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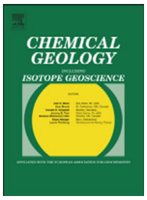

Energy yields from chemolithotrophic metabolisms in igneous basement of the Juan de Fuca ridge flank system

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ABSTRACT

The permeable rocks of the upper oceanic basement contain seawater-sourced fluids estimated to be ~2% of the global ocean volume. This represents a very large potential subsurface biosphere supported by chemosynthesis. Recent collection of high integrity samples of basement fluid from the sedimented young basaltic basement on the Juan de Fuca Ridge flanks, off the coasts of Vancouver Island (Canada) and Washington (USA), and subsequent chemical analyses permit numerical modeling of metabolic redox reaction energetics. Here, values of Gibbs free energy for potential chemolithotrophic net reactions were calculated in basement fluid and in zones where basement fluid and entrained seawater may mix; the energy yields are reported both on a per mole electrons transferred and on a per kg of basement fluid basis. In pure basement fluid, energy yields from the anaerobic respiration processes investigated are anemic, releasing <0.3 J/kg basement fluid for all reactions except methane oxidation by ferric iron, which releases ~0.6 J/kg basement fluid. In mixed solutions, aerobic oxidation of hydrogen, methane, and sulfide is the most exergonic on a per mole electron basis. Per kg of basement fluid, the aerobic oxidation of ammonia is by far the most exergonic at low temperature and high seawater:basement fluid ratio, decreasing by more than two orders of magnitude at the highest temperature (63 °C) and lowest seawater:basement fluid ratio investigated. Compared with mixing zones in deep-sea hydrothermal systems, oceanic basement aquifers appear to be very low energy systems, but because of their expanse, may support what has been labeled the 'starving majority'.

1. Introduction

1.1. Hydrothermal fluids and the basement biosphere

Hydrothermal fluids that flow through the oceanic crust alter the regional geochemistry, thermal gradients and heat transport, diagenetic processes, seismic events, and ore bodies (Fisher et al., 2010). Despite their low permeability (10^{-12}–10^{-14} m^2), oceanic crustal aquifers in the upper 500 m contain ~2% of the global ocean volume (Becker and Fisher, 2000; Johnson and Pruis, 2003). The entire ocean volume cycles through the crust every 10^5–10^6 years, mostly in the cooler regions of the ridge flank systems, away from the axes (Elderfield and Schultz, 1996; Johnson and Pruis, 2003; Mottl, 2003). This rapid and extensive hydrothermal circulation substantially impacts ocean biogeochemistry, providing significant sources and sinks for both inorganic (Wheat and Mottl, 2000) and organic (Lang et al., 2006; Lin et al., 2012) species. Thick sediment cover retards or prevents further direct interaction between oceanic crust and seawater (Underwood et al., 2005). Consequently, seawater entrainment into the basement aquifer occurs predominantly at mid-ocean ridges, unsedimented recharge seamounts, and young ridge flanks with minimal sediment cover. Seawater circulation, water–rock interactions, and subsurface fluid mixing generate aqueous solutions that, in conjunction with mineral surfaces, may provide habitats for a host of microorganisms. It has been argued that minerals provide most of the energy to the biosphere in deep ocean crust, either by direct reduction by microbes of Fe and S minerals, or by production of H_2 during serpentinization reactions (Bach and Edwards, 2003; Edwards et al., 2005; Jørgensen and Boetius, 2007).

The presence of a deep biosphere, supported by geochemical energy sources was posited two decades ago (Gold, 1992). Whitman et al. (1998) expanded on this concept by collating the available microbial cell count data from marine and terrestrial subsurface samples, concluding that in mass and volume, subsurface life may be comparable to surface life. A reassessment, including new data from mid-ocean sediment samples, lowered the estimated global microbial cell numbers by up to nearly 80% (Kallmeyer et al., 2012). Other direct and circumstantial evidence of an extensive oceanic subsurface ecosystem comes from surveys of microbial communities in terrestrial basalt

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aquifers, mineral alteration textures, 16S rRNA gene sequence data, carbon isotope fractionation, predicted chemotrophic metabolism energetics, and direct culturing attempts (Stevens and McKinley, 1995; Kelley et al., 2002; Cowen et al., 2003; Cowen, 2004; Amend and Teske, 2005; Steinsbu et al., 2010; Jungbluth et al., in press). To date, most of the studies on microbial life in the marine subsurface have, by necessity, targeted sediment habitats (D'Hondt et al., 2004; Schippers et al., 2005; Jørgensen and D'Hondt, 2006; Biddle et al., 2008; Lipp et al., 2008; Kallmeyer et al., 2012; Lomstein et al., 2012), but exploration of the biota inhabiting the igneous ocean crust, while still technically challenging, is becoming tractable (Edwards et al., 2005; Orcutt et al., 2011; Cowen et al., 2012; Lin et al., 2012; Jungbluth et al., in press). The aim of the present study is to model reaction energetics of chemolithotrophic metabolisms in Juan de Fuca ridge flank basement fluid and in zones where the basement fluid mixes with seawater. This study builds on the approach developed by McCollom and Shock (1997) and employed by several others (e.g. Amend et al., 2003; Jin and Bethke, 2005; McCollom and Amend, 2005; Rogers and Amend, 2006; McCollom, 2007; Amend et al., 2011).

1.2. Study site: Juan de Fuca Ridge fl`ank

Numerous Deep-Sea Drilling Program (DSDP), Ocean Drilling Program (ODP), and Integrated Ocean Drilling Program (IODP) boreholes penetrate through marine sediment into the basement. Fewer than 20 of these holes are equipped with CORK (Circulation Obviation Retrofit Kit) observatories (K. Becker, pers. comm.), which arguably provide the best opportunities for sampling and studying marine basement fluids. The eastern flank of the Juan de Fuca ridge on the East Pacific Rise, off the coasts of Washington (USA) and British Columbia (Canada), offers several advantages as a location for an integrated basement biosphere investigation. There, pre-drilling reconnaissance surveys, drilling operations and CORK installations, and post-drilling studies have provided a wealth of data (Davis et al., 1989, 1992; Mottl and Wheat, 1994; Wheat and Mottl, 1994; Fisher et al., 1997; Wheat et al., 1997; Mottl et al., 1998; Davis et al., 1999; Elderfield et al., 1999; Fisher and Becker, 2000; Wheat and Mottl, 2000; Fisher et al., 2003; Fisher, 2005). A transect of boreholes was drilled and equipped with CORK observatories during ODP Expedition 168 (holes 1024C, 1025C, 1026B, 1027C) and IODP Expeditions 301 (holes 1301A and 1301B) and 327 (holes 1362A and 1362B)—for discussions of CORK design, deployment, and fluid sampling, see Fisher et al. (2011) and Wheat et al. (2011).

Hole 1301A, the focus of this communication, is located on a buried basement ridge of oceanic crust, ~100 km from the Juan de Fuca Ridge spreading axis (Expedition 301 Scientists, 2005). Local crustal properties, hydrogeology, solid and fluid chemistry, and microbiology have been described (Cowen et al., 2003; Fisher et al., 2004; Expedition 301 Scientists, 2005; Wheat et al., 2010; Lin et al., 2012). The site consists of relatively impermeable sediments overlying permeable, moderately-altered 3.5 Ma old basalts (Expedition 301 Scientists, 2005; Fisher, 2009). Hydrothermal circulation occurs via unsedimented ridge flanks and exposed seamounts which guide subsurface recharge by seawater and discharge into the bottom ocean (Hutnak et al., 2006). Microbial biomass has been documented throughout the sediments and into the basement, with microbial counts increasing near the sediment–seawater and sediment–basement interfaces; both aerobes and anaerobes were identified near the sediment–seawater interface, but anaerobes dominate near the basement (Engelen et al., 2008). Various chemotrophic metabolisms are known to occur at the site, including sulfate reduction and anaerobic oxidation of methane (AOM) (Engelen et al., 2008; Steinsbu et al., 2010), and geochemical evidence for microbial oxidation of organic carbon has also been found (Lin et al., 2012). Reports of several different oxidants and reductants might suggest the possibility of several metabolic strategies, but their relative energetics at the site—the focus of this investigation—are not known. Bach and Edwards (2003) modeled energetics for selected chemolithoautotrophic metabolisms in basaltic ocean crust, focusing in particular on iron and sulfur oxidation.

Fig. 1 depicts a generalized schematic of a region of sedimented basement and the potential flow associated with recharge and discharge seamounts superimposed on an overall lateral flow, a scenario that is similar to that postulated for the region of the Juan de Fuca Ridge flank system (Wheat et al., 2002; Fisher et al., 2003; Walker et al., 2008). Borehole 1301A is located ~50 km northeast of a recharge seamount (Grizzly Bare) and ~5 km northeast of the discharge seamount Baby Bare. The CORK at 1301A allows collection of warm basement fluids (~65 °C). The present study models the mixing zone of oxidized recharge fluids with reduced basement fluids. Aqueous species of particular interest in this study include HCO_3^-, O_2, NO_3^-, SO_4^{2-}, CH_4, Fe^{2+}, H_2S, H_2 and NH_4^+. The energy calculations described below rely on temperature and chemical analyses (Table 1) reported by Lin et al. (2012).

2. Methods

2.1. Mixing model

The software package Geochemist's Workbench™ (Bethke, 1996, 2002) was used to model a two-fluid reaction path in which small aliquots of basement fluid were titrated into seawater. The chemical speciation of the mixed solution was reevaluated after each step. Mineral precipitation as a result of mixing was prohibited. Note that this does not affect most reactions considered here, as few redox-active minerals are oversaturated in the model solutions. Allowing mineral precipitation only slightly alters the energy available from aqueous iron oxidation reactions, with some of the energy transferred to reactions involving iron minerals instead (McCollom, 2000; Amend et al., 2011). Acid–base reactions were allowed to equilibrate on the timescales of mixing, but redox reactions were not; at the temperatures considered in this study, the kinetics of abiotic redox reactions are slow relative to speciation and mixing kinetics (Jannasch and Mottl, 1985; McCollom and Shock, 1997). The temperature of the modeled mixed fluid was assumed to scale linearly with the end-member fluid temperatures because the heat capacities of the dilute fluids under consideration will not differ significantly (Amend et al., 2011).

2.2. Thermodynamic calculations

The potential energy yield for a specific net metabolism can be evaluated as the Gibbs energy of reaction (ΔG_r), using the relation

$$\Delta G_r = \Delta G_r^\circ + RT \ \ln Q_r, \tag{1}$$

where $\Delta G_r°$ denotes the standard Gibbs energy at the pressure and temperature of interest, R and T represent the ideal gas constant and temperature in Kelvin, respectively, and Q_r stands for the reaction quotient. Q_r can be calculated with the relation

$$Q_r = \Pi\left(a_i^{\nu_{i,r}}\right), \tag{2}$$

where a_i is the activity of species i and $\nu_{i,r}$ is its stoichiometric coefficient in reaction r.

Values of $\Delta G_r°$ were calculated at 250 bar and 0–63 °C using the thermodynamic software package SUPCRT92 (Johnson et al., 1992). SUPCRT92 employs the revised Helgeson–Kirkham–Flowers equations of state and thermodynamic data compiled in numerous publications (for a detailed review of the approach, see Amend and Shock (2001)). Differences between the chosen pressure of the