

REVIEW

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Theoretical constraints of physical and chemical properties of hydrothermal fluids on variations in chemolithotrophic microbial communities in seafloor hydrothermal systems

Kentaro Nakamura^{1,2*} and Ken Takai^{1,3}

Abstract

In the past few decades, chemosynthetic ecosystems at deep-sea hydrothermal vents have received attention as plausible analogues to the early ecosystems of Earth, as well as to extraterrestrial ecosystems. These ecosystems are sustained by chemical energy obtained from inorganic redox substances (e.g., H_2S , CO_2 , H_2 , CH_4 , and O_2) in hydrothermal fluids and ambient seawater. The chemical and isotope compositions of the hydrothermal fluid are, in turn, controlled by subseafloor physical and chemical processes, including fluid–rock interactions, phase separation and partitioning of fluids, and precipitation of minerals. We hypothesized that specific physicochemical principles describe the linkages among the living ecosystems, hydrothermal fluids, and geological background in deep-sea hydrothermal systems. We estimated the metabolic energy potentially available for productivity by chemolithotrophic microorganisms at various hydrothermal vent fields. We used a geochemical model based on hydrothermal fluid chemistry data compiled from 89 globally distributed hydrothermal vent sites. The model estimates were compared to the observed variability in extant microbial communities in seafloor hydrothermal environments. Our calculations clearly show that representative chemolithotrophic metabolisms (e.g., thiotrophic, hydrogenotrophic, and methanotrophic) respond differently to geological and geochemical variations in the hydrothermal systems. Nearly all of the deep-sea hydrothermal systems provide abundant energy for organisms with aerobic thiotrophic metabolisms; observed variations in the H_2S concentrations among the hydrothermal fluids had little effect on the energetics of thiotrophic metabolism. Thus, these organisms form the base of the chemosynthetic microbial community in global deep-sea hydrothermal environments. In contrast, variations in H_2 concentrations in hydrothermal fluids significantly impact organisms with aerobic and anaerobic hydrogenotrophic metabolisms. Particularly in H_2 -rich ultramafic rock-hosted hydrothermal systems, anaerobic and aerobic hydrogenotrophy is more energetically significant than thiotrophy. The CH_4 concentration also has a considerable impact on organisms with aerobic and anaerobic methanotrophic metabolisms, particularly in sediment-associated hydrothermal systems. Recently clarified patterns and functions of existing microbial communities and their metabolisms are generally consistent with the results of our thermodynamic modeling of the hydrothermal mixing zones. These relationships provide important directions for future research addressing the origin and early evolution of life on Earth as well as for the search for extraterrestrial life.

Keywords: Deep-sea hydrothermal systems; Chemosynthetic ecosystems; Hydrothermal fluid chemistry; Host rock geochemistry; Geochemical modeling; Bioavailable energy yield

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Review

Introduction

Deep-sea hydrothermal vents host some of the most diverse microbial communities on Earth (Takai and Nakamura 2011). Since the first discovery of black smoker vents inhabited by dense and unique chemosynthetic macrofaunal communities (Spiess et al. 1980), submarine hydrothermal systems and their associated biota have attracted great interest (e.g., Humphris et al. 1995; Van Dover 2000; Wilcock et al. 2004). Unlike most biological communities, in which photosynthetic organisms are the base of the food web, deep-sea hydrothermal vent ecosystems are dependent on primary production by symbiotic and free-living chemolithoautotrophic microorganisms that obtain energy from inorganic redox substances (e.g., H_2S , CO_2 , H_2 , CH_4 , and O_2) in hydrothermal fluids and ambient seawater (Karl, 1995; Kelley et al. 2002). Because of the unique features of deep-sea hydrothermal vent ecosystems, they are considered plausible analogues to the early ecosystems of Earth and also to extraterrestrial life on other planets and moons (e.g., Jannasch and Mottl 1985; Nealson et al. 2005; Takai et al. 2006a).

To date, more than 300 high-temperature hydrothermal vent systems have been identified at mid-ocean ridges (MOR), island arcs, and back-arc spreading centers (Hannington et al. 2011). Deep-sea hydrothermal fluids vary greatly in their chemical compositions due to seafloor physical and chemical processes such as fluid-rock interactions, magmatic volatile inputs, and phase separation of hydrothermal fluids (Von Damm 1995; Butterfield et al. 2003; German and Von Damm 2004; Tivey 2007). Compositional variations in hydrothermal fluids (particularly energy and carbon sources) in turn affect biomass production and the diversity of hydrothermal vent-endemic communities. Consequently, clarifying the relationships among the geological background of hydrothermal environments, physical and chemical variations in hydrothermal fluids, and the compositional and functional diversity of chemosynthetic ecosystems has provided important information on the diversification and development of extant deep-sea hydrothermal ecosystems as well as the generation and sustenance of early ecosystems and possible extraterrestrial life forms.

In deep-sea hydrothermal vents, rapid mixing between hot reduced hydrothermal fluids and cold oxidized seawater provides chemical energy for microbial activity and biomass production. To quantify the in situ energetics of chemolithotrophic microorganisms in hydrothermal mixing environments, a thermodynamic model was first proposed and applied to a basalt-hosted hydrothermal system at 21° N on the East Pacific Rise (EPR) (McCollom and Shock 1997). Using batch-mixing models modified

from this original model, thermodynamic calculations have been conducted for several hydrothermal vent systems at MOR and arc-backarc (ABA) hydrothermal systems (Shock and Holland 2004; Tivey 2004; McCollom 2007; Amend et al. 2011). These studies have demonstrated differing patterns in the potential energy yields of various in situ metabolic reactions in the mixing zones of these habitats, providing the theoretical basis for relationships between hydrothermal fluid chemistry and the diversity of hydrothermal vent-endemic biological communities. However, the hydrothermal systems studied were quite limited. In addition, the structures and functions of extant chemosynthetic biological communities, which have been characterized in many previous investigations, have not yet been integrated into development of these theoretical relationships.

Many studies have identified high compositional and functional diversity of chemosynthetic ecosystems in geographically and geologically diverse hydrothermal systems (e.g., in reviews by Huber and Holden 2008; Nakagawa and Takai 2008; Takai et al. 2006b). Some of these studies have noted possible relationships between the metabolic abundances and compositions of hydrothermal vent-endemic microbial communities and the chemical characteristics of hydrothermal vent fluids in deep-sea hydrothermal systems (Perner et al. 2007, 2010; Reysenbach and Shock 2002; Takai and Horikoshi 1999; Takai et al. 2001, 2004a). However, most of these studies were qualitative and focused mainly on the genetic and phylogenetic diversity of microbial communities and their constituents. Thus, the relationships between the abundance and composition of chemolithotrophic microbial communities and the geological and geochemical environments of global deep-sea hydrothermal systems remain unclear.

Takai and Nakamura (2010, 2011) first provided clear evidence of biogeochemical relationships among microbiological community development, the chemical composition of hydrothermal fluids, and the geological environment of deep-sea hydrothermal systems through both thermodynamic calculations of the potential energy yields of various in situ metabolic reactions and observed compositional and functional diversity of chemosynthetic ecosystems in the mixing zones of these habitats. However, examples of hydrothermal systems for this comparison were still scarce; thus, only microbial populations in chimney habitats adjacent to high-temperature hydrothermal fluids were characterized by quantitative cultivation techniques and included. In the present study, we conducted a more comprehensive evaluation of the relationships among variations in geology, geochemistry, and microbial metabolisms and the diversity of communities in global deep-sea hydrothermal environments, based on compilation of a substantial

hydrothermal fluid chemistry data set and microbial communities in the mixing zones of a wide variety of habitats.

Methods

We compiled end-member fluid chemistry data for 89 hydrothermal vent sites (Additional file 1). Hydrothermal vent sites were included only if the data set contained complete chemical composition data essential for the thermodynamic calculations performed in this study, including H₂, H₂S, CH₄, CO₂, Na, Cl, Ca, K, Fe, Mn, and Si. In addition, the data set included representative geological settings such as MOR hydrothermal systems in the Pacific, Atlantic, and Indian Oceans; ABA hydrothermal systems in the western Pacific region; and the sediment-associated (SED) hydrothermal systems in the eastern Pacific and Okinawa Trough (Figure 1).

The amount of metabolic energy available for production by chemolithotrophic microorganisms was evaluated as in Takai and Nakamura (2010, 2011). Four aerobic and anaerobic reactions were considered representative of chemolithotrophic energy metabolisms (Table 1). To simulate mixing of hydrothermal fluids with seawater in a seafloor hydrothermal system, we employed a thermodynamic reaction path model, following McCollom and Shock (1997), Shock and Holland

(2004), and McCollom (2007). The compositions of the hydrothermal solutions in the mixing zones were calculated from those of the end-member vent fluids and seawater (Additional file 1). The model calculation began with 1 kg of vent fluid and continued with addition of successive increments of seawater until a seawater to vent fluid mixing ratio of 1,000:1 was reached. In the mixing calculations, minerals were not allowed to precipitate and all redox reactions were prohibited, while acid-base reactions were allowed to equilibrate. In addition, the temperatures of the calculated mixed solutions were assumed to scale linearly with the temperatures of the end-members, ignoring conductive cooling and/or heating.

The overall Gibbs free energy for the metabolic reactions was calculated using the following equation:

$$\Delta G_r = \Delta G_r^\circ + RT \ln Q_r \quad (1)$$

where ΔG_r is the Gibbs free energy of the reaction, ΔG_r° is the standard-state Gibbs free energy of the reaction, R is the universal gas constant, T is the temperature in Kelvin, and Q_r is the activity quotient of the compounds involved in the reaction. The Q_r term takes into account the contribution of the fluid composition to the Gibbs free energy of each reaction, determined based on the

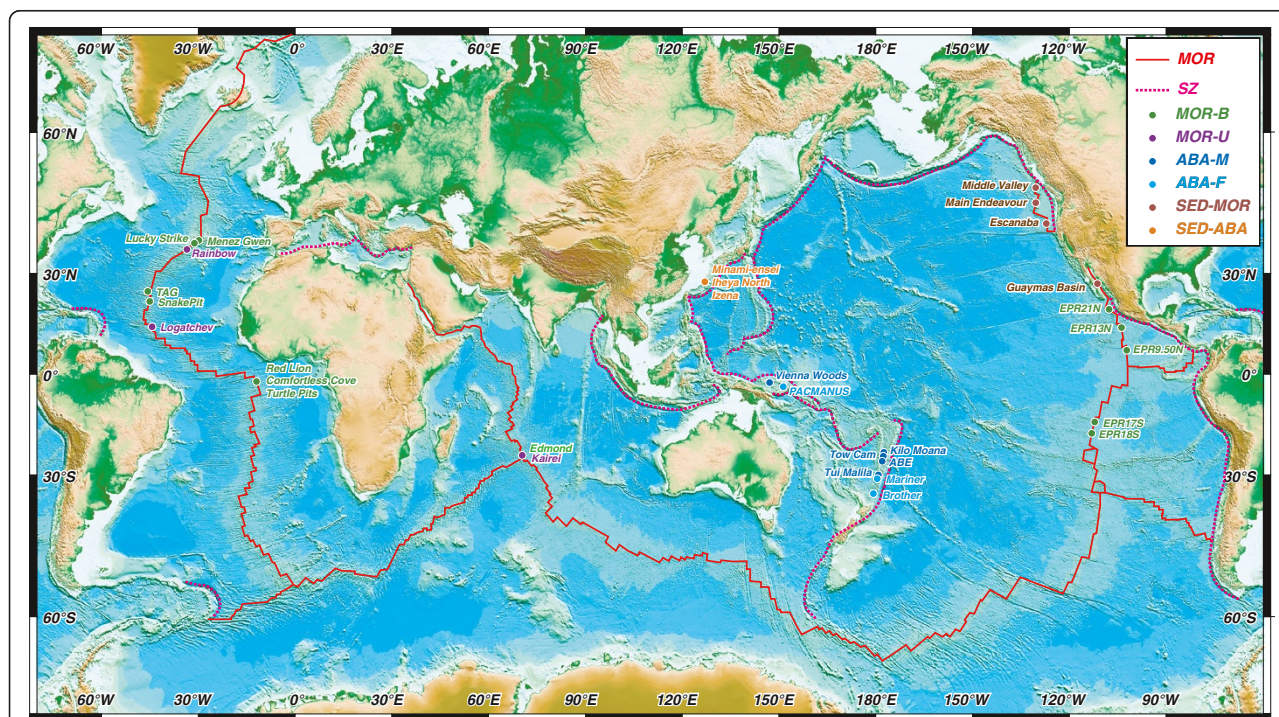


Figure 1 Index map showing mid-ocean ridges and subduction zones with active hydrothermal vents used in this study. Abbreviations: MOR, mid-ocean ridge; SZ, subduction zone; MOR-B, basalt-hosted system in a mid-ocean ridge setting; MOR-U, ultramafic rock-hosted system in a mid-ocean ridge setting; ABA-M, mafic rock-hosted system in an arc-backarc setting; ABA-F, felsic rock-hosted system in an arc-backarc setting; SED-MOR, sediment-associated system in a mid-ocean ridge setting; SED-ABA, sediment-associated system in an arc-backarc setting.

Table 1 Metabolic reactions for chemolithoautotrophy considered in this study

| Energy metabolism | Overall chemical reaction | Identified (I)/cultured (C) | $\Delta G_r^{\circ}, 250$ (KJ) ^a |
|---|---|-----------------------------|---|
| <i>Aerobic reactions</i> | | | |
| Aerobic methanotrophy | $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$ | I and C | -860.7 |
| Hydrogenotrophic O ₂ reduction | $\text{H}_2 + 1/2\text{O}_2 = \text{H}_2\text{O}$ | I and C | -264.4 |
| Thiotrophic (H ₂ S-oxidizing) O ₂ reduction | $\text{H}_2\text{S} + 2\text{O}_2 = \text{SO}_4^{2-} + 2\text{H}^+$ | I and C | -758.2 |
| Fe(II)-oxidizing O ₂ reduction | $\text{Fe}^{2+} + 1/4\text{O}_2 + \text{H}^+ = \text{Fe}^{3+} + 1/2\text{H}_2\text{O}$ | I and C | -52.6 |
| <i>Anaerobic reactions</i> | | | |
| Hydrogenotrophic methanogenesis | $\text{H}_2 + 1/4\text{CO}_2 = 1/4\text{CH}_4 + 1/2\text{H}_2\text{O}$ | I and C | -49.2 |
| Hydrogenotrophic SO ₄ reduction | $\text{H}_2 + 1/4\text{SO}_4^{2-} + 1/2\text{H}^+ = 1/4\text{H}_2\text{S} + \text{H}_2\text{O}$ | I and C | -74.9 |
| Hydrogenotrophic Fe(III) reduction | $\text{H}_2 + 2\text{Fe}^{3+} = 2\text{Fe}^{2+} + 2\text{H}^+$ | I and C | -159.2 |
| Anoxic methanotrophy with SO ₄ reduction | $\text{CH}_4 + \text{SO}_4^{2-} = \text{HCO}_3^- + \text{HS}^- + \text{H}_2\text{O}$ | I but not yet C | -30.1 |

^aStandard-state Gibbs free energy of the metabolic reactions at 2°C, 250 bar.

chemical composition of the mixed fluid estimated from the reaction path calculations. The energy available from the metabolic reactions as a function of temperature (equivalent to the mixing ratio) was calculated by multiplying the calculated Gibbs free energy for the reaction at each temperature by the concentrations of the reactants in the mixed fluid. This method takes into account the stoichiometry of the reaction and the reactants that are limiting, multiplied by the total amount of mixed fluid at that temperature (McCollom and Shock 1997; McCollom 2007).

This calculation yields an estimate of the maximum energy that is potentially available from the metabolic reactions per kilogram of mixed fluid. We used the average ΔG_r values for four temperature ranges: <25°C, 25°C to 45°C, 45°C to 80°C, and 80°C to 125°C, representing the chemolithotrophic metabolisms of psychrophilic, mesophilic, thermophilic, and hyperthermophilic microbial organisms, respectively.

Geological settings and geochemical characteristics of seafloor hydrothermal systems

As noted above, we compiled data for 89 deep-sea hydrothermal vent sites located in various geological settings (Figure 1), including MOR, ABA, and SED hydrothermal systems. These can be further subdivided into the following six categories: basalt-hosted systems in MOR settings (MOR-B), ultramafic rock-associated systems in MOR settings (MOR-U), mafic rock-hosted systems in ABA settings (ABA-M), felsic rock-hosted systems in ABA settings (ABA-F), SED systems in MOR settings (SED-MOR), and SED systems in ABA settings (SED-ABA).

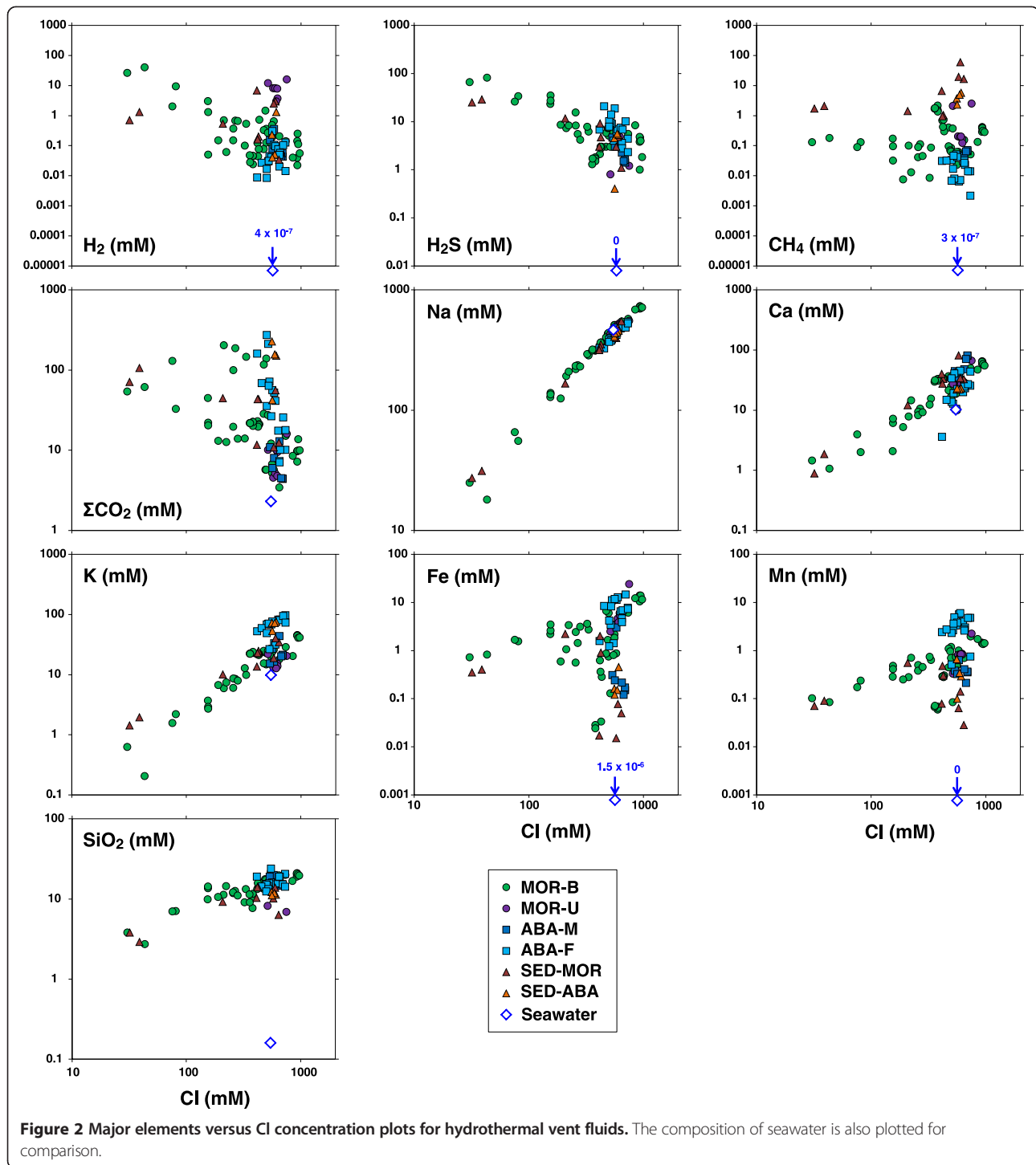
The molecular and elemental compositions of H₂, H₂S, CH₄, CO₂, Na, Ca, K, Fe, Mn, and Si as well as the pH values of the end-member hydrothermal fluids from these sites are plotted against the Cl content in Figure 2. Nearly all substances exhibited some degree of positive

or negative correlation to the Cl content, reflecting the influence of phase separation of hydrothermal fluids. Here, we focus on hydrothermal fluids with similar Cl concentrations to seawater in providing a brief overview of the geological settings and corresponding principal characteristics of their hydrothermal environments.

MOR hydrothermal systems

The global MOR system is the largest mountain chain in the world, with a total length of more than 60,000 km. Magma production in the MOR system far exceeds that in any other tectonic environment, accounting for more than 60% by volume of the total annual flux of magma from the mantle to the crust (Fisher and Schmincke 1984; Schmincke 2004). Therefore, the MOR system is the locus of the greatest amount of hydrothermal activity on Earth. Most MOR hydrothermal vents are hosted by basalt (often termed mid-ocean-ridge basalt). Therefore, many studies of deep-sea hydrothermal systems have focused mainly on basalt-hosted hydrothermal systems (Karl 1995; Kelley et al. 2002). However, in recent years, increasing attention has been paid to hydrothermal systems associated with ultramafic rocks present in the MOR (Kelley et al. 2001, 2005; Früh-Green et al. 2004), because the geochemical characteristics of ultramafic rock-hosted hydrothermal fluids are significantly different from those of basalt-hosted ones (Charlou et al. 2002).

Hydrothermal fluids from basalt-hosted systems are characterized by enrichment in base metals, a generally neutral or weakly acidic in situ pH, and strongly reducing conditions compared to seawater, due to subsurface hydrothermal reactions between basaltic rocks and seawater at high temperature and pressure (Seyfried et al. 1991; Wetzal and Shock 2000). However, the fluids from ultramafic rock-associated systems are often characterized by an abundance of dissolved H₂ and CH₄ compared to basalt-hosted hydrothermal fluids (Figure 2)



(Charlou et al. 1998, 2002). This is attributed to differences in the mineralogy and bulk chemistry of the rocks, resulting in a substantially different alteration reaction known as serpentinization (Janecky and Seyfried 1986; Wetzel and Shock 2000; Allen and Seyfried 2003). H₂ concentrations of 12 to 16 mmol/kg (roughly 1 to 2

orders of magnitude higher than in basalt-hosted hydrothermal fluids) due to serpentinization have been reported in ultramafic rock-hosted deep-sea hydrothermal vent fluids (Additional file 1) (Charlou et al. 2002; Kelley et al. 2005). In addition, enrichment of CH₄ in ultramafic rock-associated systems is likely associated with

reduction of CO₂ to CH₄ under highly reducing (high H₂) conditions.

ABA hydrothermal systems

Although significant global magma production occurs in the MOR, the second most active volcanic area is the subduction zone (Fisher and Schmincke 1984; Schmincke 2004), where ABA volcanic systems develop. Some arc volcanoes are subaerial, particularly in continental arc settings, whereas more than 40% of volcanic arcs are oceanic island arcs where most volcanoes are submarine (Leat and Larter 2003). In oceanic island arcs and associated back-arc basins, many deep-sea hydrothermal vent sites hosted by active submarine ABA volcanisms have been discovered (Ishibashi and Urabe 1995; Gamo et al. 2006). The chemical characteristics of these ABA hydrothermal systems are significantly different from those of MOR hydrothermal systems, although they share many common features derived from the basic reactions and processes of seafloor hydrothermal circulation. In particular, ABA hydrothermal fluids are characterized by large variations in chemical composition (Ishibashi and Urabe 1995; Gamo et al. 2006). This chemical variability is primarily attributed to a variety of host-rock compositions (from basaltic to rhyolitic), abundant input of volatile elements from magmas (e.g., CO₂ and SO₂), and the variable water depth (shallow to deep) of the submarine volcanoes.

ABA hydrothermal systems hosted by mafic rocks exhibit chemical characteristics similar to those of basalt-hosted hydrothermal systems at the MOR (Figure 2). In contrast, systems hosted by felsic rocks are generally characterized by lower pH, higher metal concentrations, and a variable redox state compared to mafic rock-hosted hydrothermal systems (Figure 2). In addition, because of the subduction of hydrated ocean crust beneath volcanic arcs and back-arc basins as well as the potential involvement of more evolved felsic magmas, the volatile content (H₂O, CO₂, and SO₂) of magmas in ABA settings is much higher than that in MOR settings (e.g., Gamo et al. 1997; Embley et al. 2007). ABA hydrothermal systems are also characterized by wide variations in water depth, and most are significantly shallower than typical MOR hydrothermal systems (Figure 3). This results in variations in phase separation (boiling) and hydrothermal fluid temperatures in the seafloor reaction zones, which significantly affect the chemical composition of the hydrothermal fluids. The maximum temperatures of the hydrothermal vent fluids in the compiled data were clearly controlled by the two-phase boundary of seawater (Figure 3).

SED hydrothermal systems

Some hydrothermal vent sites are covered with sediments, which influence the chemical composition of

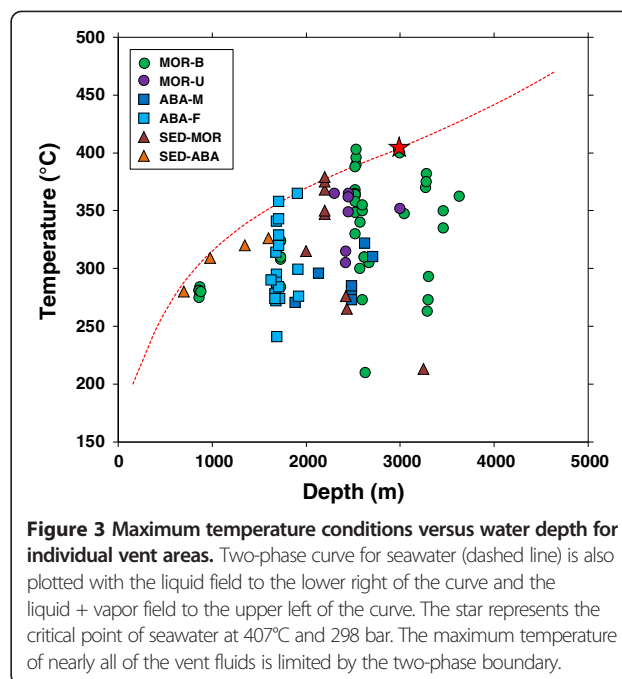


Figure 3 Maximum temperature conditions versus water depth for individual vent areas. Two-phase curve for seawater (dashed line) is also plotted with the liquid field to the lower right of the curve and the liquid + vapor field to the upper left of the curve. The star represents the critical point of seawater at 407°C and 298 bar. The maximum temperature of nearly all of the vent fluids is limited by the two-phase boundary.

their hydrothermal fluids. SED hydrothermal systems are found in both MOR (e.g., Juan de Fuca, Middle Valley, Escanaba Trough, and Guaymas Basin) and ABA (e.g., Okinawa Trough) settings in which hydrothermal vent sites are in close proximity to continental runoff sources. Irrespective of differences in tectonic setting or host-rock composition, SED hydrothermal systems have characteristic chemical compositions, e.g., relatively high pH, low metal content, and high CH₄ and NH₃ concentrations (German and Von Damm 2004). There are only minor differences in chemical composition between SED hydrothermal systems in MOR and ABA settings (Figure 2). Thus, the chemical features of SED hydrothermal vent fluids are more strongly affected by the sediment than by the tectonic setting or host-rock composition.

Factors controlling hydrothermal fluid chemistry

It is believed that hydrothermal fluid flux is primarily controlled by the crust (magma) production rate, because magmatic heat derived from creation of new oceanic crust (cooling from 1,200°C to 350°C) heats hydrothermal fluids from 2°C to 350°C (e.g., Elderfield and Schultz 1996). Based on this, Kawahata et al. (2001) estimated that the maximum volume of high-temperature hydrothermal fluid is twice that of the upper oceanic crust (the volcanic and sheeted dike sequence) and if 65% to 85% of the rocks are altered to secondary minerals, the volumetric water/rock ratio would be 2.3 to 3.1. This clearly suggests that high-temperature hydrothermal fluids are generated under rock-dominated (low water/rock ratio) conditions (Kawahata et al. 2001). Therefore, the chemical compositions of hydrothermal fluids are

predominantly controlled by water-rock reactions and fluid-mineral equilibria (Seyfried et al. 1991; Shock 1992; Seyfried and Ding 1995). Thus, host-rock geochemistry is one of the most important factors controlling hydrothermal fluid chemistry. In addition to the chemical compositions of host rocks, however, other processes such as input of volatiles from magmas, phase separation of hydrothermal fluids, and interactions with sediment also have a significant impact on the observed compositions of hydrothermal fluids.

Chemical composition of host rocks

Differences in the rock types in the reaction zone can lead to large variations in the hydrothermal fluid chemistry, because the bulk chemical composition and primary minerals in the source rock control the reaction sequences and their chemical equilibria.

Mafic rocks Most ocean basins (including MOR and ABA settings) are of mafic composition (mainly basaltic). The chemical systematics of mafic rock-seawater systems (particularly basalt-seawater systems) have been well characterized based on field observations, hydrothermal experiments, and theoretical studies (Bischoff and Dickson 1975; Mottl and Holland 1978; Seyfried and Mottl 1982; Mottl 1983; Reed 1983; Bowers and Taylor 1985; Seyfried 1987; Von Damm 1990, 1995; Seyfried et al. 1988, 1991; Shock 1992; Saccocia et al. 1994; Wetzel and Shock 2000; Butterfield et al. 2003; Nakamura et al. 2007).

Basalt-hosted hydrothermal fluids have relatively low pH at 25°C and 1 atm (generally 3 to 4) and notable enrichment in base metals (e.g., Fe and Mn) and dissolved gases (e.g., H₂, CO₂, and CH₄) compared to seawater (Figure 2). The in situ pH of the basalt-hosted vent fluids are neutral to weakly acidic, significantly different from the pH measured at 25°C and 1 atm in laboratory experiments (German and Von Damm 2004). This discrepancy is mainly caused by dissociation of H⁺-bearing aqueous complexes (e.g., HCl⁰) due to cooling during sample processing (Shock et al. 1989; Seyfried et al. 1991; Ding and Seyfried 1992; Ding et al. 2005). Another possible mechanism of pH change is precipitation of metal sulfides below the seafloor, producing protons (German and Von Damm 2004).

In high-temperature MOR vent fluids, most metals are enriched by up to 7 to 8 orders of magnitude compared to seawater. The stability of chloride complexes (e.g., FeCl₂⁰) increases with increasing temperature, and therefore, most metal ions are present in high-temperature fluids as chloride complexes (Helgeson et al. 1981; Ding and Seyfried 1992). The substantial increase in the metal solubility produces the high concentrations in the vent fluids.

Basalt-hosted hydrothermal fluids are also highly reducing, as evidenced by the presence of H₂S rather than SO₄, as well as by significant amounts of H₂, CH₄, Fe²⁺, and Mn²⁺. These chemical features are generally consistent with phase-equilibrium calculations involving the observed primary and secondary minerals (feldspar, chlorite, epidote, quartz, magnetite, anhydrite, pyrite, and pyrrhotite) and seawater at in situ hydrothermal fluid temperatures and pressures (Bowers et al. 1988; Seyfried et al. 1988, 1999; Saccocia and Seyfried 1990; Seyfried and Ding 1995; McCollum and Shock 1998; Wetzel and Shock 2000). Time-series measurements of chemical compositions of hydrothermal fluids in MOR regions have indicated steady-state concentrations of dissolved species (Campbell et al. 1988; Bowers et al. 1988; Butterfield et al. 1994; Von Damm 1988, 1995, 2000), reflecting clear solubility control by mineral phases in the subseafloor reaction zones and recharge zones.

Ultramafic rocks Compared with hydrothermal fluids in mafic rock-hosted systems, ultramafic rock-associated hydrothermal fluids are characterized by conspicuous enrichment in H₂ in the presence or absence of phase separation processes (Figure 2). Production of H₂ during serpentinization of ultramafic rocks results from reaction of water with Fe²⁺-bearing minerals, primarily olivine and pyroxene. In these reactions, Fe²⁺ is partially oxidized to Fe³⁺ by the water, resulting in precipitation of magnetite in the serpentinite. The water reduced by the Fe²⁺ also produces H₂. One of the important chemical features of ultramafic rocks that constrains abundant H₂ production during serpentinization is relatively low Al concentrations. Low Al activity results in formation of alteration minerals (particularly serpentines and brucite) that have a tendency to exclude Fe²⁺ from their structure. This leads to oxidation of Fe²⁺ by water to form magnetite. In contrast, because mafic rocks have higher Al contents than ultramafic rocks, a much greater proportion of the Fe²⁺ is sequestered in Al-bearing alteration minerals (e.g., chlorite), limiting oxidation of Fe²⁺ to Fe³⁺. Thus, hydrothermal alteration of mafic rocks generates much lower amounts of H₂ and magnetite than serpentinization of ultramafic rocks, even though the Fe content of basaltic rocks is higher than that of ultramafic rocks. Basaltic rock-hosted vent fluids typically exhibit H₂ concentrations of <1 mmol/kg, whereas >10 mmol/kg H₂ has frequently been reported for ultramafic rock-associated fluids (Additional file 1). The potential for even higher H₂ concentrations (>100 mmol/kg) has been suggested by both petrological (Frost 1985; Alt and Shanks 1998) and experimental (Berndt et al. 1996; McCollom and Seewald 2001) studies.

In addition, ultramafic rock-associated hydrothermal fluids are often characterized by CH₄ enrichment (Figure 2). Although the origin of CH₄ in these fluids is controversial, it is generally thought to be derived from reduction of CO₂ by high concentrations of H₂ through abiotic methanogenesis (Nakamura et al. 2009). However, the hydrothermal fluid CH₄ concentrations are always disequibrated with the concomitant H₂ and CO₂ concentrations, suggesting that the subseafloor hydrothermal circulation system is an open system with respect to CH₄ content. Enriched CH₄ (>0.5 mmol/kg) has also been observed in hydrothermal fluids from certain basalt-hosted systems at the MOR (Figure 2; Lucky Strike and Menez Gwen hydrothermal fields) (Additional file 1). Both of these fields are located in the northern Mid-Atlantic Ridge, where several ultramafic rock-associated hydrothermal systems have been discovered. Based on geological and geochemical lines of evidence, it has been suggested that the high CH₄ concentrations in these basalt-hosted hydrothermal fluids were caused by serpentinization of ultramafic rocks somewhere in the subseafloor (Charlou et al. 2000).

Felsic rocks Hydrothermal systems hosted by felsic rocks have been identified only in ABA settings (Figure 1). Felsic rock-hosted hydrothermal fluids are characterized by relatively low pH and enrichment in H₂S, CO₂, K, Mn, and Fe compared to mafic rock-hosted fluids (Figure 2). The chemical characteristics of felsic rock-hosted hydrothermal fluids are generally consistent with experimental results for seawater-felsic rock interactions (e.g., Hajash and Chandler 1981). For example, felsic rocks contain high concentrations of incompatible elements such as K. Enrichment of K in felsic rock-hosted fluids originates from the bulk rock composition. In addition, the lower pH is attributed to the low ability of felsic rocks to consume H⁺ in solution. The pH of a hydrothermal solution is lowered by removal of Mg²⁺ via precipitation of Mg-hydroxysulfate during heating of the seawater (Bischoff and Seyfried 1978) and by formation of Mg-bearing alteration minerals (e.g., smectite and chlorite) during seawater-rock interactions (Mottl 1983). In a basalt–seawater system, the H⁺ generated in the fluid is consumed by dissolution of Ca from the reacted rocks (Seyfried and Mottl 1982; Mottl 1983). Mg–Ca exchange reactions control the fluid pH to approximately neutral under in situ conditions (Seyfried and Mottl 1982; Wetzel and Shock 2000). However, because felsic rocks are relatively depleted in Ca, their ability to buffer pH changes is significantly lower than that of their mafic counterparts.

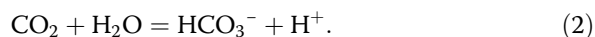
Low pH in hydrothermal fluids promotes leaching of heavy metals through water-rock interactions. This ultimately results in high concentrations of heavy metals, although the initial concentrations of heavy metals in

felsic rocks are lower than those in basaltic rocks. The Fe and Mn concentrations in deep-sea hydrothermal fluids are correlated not only with Cl concentrations but also with pH (Figure 4). Moreover, the Fe/Cl and Mn/Cl ratios for hydrothermal fluids exhibit strong correlations with pH (Figure 4). This clearly shows that the concentrations of heavy metals in deep-sea hydrothermal fluids are mainly controlled by the pH of the hydrothermal fluids.

Inputs of magmatic volatiles

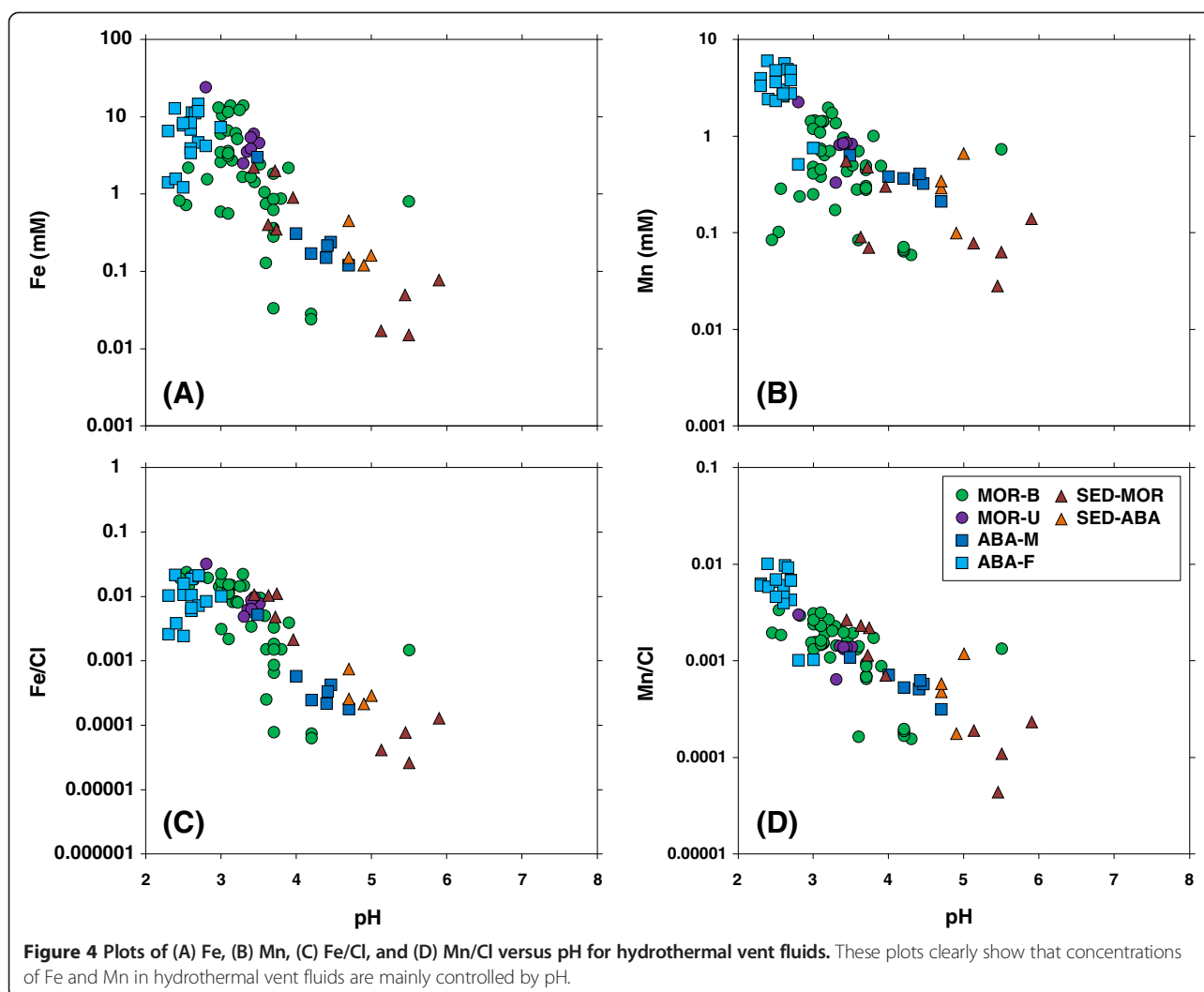
Enrichment of H₂S and CO₂ in felsic rock-hosted hydrothermal fluids cannot be explained only by water-rock interactions. Instead, enrichment in these volatiles can be caused by inputs of magmatic volatiles into hydrothermal systems. ABA magmas (particularly those that are felsic in composition) have very high concentrations of volatile elements and molecules, and hydrothermal fluids that are highly enriched in sulfur and/or CO₂ have been observed in ABA hydrothermal systems, mainly hosted by more siliceous rocks, e.g., andesite, calcite, and rhyolite rather than by basalt (Gamo et al. 1997; Sakai et al. 1990; Inagaki et al. 2006; Lupton et al. 2006, 2008). Therefore, enrichment in CO₂ and H₂S of felsic rock-hosted hydrothermal fluids is likely due to significant inputs of magmatic volatiles into these hydrothermal systems.

Dissolution of CO₂ gas into a hydrothermal fluid results in production of H⁺ in the fluid via the following reaction:

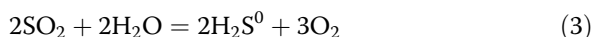


Compared to that for SO₂ (see below), the dissociation constant of this reaction is much smaller, particularly under high-temperature conditions. It is therefore believed that the effect of CO₂ on the fluid pH is not very significant. However, segregation of CO₂ from upwelling hydrothermal fluids in the subseafloor can result in consumption of H⁺ in the fluid, increasing the pH. Even a small pH increase during ascent of the hydrothermal fluid can cause subseafloor precipitation of metal-sulfide minerals, resulting in low heavy metal concentrations in the hydrothermal fluids. This process would be expected in hydrothermal systems with significant inputs of CO₂ but not SO₂ from magma, such as hot spot-influenced MOR hydrothermal systems and basalt-hosted arc-backarc hydrothermal systems.

Volatile sulfur species in the magma have a more significant effect on deep-sea hydrothermal systems. The predominant gaseous sulfur species in magma are SO₂ and H₂S (Wallace and Edmonds, 2011). Although dissolution of H₂S does not significantly affect hydrothermal fluid chemistry, that of SO₂ into hydrothermal fluids



increases the f_{O_2} and sulfuric acid in the fluids via the following reactions:



Once the f_{O_2} of the hydrothermal fluid reaches the sulfate-sulfide boundary via reaction (3), sulfuric acid is produced by reaction (4). The presence of sulfuric acid can cause a significant decrease in pH. Because the solubility of heavy metals is quite sensitive to pH, the pH decrease caused by SO_2 promotes dissolution of heavy metals from the reacted rocks. Volatile inputs from magmas occur intermittently, and even during such activity, the chemistry of hydrothermal fluids is controlled by reactions induced by both volatile inputs and water-rock interactions. Therefore, it is likely that the chemical composition of the fluids, as is typical of open and dynamic systems, significantly varies with space and time.

Nevertheless, felsic rock-hosted hydrothermal systems affected by magmatic volatile inputs clearly exhibit high concentrations of base metals and low pH (Figure 4).

Phase separation

As described above, the concentrations of all components in hydrothermal fluids exhibited positive or negative correlations with Cl, except for H_2 , CO_2 , and CH_4 in several samples affected by serpentinization of ultramafic rocks, CO_2 inputs from magma, and CH_4 inputs from sedimentary organic matter and/or microbial processes (Figure 2). Deep-sea hydrothermal fluids often reach temperatures high enough that they separate into vapor and brine phases. The phase separation temperature depends primarily on the pressure conditions (i.e., water depth) of the hydrothermal system. The observed temperatures of hydrothermal fluids from various vent sites were clearly limited by the two-phase boundary of seawater (Bischoff and Pitzer 1989) (Figure 3). Phase separation and subsequent remixing of the vapor

and brine phases produce hydrothermal fluids with a wide range of salinities, from 1 order of magnitude lower to several times higher than that of seawater (Figure 2).

The chemical properties of the vapor and brine phases are quite different from each other and from their parent fluid, because each of the chemical species in the parent fluid is distributed preferentially into the vapor and liquid phases according to their physical and chemical properties during phase separation (Butterfield et al. 2003; Foustoukos and Seyfried 2007). The concentrations of gaseous species greatly increased with decreasing Cl concentration, indicating the strong affinity of these volatile components for the vapor phase (Figure 2). In contrast, the positive correlations between the Cl concentration and other dissolved species that are primarily ionic (e.g., Na^+ and Cl^-) indicate the strong affinity of these species for the liquid phase. In addition, the relationships between the Cl concentration and the ratios of elements to chloride clearly showed a strong increase in the ratios of gaseous species to chloride with decreasing Cl concentration (Figure 5). The Si/Cl ratio also slightly increased with decreasing Cl concentration. This indicates that, in addition to gaseous species, neutral species such as SiO_2^0 have some affinity for the vapor phase. On the other hand, there was little change in the ratios of ionic species with Cl concentration as a result of phase separation, indicating that they all partition strictly into the brine phase. These chemical behaviors of the dissolved species during the phase separation and partitioning into hydrothermal fluids result in formation of low-Cl, vapor-dominated fluids enriched in gases and of residual brines enriched in ionic species and depleted in gases.

Presence of sediments

SED hydrothermal systems have chemical compositions distinct from those of other hydrothermal fluids. Compared to those of sediment-starved MOR and ABA hydrothermal systems, SED hydrothermal fluids generally have relatively high pH, lower heavy metal contents, and higher CH_4 and NH_4^+ concentrations (Figure 2) (German and Von Damm, 2004). The very high CH_4 concentrations of hydrothermal fluids in SED systems are attributed to thermal decomposition of organic matter at high temperatures during hydrothermal reactions at discharge zones and/or microbial methanogenesis at relatively low temperatures at sedimentary recharge zones (Lilley et al. 1993; Kawagucci et al. 2011, 2013). Likewise, the source of NH_4^+ in SED hydrothermal systems is considered to be thermal decomposition and microbial ammonification of organic matter (Kawagucci et al. 2011, 2013). High concentrations of NH_4^+ in these hydrothermal fluids provide an $\text{NH}_3/\text{NH}_4^+$ buffer that maintains the relatively high pH of the fluid (German

and Von Damm, 2004). This greatly decreases the solubility of metal-sulfide minerals, leading to low heavy metal concentrations in the hydrothermal-vent fluids.

Effects of hydrothermal fluid chemistry on the bioavailable energy yield

The chemosynthetic primary producers that sustain deep-sea hydrothermal vent ecosystems utilize inorganic substances (e.g., H_2S , CO_2 , H_2 , and CH_4) derived from hydrothermal vent fluids as energy and carbon sources. Thus, deep-sea hydrothermal vent ecosystems should be at least partially controlled by the chemical composition of the hydrothermal fluids. The effects of hydrothermal fluid compositions on deep-sea hydrothermal vent ecosystems based on the energy yields available to various chemolithotrophic metabolisms are described below.

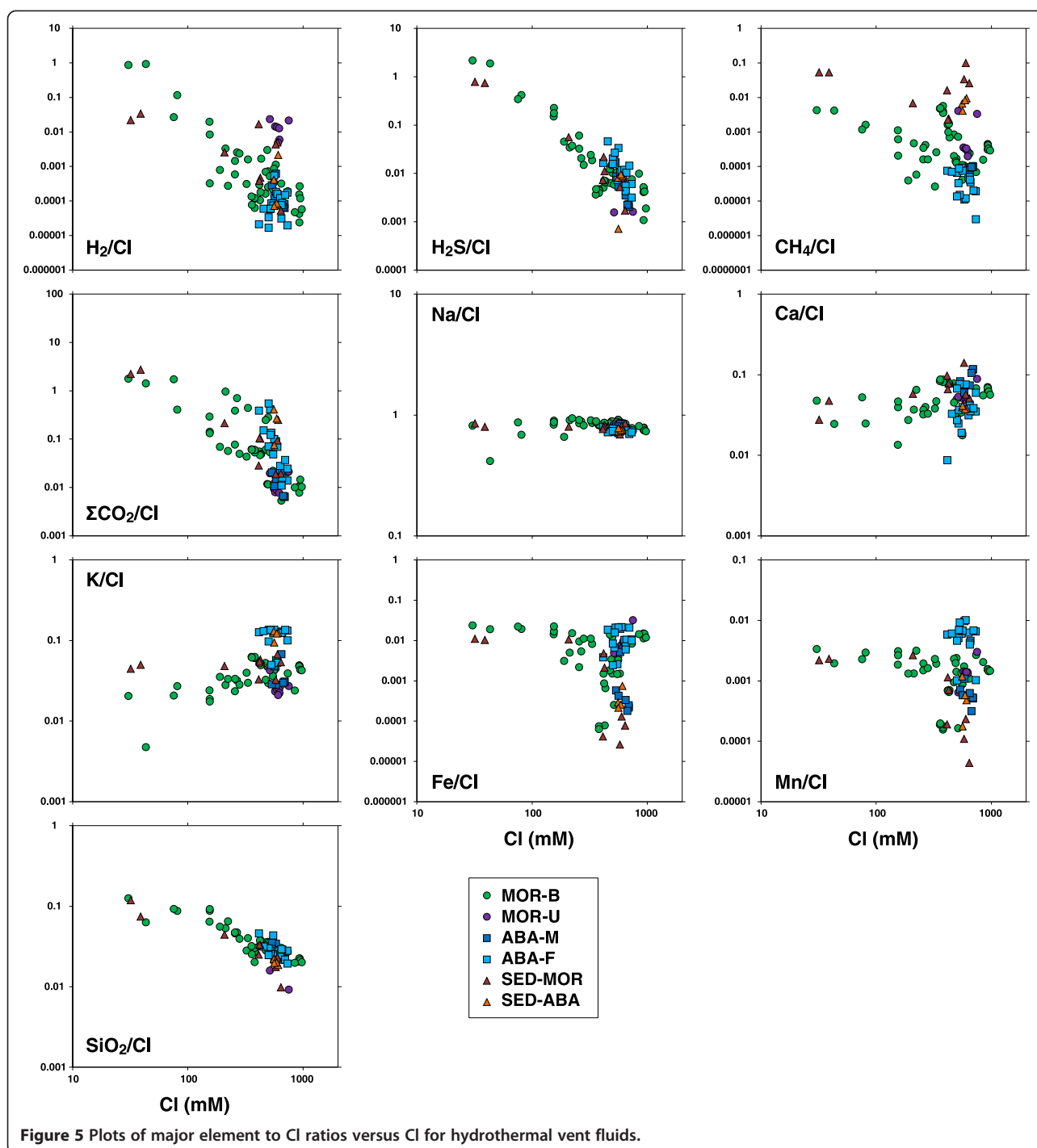
Hydrogen sulfide (H_2S)

In all of the deep-sea hydrothermal systems in all settings, the potential energy yields for sulfur-oxidizing chemolithotrophy (thiotrophy) using H_2S in the hydrothermal fluids were uniformly high at >10 J/kg mixed fluid (Figure 6A). Even in ultramafic rock-associated hydrothermal systems with relatively low H_2S concentrations, the metabolic energy of sulfur oxidation (H_2S oxidation) was nearly identical to that in other types of hydrothermal systems, some of which had 2 orders of magnitude higher H_2S concentrations (Figure 6A). This uniformity is attributed to the relatively high concentrations of H_2S (mostly >1 mmol/kg) present in hydrothermal fluids in all of the hydrothermal systems. As a result, the amount of H_2S always exceeded the O_2 concentration throughout the habitable temperature range in the mixing zones, except at very low temperatures (several degrees Celsius). The potential energy yield of sulfur-oxidizing chemolithotrophy is therefore solely controlled by the dissolved O_2 concentration in the seawater (which is globally similar in all deep-sea water). Thus, concentrations of H_2S in end-member hydrothermal fluids may not significantly affect the abundance and composition of sulfur oxidizers.

The exception is in hydrothermal plumes, where much higher seawater mixing ratios (>1000) and low temperatures (up to several degrees Celsius) are found. In hydrothermal plume environments, the concentration of H_2S in the source hydrothermal fluid, rather than the seawater-dissolved O_2 , becomes the limiting factor for sulfur-oxidizing chemolithotrophic metabolism.

Hydrogen (H_2)

In contrast to H_2S , variations in the H_2 concentration directly affected the potential energy for the chemolithotrophic microbial population, not only for aerobic H_2 oxidation but also for most anaerobic energy metabolisms



other than anaerobic methane oxidation. This feature is partially attributed to the wide range of H_2 concentrations in hydrothermal fluids. For example, typical basalt-hosted hydrothermal fluids had H_2 concentrations of <1 mmol/kg (Figure 2). In contrast, ultramafic rock-hosted hydrothermal fluids had H_2 concentrations 1 to 2 orders of magnitude higher, whereas hydrothermal fluids in ABA settings had H_2 concentrations 1 order of magnitude

lower (Figure 2). Thus, potential energy yields for aerobic and anaerobic H_2 -oxidizing (H_2 -trophic) metabolisms were directly correlated with H_2 concentrations in the end-member hydrothermal fluids (Figure 6B, C, D). For aerobic H_2 -oxidizing metabolism, nearly the same amount of metabolic energy was available irrespective of the H_2 concentration in the end-member hydrothermal fluid (Figure 6B), when the H_2 concentration exceeded

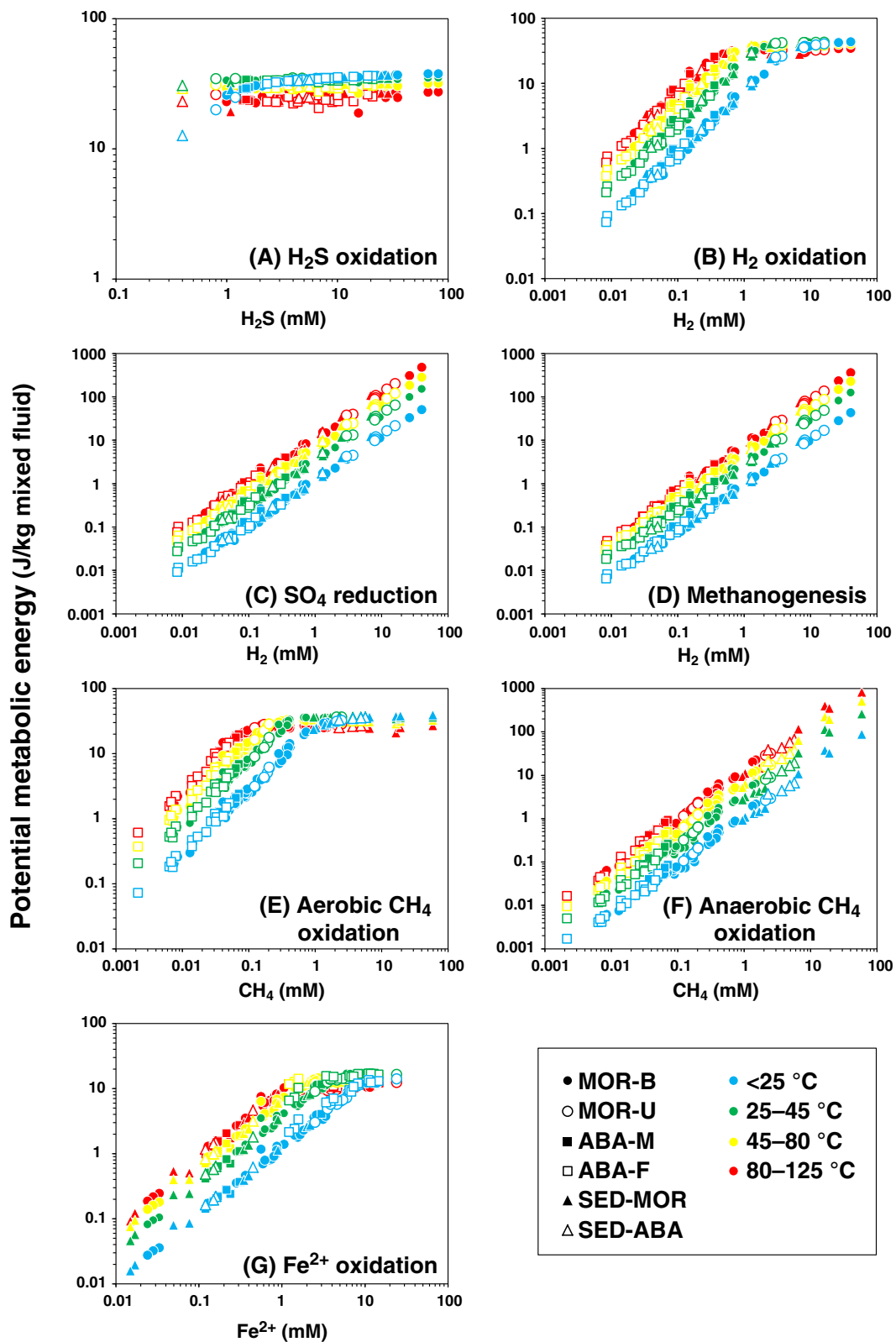


Figure 6 (See legend on next page.)

(See figure on previous page.)

Figure 6 Metabolic energy yields versus H₂S, H₂, CH₄, and Fe²⁺ concentrations in hydrothermal fluids. Potential metabolic energy available from (A) thiotrophic (H₂S-oxidizing) O₂ reduction as a function of the H₂S concentration in the end-member hydrothermal fluid; (B) hydrogenotrophic O₂ reduction, (C) hydrogenotrophic SO₄ reduction, and (D) hydrogenotrophic methanogenesis as a function of the H₂ concentration in the end-member hydrothermal fluid; (E) aerobic methanotrophy and (F) anoxic methanotrophy as a function of the CH₄ concentration in the end-member hydrothermal fluid; and (G) Fe²⁺-oxidizing O₂ reduction as a function of the Fe²⁺ concentration in the end-member hydrothermal fluid are plotted for each kilogram of mixing water for four temperature ranges. The temperature ranges of <25°C, 25°C to 45°C, 45°C to 80°C, and 80°C to 125°C generally correspond to psychrophilic, mesophilic, thermophilic, and hyperthermophilic microbial components, respectively.

approximately 1 mmol/kg (for hyperthermophiles at relatively high temperatures) to approximately 10 mmol/kg (for psychrophiles to hyperthermophiles at all temperature ranges). As with H₂S oxidation, this occurs because seawater-dissolved O₂ rather than H₂ becomes the limiting factor for aerobic H₂-oxidizing metabolism.

However, because most seafloor hydrothermal fluids had H₂ concentrations <1 mmol/kg, except for ultramafic rock-hosted and highly vapor phase-enriched hydrothermal fluids (Figure 2), variations in the H₂ concentration of the end-member hydrothermal fluid significantly affected the potential energy yields of nearly all H₂-trophic chemolithotrophs (Figure 6B, C, D). This variation is expected to have a strong impact on biomass production and the compositional structure of most H₂-trophic microbial populations as well as the entire microbial community. As described above, the abundance of H₂S in hydrothermal fluids is relatively constant among most hydrothermal systems, tectonic settings, and geological conditions. In addition, H₂S is coupled only to aerobic (both O₂- and NO₃-reducing) sulfur-oxidizing metabolisms. In contrast, the abundance of H₂ in end-member hydrothermal fluids is highly variable and constrains various aerobic and anaerobic chemolithotrophic energy metabolisms for primary production.

Although ultramafic rock-associated hydrothermal fluids are significantly enriched in H₂ (Charlou et al. 2002), in several phase separation-influenced (vapor phase-abundant) hydrothermal fluids hosted by MOR-B, H₂ can also be comparably enriched (Lilley et al. 2003) (Figure 2). In these hydrothermal systems, therefore, the energy yield of H₂-trophic metabolisms was similar to that in ultramafic rock-hosted hydrothermal systems (Figure 6B, C, D). However, the abundant availability of H₂ (as well as other gaseous species) induced by phase separation in MOR-B-hosted hydrothermal fluids is generally transient and lasts several weeks to several months (Lilley et al. 2003). Thus, the effect of temporal enrichment of hydrothermal fluid H₂ on biomass production and compositional structure of the entire microbial community is likely transient and minor.

Methane (CH₄)

The CH₄ concentration in seafloor hydrothermal fluids was also variable, ranging from the nanomole per

kilogram level in ABA hydrothermal fluids to the millimole per kilogram level in SED and ultramafic rock-hosted fluids. Variations in the CH₄ concentration in hydrothermal fluids could affect both aerobic and anaerobic methane oxidizers (Figure 6E, F).

The potential metabolic energy from anaerobic CH₄ oxidation (methanotrophy) was directly correlated with the CH₄ concentration in the hydrothermal fluid (Figure 6F), suggesting that the anaerobic methanotrophic population is likely affected by CH₄ concentrations in end-member hydrothermal fluids. This is attributable to the large amount of SO₄²⁻ in seawater; these high levels of SO₄²⁻ are always present in seawater-hydrothermal fluid mixing zones in all habitable temperature ranges. For aerobic CH₄ oxidation reactions, the potential energy yield was also affected by the CH₄ concentration in end-member hydrothermal fluids, except for hydrothermal fluids with high CH₄ concentrations (>0.2 mmol/kg for hyperthermophiles to >2 mmol/kg for psychrophiles) (Figure 6E).

Iron (Fe)

Variation in the Fe²⁺ concentration of the hydrothermal fluids was also large, from the nanomole per kilogram level to the millimole per kilogram level (comparable to the ranges for H₂ and CH₄ concentrations). This variation in the Fe²⁺ concentration of the hydrothermal fluids could affect aerobic iron-oxidizing chemolithotrophy. The potential energy yield from the aerobic Fe oxidation reaction was well correlated with the Fe²⁺ concentration in the hydrothermal fluid (Figure 6G). However, for highly Fe²⁺-enriched hydrothermal fluids (>0.2 mmol/kg for hyperthermophiles to >2 mmol/kg for psychrophiles), the amount of available metabolic energy was saturated with respect to the Fe²⁺ concentration in the end-member hydrothermal fluid (Figure 6G). The metabolic energy yield potentially obtained from aerobic oxidation of 1 mol of Fe²⁺ was several times smaller than that from aerobic oxidation of 1 mol of H₂S, H₂, or CH₄ (Figure 6). This may affect the relative abundance of aerobic Fe-oxidizer populations in deep-sea hydrothermal vent ecosystems.

In contrast to aerobic Fe-oxidizing chemolithotrophy, there was an essentially negligible energy yield predicted for anaerobic Fe³⁺ reduction using H₂ or CH₄ for all

types of deep-sea hydrothermal fluids and systems. This is attributed to an extremely low concentration of Fe^{3+} in both seawater and hydrothermal fluids.

Effect of the geological setting of the hydrothermal system on the bioavailable energy yield

In the MOR-B and all ABA settings (comprising most deep-sea hydrothermal systems), almost all potentially bioavailable energy can be obtained from aerobic metabolism (Figure 7). The end-member hydrothermal fluids in these settings contain only small amounts of H_2 and CH_4 (other than highly vapor-enriched hydrothermal fluids). The most energetically favorable chemolithotrophic metabolism was aerobic sulfur oxidation (Figure 8A). Thus, aerobic sulfur oxidizers are the chemolithoautotrophic population most likely to sustain primary production in these deep-sea hydrothermal vent ecosystems.

In the MOR-B and ABA-M settings, aerobic oxidation of H_2 and CH_4 were the second most available metabolic reactions, particularly at higher temperatures (lower mixing ratios). On the other hand, in the ABA-F setting, aerobic Fe^{2+} oxidation was the second most favorable chemolithotrophic metabolism (Figure 8A). These differences are directly related to the different chemical compositions of the end-member hydrothermal fluids (e.g., H_2 , CH_4 , and Fe^{2+} concentrations) in these settings, ultimately derived from the oxidation state of the magmas and/or volatile (particularly SO_2) inputs into the hydrothermal fluids. Relatively little energy was predicted to be available from anaerobic chemolithotrophic metabolisms for these settings, except for temporally and spatially limited habitats induced by phase separation of hydrothermal fluids (Figure 8B).

In the MOR-U and SED settings, the potential energy from aerobic oxidation of H_2 or CH_4 exceeded that from aerobic sulfur oxidation at higher temperatures (lower mixing ratios) (Figure 8A). More importantly, in these settings, considerable energy for primary production can be obtained from anaerobic chemolithotrophic metabolisms and populations (Figure 8B). Particularly in high-temperature habitats, anaerobic chemolithotrophs are expected to play a prominent role as primary producers (Figure 8A, B). This represents a marked difference in potential chemolithotrophic microbial communities between the MOR-U and SED settings and the more common MOR-B and ABA settings.

In the MOR-U setting, because of the high H_2 concentrations in end-member fluids, both aerobic and anaerobic H_2 -trophic population reducers were energetically dominant primary producers (Figure 8A, B). In addition, the total potentially bioavailable energy yields in the mixing zones were greater in the MOR-U setting than in the typical MOR-B and ABA settings (Figure 8A, B). Thus, the MOR-U deep-sea hydrothermal environments

may supply more abundant and diverse energy sources for biological production.

In the SED setting, aerobic methanotrophy could be competitive with aerobic sulfur oxidation in all temperature ranges (Figure 8A). Interestingly, among all possible chemolithotrophic metabolisms, anaerobic (sulfate-reducing) methanotrophy was by far the most favorable energy-generating metabolism, particularly in high-temperature habitats (Figure 8B). The total amount of potentially bioavailable energy yield in the mixing zones of habitats in the SED setting was also greater than in the typical MOR-B and ABA settings.

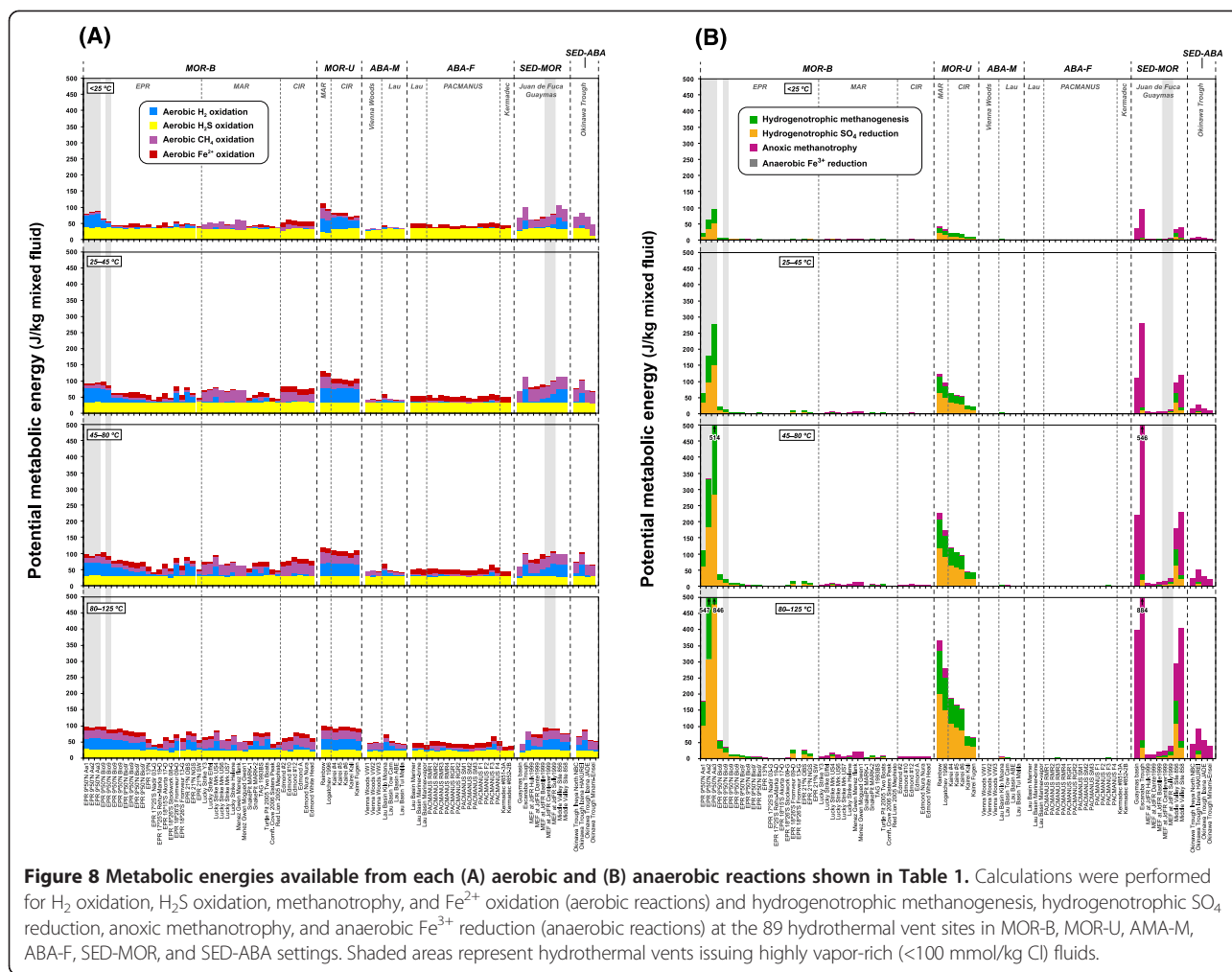
Comparison of existing chemolithotrophic microbial communities with the results of thermodynamic modeling

Above, we have provided the theoretical basis for relationships between the geological environments of hydrothermal activity (e.g., tectonic settings, basement-rock geochemistry, abundance of sediments, magmatic volatile input, and phase separation related to subseafloor hydrothermal processes), physical and chemical variations in hydrothermal fluids, and the compositional diversity of potentially bioavailable energy for various vent-endemic chemolithotrophic metabolisms estimated using thermodynamic models. We have shown that the abundance and composition of chemolithotrophic energy metabolisms in hydrothermal vent biological communities is directly constrained by the physical and chemical characteristics of the hydrothermal mixing zones of habitats, which are subject to the physical and chemical properties of end-member hydrothermal fluids. Furthermore, the physical and chemical characteristics of the end-member hydrothermal fluids are substantially controlled by the geological settings that host the hydrothermal systems. Thus, it seems likely that the abundance and composition of chemolithotrophic energy metabolisms in microbial communities located in a given deep-sea hydrothermal system could be systematized in terms of geological backgrounds based on the results of the thermodynamic models.

In typical mixing zones in deep-sea hydrothermal habitats, chemolithotrophic microbial communities consist of organisms with three typical lifestyles: surface-attached or biofilm-forming free-living entities, planktonic free-living entities, and symbiotic entities. Here, we discuss potential patterns in chemolithotrophic microbial community development delineated by recent microbiological investigations (biogeochemical, ecological, and molecular approaches) for representative hydrothermal mixing zones of habitats in which the predominant organisms have different lifestyles.

Hydrothermal plumes

Hydrothermal plumes are typical of mixing zone habitats that host planktonic free-living microbial communities



and are characterized by low temperatures and quite low mixing ratios of hydrothermal fluids (<0.1%). In hydrothermal plumes, the SUP05 group of Gammaproteobacteria is the most abundant and geographically widespread microbial component (Sunamura et al. 2004; Dick and Tebo 2010; German et al. 2010). The deep-sea vent Epsilonproteobacteria (Sunamura et al. 2004; Nakagawa et al. 2005a; German et al. 2010), methanotrophic Gammaproteobacteria (Lam et al. 2008), and ammonia-oxidizing Betaproteobacteria and Thaumarchaeota (Lam et al. 2008; Takai et al. 2004b) have been identified as other dominant microbial populations.

Although microbial communities in hydrothermal plumes have variable abundances and compositions of chemolithotrophic metabolisms, there have been few quantitative studies or functional characterizations of these communities. Thus, we still do not know much about how these microbial communities and their metabolisms respond to the varying physical and chemical states of hydrothermal plume habitats or how they are related to the geological backgrounds that produce the

source hydrothermal fluids. Nevertheless, the general landscape of metabolic abundance and composition in hydrothermal plume microbial communities has been established via biogeochemical (Cowen et al. 1986; de Angelis et al. 1993; Mandernack and Tebo, 1993; Dick et al. 2009) and microbial ecology (Sunamura et al. 2004; Takai et al. 2004b; Nakagawa et al. 2005a; Lam et al. 2008; Dick and Tebo 2010; Lesniewski et al. 2012) investigations. For example, dominance of the sulfur-oxidizing SUP05 group of Gammaproteobacteria and the deep-sea vent Epsilonproteobacteria is commonly observed in geographically and geologically diverse deep-sea hydrothermal systems. These organisms primarily sustain themselves via aerobic sulfur oxidation; considerable populations occasionally utilize aerobic H₂ oxidation for additional energy conversion if metabolically available H₂ is present. In addition, much smaller but ubiquitous populations of phylogenetically diverse bacteria also utilize Fe²⁺ and Mn²⁺ oxidation for biomass production. In contrast, in hydrothermal plumes highly enriched in CH₄ and NH₄⁺, particularly in SED hydrothermal systems, the

methanotrophic Gammaproteobacteria and ammonia-oxidizing Betaproteobacteria and Thaumarchaeota dominate the microbial communities in spatially and temporally varying hydrothermal plume habitats.

An increasing number of recent observations appear consistent with our conclusions based on thermodynamic estimates of bioavailable energy yields in low-temperature mixing zones: (1) aerobic sulfur oxidation is the most common and basic chemolithotrophic energy metabolism in global deep-sea hydrothermal systems, (2) aerobic Fe^{2+} and Mn^{2+} oxidation are less abundant but widespread metabolisms, and (3) aerobic methanotrophy and ammonia oxidizer are dominant in SED systems, respectively.

Diffusing hydrothermal fluids

Microbial communities in relatively low-temperature diffusing hydrothermal fluids have been investigated in a wide variety of geographically diverse hydrothermal systems (Huber and Holden 2008; Huber et al. 2009; Perner et al. 2011, 2013a, 2013b; Akerman et al. 2013; Campbell et al. 2013). These are mainly planktonic free-living communities under conditions in which the end-member fluids have already mixed with infiltrated seawater in relatively shallow seafloor environments in the recharge and discharge regions of hydrothermal fluids (Bemis et al. 2012). In addition to planktonic free-living populations, these microbial communities also include detached epilithic and biofilm-forming components entrained by the fluid flows.

Hydrothermal fluids diffusing at the seafloor would be expected to combine all growing, living, and dead populations and components within the entire seafloor fluid flow path in the discharge. This differs from microbial communities in hydrothermal plume habitats in which most microbial populations are indigenously growing from planktonic origins in deep-sea water (Lesniewski et al. 2012). Thus, it is challenging to clearly understand the relationships between the diversity and composition of the observed microbial populations and hydrothermal fluid chemistry based on existing biological and geochemical data for diffusing fluid habitats. However, several studies have recently suggested the dominance of sulfur oxidizers in typical MOR-B settings and the presence of hydrogen oxidizers in MOR-U settings (Perner et al. 2011, 2013a; Akerman et al. 2013). These results are generally consistent with our thermodynamic predictions of relationships among microbial metabolisms and functions, hydrothermal fluid chemistry, and geological background.

On the other hand, a very recent study producing function-focused quantitative estimates, based on H_2 and sulfide consumption and CO_2 assimilation activities as well as metagenomic 16S rRNA and functional gene

analyses, has indicated that even in H_2 -poor hydrothermal fluids in MOR-B settings, H_2 oxidation-based primary production is highly attractive despite the low H_2 content (Perner et al. 2013b). This leads us to consider that low-temperature diffusing flow is the product of complex seafloor processes (including seawater-hydrothermal fluid mixing, conductive cooling, various redox reactions, and mineral precipitation), and thus, the simple batch-mixing model employed in this study may not be able to accurately reproduce all of these processes.

Geochemical data sets for low-temperature diffusing flows remain scarce. Thus, further quantitative estimates combined with in situ or detailed chemical measurements will be needed to more accurately describe interactions among the physical and chemical processes, bioavailable energy yields from chemolithotrophic metabolisms, and community development in diffusing hydrothermal fluids.

Chemosynthetic invertebrates

Chemolithotrophic symbionts hosted by deep-sea vent-endemic chemosynthetic invertebrates represent important primary producers in global deep-sea hydrothermal ecosystems. Their biomass production and functions may be constrained by the energy states of the habitats of both the symbionts and the host animals (Dubilier et al. 2008), as productivity and energy metabolism in a tight symbiotic association are strongly regulated by the interaction of the symbiont with the physiology and ecology of the host animal (Dubilier et al. 2008). There have been numerous studies of the basic relationships between the in situ physical and chemical conditions of habitats and the abundance and composition of energy metabolisms in deep-sea hydrothermal chemosynthetic symbioses (Beinart et al. 2012; Petersen et al. 2011; Suzuki et al. 2006; Watsuji et al. 2010, 2014). However, the energy conversion yield of the primary production of chemolithotrophic symbionts is likely one of the most important factors in the establishment of chemosynthetic symbioses, affecting the selection, acquisition, and breeding of specific bacterial counterparts. In particular, episymbioses and horizontally transmitted endosymbioses, in which symbionts are acquired from the proximal environments of habitats in their larval and adult stages in each generation, would be expected to be more strongly affected by the energy states of chemolithotrophic symbiont metabolisms than vertically transmitted endosymbioses.

Recently, several studies have been conducted of the relationship between the activity of chemolithotrophic symbionts and hydrothermal fluid chemistry, e.g., a series of studies on epibiotic microbial communities in the galatheid crab *Shinkaia crosnieri* in Okinawa Trough

(Watsuji et al. 2010, 2012, 2014). The epibiotic microbial communities of *S. crosnieri* abdominal setae consist primarily of the sulfur-oxidizing Epsilonproteobacteria and Gammaproteobacteria and methanotrophic Gammaproteobacteria (Watsuji et al. 2010, 2012, 2014). These results are generally consistent with the results of our thermodynamic modeling, indicating high bioavailable energy yields from both sulfur- and CH₄-oxidizing reactions at low temperatures (high seawater mixing ratios) in the Okinawa Trough (Figure 8). The abundance of epibiotic methanotrophic gammaproteobacterial populations and methanotrophic activity vary among the *S. crosnieri* populations recovered from different hydrothermal fields (Iheya North and Hatoma Knoll fields) (Watsuji et al. 2010). As suggested by our model calculations, these variations are likely correlated with the in situ CH₄ concentrations in the *S. crosnieri* colonies. This may, in turn, be associated with the CH₄ concentrations in the end-member hydrothermal fluids, although CH₄ concentrations in the Hatoma fluids have not yet been published.

Another notable example is the dual endosymbiotic (thiotrophic and methanotrophic) populations of vent mussels living in different geological settings of deep-sea hydrothermal vent sites in the MAR and the Eastern Pacific (Petersen et al. 2011). Based on thermodynamic modeling of preferred H₂-trophic energy metabolism, genetic characterization of a key enzyme gene for H₂-trophic energy metabolism, and functional analyses of H₂ consumption and CO₂ fixation of endosymbionts in *Bathymodiolus puteoserpentis* in a typical MOR-U hydrothermal system (Logatchev field), Peterson et al. (2011) clearly demonstrated that the thiotrophic population in dual endosymbiosis of the Logatchev *B. puteoserpentis* use H₂ and H₂S comparably as energy sources for primary production. This was the first reported example of chemosynthetic symbiosis sustained by an inorganic energy source (H₂) other than H₂S (reduced sulfur species) or CH₄. In other words, this study first revealed that compositional variations in H₂, H₂S, and CH₄ in the mixing zones of chemosynthetic macrofaunal habitats affect the patterns and functions of episymbioses and endosymbioses in chemosynthetic microbial-faunal associations. Peterson et al. (2011) also showed that the thio- and H₂-trophic endosymbionts hosted by different *Bathymodiolus* populations living in geographically and geologically distinct hydrothermal systems of the MAR and Pacific (all H₂-starved MOR-B hydrothermal systems) had much lower specific H₂ consumption activities than the endosymbiotic population from the H₂-abundant MOR-U hydrothermal system (Logatchev field). Although not fully quantitative, these results provide strong evidence that the metabolic activity of chemolithotrophic symbionts is controlled by hydrothermal fluid

chemistry and is related to the geological background of the hydrothermal system, as suggested by our model calculations.

Recently, metagenomic and metatranscriptomic approaches have also been used to study possible biogeochemical associations with *Alviniconcha* (deep-sea hydrothermal-vent snail) holobionts (host/symbiont associations) that dwell in a broad region of the Eastern Lau Spreading Center (ELSC) (Beinart et al. 2012; Sanders et al. 2013). Different holobiont patterns have been found in the *Alviniconcha* populations obtained from the mixing zones of colonies in four different hydrothermal systems in the ELSC. The endosymbionts were classified into three groups: Sulfurimonas-type Epsilonproteobacteria, gamma-1-type Gammaproteobacteria, and gamma-Lau-type Gammaproteobacteria (Beinart et al. 2012), all of which are known to be typical sulfur (and H₂) oxidizers. The *Alviniconcha* holobiont and endosymbiont distributions varied from the northern to the southern region of the ELSC, which have somewhat different geological settings (Beinart et al. 2012). The ELSC has been well characterized from north to south in terms of geological properties (such as the spreading stage and rate, magmatic productivity, geochemistry, and host-rock geochemistry) (Tivey et al. 2012). Reflecting the change in geological setting, the chemical compositions of the end-member hydrothermal fluids also change from relatively reduced and H₂- and H₂S-enriched (approximately 500 μM and approximately 5 mM, respectively) in the north to relatively oxidized and H₂- and H₂S-depleted (approximately 30 μM and approximately 3 mM, respectively) in the south (Beinart et al. 2012). The endosymbiont species shift from predominantly Sulfurimonas-type Epsilonproteobacteria in the north to predominantly gamma-1-type Gammaproteobacteria and finally to both types of Gammaproteobacteria in the south (Beinart et al. 2012). Interestingly, the compositional abundance of both the endosymbiotic microbial components and the expressed key gene transcripts for various energy metabolisms vary with the regional geochemical gradient (Sanders et al. 2013). Under relatively reduced and H₂- and H₂S-enriched conditions, the compositional abundance of mRNAs related to H₂- and sulfur-oxidizing metabolisms throughout the entire endosymbiont transcriptome is highly elevated (Sanders et al. 2013). The compositional abundances of the mRNAs of these energy metabolisms throughout the entire endosymbiont transcriptome are likely associated with the activities of these energy metabolisms in the endosymbiotic populations of the *Alviniconcha* host individuals.

Our geochemical modeling suggests that changes in the H₂S concentration from north to south in the ELSC (approximately 5 mM to approximately 3 mM) should not significantly affect sulfur-oxidizing metabolisms, whereas H₂-oxidizing metabolisms could be affected by

the change in H_2 concentration (approximately 500 μM to approximately 30 μM) (Figure 6). Indeed, based on differences in the expression of hydrogenases between Epsilonproteobacteria and Gammaproteobacteria individuals, Sanders et al. (2013) suggested that H_2 oxidation may play a larger role in the energy metabolism of holobionts with Epsilonproteobacteria. Thus, the change in H_2 concentration, rather than the H_2S concentration, may account for differences in the holobiont patterns found in the Alviniconcha populations in the ELSC. Although future studies are needed to elucidate the degree to which Epsilonproteobacteria endosymbionts rely on H_2 for energy production, this may be additional evidence supporting the relationship between geological constraints on hydrothermal fluid chemistry and the compositions and functions of chemosynthetic microbial symbionts in deep-sea hydrothermal environments.

Chimney structures and sediments

The compositional and functional diversity of microbial communities has been most extensively explored in deep-sea vent chimney structures that host high-temperature hydrothermal fluid emissions (Nakagawa and Takai 2008; Takai and Nakamura 2010, 2011; Takai et al. 2006b). These microbial communities consist of typical epilithic (mineral surface-attached) and/or biofilm-forming populations and are sustained by the redox disequilibria formed in the chimney wall via diffusive mixing between the internal hydrothermal fluid and external seawater. Thus, the abundance and composition of chemolithotrophic energy metabolisms in the chimney microbial communities are directly controlled by the energy states of the chimney habitats, resulting in good approximations by the thermodynamic calculations of the simple batch-mixing model.

Using data for both end-member hydrothermal fluids and chimney microbial communities obtained from six deep-sea hydrothermal systems with different geological settings, Takai and Nakamura (2010, 2011) constructed intra-field and inter-field comparisons between the abundance and composition of chemolithotrophic energy metabolisms predicted by thermodynamic modeling and the microbial community composition determined through quantitative cultivation methods. Based on both the thermodynamic modeling and microbiological characterization, statistically significant correlations between the H_2 concentration in the hydrothermal fluid or the estimated potential energy yield of H_2 -trophic methanogenesis and the cultivatable population size of hydrogenotrophic methanogens were found. More recently, in addition to quantitative cultivation methods, statistical phylotype compositional analyses of 16S rRNA and other functional genes have also been used to demonstrate significant correlations between H_2 -trophic chemolithotrophy in chimney microbial communities and

hydrothermal fluid H_2 concentrations, particularly in MOR-U hydrothermal systems (Flores et al. 2011; Roussel et al. 2011). Our geochemical model provides consistent explanations for the results of these studies. Specifically, the energy yields of anaerobic (and aerobic, in most cases) H_2 -trophic reactions were well correlated with the H_2 concentrations of hydrothermal fluids (Figure 6). In addition, thermophilic H_2 -trophic methanogens and sulfate/sulfur reducers are predominantly found in H_2 -enriched deep-sea hydrothermal systems in the MOR-U setting (Figure 8). It is thus very likely that serpentinization-driven H_2 enrichment in hydrothermal fluids is an important geochemical factor that directly controls the thermodynamic energy potential, biomass, and productivity of H_2 -trophic chemolithotrophs.

Similar to the apparent relationship between H_2 concentrations in hydrothermal fluids and the abundance of H_2 -trophic chemolithotroph populations, our thermodynamic calculations also identified a possible relationship between CH_4 enrichment and the abundance of anaerobic methanotroph populations (particularly thermophilic methanotrophic sulfate reducers) in SED hydrothermal systems (Figure 8). In low-temperature habitats (e.g., hydrothermal plumes, diffusing fluids, and chemosynthetic animal symbioses), many molecular signals and metabolic activities of aerobic methanotrophy have been observed. However, the existence of anaerobic thermophilic methanotrophic sulfate reducers has been inferred only from lipid biomarker signals (Schouten et al. 2003). Recently, thermophilic anoxic CH_4 -oxidizing SO_4 -reducing activities have been directly verified at up to 70°C in the sediments of the Guaymas Basin hydrothermal field (Holler et al. 2011). In addition, possible microbial components of thermophilic anaerobic methane oxidizers, consortia of ANME-1a Archaea and HotSeep-1 cluster Deltaproteobacteria, have been identified via FISH analysis (Holler et al. 2011). Similar phylotypes of potentially thermophilic ANME-1a Archaea have also been found in hydrothermal sediments and diffusing fluids of SED hydrothermal systems such as the Axial Seamount and Endeavour Segment fields in the Juan de Fuca Ridge and the Yonaguni Knoll IV field in the Okinawa Trough (Nunoura et al. 2010; Merkel et al. 2013). Because these phylotypes of thermophilic anaerobic methanotrophic Archaea remain resistant to cultivation, quantitative cultivation methods are not feasible. However, other quantitative techniques targeting 16S rRNA and functional gene transcripts together with direct metabolic activity measurements are now available (e.g., Beal et al. 2009; Watsuji et al. 2012, 2014). Such quantitative estimates will provide multiple lines of evidence for the relationship between CH_4 enrichment in SED hydrothermal systems and the abundance of thermophilic methanotrophic sulfate reducers in mixing zone habitats.

Takai and Nakamura (2010) have also noted that phase separation has a considerable impact on intra-field variations in hydrothermal fluid chemistry. In microbiological studies of the Iheya North field in the middle Okinawa Trough and the Mariner field in the Lau Basin, increased populations of anaerobic and aerobic H₂-trophic chemolithotrophs (e.g., Methanococcales and Aquificales) were observed, potentially due to phase separation of hydrothermal fluids (Nakagawa et al. 2005b; Takai et al. 2008). However, in studies of the Yonaguni Knoll IV field in the Southern Okinawa Trough, H₂-trophic (and thiotrophic) chemolithotrophs (e.g., Methanococcales, Desulfurococcales, Nautiliaceae, and Thioreductoraceae) were the dominant microbial components in both vapor- and brine-rich hydrothermal fluids (Nunoura and Takai 2009). Although H₂S concentration data for the Yonaguni Knoll IV field have not yet been reported, our geochemical model calculations indicate that if the H₂ concentrations of the end-member hydrothermal fluids were well below approximately 1 mmol/kg, the metabolic energy available from both aerobic and anaerobic H₂-trophic reactions would be directly correlated with the H₂ concentration of the fluids (Figure 6). The H₂ concentrations in the vapor- and brine-rich hydrothermal fluids venting at the Iheya North field (0.045 and 0.096 mmol/kg, respectively) and the Mariner field (0.012 and 0.13 mmol/kg, respectively) are well below approximately 1 mmol/kg and thus, phase separation-induced H₂ variations may directly affect the available energy yields from aerobic and anaerobic H₂-trophic reactions. In contrast, the H₂ concentrations in the fluids at the Yonaguni Knoll IV field (0.8 to 3.6 mmol/kg) are mostly above approximately 1 mmol/kg, resulting in saturation of the metabolic energy available from aerobic hydrogenotrophic reactions, particularly at higher temperatures (Figure 6). In addition, the bioavailable energy yield from hyperthermophilic anaerobic reactions is nearly comparable to that from aerobic thiotrophic reactions, even in brine-rich hydrothermal fluids (Figure 6). This may explain why there are no major differences in abundance or composition of microbial communities between the vapor- and brine-rich hydrothermal fluids in the Yonaguni Knoll IV field (Nunoura and Takai, 2009).

Conclusions

We have provided an overview of variations in the geology, geochemistry, microbial energy metabolisms, and community development associated with global deep-sea hydrothermal systems. Relationships among the geological backgrounds of hydrothermal activities (e.g., tectonic settings, basement rock geochemistry, abundance of sediments, magmatic volatile inputs, and phase separation related to seafloor hydrothermal processes),

physical and chemical variations in hydrothermal fluids, and compositional diversity of potentially bioavailable energy for various vent-endemic chemolithotrophic metabolisms have been elucidated through thermodynamic modeling of redox states in hydrothermal mixing zone habitats. In addition, these relationships have been empirically substantiated by recent multidisciplinary biogeochemical and microbiological studies of existing microbial communities and their metabolic functions in representative deep-sea hydrothermal systems in different geographic locations and geological settings.

However, thermodynamic estimates of potential energy for possible chemolithotrophic metabolisms are based on certain simplifications, particularly with respect to quantitative representations of mixing of source hydrothermal fluids and seawater and the kinetic effects of abiotic reactions, cellular uptake and excretion of energy sources, and enzymatic functions on energy metabolism. These shortcomings may result in differences between the theoretical predictions and actual configurations and patterns in some cases. To characterize the in situ physical and chemical characteristics of hydrothermal mixing zone habitats at high spatial and temporal resolution, several electrochemical sensors have been developed and applied to various habitats such as diffusing hydrothermal fluids and chemosynthetic animal colonies. However, these sensors have some technical challenges, including multiple chemical interferences, relatively narrow dynamic ranges, and the need for in situ calibration (Luther et al. 2012). A deep-sea in situ membrane inlet mass spectrometry (MIMS) method has also been developed and used for in situ measurement of volatile and time-sensitive chemical species (Wankel et al. 2010). These newly developed in situ measurement tools will enable more precise estimates of the energy states of habitats of chemolithotrophic microbial communities. Improvement and development of biogeochemical and microbiological characterization techniques are also necessary to understand the functional and metabolic abundance and composition of microbial communities in deep-sea hydrothermal environments. It is a significant challenge to quantify the biomass, productivity, and functions of dominant microbial components in deep-sea vents. Comprehensive characterizations of in situ mRNA assemblages using such tools as GeoChip technology (Wang et al. 2009) and the metatranscriptomic approach (Dahle et al. 2013) will likely prove more objective, quantitative, and effective than employing elaborate quantitative cultivations using numerous media for intra-field and inter-field comparisons of microbial communities and their functions. Successfully overcoming these challenges is essential for clarifying the relationships between geology, geochemistry, microbial energy metabolisms, and community development associated with global deep-sea hydrothermal activities.

Additional file

Additional file 1: Chemical compositions of end-member hydrothermal fluids and seawater used in this study. Data are from 89 hydrothermal vent sites in MOR-B, MOR-U, AMA-M, ABA-F, SED-MOR, and SED-ABA settings.

Abbreviations

ABA: arc-backarc; ABA-F: felsic rock-hosted hydrothermal system in an arc-backarc setting; ABA-M: mafic rock-hosted hydrothermal system in an arc-backarc setting; MOR: mid-ocean ridge; MOR-B: basalt-hosted hydrothermal system in a mid-ocean ridge setting; MOR-U: ultramafic rock-hosted hydrothermal system in a mid-ocean ridge setting; SED: sediment-associated; SED-ABA: sediment-associated hydrothermal system in an arc-backarc setting; SED-MOR: sediment-associated hydrothermal system in a mid-ocean ridge setting.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

Both KN and KT proposed the topic, conceived of and designed the study, compiled and processed the data, and wrote the paper. Both authors read and approved the final manuscript.

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