Geochemical Constraints on Potential Biomass Sustained by Seafloor Water–Rock Interactions

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Abstract

Since the first discovery of macrofaunal and microbial communities endemic to hydrothermal vents, chemolithoautotrophic microorganisms at and beneath the seafloor have attracted the interest of many researchers. This type of microorganism is known to obtain energy from inorganic substances (e.g., reduced sulfur compounds, molecular hydrogen, and methane) derived from subsurface physical and chemical processes, such as water–rock interactions. As the primary producers, they sustain chemosynthetic ecosystems, which are fundamentally different from terrestrial and shallow marine ecosystems that are sustained by photosynthetic primary production. It is possible that the chemosynthetic ecosystems at and beneath the seafloor are vast and metabolically active, playing an important role in the global geochemical cycles of many bio-essential elements. However, even today, the spatial and temporal distributions of the unseen chemosynthetic biosphere are largely uncertain. Here, we present geochemical constraints on the estimate of the potential biomass in seafloor and subseafloor chemosynthetic ecosystems sustained by high-temperature deep-sea hydrothermal activities and low-temperature alteration/weathering of oceanic crust. The calculations are based on the fluxes of metabolic energy sources (S, H₂, Fe, and CH₄), the chemical energy yields for metabolic reactions, and the maintenance energy requirements. The results show that for deep-sea hydrothermal vent ecosystems, most bioavailable energy yields (86 %) are due to oxidation reactions of S. In contrast, for subseafloor oceanic crust ecosystems, oxidation reactions of Fe and S generally yield the same amounts of bioavailable energy (59 % and 41 %, respectively). The estimated biomass potential in the subseafloor oceanic crust ecosystems (0.14 Pg C) is one order of magnitude higher than that in global deep-sea hydrothermal vent ecosystems (0.0074 Pg C), most likely reflecting the greater flux of

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low-temperature fluids circulating within the oceanic crust than that of high-temperature focused fluids venting at ridge axes. The overall biomass potential of the chemosynthetic ecosystems, estimated to be 0.15 Pg C, corresponds to only 0.02 % of the Earth's total living biomass. This estimate suggests that chemosynthetic ecosystems comprise a rare biomass fraction of the modern Earth's biosphere, probably reflecting a significantly smaller energy flux from Earth's interior compared with that from the sun.

Keywords

Biomass potential • Chemosynthetic ecosystems • Hydrothermal activity • Low-temperature alteration/weathering • Oceanic crust

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2.1 Introduction

It was long believed that essentially all life forms on Earth were sustained by the primary production of photosynthetic organisms and substantially relied on energy supplied from the sun. In the past century, the ubiquitous presence of lithoautotrophic microorganisms on the Earth has been gradually recognized (Dworkin 2012). However, these organisms were not considered important on the global scale because they were thought to represent only a small fraction of the microbial community in most environments, and most of these organisms consume inorganic compounds produced by the degradation of biologically derived organic matter. In the late 1970s, when deep-sea hydrothermal activities first began to be explored, it became apparent that the biological communities present in the dark seafloor environments were dense in biomass and diverse in species (Corliss et al. 1979; Spiess et al. 1980). It was suggested that these organisms must rely on a different source of energy. Furthermore, in the past decade the existence of potentially vast and metabolically active microbial populations within the oceanic crust was also suggested by several studies (Bach and Edwards 2003; Cowen et al. 2003; Lever et al. 2013). In contrast to most of the surface biological communities, in which the food chains start with the primary production of photosynthetic organisms, the newly discovered deep-sea ecosystems are likely dependent on the primary production of symbiotic and free-living chemolithoautotrophic microorganisms that obtain energy from the oxidation of inorganic compounds (e.g., H_2S , CO_2 , H_2 , and CH_4) essentially provided by the subseafloor water-rock interactions. It is now hypothesized that such deep, dark ecosystems (often described as chemosynthetic communities) comprise a considerably widespread biosphere associated with the global deep-sea hydrothermal systems and perhaps an even more vast biosphere in the subseafloor igneous oceanic crust (Edwards et al. 2005; Schrenk et al. 2010; Orcutt et al. 2011).

In the past several decades, the deep-sea chemosynthetic communities at and beneath the seafloor have been extensively studied along the following three general directions of scientific interest. The first is that most of the microbial components of the deep-sea chemosynthetic communities are extremophiles that have important physiological and biochemical functions and biomaterials for understanding the limits of life and biological activities on this planet (Takai 2011). The second interest is that such microbes represent models most likely to elucidate the origin and early evolution of life on Earth and to predict possible extraterrestrial organisms and the habitability of other planets and moons (Jannasch and Mottl 1985; Nealson et al. 2005; Takai et al. 2006). The third interest is related to the estimation and quantification of how the metabolisms and functions of the deep-sea chemosynthetic communities impact the global biogeochemical cycles of C, Fe, S, and other bio-essential elements (Edwards et al. 2005; Schrenk et al. 2010; Kallmeyer et al. 2012). Despite an increasing number of studies that have been published regarding the first and second interests (Horikoshi and Tsujii 1999; McCollom 1999; Varnes et al. 2003; Hoehler 2004; Gerday and Glansdorff 2007; Takai 2011), much less is known about the third (i.e., the abundance and distribution of deep-sea and deep subseafloor chemosynthetic ecosystems and their impact on the global biogeochemical cycles of the bio-essential elements). Several authors have estimated the potential production rate of biomass by the chemosynthetic ecosystems (McCollom and Shock 1997; Bach and Edwards 2003). However, the biomass production rate cannot be used directly for the estimation of biomass. Thus, we cannot so far interpret the abundance and distribution of the deep, dark ecosystems and their role as reservoirs of the bio-essential elements. Here, we present the first theoretical estimation of the potential biomass that could be sustained by high-temperature deep-sea hydrothermal vent activity and low-temperature oceanic crust alteration/weathering.

2.2 Method to Estimate the Potential Biomass Sustained by Chemosynthetic Primary Production

In this study, we attempt to estimate the potential biomass that could be sustained by the chemosynthetic energy sources derived from high-temperature deep-sea hydrothermal activity and low-temperature oceanic crust alteration/weathering. The biomass potential of chemosynthetic communities can be calculated based on the flux of chemosynthetic energy sources, bioavailable energy yields, and maintenance energy requirements as follows:

$$BM = F_{ces} BE ME^{-1} \quad (2.1)$$

where BM is the potential biomass that could be sustained by chemosynthetic energy sources derived from high-temperature deep-sea hydrothermal activity and low-temperature oceanic crust alteration/weathering, F_{ces} is the overall flux of the chemosynthetic energy sources, BE is the bioavailable energy yield from a chemosynthetic metabolic reaction per unit of energy source, and ME is the species-independent maintenance energy requirement.

The bioavailable energy yield, BE , was determined by calculating the Gibbs free-energy change in each of the metabolic reactions following the method developed by McCollom and Shock (1997), Shock and Holland (2004), and McCollom (2007). The predominant chemolithotrophic energy metabolisms examined in this study are listed in Table 2.1. The overall Gibbs free energy of a reaction can be calculated using the following equation:

$$BE = \Delta G_r = \Delta G_r^\circ + RT \ln Q \quad (2.2)$$

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 is the activity quotient of the compounds involved in the reaction. The Q term takes into account the contribution of the fluid composition to the Gibbs energy of each reaction.

Maintenance energy, ME , is defined as the minimum rate of energy intake to maintain molecular and cellular integrities and functions, which is expressed as the energy flux required to maintain a certain amount of biomass over a certain unit of time. In this study, the maintenance energy requirement is calculated using the following equation, according to Harder (1997):

$$ME = A \cdot e^{-Ea/RT} \quad (2.3)$$

where Ea is the activation energy of 69.4 kJ/mol, R is the universal gas constant, T is the temperature in Kelvin, and A is an empirically derived constant. The constant values of A , as determined in chemostat experiments, for aerobic and anaerobic microorganisms are 8.13×10^{12} and 4.99×10^{12} kJ/g dry weight/day, respectively (Tijhuis et al. 1993; Harder 1997). However, it is known that this value is likely 3–6 orders of magnitude lower for the maintenance and survival of microorganisms in natural systems. Price and Sowers (2004) noted that the reported energy flux requirements were classified roughly into three categories, with values of ‘growth’ exceeding those of ‘maintenance’ by approximately three orders of magnitude and exceeding those of ‘survival’ by 5–6 orders of magnitude. In this study, following Hoehler (2004), we performed the calculation using values for the maintenance energy factor, A , of 8.13×10^9 and 4.99×10^9 kJ/g dry weight/day for aerobic and anaerobic reactions, respectively. These values correspond to the ‘maintenance’ state described by Price and Sowers (2004). The ‘maintenance’ state values used here are likely appropriate for the estimation of steady-state biomass potential without growth or reduction.

2.2.1 Deep-Sea Hydrothermal Vent Communities

To estimate the biomass potential of deep-sea hydrothermal vent communities, as part of the chemosynthetic ecosystems

Table 2.1 Metabolic reactions for chemolithoautotrophy considered in this study

Energy metabolism	Overall chemical reaction
<i>Aerobic reactions</i>	
1. Aerobic methanotrophy	$\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$
2. Hydrogenotrophic O_2 -reduction	$\text{H}_2 + 1/2\text{O}_2 = \text{H}_2\text{O}$
3. Thiotrophic (H_2S -oxidizing) O_2 -reduction	$\text{H}_2\text{S} + 2\text{O}_2 = \text{SO}_4^{2-} + 2\text{H}^+$
4. 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>Anaerobic reactions</i>	
5. Hydrogenotrophic methanogenesis	$\text{H}_2 + 1/4\text{CO}_2 = 1/4\text{CH}_4 + 1/2\text{H}_2\text{O}$
6. Hydrogenotrophic SO_4 -reduction	$\text{H}_2 + 1/4\text{SO}_4^{2-} + 1/2\text{H}^+ = 1/4\text{H}_2\text{S} + \text{H}_2\text{O}$
7. Hydrogenotrophic Fe(III)-reduction	$\text{H}_2 + 2\text{Fe}^{3+} = 2\text{Fe}^{2+} + 2\text{H}^+$
8. Anoxic methanotrophy with SO_4 -reduction	$\text{CH}_4 + \text{SO}_4^{2-} = \text{HCO}_3^- + \text{HS}^- + \text{H}_2\text{O}$

at and beneath the seafloor, Eq. (2.1) is converted to the following relation:

$$BM_{hydro} = F_{hydro} BE_{hydro} ME^{-1} \quad (2.4)$$

where BM_{hydro} is the potential biomass (g dry weight) that could be theoretically sustained by the total deep-sea hydrothermal fluid inputs, such as high-temperature vents; F_{hydro} is the overall flux of deep-sea hydrothermal fluid flows (kg hydrothermal fluid/year); BE_{hydro} is the sum of the predominant chemosynthetic metabolic energy yields from 1 kg of end-member hydrothermal fluid (kJ/kg hydrothermal fluid); and ME is the maintenance energy requirement, that is, the energy supply required to sustain a certain amount of biomass per unit of time (kJ/g dry weight/year).

As originally proposed by McCollom and Shock (1997), the bioavailable energy yield, BE_{hydro} , represents the amount of chemical energy potentially available from the metabolisms of chemolithotrophic microorganisms during the mixing of hydrothermal vent fluid with seawater. A source of chemical energy is a basic requirement for all organisms, and, in the case of chemolithotrophs in deep-sea hydrothermal vent environments, the energy sources arise from the chemical disequilibria that develop during the mixing of hydrothermal fluids with seawater. In this study, for the sake of convenience the average values of BE_{hydro} in four hypothetical mixing waters with temperature ranges of <25 °C, 25–45 °C, 45–80 °C, and 80–125 °C are calculated. These temperature ranges represent chemolithotrophic metabolisms of psychrophilic, mesophilic, thermophilic and hyperthermophilic microbial components, respectively. The mixing calculations were performed using the computer program EQ3/6, Version 8.0 (Wolery and Jarek 2003). The thermodynamic database necessary for the EQ3/6 operations and the values of the standard Gibbs energy for the chemolithotrophic metabolic reactions were generated using the SUPCRT92 code and database (Johnson et al. 1992). The SUPCRT92 database used here is the thermodynamic dataset for aqueous species and complexes from Shock and Helgeson (1988), Shock and Helgeson (1990), and Shock et al. (1997), with recent upgrades of the slop98.dat database (see Wolery and Jove-Colon 2004) and the OBIGT.dat database (see also <http://www.predcent.org/>).

2.2.2 Subseafloor Basaltic Oceanic Crust Communities

To estimate the biomass potential of the chemosynthetic communities in subseafloor basaltic aquifers within the oceanic crust, Eq. (2.1) is converted to the following relation:

$$BM_{awoc} = F_{awoc} BE_{awoc} ME^{-1} \quad (2.5)$$

where BM_{awoc} is the potential biomass (g dry weight) that could be theoretically sustained by low-temperature alteration/weathering of oceanic crust in the subseafloor basaltic aquifer, F_{awoc} is the overall flux of reduced iron and sulfur in the basaltic ocean crust supplied during the low-temperature alteration/weathering of oceanic crust, BE_{awoc} is the chemosynthetic metabolic energy yields of reduced iron- and sulfur-oxidation reactions in the subseafloor basaltic aquifer within the oceanic crust (kJ/mol S, Fe), and ME is the maintenance energy requirement described above (kJ/g dry weight/year).

The calculation of BE_{awoc} for the subseafloor basaltic oceanic crust communities generally follows the method described by Bach and Edwards (2003), which is in turn based on McCollom and Shock's model described above. The chemolithotrophic energy metabolisms examined in the calculation are Fe(II)- and H₂S-oxidation reactions (reactions 4 and 7 in Table 2.1). BE_{awoc} is calculated using the same equation used in the calculation for the deep-sea hydrothermal vent communities. Following Bach and Edwards (2003), the temperature and pressure conditions of the ridge flank aquifer are set at 10 °C and 250 bar, respectively. The activity quotient of the reactants and reaction products is also calculated based on the compositional data used in Bach and Edwards (2003) (see table 3 in Bach and Edwards 2003).

2.3 Potential Biomass Sustained by High-Temperature Deep-Sea Hydrothermal Systems

2.3.1 Geochemical Characteristics of Deep-Sea Hydrothermal Fluids

It is known that the variation in composition of the chemolithotrophic energy metabolisms of deep-sea hydrothermal vent microbial communities is highly affected by the chemical compositions of hydrothermal fluids (Nakamura and Takai 2014). In this study, therefore, we used the extensive dataset for the chemical compositions of 89 high-temperature end-member hydrothermal fluids compiled by Nakamura and Takai (2014) (Suppl. Table 2.1) to identify the variation of the chemical composition of deep-sea hydrothermal vent fluids. The dataset covers the sediment-starved mid-ocean ridge hydrothermal systems (MOR) in the Pacific, Atlantic, and Indian Oceans; the sediment-starved arc-backarc hydrothermal systems (ABA) in the western Pacific region; and the sediment-associated hydrothermal systems (SED) in the eastern Pacific and the Okinawa Trough (Fig. 2.1). These hydrothermal systems are further classified into basalt-hosted MOR systems (MOR-B), ultramafic rock-associated MOR systems (MOR-U), mafic rock-hosted ABA systems (ABA-M), felsic rock-hosted ABA systems (ABA-F), sediment-associated

Fig. 2.1 Index map showing the locations of the active hydrothermal vent sites used in this study with the mid-ocean ridges, intra-oceanic arcs, and active back-arc spreading centers. Abbreviations: MOR-B basalt-hosted system in mid-ocean ridge settings, MOR-U ultramafic rock-hosted system in mid-ocean ridge settings, ABA-M mafic

rock-hosted system in arc-backarc settings, ABA-F felsic rock-hosted system in arc-backarc settings, SED-MOR sediment-associated system in mid-ocean ridge settings, SED-ABA sediment-associated system in arc-backarc settings

MOR systems (SED-MOR), and sediment-associated ABA systems (SED-ABA).

The compiled data are plotted on diagrams of H_2 , H_2S , and CH_4 concentrations against the Cl concentration (Fig. 2.2). These plots show negative correlations between these gas-component concentrations and the Cl content, with the exception of the H_2 -enriched MOR-U samples and CH_4 -enriched SED samples (described below). This pattern is attributed to the phase separation and phase partitioning of hydrothermal fluids (German and Von Damm 2004). It is known that phase separation tends to generate both Cl-depleted/volatile-enriched vapor and Cl-enriched/volatile-depleted brine under subcritical or supercritical temperature and pressure conditions (Butterfield et al. 2003; Foustoukos et al. 2007). In contrast to the gas-components, the correlations between the Fe and Cl concentrations are not so clear, while some vapor-rich samples exhibit positive correlations with Cl (Fig. 2.3a). Instead, the Fe concentrations correlate well with the pH of the hydrothermal fluids (Fig. 2.3b).

Some highly Cl-depleted hydrothermal fluids (<100 mmol/kg) exhibit considerably high concentrations of H_2 , H_2S , and CH_4 (Fig. 2.2). It has been revealed that such extremely gas-enriched fluid emissions are very temporary, limited to a period of several weeks to months after a volcanic and/or seismic event (Lilley et al. 2003). Thus, the

extremely gas-enriched fluid emissions are exceptional and cannot be regarded as steady-state activities. Therefore, the chemical data of hydrothermal fluids with Cl concentrations of <100 mmol/kg are excluded from the estimation of potential biomass in this study.

The H_2 concentrations of most of the hydrothermal fluids, except for the extremely gas-enriched entities, range from ~ 0.01 to ~ 1 mmol/kg (Fig. 2.2a). Significant H_2 enrichment (>1 mmol/kg) is, however, identified in all the ultramafic rock-associated MOR-U fluids (Fig. 2.2a). It has been documented that the serpentinization reaction in ultramafic rocks during hydrothermal alteration provides significant amounts of H_2 to the hydrothermal fluids (Charlou et al. 2002; McCollom and Bach 2009; Nakamura et al. 2009). Our compilation apparently confirmed the significant H_2 enrichment in the MOR-U fluids among all types of hydrothermal fluids. In addition to the MOR-U fluids, a number of the sediment-associated SED-MOR and SED-ABA fluids also exhibit abundant dissolved H_2 (Fig. 2.2a). This can be attributed to the thermal decomposition of organic matter included in sediments under a specific hydrogeologic structure (e.g., dominant high-temperature interactions between hydrothermal fluids and sediments in the discharging stages following the subseafloor water–rock hydrothermal reactions) (Kawagucci et al. 2013). It is noteworthy that

Fig. 2.2 (a) H_2 , (b) CH_4 , and (c) H_2S versus Cl plots for hydrothermal vent fluids venting in the mid-ocean ridge and arc-backarc settings. Gray areas represent the extremely vapor-rich hydrothermal fluids with <100 mmol/kg of Cl concentration, which are excluded from the estimation of biomass potential in this study. Abbreviations: *MOR-B* basalt-hosted system in mid-ocean ridge settings, *MOR-U* ultramafic

rock-hosted system in mid-ocean ridge settings, *ABA-M* mafic rock-hosted system in arc-backarc settings, *ABA-F* felsic rock-hosted system in arc-backarc settings, *SED-MOR* sediment-associated system in mid-ocean ridge settings, *SED-ABA* sediment-associated system in arc-backarc settings

the extent of H_2 enrichment in the SED fluids is considerably lower than that in MOR-U fluids (Fig. 2.2a).

The CH_4 concentrations in most deep-sea hydrothermal fluids vary from ~ 0.001 to ~ 1 mmol/kg (Fig. 2.2b). Notable enrichment of dissolved CH_4 in the hydrothermal fluids is identified in all the SED fluids (Fig. 2.2b). The CH_4 enrichment can be attributed to the thermal decomposition of organic matter in sediments in higher temperature (>120 °C) regions (reaction and/or discharge zones) and/or to microbial methanogenesis in relatively lower temperature (<120 °C) regions (e.g., recharge zone) (Lilley et al. 1993; Kawagucci et al. 2011, 2013). Some of the MOR-U fluids also have significantly high CH_4 concentrations, most likely due to the chemical reduction of CO_2 (abiotic methanogenesis) under the highly reduced (H_2 -rich) hydrothermal conditions (Charlou et al. 2002). Our compilation shows that CH_4 enrichment in the MOR-U fluids is much less than that in the SED fluids (Fig. 2.2b, Suppl. Table 2.1).

In contrast to the H_2 and CH_4 concentrations, the H_2S levels are constantly high (>1 mmol/kg), and their variation is noticeably small (ranging from ~ 1 to ~ 10 mmol/kg) in any type of deep-sea hydrothermal fluid (Fig. 2.2c). Therefore, in deep-sea hydrothermal fluids without H_2 and CH_4 enrichment, H_2S is the most abundant reductive gas species available for the chemolithotrophic metabolisms of microbial communities. Additionally, the Fe concentrations vary from ~ 0.01 to ~ 10 mmol/kg; these values are correlated with the pH of the hydrothermal fluids (Fig. 2.3b). The felsic rock-hosted ABA-F fluids tend to have high Fe concentrations and low pH values (Fig. 2.3b), probably due to volatile input from magmas. On the other hand, sediment-associated SED fluids generally exhibit relatively low Fe concentrations and high pH values (Fig. 2.3b), probably reflecting the presence of organic matter serving as the $\text{NH}_3/\text{NH}_4^+$ buffer (German and Von Damm 2004).

Fig. 2.3 Fe versus (a) Cl and (b) pH plots for hydrothermal vent fluids venting in the mid-ocean ridge and arc-backarc settings. Gray areas represent the extremely vapor-rich hydrothermal fluids with <100 mmol/kg of Cl concentration. Abbreviations: *MOR-B* basalt-hosted system in mid-ocean ridge settings, *MOR-U* ultramafic rock-hosted system in mid-ocean ridge settings, *ABA-M* mafic rock-hosted system in arc-backarc settings, *ABA-F* felsic rock-hosted system in arc-backarc settings, *SED-MOR* sediment-associated system in mid-ocean ridge settings, *SED-ABA* sediment-associated system in arc-backarc settings

2.3.2 Bioavailable Energy Yield from Deep-Sea Hydrothermal Fluids

To address the effect of hydrothermal fluid chemistry on the biomass potential of deep-sea hydrothermal vent ecosystems, the bioavailable energy yields of various chemolithotrophic metabolisms are determined. In this study, as listed in Table 2.1, we consider potentially predominant aerobic and anaerobic chemolithotrophic energy metabolisms driven by H_2 , H_2S , Fe^{2+} and CH_4 . Note that these elements derived from hydrothermal fluids are not entirely consumed by biological activities. Indeed, it is generally considered that significant parts of the Fe^{2+} and H_2S in hydrothermal fluids are oxidized abiotically. In our calculation, however, we assume that all these elements are used for

chemolithoautotrophic metabolism to estimate the upper limit of biomass that could be sustained by deep-sea hydrothermal activities (the biomass potential).

Figure 2.4 shows the metabolic energy yields maximally obtained from 1 kg of hydrothermal fluids for each of the hydrothermal systems MOR-B, MOR-U, ABA-M, ABA-F, SED-MOR, and SED-ABA. It should be noted here that the bioavailable energy yields were calculated based on an assumption that each of the aerobic and anaerobic reactions could use all the O_2 and H_2/SO_4 in the mixed fluids. For the reason, the energy yield from each of the reactions represents the maximum energy for the reaction available from the mixing fluids, and thus the sum of the energy available from all of the metabolic reactions are larger than the actual potential energy yields from the mixing fluids. In Fig. 2.4, for the aerobic energy metabolisms the bioavailable energy yield at <25 °C is larger by far than the yields of the higher temperature conditions. The anaerobic energy metabolisms become more favorable at higher temperatures, although the bioavailable energy yields by the anaerobic metabolisms at all temperature ranges are significantly lower than those of aerobic metabolisms at <25 °C. Consequently, it is suggested that aerobic chemolithotrophs in lower temperature conditions (mostly psychrophilic) are mainly responsible for the primary production of the associated microbial and macrofaunal communities in the global deep-sea hydrothermal vent environments.

In the MOR-B, ABA-M, and ABA-F systems, aerobic thiotrophy at low-temperature conditions (<25 °C) is by far the most energetically favorable compared with the other aerobic and anaerobic metabolisms at any temperature condition (Fig. 2.4). In the H_2 -enriched MOR-U system, aerobic hydrogenotrophic metabolisms can produce much greater energy for biomass production than aerobic thiotrophic metabolisms (Fig. 2.4). This type of hydrothermal system is also characterized by significant energy yields from anaerobic hydrogenotrophic chemolithotrophs (e.g., methanogens and sulfate-reducers) under high-temperature conditions (Fig. 2.4). Similarly, the CH_4 -enriched SED-MOR and SED-ABA systems have significant potential to yield energy for aerobic methanotrophs at lower temperatures and for anaerobic methanotrophic sulfate-reducers at higher temperatures (Fig. 2.4). The aerobic $Fe(II)$ -oxidation reaction yields the second-highest metabolic energy in ABA-F systems and some hydrothermal vents in MOR-B systems, although the aerobic thiotrophy produces much higher energy than the aerobic $Fe(II)$ -oxidation (Fig. 2.4). However, very little energy is available from anaerobic $Fe(III)$ -reduction at any temperature condition in any type of hydrothermal system due to the extremely low concentration of ferric iron both in seawater and hydrothermal fluids.

Fig. 2.4 Bar chart showing metabolic energies (kJ/kg hydrothermal fluid) available from the six aerobic and anaerobic reactions (Table 2.1) in 89 hydrothermal vent sites at temperature ranges of <25, 25–45, 45–80, and 80–125 °C in the MOR-B, MOR-U, ABA-M, ABA-F, SED-MOR, and SED-ABA systems. *Shaded vent sites* are excluded from the estimation of biomass potential in this study because of their unusual chemical compositions (<100 mmol/kg of Cl). See text for more details. Abbreviations: *MOR-B* basalt-hosted system in mid-ocean ridge settings, *MOR-U* ultramafic rock-hosted system in mid-

ocean ridge settings, *ABA-M* mafic rock-hosted system in arc-backarc settings, *ABA-F* felsic rock-hosted system in arc-backarc settings, *SED-MOR* sediment-associated system in mid-ocean ridge settings, *SED-ABA* sediment-associated system in arc-backarc settings, *ABA* arc-backarc hydrothermal system, *SED* sediment-associated hydrothermal system, *H₂S-ox* aerobic H₂S-oxidation, *H₂-ox* aerobic H₂-oxidation, *CH₄-ox* aerobic CH₄-oxidation, *SO₄-re* anaerobic SO₄-reduction, *AMO* anaerobic CH₄-oxidation

Figure 2.5 shows the average values of bioavailable energy yields from each of the energy metabolisms in the MOR-B, MOR-U, ABA, and SED systems. Because there are essentially no differences in the bioavailable energy yields between the ABA-M and ABA-F systems or between the SED-MOR and SED-ABA systems (Fig. 2.4), we use the average value of the ABA and SED systems for the estimation of potential biomass described below. In the MOR-B and ABA systems, the aerobic thiotrophy at <25 °C is by far the most energetically favorable, whereas the contribution of the other energy metabolisms is essentially negligible (Fig. 2.5). In contrast, in the MOR-U system, the aerobic

hydrogen-oxidation at <25 °C is the most energetically favorable. This is due to the high concentrations of H₂ and relatively low concentrations of H₂S in the MOR-U fluids. Additionally, at high-temperature conditions anaerobic hydrogenotrophic energy metabolisms yield more energy than aerobic hydrogen-oxidation (Fig. 2.5). In the SED system, the aerobic methanotrophic energy production is comparable to thiotrophic production at low temperatures (<25 °C), whereas anaerobic methanotrophy is the most energetically favorable at high temperatures (>45 °C), reflecting the high concentration of CH₄ in the hydrothermal fluids (Fig. 2.5).

Fig. 2.5 Bar chart showing averaged metabolic energies (kJ/kg hydrothermal fluid) available from the six aerobic and anaerobic reactions (Table 2.1) at temperature ranges of <25, 25–45, 45–80, and 80–125 °C in the MOR-B, MOR-U, ABA, and SED systems. Abbreviations: MOR-B basalt-hosted system in mid-ocean ridge settings, MOR-U ultramafic rock-hosted system in mid-ocean ridge settings, ABA arc-backarc hydrothermal system, SED sediment-associated hydrothermal system, H₂S-ox aerobic H₂S-oxidation, H₂-ox aerobic H₂-oxidation, CH₄-ox aerobic CH₄-oxidation, SO₄-red anaerobic SO₄-reduction, AMO anaerobic CH₄-oxidation

2.3.3 Fluxes of Deep-Sea Hydrothermal Fluids

The total amount of high-temperature hydrothermal fluid flux from the MOR system into the ocean has been estimated as 5.6×10^{15} g/year, based on the production rate of oceanic crust (Elderfield and Schults 1996; Mottl 2003). This calculation is based on the assumption that 10 % of the hydrothermal budget results from high-temperature focused flows and that 90 % results from lower-temperature fluid flows. This assumption has recently been supported by the geochemical evidence from hydrothermally altered oceanic crust by Nielsen et al. (2006). Indeed, at least two types of alteration (high-temperature (>250 °C) with a low water/rock ratio and low-temperature (<150 °C) with a high water/rock ratio) have long been recognized in oceanic crust, in both on-axis and off-axis regions of mid-ocean ridges (Fig. 2.6) (Alt et al. 1986, 1996a, b; Nakamura et al. 2007).

In this study, therefore, we adopt this value as the total high-temperature hydrothermal fluid flux from the MOR system.

Based on the chemical characteristics of hydrothermal fluids and the bioavailable energy yields described in the previous sections, the MOR system is further divided into the following three types: (1) the ultramafic rock-associated H₂-rich MOR-U system, (2) the sediment-associated CH₄-rich SED-MOR system, and (3) the relatively H₂S-rich MOR-B system. To estimate the fluxes of the H₂-enriched, CH₄-enriched, and H₂S-enriched fluids separately, we attempted to allocate the total amount of MOR hydrothermal fluid flux into the three hydrothermal systems as follows.

In the mid-ocean ridges explored so far, the presence of ultramafic rocks is mostly recognized at slow and ultra-slow spreading ridges (Cannat et al. 2006; Escartin et al. 2008). Recent geophysical surveys have predicted that ultra-slow and slow spreading ridges occupy 20 % and 40 % of the mid-ocean ridge extent, respectively (Cannat et al. 2006; Schwartz et al. 2005). In addition, extensive chemical surveys of hydrothermal plumes have suggested that the general incidence ratio of hydrothermal activities along the mid-ocean ridge is linearly correlated with the spreading rate (Baker and German 2004; Baker et al. 2004). According to the results of Baker et al. (2004), the incidence ratios of hydrothermal plumes (activities) can be estimated as 0.08, 0.25, and 0.67 at the ultra-slow, slow, and moderate to fast spreading ridges, respectively. Given that the hydrothermal fluid fluxes are correlated with the plume incidence, as well as the ridge lengths, we can break down the total MOR hydrothermal flux (5.6×10^{15} g/year) into 2.4×10^{14} g/year, 1.5×10^{15} g/year, and 3.9×10^{15} g/year at the ultra-slow, slow, and moderate to fast spreading ridges, respectively.

Cannat et al. (2006) reported that, based on the geophysical surveys at the ultra-slow spreading ridge of the Southwest Indian Ridge, 59 % of the seafloor is a typical type covered with basaltic lava flows, whereas 37 % is smooth and 4 % is corrugated. The smooth seafloor is composed mostly of ultramafic rocks, whereas the corrugated seafloor consists of basaltic lavas on one side and ultramafic/gabbroic rocks on the other side (Cannat et al. 2006). If we assume here that (1) all of the ultra-slow spreading ridges have 37 % smooth seafloor and 4 % corrugated seafloor, as is the case for the Southwest Indian Ridge, and (2) all of the smooth-seafloor regions and half of the corrugated-seafloor regions have a potential to generate H₂-rich hydrothermal fluids, we can estimate that 39 % of ultra-slow spreading ridges can host the H₂-rich hydrothermal system.

In the slow spreading Mid-Atlantic Ridge, Escartin et al. (2008) showed that 50 % of the ridge axis regions were symmetric, and the rest were asymmetric. Based on seafloor morphology, the symmetric and asymmetric ridges can be

Fig. 2.6 Schematic illustration showing hydrothermal circulation within oceanic crust in on- and off-axis regions (modified from Nakamura et al. 2007). The red, orange, and blue arrows represent high- (>~250 °C), intermediate- (<~150 °C), and low-temperature

(<~100 °C) fluid flows, respectively. Abbreviations: UVZ upper volcanic zone, LVZ lower volcanic zone, TZ transition zone, USDZ upper sheeted dike zone, LSDZ lower sheeted dike zone, GZ gabbro zone

comparable to the typical volcanic seafloor and corrugated seafloor described by Cannat et al. (2006), respectively. Thus, the seafloor at the symmetric ridge regions can be regarded as composed mostly of basaltic lava flows, whereas the asymmetric regions consist of basaltic lavas on one side and ultramafic/gabbroic rocks on the other side. As is the case for the ultra-slow spreading ridges, therefore, we can estimate that 25 % of slow spreading ridges can host the hydrothermal systems producing H₂-enriched hydrothermal fluids.

There are also sediment-associated ridges, which are geographically located in close proximity to continents (Fig. 2.1). In this study, the Juan de Fuca Ridge, the Gorda Ridge, and the Gulf of California in the northeast Pacific Ocean and the Red Sea are defined as the sediment-associated ridges. The spreading rate of the ridges is variable: moderate to fast in the northeast Pacific Ocean but slow in the Red Sea. The total lengths of the ridges in the northeast Pacific Ocean and the Red Sea are evaluated to be each ~2,000 km, which corresponds to 8.3 % each of the total lengths of the moderate to fast spreading ridges and the slow spreading ridges.

Based on the estimations described above, the hydrothermal fluid fluxes from the H₂-rich MOR-U system, the CH₄-rich SED-MOR system, and the H₂S-rich MOR-B system can be estimated to be 4.6×10^{14} , 4.4×10^{14} , and 4.7×10^{15} g/year, respectively. It should be noted here

that, in the slow and ultra-slow spreading ridges composed both of typical basaltic seafloor and corrugated/smooth seafloor with ultramafic rocks, hydrothermal fluid flux is likely to be lower in the corrugated/smooth seafloor regions compared with the typical seafloor region. This is because corrugated/smooth seafloor is considered to be formed by tectonic (amagmatic) processes rather than magmatic processes, resulting in a lack of heat source in the corrugated/smooth seafloor regions. However, we still do not know much about the difference of hydrothermal fluxes between magmatic and amagmatic regions of the slow and ultra-slow spreading ridges. In our model calculation, therefore, we simply applied the plume incidence ratios for slow and ultra-slow spreading ridges (Baker et al. 2004), which is an average value with both magmatic and amagmatic regions. For this reason, the estimated flux of the MOR-U fluids can be regarded as the maximum value.

In contrast to the case of the MOR hydrothermal systems described above, there has been no previous estimation of the total hydrothermal fluid flux from the ABA systems. Thus, we attempt to estimate the hydrothermal flux from the ABA systems in a similar manner to the estimation of the MOR hydrothermal fluid flux. Following the method used to calculate the MOR hydrothermal fluid flux, the flux from the ABA systems was estimated from the global crustal (magma) production rate in arc-backarc settings. For arc settings, we focus only on submarine hydrothermal

activities, not on subaerial hydrothermal activities. Thus, only the intra-oceanic arcs, totaling approximately 17,000 km (nearly 40 % of the subduction margins of the Earth) (Leat and Larter 2003), are considered, although not all intra-oceanic arc volcanism is submarine. The magma (crust)-addition rate in the western Pacific island arcs (a typical intra-oceanic arc) was estimated to be 30–95 km³/km/Myr (Dimalanta et al. 2002). If we assume that all intra-oceanic arcs have the same magma-addition rate, the crustal production rate of these arcs is estimated to be 0.51–1.6 km³/year. For simplicity, we use an average value of 1.1 km³/year, which corresponds to 5.5 % of the oceanic crustal production rate at mid-ocean ridges.

It is also known that most of the intra-oceanic arcs accompany back-arc spreading or rifts, except for the Solomon and Aleutian arcs (Gerya 2011). Among these arcs, the Okinawa Trough (~1,000 km) (Hirata et al. 1991), the Mariana Trough (~1,300 km) (Hawkins and Melchior 1985), the Manus Basin (~120 km) (Reeves et al. 2011), the North Fiji Basin (~800 km) (Tanahashi et al. 1994), the Lau Basin (~2,000 km) (Parson and Wright 1996), the East Scotia Basin (~500 km) (Rogers et al. 2012), the Bransfield Basin (~300 km) (Janik 1997), the Andaman Basin (~80 km) (Rao et al. 1996), and the Marsili Basin (~70 km) (Ventura et al. 2013) are known to be currently active (Fig. 2.1). Thus, we assume here that all these currently active back-arc spreading centers (total length of ~6,200 km) have an average crustal thickness of 6 km and an average spreading rate of 5 cm/year (both values are the same as the mid-ocean ridge average), although their spreading rates and crustal thicknesses are known to be variable (slow to fast spreading and crustal thicknesses of a few km to >10 km). Consequently, the crustal production rate of the back-arc spreading is estimated to be 2.1 km³/year, corresponding to 10 % of the oceanic crustal production rate.

It is also important to note that no active H₂-enriched hydrothermal system associated with ultramafic rocks have ever been discovered in arc-backarc settings. However, the SED hydrothermal system characterized by CH₄-enriched fluids is known in the Okinawa Trough (Kawagucci et al. 2011), which has ~1,000 km each of arc and back-arc systems. Taking into account the total crustal production rate and the fraction of the sediment-associated region, the hydrothermal fluid fluxes from the sediment-associated SED-ABA system and the rest of the ABA system are estimated to be 1.1×10^{14} and 7.8×10^{14} g/year, respectively.

A summary of the estimated hydrothermal fluid fluxes from the global MOR and ABA systems is shown in Fig. 2.7. It is evident that the largest hydrothermal fluid flux (72.4 %) is provided by the MOR-B system. In contrast, the mass contributions of the ABA (12.0 %), MOR-U (7.1 %), and SED (8.5 %) systems are quite limited.

Fig. 2.7 Hydrothermal fluid fluxes from MOR-B, MOR-U, ABA, and SED systems. Abbreviations: MOR-B basalt-hosted system in mid-ocean ridge settings, MOR-U ultramafic rock-hosted system in mid-ocean ridge settings, ABA arc-backarc hydrothermal system, SED sediment-associated hydrothermal system

2.3.4 Biomass Potential in Deep-Sea Hydrothermal Vent Ecosystems

In the above sections, we described the estimates of the hydrothermal fluid fluxes and the bioavailable energy yields of various chemolithotrophic metabolisms in different types or settings of deep-sea hydrothermal systems. Here, using Eq. (2.4), we approach an estimate of the biomass potential sustained by deep-sea hydrothermal fluid inputs from the MOR-B, MOR-U, ABA, and SED systems. As mentioned above, the total amounts of energy available from all the metabolic reactions are larger than the actual potential energy yields from the mixing fluids because of the assumption that each of the aerobic and anaerobic reactions can use all the O₂ and H₂/SO₄ in the mixed fluids, respectively. Therefore, to provide the maximum estimate of biomass in these deep-sea hydrothermal vent ecosystems, the most energetically favored metabolisms under the aerobic and anaerobic conditions (using O₂ and H₂/SO₄, respectively) are chosen.

The only exception is the SED system, where the psychrophilic aerobic thiotrophy and methanotrophy can produce nearly the same bioavailable energy yield (Fig. 2.5). For hydrothermal vent sites, the most energetically favored aerobic metabolism is psychrophilic aerobic thiotrophy at some sites and psychrophilic aerobic methanotrophy at other sites, although hyperthermophilic anoxic methanotrophy with SO₄-reduction is the most energetically favorable anaerobic metabolism at all sites (Fig. 2.4). Indeed, biological investigations of the hydrothermal vents of the SED system have revealed the presence of significant amounts of aerobic methanotrophs (Watsuji et al. 2010; Lesniewski et al. 2012). For this reason, in the estimation we use methane-oxidation reactions as the most energetically favored metabolisms for the SED system. In this case, methane in the mixing fluid is competitively used for both aerobic and anaerobic methanotrophy, resulting in

lower total amounts of energy obtained from the mixing fluid. However, the assumption's influence on the estimation of biomass is thought to be limited for the following reasons: (1) the effect of anaerobic methanotrophy on total bioavailable energy yield is relatively minor, and (2) a shortage of aerobic methanotrophy can be supplemented with aerobic thiotrophy. Therefore, for the sake of convenience, we separately estimated the maximum amounts of energy available from aerobic and anaerobic methane-oxidation reactions based on the assumption that each reaction can use all the CH_4 in the mixing fluid. Finally, the sum of the estimated values is used as the potential bioavailable energy yield of the SED system.

Consequently, the most energy-yielding metabolisms for the biomass development are assumed to be psychrophilic aerobic thiotrophy and hyperthermophilic hydrogenotrophic sulfate reduction in the MOR-B and ABA systems, psychrophilic aerobic hydrogenotrophy and hyperthermophilic hydrogenotrophic sulfate-reduction in the MOR-U system, and psychrophilic aerobic methanotrophy and hyperthermophilic methanotrophic sulfate-reduction in the SED system.

The calculated biomass potential is shown in Fig. 2.8. The result indicates that almost all the biomass estimated is sustained by aerobic psychrophilic chemolithotrophic production, and the contributions of anaerobic hyperthermophilic chemolithotrophs are essentially negligible (Fig. 2.8a). This is attributed to the lower abundances of H_2 - and CH_4 -rich hydrothermal systems (MOR-U and SED), lower energy yields of high-temperature anaerobic reactions per a given amount of hydrothermal fluids, and a higher maintenance cost at higher temperatures as shown in Eq. (2.3).

The biomass potentials in the MOR-B, MOR-U, ABA, and SED hydrothermal systems are calculated to be 5.5×10^{12} g C, 4.9×10^{11} g C, 8.4×10^{11} g C and 5.9×10^{11} g C, respectively. It is clear that most of the overall biomass is sustained by the MOR-B system (Fig. 2.8b), reflecting the largest hydrothermal fluid flux from the MOR-B system among all the systems (Fig. 2.7). The biomass potentials sustained by each energy metabolism are calculated to be 6.4×10^{12} g C for aerobic thiotrophy, 4.9×10^{11} g C for aerobic hydrogenotrophy, 5.9×10^{11} g C for aerobic methanotrophy, 3.4×10^8 g C for hydrogenotrophic sulfate reduction, and 2.9×10^8 g C for anaerobic methanotrophic sulfate reduction. As shown in Fig. 2.8c, more than 85 % of the overall estimated biomass for the global deep-sea hydrothermal vent ecosystems is sustained by aerobic thiotrophic populations. This result clearly indicates the significance of inorganic reduced-sulfur compounds entrained from hydrothermal fluid emissions for biomass production in the global deep-sea hydrothermal vent ecosystems of the modern Earth. The biomass potentials sustained by the aerobic oxidations of H_2 and CH_4 in the hydrothermal fluids are

Fig. 2.8 Relative amounts of potential biomass sustained by (a) low-temperature aerobic reactions and high-temperature anaerobic reactions, (b) MOR-B, MOR-U, ABA, and SED systems, and (c) $\text{H}_2\text{S-ox}$, $\text{H}_2\text{-ox}$, $\text{CH}_4\text{-ox}$, $\text{SO}_4\text{-red}$, and AMO reactions. Abbreviations: MOR-B basalt-hosted system in mid-ocean ridge settings, MOR-U ultramafic rock-hosted system in mid-ocean ridge settings, ABA arc-backarc hydrothermal system, SED sediment-associated hydrothermal system, $\text{H}_2\text{S-ox}$ aerobic H_2S -oxidation, $\text{H}_2\text{-ox}$ aerobic H_2 -oxidation, $\text{CH}_4\text{-ox}$ aerobic CH_4 -oxidation, $\text{SO}_4\text{-red}$ anaerobic SO_4 -reduction, AMO anaerobic CH_4 -oxidation

one order of magnitude lower than that sustained by the hydrothermal sources of reduced-sulfur compounds. In contrast, the impact of anaerobic (hyper)thermophilic chemolithotrophs on the biomass potential of global deep-sea hydrothermal vent ecosystems are essentially negligible on the modern Earth.

2.4 Potential Biomass Sustained by Low-Temperature Alteration/Weathering of Oceanic Crust

In addition to the high-temperature hydrothermal systems at the mid-ocean ridge axis, we now know that low-temperature water–rock interactions (low-temperature alterations including so-called ocean floor weathering) occur in both on-axis and off-axis regions (Fig. 2.6) (e.g., Alt et al. 1986, 1996a, b; Mottl and Wheat 1994; Nakamura et al. 2007). It is considered that the low-temperature fluid-flows and water–rock interactions play pivotal roles in heat and chemical exchanges between the ocean and oceanic crust (Wheat and Mottl 2000). Even at the mid-ocean ridge axis, most of the hydrothermal budget (~90 %) is driven by low-temperature fluid circulation (Elderfield and Schults 1996; Nielsen et al. 2006). Furthermore, most of the global hydrothermal budget is likely led by the low-temperature fluid flows on the mid-ocean ridge flanks, where approximately 2–3 times greater heat loss occurs than on the axis (Stein et al. 1995; Elderfield and Schults 1996). This estimation leads us to consider that there may be a spatially enormous, previously unseen biosphere in the ridge-flank regions. However, to date, exploration of the potentially habitable igneous ocean crust, mostly at the mid-ocean ridge flanks, remains insufficient (Edwards et al. 2012; Lever et al. 2013).

The igneous ocean crust is known to harbor the largest aquifer system on Earth, potentially representing approximately 2 % of the ocean's fluid volume (Johnson and Priuis 2003). It has been noted that the oceanic crust aquifer is hydrothermally driven (Sclater et al. 1980; Stein and Stein 1994) and that fluids are exchanged with the overlying oceans on the order of every 100,000 years (Elderfield and Schults 1996). Surprisingly, the estimated fluid flux from the oceanic crust to the deep ocean is roughly equivalent to the global annual flux of riverine inputs to the oceans (Elderfield and Schults 1996). In contrast to the high-temperature on-axis hydrothermal systems, however, both the chemical composition and the physical properties of the low-temperature crustal fluids are largely uncertain because of difficulty in accessing the low-temperature fluid-flow systems within the oceanic crust. Therefore, it is quite difficult to estimate the flux of chemosynthetic energy sources derived by the low-temperature fluid flows based on the direct investigation of the fluids.

In addition to the chemistry of the low-temperature crustal fluids, the petrological and geochemical properties of altered oceanic crust (the other product of water–rock interactions in the on- and off-axis regions of the mid-ocean ridge) can provide important insights into the chemical exchange processes during the low-temperature

water–rock interactions (e.g., Alt et al. 1996a, b; Staudigel et al. 1996; Teagle et al. 1996; Nakamura et al. 2007). Indeed, Bach and Edwards (2003) estimated the bioavailable energy yield by low-temperature water–rock interactions at the ridge-flank regions based on geochemical data for altered oceanic crust. Following the method proposed by Bach and Edwards (2003), we can estimate the bioavailable energy yield and fluxes of the energy sources from the low-temperature alteration of oceanic crust. This estimate, in turn, leads to the estimation of the biomass potential sustained by the low-temperature water–rock interactions within the oceanic crust.

2.4.1 Processes and Fluxes of Elemental Exchange Between Seawater and Oceanic Crust During Low-Temperature Alteration/Weathering

The uppermost 200–500 m of basaltic ocean crust is known to be characterized by a high permeability that facilitates the circulation of large quantities of seawater (Fisher 1998; Fisher and Becker 2000). Within the oceanic crust aquifer, basaltic rocks react with oxygenated deep-sea water to form secondary minerals, replacing primary phases (e.g., glass, olivine, and metal sulfides) and/or filling fractures and void spaces (Alt et al. 1996a, b; Teagle et al. 1996; Talbi and Honnorez 2003). This process changes the composition of both the seawater and the oceanic crust (Hart and Staudigel 1986; Alt et al. 1996a, b; Staudigel et al. 1996; Elderfield et al. 1999; Nakamura et al. 2007). During the low-temperature alteration/weathering of oceanic crust, chemical energy for lithoautotrophy can arise from the redox reactions between the reduced basaltic rocks and relatively oxidized seawater. In this environment, reduced forms of elements (e.g., ferrous iron, sulfide sulfur, and divalent manganese) in the rocks are out of equilibrium with oxidants, such as O_2 and NO_3 , in the seawater because low-temperature water–rock reactions are kinetically sluggish. This provides an opportunity for microorganisms to catalyze the reactions and to exploit the components for metabolism and growth (Bach and Edwards 2003).

Because of the significantly higher abundances of Fe and S than Mn and other reduced forms of metals in basalt, the oxidations of Fe and S become the most abundant energy sources for chemolithotrophic metabolism (Bach and Edwards 2003). Another potential energy source is H_2 , which is generated via hydrolysis by Fe in basaltic glass or Fe-rich minerals (Bach and Edwards 2003). It has been suggested that a portion of ridge-flank aquifer in the SED system could host sulfate reducers (Lever et al. 2013).

However, under the entirely oxidizing conditions with the high seawater/rock ratio expected for the oceanic crust aquifer (Alt et al. 1996a, b; Teagle et al. 1996), the occurrence of hydrolysis by Fe seems to be limited during low-temperature alteration/weathering. Moreover, it is unlikely that such highly oxidized aquifer systems provide widespread habitats for anaerobic chemolithotrophs (e.g., methanogens and sulfate reducers). Indeed, the incidence of low-temperature H_2 -based microbial communities in the terrestrial subsurface basaltic aquifers is highly controversial (Stevens and McKinley 1995, 2000, 2001; Anderson et al. 1998, 2001). In the present contribution, therefore, we adopt only the aerobic oxidation of Fe and S during the low-temperature water–rock interactions within the oceanic crust. Additionally, as noted in the previous section of hydrothermal vent ecosystems, not all the Fe and S is used for biological activities. More likely, it is possible that most of the Fe and S in basaltic ocean crust is oxidized abiotically. In our calculation, however, we assume that all these elements are used for chemolithoautotrophic metabolism (aerobic oxidation of Fe and S) to estimate the biomass potential (i.e., the upper limit of biomass) of the deep subsurface biosphere in igneous ocean crust.

2.4.1.1 Iron

Here, we estimate the degree, extent, and timing of Fe-oxidation during low-temperature alteration/weathering of basaltic ocean crust based on the geochemical data from DSDP, ODP, and IODP, which were compiled by Bach and Edwards (2003) (Suppl. Table 2.2). The oxidation state ($Fe(III)/\Sigma Fe$) of fresh basaltic ocean crust is known to be 0.15 ± 0.05 (Christie et al. 1986; Bach and Erzinger 1995). In this study, therefore, the original $Fe(III)$ content of the fresh oceanic crust is estimated based on the total Fe content and the oxidation state. Then, using the estimated original $Fe(III)$ and the observed $Fe(III)$ contents, we calculate the amounts of $Fe(II)$ oxidized to $Fe(III)$ during low-temperature alteration/weathering.

Figure 2.9a shows a change in the amounts of $Fe(II)$ that oxidized to $Fe(III)$ in basalt with crust age. The figure clearly indicates that the $Fe(II)$ in basaltic ocean crust is gradually oxidized to $Fe(III)$ during low-temperature alteration/weathering in off-axis regions. The oxidation of Fe is continuous but wanes with a time-dependent logarithm (Fig. 2.9a). This is consistent with geophysical (Stein and Stein 1994; Fisher and Becker 2000; Jarrard 2003) and geochemical (Hart and Staudigel 1986; Peterson et al. 1986; Booij et al. 1995) lines of evidence suggesting that vigorous seawater circulation and oxidative alteration take place especially in young crust. Although the timing for the termination of the circulation and alteration is still uncertain, a simple model of age-dependent oxidative alteration was

Fig. 2.9 Changes in (a) the amounts of $Fe(II)$ oxidized to $Fe(III)$ and (b) the Fe -oxidation rate of basaltic ocean crust with crust age

employed in this study, based on the change in geophysical parameters sensitive to crustal hydration (Jarrard 2003).

Based on the relationship of the Fe -oxidation with crust age in oceanic crust (Fig. 2.9a) and the average age of subducted oceanic crust (60 Ma) (Schubert et al. 2001), we can estimate the average amounts of $Fe(II)$ oxidized to $Fe(III)$ in oceanic crust during low-temperature alteration/weathering to be 0.33 mol Fe/kg basalt. The Fe -oxidation budget can be converted to a steady-state oxidation rate of Fe by multiplying by the annual mass of basaltic ocean crust produced. Following the assumptions provided by Bach and Edwards (2003) (a seafloor production rate of $3.0 \text{ km}^2/\text{year}$, a depth extent of oxidation of 500 m, an upper crustal porosity of 0.10, and a basalt density of $2,950 \text{ kg/m}^3$), the annual production mass of the altered oceanic crust is estimated to be $4.0 \times 10^{12} \text{ kg/year}$. With the estimated Fe -oxidation budget (0.33 mol Fe/kg basalt) and the annual production rate of altered oceanic crust ($4.0 \times 10^{12} \text{ kg/year}$), we calculated global upper ocean-crust oxidation rates of $1.3 \times 10^{12} \text{ mol } Fe/\text{year}$. In addition to the steady-state oxidation rate, we also calculate the specific Fe -oxidation rate at the each age of oceanic crust (Fig. 2.9b) by differentiating the curve of the Fe -oxidation progress with crust age (Fig. 2.9a).

The result clearly shows that a much higher Fe-oxidation rate occurs in younger oceanic crust (Fig. 2.9b).

2.4.1.2 Sulfur

Even today, data for S concentrations in altered oceanic crust are quite scarce. In this study, we use S-concentration data from DSDP, ODP, and IODP. These data were compiled by Bach and Edwards (2003) and more recently provided by Miller and Kelley (2004), Rouxel et al. (2008), and Alt and Shanks (2011) (Suppl. Table 2.2). It is known that the speciation of S in basaltic magma is dominated by sulfide. Because sulfide has a strong affinity for FeO in the melt, the solubility of S is essentially controlled by the concentration of Fe (Mathez 1976; Wallace and Carmichael 1992). Thus, we can estimate the primary S concentration in basaltic ocean crust using the following empirical relationship between total Fe and S concentrations for sulfide-saturated basaltic magma (Mathez 1979):

$$S [\text{wt}\%] = 0.023 \text{ Fe} [\text{wt}\%] - 0.059 \quad (2.6)$$

During low-temperature alteration/weathering of basaltic ocean crust, the sulfide in the basalt is oxidized to sulfate. Because of the high solubility of sulfate in seawater, the oxidized S during the alteration/weathering is leached from the basalt, resulting in a decrease of total sulfur content. Thus, the differences between the calculated initial S concentrations and the observed S concentrations in altered oceanic crust can be regarded as the amounts of S oxidized during alteration/weathering. Figure 2.10a shows that the amount of oxidized S in oceanic crust changes with the age of oceanic crust, although the extent of S-oxidation in oceanic crust is much more variable compared with that of Fe-oxidation (Fig. 2.9a).

The compiled DSDP, ODP, and IODP data generally show a correlation between the amounts of oxidized S and the logarithmic age of oceanic crust (Fig. 2.10a). Thus, we also employ a simple model of age-dependent oxidative alteration, as in the case for the Fe-oxidation described above. In this model, the S-oxidation rate decreases in proportion to the logarithmic age of oceanic crust. Following the same method used in the calculation of the Fe-oxidation budget, we can estimate the average amounts of oxidized S during low-temperature alteration/weathering of oceanic crust to be 0.02 mol S/kg basalt. The S-oxidation budget can be converted to a steady-state oxidation rate of 8.1×10^{10} mol S/year by multiplying by the mass of the annual production of altered oceanic crust. We can also calculate the specific S-oxidation rate at each age of oceanic crust, showing that a much higher S-oxidation rate is achieved in younger oceanic crust (Fig. 2.10b), as in the case for Fe-oxidation.

Fig. 2.10 Changes in (a) the amounts of reduced sulfur oxidized to sulfate and (b) the sulfur-oxidation rate of basaltic ocean crust with crust age

2.4.2 Bioavailable Energy Yield from Low-Temperature Alteration/Weathering of Oceanic Crust

Following Bach and Edwards (2003), the metabolic energy yields for Fe- and S-oxidation reactions in the low-temperature basalt aquifer are calculated to be 66.2 kJ/mol Fe and 751 kJ/mol S, respectively. Then, using the metabolic energy yields and the Fe- and S-oxidation rates (1.3×10^{12} mol Fe/year and 8.1×10^{10} mol S/year, respectively) estimated in the previous section, the amounts of energy for chemolithotrophic Fe- and S-oxidizing metabolisms during low-temperature alteration/weathering of basaltic ocean crust are estimated to be 8.8×10^{13} kJ/year and 6.1×10^{13} kJ/year, respectively. In this case, the requisite amounts of oxygen for the Fe- and S-oxidation reactions (3.3×10^{11} mol O_2 /year and 1.6×10^{11} mol O_2 /year, respectively) are much smaller than the supply rate (1.4×10^{12} mol O_2 /year) calculated from the fluid flux through oceanic crust. It is noteworthy that, although the S-oxidation rate (0.81×10^{11} mol S/year) is one order of magnitude lower than the Fe-oxidation rate (1.3×10^{12} mol Fe/year), the energy yield of the S-oxidizing metabolisms is comparable to that of the Fe-oxidizing metabolisms. This

Fig. 2.11 Relative amounts of potential biomass sustained by (a) Fe(II)- and H₂S-oxidation reactions and (b) high-temperature hydrothermal activity and low-temperature oceanic crust alteration/weathering

reflects a much higher energy yield per mole of electron acceptor from the S-oxidation reaction than the Fe-oxidation reaction. This suggests that for both the high-temperature hydrothermal systems and the low-temperature oceanic crust aquifer systems, the reduced form of S is an important energy source for chemosynthetic ecosystems on the modern Earth, while the Fe-oxidation reaction is the most energetically favorable in the basaltic ocean crust aquifer.

2.4.3 Biomass Potential in Oceanic Crust Ecosystems

Based on Eq. (2.5), we calculated the biomass potential sustained by the low-temperature alteration/weathering using the estimated values of the bioavailable energy yields, the rates of Fe- and S-oxidations, and the maintenance energy requirement. The potential biomass sustained by the Fe- and S-oxidation reactions is calculated to be 8.5×10^{13} g C and 5.9×10^{13} g C, respectively. The results show that nearly the same population sizes can be fostered by the Fe- and S-oxidizing energy metabolisms during the low-temperature alteration/weathering of basaltic ocean crust (Fig. 2.11a). This implies that both the aerobic Fe-oxidizers and the aerobic S-oxidizers play important biogeochemical and ecological roles in the subseafloor crust

ecosystems. Moreover, it is interesting that the overall biomass potential in the oceanic crust ecosystems (1.4×10^{14} g C) is one order of magnitude higher than that in the high-temperature hydrothermal vent ecosystems (0.74×10^{13} g C) (Fig. 2.11b). The difference in overall biomass potentials is likely dependent on the difference in hydrothermal heat fluxes between the low-temperature on- and off-axis flows (~ 9 TW) and the high-temperature axial flow (~ 0.3 TW) (Elderfield and Schults 1996). Note here that the biomass potential estimation of the oceanic crust ecosystems is completely independent of the heat flux data.

In addition to the amount of biomass in the oceanic crust, we can also calculate the cell abundances (6.1×10^{27} cells for aerobic Fe-oxidizers and 4.2×10^{27} cells for aerobic S-oxidizers) and the possible average cell densities in the hypothetically habitable spaces (6.7×10^4 cells/cm³ for aerobic Fe-oxidizers and 4.7×10^4 cells/cm³ for aerobic S-oxidizers) using a carbon content value of 14 fg C/cell (Kallmeyer et al. 2012) together with average values of density, porosity, and age of oceanic crust. The estimated total cell abundance in igneous oceanic crust (1.0×10^{28} cells) is much lower than the recently estimated global subseafloor sedimentary microbial abundance (2.9×10^{29} cells) (Kallmeyer et al. 2012). The average cell density in oceanic crust ($\sim 1.1 \times 10^5$ cells/cm³) is comparable to that in subseafloor sedimentary habitats in the mid-ocean gyres (Fig. 2.12) (Kallmeyer et al. 2012). It is worth noting that the cell density in oceanic crust is much higher in younger oceanic crust (e.g., <1 Ma) than in older oceanic crust (e.g., >100 Ma) (Fig. 2.12) because of the difference in Fe- and S-oxidation rate with crustal age. This leads us to propose that the exploration and investigation of deep subseafloor oceanic crustal microbial communities should be performed in the young oceanic crust.

2.5 Microbial Biomass Potentials Associated with Fluid Flows in Ocean and Oceanic Crust and the Impact on Global Geochemical Cycles on the Modern Earth

In the present contribution, we estimate the biomass potentials of ecosystems associated with the global high-temperature hydrothermal and low-temperature crustal fluid flow systems in the deep ocean and oceanic crust (0.0074 and 0.14 Pg C, respectively). The results lead to a grand total of 0.15 Pg C, which represents the overall biomass potential of the deep-sea and deep-subseafloor biospheres sustained by inorganic compounds provided by subseafloor water-rock interactions. The estimated biomass potential comprises no more than 0.02 % of the total living biomass on modern Earth (Fig. 2.13a) (Kallmeyer et al. 2012). It should be

Fig. 2.12 Comparison of cell concentrations in the subseafloor sediment biosphere with that in the oceanic crust biosphere (modified from Kallmeyer et al. 2012). The maximum estimate of cell concentrations of the oceanic crust biosphere is generally comparable to the subseafloor sediment in the North and South Pacific Gyres. Note that the cell concentration of the oceanic crust biosphere is the maximum estimate, whereas that of subseafloor sediment biosphere is the actual observed value

noted that because our biomass potential estimations are the maximum estimation, the real biomass abundances are likely to be significantly lower than the estimated values.

In addition to the subseafloor crustal ecosystems, subseafloor sedimentary ecosystems have attracted much attention (Whitman et al. 1998). The latest estimation has revealed that the subseafloor sedimentary biomass of microorganisms may represent 0.6 % of the Earth's total biomass (Fig. 2.13a) (Kallmeyer et al. 2012). It should be noted here that the subseafloor sedimentary biomass would be substantially sustained by the solar energy input through organic carbon sources derived from terrestrial and shallow marine phototrophic production, as suggested by a general trend of decreasing cell abundance in subseafloor sediments with increasing depth (Parkes et al. 1994; Kallmeyer et al. 2012). Even compared with the subseafloor sedimentary biomass, the estimated biomass potential of the chemosynthetic ecosystems sustained by the subseafloor high-temperature and low-temperature water–rock interactions is quite small, only 3.7 % of the sedimentary biomass (Fig. 2.13b). It is, therefore, very likely that most of the Earth's total biomass, including the subseafloor sediment biosphere, is sustained by solar energy via photosynthetic

Fig. 2.13 Comparisons of the estimated potential biomass of the oceanic crust biosphere (including the high-temperature hydrothermal vent biosphere and the low-temperature oceanic crust biosphere) with the amounts of biomass in (a) terrestrial, marine, and subseafloor sediment biospheres and (b) subseafloor sediment biosphere

primary production in the terrestrial and ocean surface biospheres. This is consistent with the large difference in energy mass balance on the modern Earth between the whole solar energy flux (174,260 TW) (Smil 2008) and the oceanic heat flux (~9 TW) (Elderfield and Schults 1996).

The present study shows that the potential biomass of the deep-sea and deep subseafloor ecosystems sustained by the inorganic substrates provided by crust–seawater interactions is a tiny fraction of the global biomass on the modern Earth. This suggests that there are no large chemosynthetic communities in the deep-sea and deep subseafloor crust region that might comprise an unseen majority of the modern Earth's biosphere. It should be noted, however, that the very small biomasses of the deep-sea and deep subseafloor ecosystems do not mean they have insignificant functions and roles in the global biogeochemical cycles of C, Fe, S, and other bio-essential elements throughout the long history of the co-evolution of the Earth and life. The present contribution invites future quantitative investigations into the global biogeochemical cycles.

Moreover, our estimate of biomass potentials and compositional patterns in different geological settings of deep-sea hydrothermal systems and chemolithotrophic energy metabolisms suggests potentially strong interrelationships among the geological settings, the physical-chemical conditions of hydrothermal fluids (and seawater), and the dominant energy metabolisms for the biomass potential in the global deep-sea hydrothermal and ridge-flank aquifer environments. These interrelationships will provide key insights into the evolutionary implications of the energy mass balance and biomass production in the origin and evolution of life on Earth as well as future exploration of extraterrestrial life on other planets and moons.

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