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# Dissolved hydrogen and methane in the oceanic basaltic biosphere

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ABSTRACT

The oceanic basaltic crust is the largest aquifer on Earth and has the potential to harbor substantial subsurface microbial ecosystems, which hitherto remains largely uncharacterized and is analogous to extraterrestrial subsurface habitats. Within the sediment-buried 3.5 Myr old basaltic crust of the eastern Juan de Fuca Ridge flank, the circulating basement fluids have moderate temperature (~65 °C) and low to undetectable dissolved oxygen and nitrate concentrations. Sulfate, present in high concentrations, is therefore expected to serve as the major electron acceptor in this subsurface environment. This study focused on the availability and potential sources of two important electron donors, methane ($CH_4$) and hydrogen ($H_2$), for the subseafloor biosphere. High integrity basement fluids were collected via fluid delivery lines associated with Integrated Ocean Drilling Program (IODP) Circulation Obviation Retrofit Kits (CORKs) that extend from basement depths to outlet ports at the seafloor. Two new CORKs installed during IODP 327 in 2010, 1362A and 1362B, were sampled in 2011 and 2013. The two CORKs are superior than earlier style CORKs in that they are equipped with coated casing and polytetrafluoroethylene fluid delivery lines, reducing the interaction between casing materials with the environment. Additional samples were collected from an earlier style CORK at Borehole 1301A.

The basement fluids are enriched in $H_2$ (0.05–1.8 μmol/kg), suggesting that the ocean basaltic aquifer can support $H_2$-driven metabolism. The basement fluids also contain significant amount of $CH_4$ (5–32 μmol/kg), revealing $CH_4$ as an available substrate for subseafloor basaltic habitats. The $\delta^{13}C$ values of $CH_4$ from the three boreholes ranged from −22.5 to −58‰, while the $\delta^2H$ values ranged from −316 to 57‰. The isotopic compositions of $CH_4$ and the molecular compositions of hydrocarbons suggest that $CH_4$ in the basement fluids is of both biogenic and abiotic origins, varying among sites and sampling times. The $\delta^2H$ values of $CH_4$ in CORK 1301A fluid samples are much more positive than found in all other marine environments investigated to date and are best explained by the partial microbial oxidation of biogenic $CH_4$. In conclusion, our study shows that $CH_4$ and $H_2$ are persistently available to fuel the deep biosphere and that $CH_4$ is both produced and potentially consumed by microorganisms in the oceanic basement.



## 1. Introduction

The upper (40–500 m) oceanic basaltic crustal aquifer holds an amount of seawater-derived hydrothermal fluids equal to approximately 2% of the global ocean volume, and thus represents the largest aquifer on earth (Johnson and Pruis, 2003). Heat flow data indicate that thermally driven circulation of seawater persists within the upper basaltic crust (basement) to a global average age of at least 65 million-year (Myr) old (Parsons and Sclater, 1977). Basement fluids are primarily recharged by bottom seawater that penetrates highly permeable basement at mid-ocean ridges and through thinly sedimented young ridge flanks and unsedimented rocky seamounts. Most of the flow occurs through ridge flanks at relatively low temperature (Expedition 327 Scientists, 2010). This immense low temperature subseafloor basalt-aquifer provides an analogy to extraterrestrial subsurface microbial ecosystems (Sleep et al., 2004; Nealson et al., 2005; Sherwood Lollar et al., 2007).

*Abbreviations:* JFR, Juan de Fuca Ridge; IODP, Integrated Ocean Drilling Program; ODP, Ocean Drilling Program; CORK, Circulation Obviation Retrofit Kit; FDL, fluid delivery line; MPS, mobile pump system; MVBS, medium volume bag sampler; LVBS, large volume bag sampler; PTFE, polytetrafluoroethylene; mbsf, meters below seafloor; msb, meters sub-basement; Ti-major, titanium major sampler.

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Evidence from the alteration of basaltic glass and rocks, including their texture (Fisk et al., 1998; Furnes and Staudigel, 1999; Furnes et al., 2001b), chemical (Alt and Mata, 2000; Furnes et al., 2001a; Bach and Edwards, 2003; Thorseth et al., 2003) and isotopic compositions (Thorseth et al., 1995; Torsvik et al., 1998; Alford et al., 2011; Alt and Shanks, 2011), suggest a subseafloor biosphere within the ridge flank basement. Microbial analyses of ridge flank basement fluids indicate the presence of diverse and dynamic bacterial and archaeal communities (Cowen et al., 2003; Huber et al., 2006; Orcutt et al., 2011; Smith et al., 2011; Jungbluth et al., 2013). Thermodynamic modeling based on geochemical analysis (Lin et al., 2012) also indicates that the conditions in the ridge flank basement, though quite low in the energy-yields, are still conducive for diverse microbial metabolisms (Boettger et al., 2013). Microbial activity in the basement may in turn play an important role in regulating global biogeochemical cycles, such as the removal of phosphate (Wheat et al., 1996) and refractory dissolved organic carbon (Lang et al., 2006; Lin et al., 2012) from the deep ocean.

Basement fluids circulating in sedimented ridge-flanks have been shown to contain significant amount of electron acceptors, including sulfate (eastern flank of Juan de Fuca, Elderfield et al., 1999; Wheat et al., 2004, 2010; Lin et al., 2012), nitrate (South Pacific Gyre, D'Hondt et al., 2013) and oxygen (South Pacific Gyre, D'Hondt et al., 2013; North Pond, Orcutt et al., 2013). Yet, it is still unclear whether there are sustainable sources of common electron donors such as hydrogen ($H_2$) and methane ($CH_4$) in the basement environment. $H_2$-driven lithoautotrophic microbial ecosystems have been suggested to be present in continental basaltic aquifers and fractures (Stevens and McKinley, 1995; Chapelle et al., 2002; Lin et al., 2006) and in serpentine-hosted aquifers (Charlou et al., 2002; Kelley et al., 2005; Proskurowski et al., 2008b), encouraging the search for similar microbial communities in the ridge-flank oceanic basaltic environment, where temperature is moderate and suitable for life (Cowen et al., 2003; Cowen, 2004).

Many diverse chemolithoautotrophic microorganisms living in hydrothermal systems can use $H_2$ as an electron donor (Jannasch, 1995), coupled with electron acceptors such as sulfate (Fichtel et al., 2012), sulfur (Takuro et al., 2008), carbon dioxide (Kurr et al., 1991; Takai et al., 2002), or iron (e.g. Kashefi et al., 2002) to produce organic matter. $H_2$ has also been shown to limit the growth, abundance and distribution of hyperthermophilic methanogens at deep-sea hydrothermal vents (Ver Eecke et al., 2012). Few studies have addressed the presence of $H_2$ in the sedimented-ridge flank subseafloor aquifer. However, these samples were collected from sediment influenced vent fluids (Mottl et al., 1998; Lang et al., 2006), or through rusty iron casing or stainless steel tubing (Lin et al., 2012). In this study, we have improved sampling methods over these previous studies, and present $H_2$ concentrations from multiple high integrity basement fluid samples.

Methane is another important electron donor and carbon source for a wide variety of methanotrophs (e.g. Balch et al., 1979; Hinrichs et al., 1999; Boetius et al., 2000; Biddle et al., 2006; Inagaki et al., 2006; Knittel and Boetius, 2009; Merkel et al., 2013). The importance of $CH_4$ in the global carbon cycle has been widely recognized in various settings such as coastal ocean, marine sediment, and deep-ocean and hydrothermal systems (Claypool and Kvenvolden, 1983; Crill and Martens, 1986; Valentine et al., 2001; Cowen et al., 2002; Biddle et al., 2006). Significant accumulation of $CH_4$ produced via anaerobic organic matter degradation occurs in zones where sulfate is exhausted ($<1$ mM, versus seawater concentration of $\sim$28 mM), likely due to removal of $CH_4$ by sulfate reducers (Reeburgh and Heggie, 1977; Claypool and Kvenvolden, 1983; Boetius et al., 2000; Shipboard Scientific Party, 2004) and is widely observed in organic-rich coastal and continental margin marine sediments (e.g. Barnes and Goldberg, 1976; Claypool and Kvenvolden, 1983; Crill and Martens, 1986; Hoehler et al., 1994, 1998; D'Hondt et al., 2002). In contrast to organic-rich marine sediments, the 3.5 Myr old basaltic basement along the Juan de Fuca Ridge flank is a relatively organic carbon-poor (12 μM) but sulfate-rich (18 mM) environment (Lin et al., 2012). Despite low organic carbon and abundant sulfate, small amounts of $CH_4$ (1.5 μmol/kg) have been observed in this environment (Lin et al., 2012). However, the source of such $CH_4$ remains unclear. In this study, we present $CH_4$ concentrations, its isotopic composition, and the molecular compositions of hydrocarbons in order to shed light on potential sustainable sources of $CH_4$ in the basement environment.

## 2. Materials and methods

### 2.1. Sampling sites

Most of the eastern flank of the Juan de Fuca Ridge is covered by hemipelagic mud and turbidite sediment transported from the nearby continental margin during the Pleistocene, resulting in rapid burial of basement rocks at a relatively young age (Davis et al., 1992; Underwood et al., 2005). Sediment is $\sim$250 m thick overlying $\sim$3.5 Myr old basement at our study sites (Fig. 1). The thick sediment layer acts as a hydraulic seal, preventing direct exchange between bottom seawater and the basement (Davis et al., 1992; Wheat and Mottl, 1994; Shipboard Scientific Party, 1997; Becker and Fisher, 2008). Direct exchange with bottom seawater is limited to seamounts and smaller basement outcrops protruding through the sediments to the north (Mama Bare) and south (Baby Bare and Grizzly Bare) of the study site (Fig. 1).

Despite the immense volume of the ocean crustal aquifer, access to ocean basement fluids for sampling and study is limited. Unprecedented opportunities to collect basement fluids from sediment-covered ridge flanks are provided by Circulation Obviation Retrofit Kit (CORK) observatories (Becker and Davis, 2005; Wheat et al., 2011). A cluster of CORKs have been installed in selected Ocean Drilling Program (ODP) and Integrated Ocean Drilling Program (IODP) boreholes on the eastern flank of the Juan de Fuca Ridge. CORKs penetrate through sediment and into basement (Fig. 1) and thus allow the monitoring and testing of hydrogeological parameters and the collection of basement fluids for geochemical and biological studies.

This study mainly utilizes two new sites, 1362A and 1362B (Fig. 1a and b), drilled and new-style advanced CORKs (Wheat et al., 2011) installed during IODP Expedition 327 in 2010 (Expedition 327 Scientists, 2010). Fluid samples for $CH_4$ isotopic analysis were also collected from borehole 1301A, drilled and equipped with an older-style advanced CORK during IODP Expedition 301 in 2004 (Shipboard Scientific Party, 2004). These advanced CORKs are equipped with fluid delivery lines (FDLs, Fig. 2a–c) that run exterior to the CORK's casing from basement depths to the outlet port at the seafloor. CORKs 1362A and 1362B are equipped with coated casing and polytetrafluoroethylene (PTFE) FDLs, reducing the interaction between casing materials with the environment whereas CORKs 1301A is equipped with stainless steel FDL. The three boreholes were positioned along a hypothesized basement fluid flow path, from the recharge seamount Grizzly Bare in the southwest toward the discharge outcrop Baby Bare in the northeast. The CORKs penetrate to different depths within the basaltic basement, permitting fluid circulation to be monitored at multiple depths (Fig. 1).

### 2.2. Sampling methods

A mobile pump system (MPS, Fig. 2c; Cowen et al., 2012; Lin et al., 2012) equipped with a mating connector for CORKs