dog fields, fluids with maximum measured exit temperatures of 270°C vent through anhydrite chimneys found atop mounds of sulfide mineral rubble (AMES et al., 1993). To the south of the Dead Dog field, venting of fluids at temperatures estimated to be in the vicinity of 400°C resulted in the formation of the Bent Hill massive sulfide deposit, which contains an estimated 8 million tons of ore (ZIERENBERG et al., 1998). Although high temperature venting has ceased, ~270°C fluids do vent from small spires and chimneys near the ODP Mound, a smaller massive sulfide deposit located ~300 m south of Bent Hill. The ODP Mound vent field has apparently undergone rapid changes on time scales of only 1-2 years, with several new small spires and chimneys having formed across the surface of the mound as a result of puncturing of a hydrologic seal in the subsurface during ODP Leg 169 drilling operations.

Chloride systematics in vent fluids indicate that the ODP Mound field is characterized by subsurface reaction zone temperatures that are hotter than those at the Dead Dog field. Temperatures calculated from the relative abundances of C₂-C₃ alkanes and alkenes are consistent with temperatures required to produce the observed Cl concentrations and suggest that equilibrium between these organic compounds occurs in nature. The abundances and isotopic compositions of C₁-C₄ alkanes, benzene and toluene

indicate that the aqueous organic compounds have undergone a greater extent of alteration in the ODP Mound vent fluids in response to the hotter subsurface temperatures or longer reaction times. Abiotic oxidation of methane and other organic compounds is a key process influencing the concentration and isotopic composition of carbon dioxide in the Middle Valley vent fluids. Chemical and isotopic equilibrium between methane and carbon dioxide has likely occurred in the subsurface reaction zones of these two vent fields, driven by an approach to equilibrium from excess methane. Oxidation of organic compounds is also hypothesized to lead to the very high aqueous H₂ concentrations observed in the ODP Mound fluids. That the sediments from Middle Valley contain relatively low levels of organic carbon relative to the sediments that overlie other mid-ocean ridges such as at Guaymas Basin, Gulf of California, yet can still affect the concentrations of such inorganic species as CO₂ and H₂, indicates the importance of further investigation of organic compounds in other hydrothermal systems and their inclusion in models of crustal alteration.

Chapter 4. Temporal variability of fluid compositions at Middle Valley.

Vent fluid compositions in some locations such as at the MEF, northern Juan de Fuca Ridge, and 21°N, on the East Pacific Rise, have exhibited stability at time scales of up to six years (BUTTERFIELD et al., 1994b; CAMPBELL et al., 1988). Large changes observed in fluid compositions at the Main Endeavour field from 1999 and 2000 following seismic activity indicate the sensitivity of the fluid chemistry to changes in subsurface conditions (SEEWALD et al., 2002; SEYFRIED et al., 2002). The temporal variability of vent fluid compositions at Middle Valley can be investigated at the yearly and decadal scales. Fluid chemistries from active vents in the Dead Dog field were sampled in 1990 and 1991 by Butterfield et al. (1994a). Heineken Hollow, Dead Dog Mound, Inspired Mounds and Chowder Hill vents were sampled in both that study and this thesis, providing a ten-year interval over which to compare changes in the major ion chemistry. Lone Star vent was sampled by Butterfield et al. (1994a) at the ODP Mound in 1990, but was not sampled as part of this thesis, precluding an assessment of the temporal variability of vent fluid compositions at the scale of individual vents. However,

