



The Lost City hydrothermal system: Constraints imposed by vent fluid chemistry and reaction path models on subseafloor heat and mass transfer processes

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Received 18 February 2015; accepted in revised form 22 April 2015; available online 29 April 2015

Abstract

Since the first reported discovery of the Lost City hydrothermal system in 2001, it was recognized that seawater alteration of ultramafic rocks plays a key role in the composition of the coexisting vent fluids. The unusually high pH and high concentrations of H₂ and CH₄ provide compelling evidence for this. Here we report the chemistry of hydrothermal fluids sampled from two vent structures (Beehive: ~90–116 °C, and M6: ~75 °C) at Lost City in 2008 during cruise KNOX18RR using ROV *Jason 2* and R/V *Revelle* assets. The vent fluid chemistry at both sites reveals considerable overlap in concentrations of dissolved gases (H₂, CH₄), trace elements (Cs, Rb, Li, B and Sr), and major elements (SO₄, Ca, K, Na, Cl), including a surprising decrease in dissolved Cl, suggesting a common source fluid is feeding both sites. The absence of Mg and relatively high concentrations of Ca and sulfate suggest solubility control by serpentine–diopside–anhydrite, while trace alkali concentrations, especially Rb and Cs, are high, assuming a depleted mantle protolith. In both cases, but especially for Beehive vent fluid, the silica concentrations are well in excess of those expected for peridotite alteration and the coexistence of serpentine–brucite at all reasonable temperatures. However, both the measured pH and silica values are in better agreement with serpentine–diopside–tremolite–equilibria. Geochemical modeling demonstrates that reaction of plagioclase with serpentinized peridotite can shift the chemical system away from brucite and into the tremolite stability field. This is consistent with the complex intermingling of peridotite and gabbroic bodies commonly observed within the Atlantis Massif. We speculate the existence of such plagioclase bearing peridotite may also account for the highly enriched trace alkali (Cs, Rb) concentrations in the Lost City vent fluids. Additionally, reactive transport modeling taking explicit account of temperature dependent rates of mineral dissolution and precipitation clarifies the feedback between permeability, heat loss, and changes in the dissolved Si of the vent fluids. Assuming both the Beehive and M6 vent fluids were sourced at similar subseafloor conditions (tremolite buffered at 200 °C), model results indicate loss of approximately 30% Si upon cooling to ~150 °C during upflow. However, Si concentrations remained largely conservative with continued cooling to lower temperatures owing to unfavorable reaction kinetics. While consistent with the Beehive endmember composition, these results fail to explain the relative Si depletion in the lower temperature M6 fluids. Thus, it may be that more robust kinetic models for silicates are needed to accurately account for the mechanism and rate of silica removal in the unusually high pH of the Lost City vent fluids.

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1. INTRODUCTION

The Lost City hydrothermal field (LCHF) (30°07'N, 42°07'W) is hosted in ultramafic rocks exposed along the southern face of the Atlantis Massif, which is offset

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~15 km from the Mid-Atlantic Ridge (Kelley et al., 2001, 2005; Blackman et al., 2002, 2014; Früh-Green et al., 2003; Karson et al., 2006; Proskurowski et al., 2008; Blackman et al., 2014). Carbonate-brucite chimneys within the hydrothermal field rise up to 60 m above the faulted structural ledges upon which they are perched (Kelley et al., 2001, 2005), providing evidence of permeable conduits for discharge of hydrothermal fluids sourced beneath the seafloor (Ludwig et al., 2006). The hydrothermal fluid that flows from the chimneys is noteworthy in its high pH and H₂ concentrations, as well as abundant and diverse concentrations of dissolved organic compounds, especially methane and organic acids (Kelley et al., 2005; Ludwig et al., 2006; Proskurowski et al., 2006, 2008; Konn et al., 2009; Lang et al., 2010, 2012). These characteristics of the hydrothermal fluid chemistry strongly implicate peridotite alteration, serpentinization, and in the case of the organics, Fischer Tropsch Type (FTT) synthesis (Kelley et al., 2001; Allen and Seyfried, 2004; Ludwig et al., 2006; Proskurowski et al., 2006, 2008; Seewald et al., 2006; Foustoukos et al., 2008; Konn et al., 2009; Lang et al., 2010). The role of peridotite and associated ultramafic rocks in the chemical evolution of Lost City vent fluids is further strengthened by the recovery of serpentinites, partially altered peridotite, and olivine-rich gabbro from the southern Atlantis Massif by DSRV *Alvin* during both reconnaissance and targeted studies in 2001 and 2003 (Kelley et al., 2001, 2005; Schroeder et al., 2002; Früh-Green et al., 2003; Boschi et al., 2008). The absence of brucite and relative abundance of pyrite in the recovered alteration assemblages, however, are important observations, suggesting more complex geochemical processes than simple peridotite hydrolysis and redox disequilibrium, respectively, if these mineral associations can be directly linked to the chemistry of the Lost City vent fluids (Früh-Green et al., 2003; Boschi et al., 2006, 2008; Delacour et al., 2008b). Results from the Integrated Drilling Program at Site U1309 (immediately north of the LCHF) show that the central dome is mainly composed of gabbroic rocks with minor peridotite (Blackman et al., 2006, 2014; Delacour et al., 2008a). Mineral assemblages in the core record a complex alteration history that is largely dominated by greenschist facies conditions, providing additional insight on sources of heat and mass transfer reactions in the seafloor, with implications for the temporal evolution of LCHF (Früh-Green et al., 2003; Allen and Seyfried, 2004). Thus, based on these and similar investigations, it is now clear that Lost City reveals an important type of hydrothermal activity, one that is dominated by alteration of mantle peridotite, and perhaps gabbro, at moderately low fluid temperatures, although higher temperatures in the subsurface and in the geological past cannot be ruled out (Blackman et al., 2002; Schroeder et al., 2002; Früh-Green et al., 2003; Allen and Seyfried, 2004; Boschi et al., 2006; Karson et al., 2006; McCaig et al., 2007, 2010; Foustoukos et al., 2008; Proskurowski et al., 2008).

There has been great progress made in understanding the effect of temperature and composition on mass transfer processes that could result in the formation of Lost City hydrothermal fluid, although the qualitative and quantitative controls on phase equilibria remain uncertain. For

example, in the absence of data for dissolved silica, it is not possible to constrain unambiguously peridotite alteration reactions buffering the pH of Lost City hydrothermal fluids. Similarly, data on trace alkali concentrations are also unavailable. This limits our ability to infer the source or composition of the (unaltered) protolith, with implications for the fluid/rock mass ratio attending hydrothermal alteration. Although the fluid/rock mass ratio can be estimated using strontium and oxygen isotopes in the vent fluids (Boschi et al., 2008; Foustoukos et al., 2008), other dissolved components provide additional information with which the datasets can be compared, enhancing broader applications. Here we report the concentrations of dissolved species for selected vents in the Lost City hydrothermal system. These data not only augment existing datasets, but can also be used to inform coupled heat and reactive mass transport models, providing information critical to understanding the dynamic feedback between mineral alteration, temperature, permeability, and changes in fluid chemistry between the subsurface and vent sites for this important type of marine hydrothermal system.

2. GEOLOGIC SETTING

The Lost City hydrothermal field is located at a water depth of approximately 750–850 m on the southern wall of the Atlantis Massif, approximately 15 km west of the Mid-Atlantic Ridge (Kelley et al., 2001, 2005). On the basis of magnetic data, the massif has been undergoing uplift for the past 1.5 m.y., motion that is consistent with the existence of well-developed surficial corrugations (Blackman et al., 2002).

Lost City is located near the central summit of the massif, in close association with normal faults that produce a series of bench-like structures (Fig. 1). These faults provide pathways for circulation and venting of hydrothermal fluid (Kelley et al., 2001, 2005; Ludwig et al., 2006). On the seafloor, mixing of high pH and Ca-rich hydrothermal fluid with seawater results in precipitation of variable mixtures of aragonite and brucite. During aging of the chimneys, aragonite is replaced by calcite, while at the same time brucite is rendered unstable in seawater-type fluids and ultimately dissolves (Ludwig et al., 2006). The deposits range from tall pinnacles to flanges and delicate precipitates that grow outward from fissures in the bedrock (Kelley et al., 2001; Allen and Seyfried, 2004; Kelley et al., 2005; Ludwig et al., 2006, 2011). Radiometric dating suggests hydrothermal activity at Lost City has been on-going for at least 30–35 kyr (Früh-Green et al., 2003), and perhaps as long as 120 kyr (Ludwig et al., 2011).

Observed sites of venting at Lost City occur largely within a region of approximately ~500 m². This hydrothermally active area constitutes the core of the field. These and numerous other vents and seeps are generally associated with the intersection of two major faults, one striking east–west, while the other strikes ~020° (Kelley et al., 2005; Karson et al., 2006; Ludwig et al., 2011). Previous studies have explored in detail the vent locations in the context of structural and tectonic controls, which, in part, resulted in the high resolution bathymetric map shown here

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