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Stealth export of hydrogen and methane from a low temperature serpentinization system

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ABSTRACT

Chemical input to the deep sea from hydrothermal systems is a globally distributed phenomenon. Hydrothermal discharge is one of the primary mechanisms by which the Earth's interior processes manifest themselves at the Earth's surface, and it provides a source of energy for autotrophic processes by microbes that are too deep to capitalize on sunlight. Much is known about the water-column signature of this discharge from high-temperature mid-ocean Ridge (MOR) environments and their neighboring low-temperature counterparts. Hydrothermal discharge farther away from the ridge, however, has garnered less attention, owing in part to the difficulty in finding this style of venting, which eludes methods of detection that work well for high-temperature 'black smoker'-type venting. Here we present a case study of the plume from one such 'invisible' off-axis environment, The Lost City, with an emphasis on the dissolved volatile content of the hydrothermal plume. Serpentinization and abiotic organic synthesis generate significant concentrations of H_2 and CH_4 in vent fluid, but these species are unevenly transported to the overlying plume, which itself appears to be a composite of two different sources. A concentrated vent cluster on the talus slope channels fluid through at least eight chimneys, producing a water-column plume with the highest observed concentrations of CH_4 in the field. In contrast, a saddle in the topography leading up to a carbonate cap hosts broadly distributed, nearly invisible venting apparent only in its water-column signals of redox potential and dissolved gas content, including the highest observed plume H_2. After normalizing H_2 and CH_4 to the ^{3}He background-corrected anomaly ($^3He^{\Delta}$) to account for mixing and relative amount of mantle input, it appears that, while a minimum of 60% of CH_4 is transported out of the system, greater than 90% of the H_2 is consumed in the subsurface prior to venting. The exception to this pattern occurs in the plume originating from the area dubbed Chaff Beach, in which somewhat more than 10% of the original H_2 remains, indicating that this otherwise unremarkable plume, and others like it, may represent a significant source of H_2 to the deep sea.

1. Introduction

The Lost City field is a manifestation of low temperature (<250 °C) circulation through ultramafic rocks and remains, thus far, a unique oceanographic expression of serpentinization related venting. The field features up to 60 m high carbonate edifices that vent <91 °C, pH 9–11, metal-poor fluids (Kelley et al., 2001, 2005; Früh-Green et al., 2003; Ludwig et al., 2006). Fluid-rock reactions in the underlying ultramafic rocks result in highly reducing fluids with milli-molar concentrations of hydrogen (H_2). Fluids also contain high concentrations of methane (CH_4), C_2^+ alkanes, and formate, whose formation has been attributed to abiological synthesis based on their relative concentrations, stable isotopes (^{13}C, ^{2}H), and radiocarbon content (Proskurowski et al., 2008; Lang et al., 2010). The porous carbonate chimneys are dominated by novel CH_4-cycling archaea (Schrenk et al., 2004). Similar low temperature water–rock reactions are increasingly being identified in continental systems, where the physical manifestations in the form of large travertine deposits and alkaline springs are more readily observed. High pH springs have now been identified in Oman, California, Italy, Newfoundland, New Caledonia, Yougoslavia, Turkey, and the Philippines (Barnes et al., 1978; Neal and

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Stanger, 1983; Abrajano et al., 1988, 1990; Fritz et al., 1992; Cipolli et al., 2004; Hosgormez et al., 2008; Marques et al., 2008; Blank et al., 2009; Etiope et al., 2011; Schwarzenbach et al., 2013; Szponar et al., 2013).

The high concentrations of CH_4 and H_2 derived from the serpentinization of ultramafic rocks result in large export fluxes to the deep sea in amounts far greater than that from basalt-hosted systems (Cannat et al., 2010; Charlou et al., 2010; Keir, 2010). Approximately 70% of the total mid-ocean flux of these gases is due to serpentinite-hosted water–rock interactions, despite the fact that the total subsurface water flow through these systems is significantly smaller (~8%; Keir, 2010). The majority of identified systems impacted by serpentinization, such as Rainbow and Logatchev, are high temperature (>350 °C) and share some features with basalt hosted hydrothermal systems such as low pHs and fluids rich in iron and manganese (Charlou et al., 2010). The concentrations of CH_4 and H_2 in endmember vent fluids from Lost City are similar to those of Rainbow and Logatchev but, due to the lower exit temperatures, the CH_4/heat and H_2/heat ratios are ~3–7 times higher (Cannat et al., 2010).

Low temperature serpentinization systems are expected to occur in other oceanographic locations where ultramafic rocks are exposed to seawater, but other such systems have eluded detection. One possible exception is the extinct 'Ghost City,' adjacent to the high temperature Rainbow field, where carbonate chimneys may be indicative of a formerly active low temperature, high pH type of system (Lartaud et al., 2011).

It is possible that Lost City type circulation is unique, making such an environment relatively unimportant in terms of chemical fluxes to the deep sea. Given the high incidence of similar continental springs, as well as the wide exposure of ultramafic rocks on the seafloor, this seems unlikely however. Instead, such circulation may be widespread but undiscovered. Most oceanographic hydrothermal fields are identified by instrument packages towed by surface ships. Warm fluids rise buoyantly and mix with deep seawater, and the resulting plume has diagnostic characteristics that can be detected such as small increases in temperature or suspended particulates due to the precipitation of metal rich particles in the water column (German and Von Damm, 2003). Vent fluids from Lost City, however, are of lower temperature (≤91 °C) than those from most magmatically driven systems (>300 °C), and lack the significant concentrations of dissolved iron and manganese that would lead to particle formation (Kelley et al., 2005). Lost City type hydrothermal systems will therefore be difficult to detect by traditional methods.

The relative fate of reduced chemical species such as CH_4 and H_2 has implications for fluxes to the deep sea from systems typified by the Lost City field, and for the microbial communities that utilize these reduced compounds as a source of energy or carbon. Within the endmember fluids of the Lost City field itself, hydrogen concentrations vary widely (0.5–14 mM) and are believed to support subsurface microbial sulfate reduction (Proskurowski et al., 2006; Lang et al., 2012). In contrast, much smaller concentration differences in methane (1–2 mM) are strongly associated with the relative amount of mantle input, as identified by concentrations of ^3He (Proskurowski et al., 2008).

The goals of this work are two-fold: (1) to characterize the water column features of this particular system as an aid to future exploration for similar systems; and (2) to identify the fate of the reduced volatiles H_2 and CH_4 as vent fluids mix with oxygenated seawater, particularly in relation to subsurface processes. During a 2003 cruise to the Lost City field, we used 14 vertical hydrocasts to characterize the plume over the Lost City field. We report here on the water column characteristics of serpentinization-related venting including potential temperature, turbidity, *Eh*, and concentrations of CH_4, H_2, and helium (He).

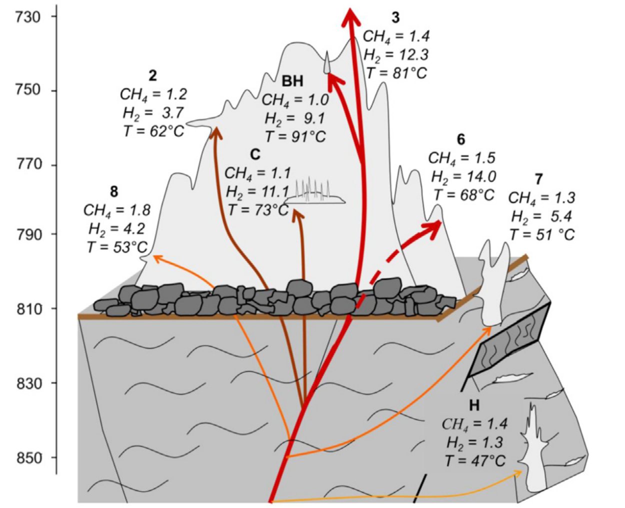

Fig. 1. Schematic sketch of the distribution of venting chimneys from the Lost City field with gas concentrations in mmol/kg (sketch modified from Lang et al., 2012; gas data from Proskurowski et al., 2006, 2008). The field rests on a down-dropped terrace and the top of the massif (labeled 'cap') is capped by a ~1 m thick layer of carbonate ooze that has been hydrothermally cemented (Kelley et al., 2001; 2005; Blackman et al., 2002; Früh-Green et al., 2003; Karson et al., 2006).

2. Background

2.1. Geological setting

Geologic investigations of the Atlantis Massif ocean core complex resulted in the serendipitous discovery of large carbonate-brucite towers and the Lost City hydrothermal field in December 2000 (Kelley et al., 2001). The ~3800 m high seamount is located at 30°N, on the inside corner high of the Mid-Atlantic Ridge and the Atlantis transform fault. It is composed of ~1–2 Myr-old ultramafic rocks with lesser gabbro that have been exposed by long-lived detachment faulting (Kelley et al., 2001; Blackman et al., 2002; Früh-Green et al., 2003; Karson et al., 2006; Boschi et al., 2008).

The field rests on a down-dropped terrace at a water depth of 750–850 m; active venting is found along a broadly linear east–west zone, with 8 identified locations where fluids are focused through large, up to 60 m high, carbonate-brucite chimneys (Fig. 1; Kelley et al., 2001, 2005; Früh-Green et al., 2003; Karson et al., 2006). The top of the massif is capped by a ~1 m thick layer of carbonate ooze that has been hydrothermally-cemented (Kelley et al., 2001, 2005; Blackman et al., 2002; Früh-Green et al., 2003; Karson et al., 2006). Radiocarbon and U–Th dating of the carbonate chimneys indicates the field has been present for up to 120 kyr (Früh-Green et al., 2003; Ludwig et al., 2011).

2.2. Vent sites

The chimneys at the center of the Lost City field (Fig. 1) are hotter and have fluids with higher hydrogen concentrations than those at the periphery of the field (Proskurowski et al., 2006). The decrease in hydrogen concentrations, from 14 to 0.5 mmol/kg, corresponds with a decrease in sulfate and an increase in sulfide concentrations in the ratio expected for microbial sulfate reduction (Proskurowski et al., 2006; Lang et al., 2012). Chimneys on the outer rim of the field, are at greater water depths, and host lower-temperature fluids with lower hydrogen concentrations (Proskurowski et al., 2006).

3. Methods

Following the initial discovery of the Lost City hydrothermal field in 2000, a research cruise was undertaken in 2003 to characterize the field using the manned submersible, ALVIN, for