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

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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

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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 seafloor 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.

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 ~15 km from the Mid-Atlantic Ridge (Blackman et al., 2002; Blackman et al., 2014; Früh-Green et al., 2003; Karson et al., 2006; Kelley et al., 2001; Kelley et al., 2005; Proskurowski et al., 2008). 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; Kelley et al., 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; Konn et al., 2009; Lang et al., 2010; Lang et al., 2012; Ludwig et al., 2006; Proskurowski et al., 2008; Proskurowski et al., 2006). These characteristics of the hydrothermal fluid chemistry strongly implicate peridotite alteration, serpentinization, and in the case of the organics, Fischer Tropsch Type (FTT) synthesis (Allen and Seyfried, 2004; Foustoukos et al., 2008; Kelley et al., 2001; Konn et al., 2009; Lang et al., 2010; Ludwig et al., 2006; Proskurowski et al., 2008; Proskurowski et al., 2006; Seewald et al., 2006). 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 (Boschi et al., 2008; Früh-Green et al., 2003; Kelley et al., 2001; Kelley et al., 2005; Schroeder et al., 2002). 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 (Boschi et al., 2008; Boschi et al., 2006; Delacour et al., 2008b; Früh-Green et al., 2003). 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; Blackman et al., 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 (Allen and Seyfried, 2004; Früh-Green et al., 2003). 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 (Allen and Seyfried, 2004; Blackman et al., 2002; Boschi et al., 2006; Foustoukos et al., 2008; Früh-Green et al., 2003; Karson et al., 2006; McCaig et al., 2007; McCaig et al., 2010; Proskurowski et al., 2008; Schroeder et al., 2002).

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 meters on the southern wall of the Atlantis Massif, approximately 15 km west of the Mid-Atlantic Ridge (Kelley et al., 2001; Kelley et al., 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; Kelley et al., 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 (Allen and Seyfried, 2004; Kelley et al., 2001; Kelley et al., 2005; Ludwig et al., 2006; Ludwig et al., 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° (Karson et al., 2006; Kelley et al., 2005; 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 (Fig. 1) (Blackman et al., 2002; Karson et al., 2006; Kelley et al., 2001; Kelley et al., 2005; Ludwig et al., 2006; Proskurowski et al., 2008). In 2008 our program focused on two vent structures: the Beehive (BH) and Marker #6 (M6). Fluid was venting

vigorously at the Beehive, having exit temperatures ranging from 91-116°C. Lower temperatures (53-78°C) were measured at M6 (E-NE of BH, Fig. 1b), where hydrothermal fluid was escaping more diffusively.

3. SAMPLE COLLECTION AND ANALYSIS OF HYDROTHERMAL FLUIDS

Hydrothermal fluids sampled from the carbonate-brucite structures at Lost City during cruise *KNOX18RR* were collected by *ROV Jason-2* using two types of pressurized, piston driven sampling devices (denoted IGT or CGT) constructed entirely of titanium. These devices, similar in design, use a back pressure of compressed nitrogen to maintain each sample at seafloor pressure during both acquisition and ship-board processing, allowing continuous sub-sampling without degassing any fluid remaining in the sampler. The IGT (isobaric, gas-tight) samplers (Seewald et al., 2002) operate remotely using computer controlled software and ICL (inductively coupled link) hardware that permits non-contact serial communication (Bradley et al., 1995; Fornari et al., 1997) with a mechanical valve that serves as a fluid inlet to the sampler (Fig. 2). Accordingly, opening and closing the valve for timed cycles is possible, thereby assuring complete filling of the 150 ml sampler. The other sampler utilized (Wu et al., 2011)(CGT) has a lower volume (~120 ml), while the valve is opened and closed via action of the submersible manipulator arm in a manner similar to the “majors sampler” (Von Damm et al., 1985), which has long been used during submersible studies of deep sea vents. For both samplers, however, the inherent capability of ICL communication permits monitoring of fluid temperature as the sampler is being filled.

The vent sampling strategy deployed was not to sample the numerous individual vent structures throughout the Lost City hydrothermal field, but rather to focus on just two, as described above. The reason for this involved broader aspects of the dive plan, which required deployment of in-situ chemical sensors at selected vent sites. To verify the chemical sensor data, it was necessary to re-visit and re-sample the vent fluids over the 4 days during which the ship (*R/V Roger Revelle*) and ROV (*Jason 2*)

were at the Lost City site. Seven samples of the Beehive vent fluid were obtained, while three fluid samples were obtained at Marker #6. The repeated measurements at both vent sites occurred on separate dives at different times, and with different samplers. This is useful, in that it provides a more complete measure of sampling related variability that can contribute to the reported concentrations of hydrothermal fluid chemistry. Ambient bottom seawater was also collected at Lost City in 2008 to facilitate more accurate endmember extrapolations (section 4.1).

On-board processing of fluid samples typically occurred within hours of recovery, with priority given to the most labile components. In general, sub-samples were immediately taken for determination of pH and dissolved gases (e.g., H_2 , H_2S , and CH_4). These samples were drawn into glass, gas-tight syringes adapted with PEEK valves that effectively preclude gas loss during subsequent sample handling. Repeated pH measurements (± 0.05 units) were made with a Thermo-RossTM glass electrode, which was standardized daily before each sampling session. Total dissolved sulfide was determined by injection of 1 to 3 ml aliquots into a high pH antioxidant buffer solution (SAOB, Fisher Scientific) that was subsequently titrated with a standardized $Pb(NO_3)_2$ solution using a sulfide specific (Ag^+/S^{2-}) electrode. The low concentrations observed, however, limited resolution using this approach (Table 1). Accordingly, we report dissolved sulfide concentrations only for samples with which there existed reasonable consistency between replicate measurements ($< 10\%$ RSD, 2σ). Dissolved H_2 and CH_4 were analyzed after head space extraction using a gas chromatograph equipped with a molecular sieve column and sequential thermal conductivity and flame ionization detectors. Replicate measurements and standardization protocols suggest an analytical precision in reported values of these gases of $\pm 5\%$ (2σ).

Sub-samples of vent fluid were preserved for shore based analysis at the University of Minnesota. Chlorinity (Cl + Br) was determined by electrochemical titration using a standardized $AgNO_3$ solution. Based on replicate measurements of seawater standards (IAPSO) and standard-sample-blank protocol, an analytical precision of $\pm 0.5\%$ (2σ) is indicated. Additional anions (SO_4 , Br), major cations (Na, K, Ca, Mg), and minor/trace components (Li, Rb, Cs, Sr, Si, B, Fe) were analyzed by a combination of ion

chromatography (IC), inductively coupled plasma optical emission spectrometry (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS). The analytical uncertainty that attends these measurements is on the order of 2-10% (2σ) of the reported concentrations, with lower concentration components carrying the greater uncertainty (Pester et al., 2011; Seyfried et al., 2011; Seyfried et al., 2003). These analyses were also calibrated against IAPSO seawater for appropriate elements; and overlapping measurements of major cations by both IC and ICP-OES showed excellent agreement. The analytical uncertainty for Cs and Fe, however, was much higher, up to 30 and 40%, respectively. In the case of Cs, this is caused by the inherently low concentration and associated analytical challenges. Cs, however, inversely correlates with Mg, as predicted, underscoring the meaningfulness of the data. Fe, on the other hand, has a higher concentration, but fails to correlate with Mg. Moreover, the Fe data represent a composite of the dissolved fraction and the particulate fraction recovered by filtration (0.45 μ nylon) of the residual fluid in the Ti-samplers. Considering the relatively low total Fe concentration it would take very little “contaminant” Fe (Fe particles unrelated to the intrinsic composition of the Lost City vent fluid) to cause the scatter in the Fe-Mg data, as observed. Thus, although we provide these data, in the absence of a clear Fe-Mg correlation, the data should be considered uncertain. While within analytical error of chlorinity (by titration), reported Cl concentrations nonetheless reflect subtraction of associated Br as determined by IC. The fluid chemistry of the Lost City vent fluids sampled during cruise *KNOX18RR* and analyzed as described above is reported in Tables 1 and 2.

4. RESULTS AND DISCUSSION

4.1 The Lost City Hydrothermal Fluid Endmember

End member concentrations of LCHF vent fluids were calculated by linear regression of seawater and sample compositions to zero Mg (e.g., Von Damm et al. (1985)). Our use of isobaric gas-tight samplers (Seewald et al., 2002; Wu et al., 2011), however, effectively minimized seawater mixing as indicated by the relatively low Mg concentrations in the vent fluids sampled from LCHF in 2008 (Table

1). One sample at the Marker #6 site had a temperature of 53°C, but near seawater Mg concentration. This can only occur if the thermocouple and sample inlet tube became decoupled during sampling. Accordingly, this is clearly a failed vent fluid sample, but one that is still useful in that it provides us with another sample of seawater at LCHF with which the hydrothermal vent fluids can be compared. Although the sampled vents were located within relatively close proximity to one another (~20 m, Fig. 1b), it is still interesting that these fluids reveal such similar chemistry, especially considering clear differences in temperature and fluid flow rate. In general, the overall compositional similarity of the vent fluids reported here is largely in keeping with observations made by previous workers studying related aspects of the LCHF (Kelley et al., 2001; Kelley et al., 2005; Lang et al., 2013; Lang et al., 2012; Proskurowski et al., 2008; Proskurowski et al., 2006). This is particularly true for relatively high-temperature vent fluids and for components affected less by microbial utilization (Lang et al., 2012). Thus, it can be argued that a source fluid common to these two vents, and perhaps others, ascends from a region in the seafloor undergoing active serpentinization at a common temperature and pressure. This fluid is then dispersed, conductively cooling to variable extents in response to local controls on permeability.

4.1.1 Anions

The dissolved concentration of endmember sulfate in hydrothermal fluid from the two sites sampled in 2008 is approximately 3.3 mmol/kg (Fig. 3a; Tables 1 and 2). These data are broadly analogous to values reported earlier for LCHF vent fluids, especially for similarly located vents (Kelley et al., 2005; Lang et al., 2012). Overall, endmember sulfate concentrations throughout the entire Lost City vent field have been reported to range from approximately 1 to 4 mmol/kg (Kelley et al., 2005; Lang et al., 2012). These earlier studies have also demonstrated that the vent fluids with the highest sulfate concentrations tend to have relatively low total dissolved sulfide concentrations (~0.25 mmol/kg) (Kelley et al., 2005; Lang et al., 2012), and might better represent the inventory of dissolved sulfur species intrinsic to the source fluid feeding LCHF (Lang et al., 2012). In contrast, the low sulfate and high sulfide vent fluids (not sampled during the present study) appear to be affected by microbially mediated sulfate

reduction (Lang et al., 2012). This is consistent with the moderately low temperature of these fluids, the $\delta^{34}\text{S}$ sulfate values in excess of +30‰ (Vienna Canyon Diablo troilite) (Kelley et al., 2005), and biomass abundance and carbon isotopic composition (Lang et al., 2012).

Considering the well-known hydration effects that accompany serpentinization of peridotite (Frost and Beard, 2007; Früh-Green et al., 2004; Sanford, 1981), dissolved chloride concentrations in Lost City vent fluids might be expected to exceed seawater values. Previously reported values, however, are similar to seawater (Kelley et al., 2001). The chloride endmember of fluids sampled during the present investigation again demonstrate near seawater concentrations, but a statistically significant negative correlation with Mg is apparent (Fig. 3b). Indeed, the endmember Cl concentrations in fluids from both BH and M6 are approximately 10-15 mmol/kg below that of bottom seawater at Lost City (Table 1, 2; Fig. 3b). One well known mechanism to account for this involves chloride uptake by serpentine (Mevel, 2003; Sharp and Barnes, 2004). Serpentinized peridotite from submarine and even subareal settings often shows chloride enrichment. In this case the enrichment can occur either as water soluble phase within serpentine, or by isomorphic substitution of Cl for OH, potentially resulting in formation of an iowaite component in the serpentine structure. Sharp and Barnes (2004) determined the existence of nearly equivalent amounts of water and non-water soluble Cl in serpentinites from ODP cores, totaling approximately 0.5% Cl. At a fluid/rock mass ratio of approximately 2-4 (Foustoukos et al., 2008), a value of approximately 0.07 - 0.14% Cl can be estimated for the coexisting serpentine if the compositional change in the vent fluid and serpentine can be directly linked in time and space. This is a generous assumption considering the complex tectonic and hydrothermal history at the southern wall of the Atlantis Massif and the associated Lost City hydrothermal field (Boschi et al., 2008; Boschi et al., 2006). In contrast to Cl uptake by serpentine minerals, it is also possible that the slight decrease in Cl observed in the Lost City vent fluids occurs indirectly in association with dehydration of minerals, such as brucite. The lack of brucite associated with serpentinites recovered from the southern wall of the Atlantis Massif is well known (Boschi et al., 2008), and may provide a mechanism by which water is remobilized,

diluting Cl and similarly conservative elements. As emphasized below, changes in bulk composition during hydrothermal alteration of Al-bearing peridotite can be expected to render brucite unstable, enhancing serpentine formation, while releasing water. An analogous process involving serpentine dehydration to talc to account for the change in concentration and isotopic composition of boron associated with the Atlantis Massif detachment fault and oceanic core complex has been emphasized by Boschi et al. (2006). Thus, both direct (Cl metasomatism) and indirect (dehydration reactions) mechanisms can account for the slight but significant decrease in Cl that we have observed in Lost City vent fluids. Either scenario is unavoidably complicated in space and time, potentially involving a change in the physicochemical environment governing fluid-mineral exchange. Although the mechanism is not entirely clear, such Cl depletion is important in that it provides a previously unrecognized clue that can be used with other data to decipher the chemical and mineralogical evolution of the Lost City hydrothermal system.

Relative to the high precision of the chlorinity titration, dissolved Br analysis by IC carries a more modest precision ($\sim 3\%$, 2σ); and nearly all Br concentrations, as well as the associated Br/Cl ratios, fall within error of seawater (Tables 1 and 2).

4.1.2 Major cations

Dissolved concentrations of the major alkali elements, Na and K, in Lost City vent fluids are in excess of ambient seawater values (Table 1, 2, Fig. 4). The observed increase in the concentration of Na is particularly interesting in light of the previously discussed decrease in dissolved Cl, enhancing further the Na addition to solution when normalized to Cl, as is typically done for hydrothermal vent fluids (Pester et al., 2012; Von Damm, 2000). Sodium is likely derived from dissolution of a Na component in pyroxene or plagioclase during fluid-rock interaction at depth. Results of peridotite-seawater experiments conducted previously at a range of temperatures often reveal the release of Na to the fluid, likely in exchange for seawater Ca or Mg (Allen and Seyfried, 2003; Seyfried et al., 2007). Although it is often difficult to quantify the magnitude of Na release from unstable silicate minerals in seawater in light of on-

going hydration effects, Seyfried et al. (2007) showed this clearly by linking the increase in dissolved Na to corresponding changes in pH. Potassium, in contrast, has long been recognized as a so-called “soluble element” in both mafic and ultramafic chemical systems, although the extent to which it partitions into the fluid is considerably better established for basalt than for more ultramafic lithologies. That the Lost City vent fluids reveal such a small increase in potassium concentration relative to seawater (within analytical error) provides qualitative evidence of a relatively high fluid/rock mass ratio attending subseafloor exchange reactions, and/or an appreciably low K concentration in the protolith.

Endmember Ca in the Lost City vent fluids is clearly elevated relative to seawater (Table 1, 2; Fig 4b). In general, the data reported here are consistent with analogous data reported earlier by Kelley et al. (2001). Owing to the relative abundance of clinopyroxene (Cpx) in mantle peridotite, Mg (seawater derived) for Ca (rock derived) exchange accounts best for the observed increases in dissolved Ca, as follows:

The dissolved silica produced can be expected to be controlled by coexisting alteration reactions involving these and other silicate minerals. Numerous experimental and theoretical peridotite alteration studies at a range of temperatures and pressures support variants of reaction (1) (Allen and Seyfried, 2003, 2005; Berndt et al., 1988; Janecky and Seyfried, 1986; Klein et al., 2013; Seyfried et al., 2007). Because of chemical and physical conditions intrinsic to the Lost City hydrothermal system it can be inferred that diopside, tremolite, anhydrite, and perhaps even plagioclase (see below) can affect Ca solubility, each mineral precipitating and/or dissolving with reaction progress between seawater derived aqueous fluid and a largely ultramafic protolith. We cannot, however, rule out reactions involving a wide range of other Ca-bearing primary and secondary mineral that may also play a role at some stage in the chemical evolution of dissolved Ca in Lost City vent fluids (Beard and Hopkinson, 2000; Klein et al., 2013).

4.1.3 Trace elements

Trace alkali elements in basalt hosted hydrothermal systems have long been recognized for their lack of solubility control, especially at elevated temperatures (Berndt and Seyfried, 1990; Pester et al., 2008; Seyfried et al., 1984). At Lost City these elements show clear enrichment relative to seawater, though the magnitude differs for each element (Fig. 5a-c). As with many other components measured in the Lost City vent fluids, no significant differences can be discerned for the trace alkali elements between the BH and M6 in keeping with a common source. This is also true of dissolved Sr, which shows slight increases relative to seawater (Fig. 5d), consistent with data previously reported by Ludwig et al. (2006) in connection with their study of the chemical and mineralogical evolution of the carbonate chimneys at Lost City. Importantly, Foustoukos et al. (2008) combined the Sr concentration and isotope data with the reaction path model of Berndt et al. (1988) to calculate a fluid/rock mass ratio of 2-4 for the Lost city hydrothermal system. If the trace alkali elements in the Lost City vent fluids are extracted quantitatively from a depleted mantle source (Salters and Stracke, 2004), fluid/rock mass ratios of approximately 5, 0.6, and 0.9 can be estimated from the observed enrichments (relative to seawater) of Li, Cs and Rb, respectively. An extraction efficiency of less than 100%, however, would result in lower values, as is typically the case for Li. For example, both basalt alteration experiments and data from exposed dikes at Hess Deep exhibit only 50 - 70% Li removal from the rock (Brant et al., 2012; James et al., 2003; Seewald and Seyfried, 1990; Seyfried et al., 1984). Assuming similar Li solubility constraints for Lost City, associated fluid/rock ratios are lower (2.5 - 3.5), and therefore consistent with the range of values predicted by Sr isotopes. While their extraction efficiencies are indeed higher than that of Li, the low fluid/rock ratios estimated using Cs and Rb still contrast sharply with those predicted by both Li and Sr. One interpretation is that there exists sources of Cs and Rb in amounts greater than typical of depleted mantle. For example, basalts from the nearby Lucky Strike seamount (37°N) exhibit typical (MORB) bulk Li concentrations, yet they are highly enriched in Rb and Cs, having average Rb/Li and Cs/Li ratios approximately 10 times higher (max ~20x) than normally observed (Pester et al., 2012). Though we do

not suggest any connection with the Lucky Strike regime, these data nonetheless demonstrate the existence of a protolith uniquely enriched to a degree that can possibly explain the trace alkali ratios in Lost City vent fluids.

Although there are uncertainties with estimating the relative mobility of trace elements, especially when dealing with an inferred composition of mantle rocks, reliance on constraints imposed by the actual endmember concentrations of mobile elements and isotopes of elements (Sr) in Lost City vent fluid is advantageous in this regard. Estimates of fluid/rock mass ratio based on the chemical and/or isotopic composition of rock samples obtained by dredging are similarly useful, but measure the end-product or integrated effects of potentially long-lived hydrothermal activity that could vary in space and time. The integrated fluid/rock ratios based on Sr and Nd isotopes measured for rocks recovered from the southern Atlantis Massif, for example, are substantially higher than those based on geochemical data from the active (present-day) stage of metamorphism resulting in Lost City vent fluid chemistry (Boschi et al., 2008; Boschi et al., 2006; Delacour et al., 2008b). Thus, the very different conclusions reached in terms of alteration temperature and/or fluid/rock mass ratio based on the two different perspectives (altered rock or fluid composition) are not altogether surprising.

Boron in Lost City vent fluids is well below seawater values with the two vent sites virtually indistinguishable with respect to their endmember concentrations (Fig. 6). This is consistent with previously reported data (Boschi et al., 2008; Foustoukos et al., 2008; Kelley et al., 2001; Kelley et al., 2005). This is also consistent with results of experimental peridotite alteration studies at a wide range of temperatures and pressures, which have long confirmed B solubility limits in fluids coexisting with hydrous magnesium silicates, such as serpentine (Janecky and Seyfried, 1986; Seyfried and Dibble, 1980; Seyfried et al., 2007). The relatively high pH that attends peridotite alteration by seawater, especially at low to moderate temperatures, likely plays a key role in B uptake by serpentine and coexisting hydrous silicates. That is, pH governs the coordination chemistry of dissolved boron with the trigonal ($\text{B}(\text{OH}_3)$) and tetragonal ($\text{B}(\text{OH})_4^-$) species dominating at relatively low and high pH, respectively (Palmer et al.,

1992; Palmer et al., 1987; Spivack and Edmond, 1987). Thus, the incorporation of boron in serpentine likely entails borate species replacing silicon in the crystal lattice, as opposed to simple adsorption. Not surprisingly, serpentinized peridotite samples recovered by submersible in the vicinity of the Atlantis Massif are enriched in boron (Boschi et al., 2008). Moreover, boron removal from seawater during serpentinization is positively correlated with $\delta^{11}\text{B}$, while showing little or no correlation with $\delta^{18}\text{O}$, adding strength to the argument that B uptake is largely controlled by the prevailing pH conditions in the seafloor reaction zone at Lost City (Boschi et al., 2008; Foustoukos et al., 2008).

4.1.4 Dissolved silica

In contrast with virtually all other elements, dissolved silica in Lost City vent fluids shows a relatively complex range of concentrations, yielding different endmembers for the two sites sampled (Table 1, 2 and Fig. 7). For example, the endmember Si concentration in fluids diffusively venting from the M6 site is similar to background seawater ($\sim 25 \mu\text{mol/kg}$) in spite of moderately high temperatures ($\sim 75\text{--}78^\circ\text{C}$) and the absence of seawater mixing effects for all but the one failed M6 sample. In sharp contrast with M6, hydrothermal fluid venting more vigorously from the Beehive (BH) structure is characterized by Si concentrations approximately 3 times greater than seawater, with a maximum of $94 \mu\text{mol/kg}$. Although these Si concentrations might be interpreted as low, especially in comparison with basalt hosted hydrothermal systems (Butterfield et al., 2003; Von Damm, 1995, 2000; Von Damm et al., 1998), higher values should not be expected for fluids coexisting with ultramafic minerals and their hydrous alteration products at low to moderate temperatures (Allen and Seyfried, 2004; Frost and Beard, 2007). Furthermore, the data for dissolved Si provide information critical to the accurate interpretation of the chemical evolution of the Lost City vent fluids. The relatively low Si concentrations of fluids venting from M6, for example, may reflect the effect of longer residence times along fluid flow path in the subsurface with the potential for Si removal by re-equilibration processes. That M6 vent fluids are also cooler is consistent with such an interpretation, since the lower temperature could be expected to decrease Si solubility. The higher Si concentrations expressed in BH vent fluid are in keeping with better

preservation of Si buffering reactions directly associated with the subseafloor source conditions, although, even here, Si loss cannot be ruled out entirely. As emphasized below, the Si concentrations of both vent fluids, but especially BH, are well in excess of those likely if controlled by the coexistence of brucite-serpentine-diopside, an alteration assemblage often associated with serpentinization of mantle peridotite (Frost and Beard, 2007; Janecky and Seyfried, 1986; McCollom and Bach, 2009; Palandri and Reed, 2004; Seyfried et al., 2007; Wetzel and Shock, 2000). Thus, the moderately high dissolved silica in conjunction with trace alkali element concentrations, especially dissolved Cs and Rb, point to the existence of subseafloor reactions at Lost City considerably more complex than would be suggested by simple olivine hydrolysis.

4.1.5 Dissolved gases

One of the more interesting and important aspects of the Lost City hydrothermal system is the high concentrations of dissolved H_2 and CH_4 in the endmember vent fluids (Bradley et al., 2009; Kelley et al., 2001; Kelley et al., 2005; Lang et al., 2010; Proskurowski et al., 2008; Proskurowski et al., 2004; Proskurowski et al., 2006; Seewald et al., 2006). All of the fluid samples reported here similarly show high H_2 and CH_4 concentrations, providing additional time series data bearing on the geochemical stability of the hydrothermal system (Table 1, 2, Fig. 8). The high H_2 concentrations are almost certainly a result of olivine hydrolysis with H_2 buffering likely provided by the coexistence of Fe bearing serpentine and magnetite (Frost and Beard, 2007; Klein et al., 2009; Klein et al., 2013; McCollom and Bach, 2009; Seyfried et al., 2007; Sleep et al., 2004). The noteworthy concentrations of dissolved CH_4 might be linked to H_2 by abiotic synthesis, but also to microbial metabolism, especially for fluids that vent less vigorously from seeps throughout the vent field (Konn et al., 2009; Lang et al., 2010; Lang et al., 2013; Proskurowski et al., 2006). The focused flow fluids at Lost City, however, provide clearer insight into deeper and higher temperature reactions, and an abiotic origin of methane and other low molecular weight hydrocarbons (Bradley et al., 2009; Lang et al., 2012; Proskurowski et al., 2006). The distinct “inverse” trend in stable carbon and hydrogen isotopic composition of C_1 to C_4 hydrocarbons is

consistent with FTT synthesis. Radiocarbon data suggest mantle-derived inorganic carbon is the source of carbon for methane synthesis as opposed to seawater derived bicarbonate (Proskurowski et al., 2006).

4.2 Geochemical Modeling and Phase Equilibria Constraints at Lost City

Geochemical modeling of peridotite alteration by seawater and other aqueous fluids has long been used to illustrate the effect of temperature, mineral composition, or fluid/rock mass ratio on the chemical and mineralogical evolution of peridotite, peridotite alteration minerals, and the composition of the coexisting aqueous phase (Allen and Seyfried, 2003; Alt and Shanks, 2003; Foustoukos et al., 2008; Janecky and Seyfried, 1986; Klein et al., 2013; Ludwig et al., 2006; McCollom and Bach, 2009; Palandri and Reed, 2004; Wetzel and Shock, 2000). Results of such simulations have provided critical insight on: (1) The role of temperature and peridotite composition on H₂ generation that can be linked to alteration mineral pathways, microbial metabolism, and organic synthesis (Amend et al., 2011; Klein et al., 2013; McCollom and Bach, 2009; Seewald et al., 2006); (2) The effect of mixing between seawater and hydrothermal fluid buffered by peridotite alteration products on the formation and mineralogical evolution of carbonate hosted chimney deposits at Lost City and elsewhere (Allen and Seyfried, 2004; Ludwig et al., 2006; McCollom and Bach, 2009); and (3) The effectiveness of peridotite alteration products (e.g., brucite, serpentine, diopside) in buffering aspects of the fluid chemistry at a range of temperatures and fluid/rock mass ratios applicable to the Lost City hydrothermal system. It is this third point that is of most interest to us here, especially regarding the dissolved silica concentrations.

To assess phase equilibria controls on dissolved silica and/or other components in Lost City vent fluids it is necessary to calculate the distribution of aqueous species at conditions applicable to LCHF. The thermodynamic database for aqueous species and minerals used for this was created using the DBCreate software package (Kong et al., 2013). These data are largely consistent with the standard SUPCRT92 dataset (Johnson et al., 1992; Sverjensky et al., 1997; Tutolo et al., 2014), with exceptions outlined in other geochemical modeling studies that take advantage of more recent experimental data (Allen and Seyfried, 2004; Foustoukos et al., 2008; Seyfried et al., 2007; Seyfried et al., 2010; Tutolo et

al., 2014). Ion activities for charged species were calculated using the extended form of the Debye Hückel equation as described by Helgeson (1969) and Helgeson and Kirkham (1974). The activity coefficients for all uncharged species, however, were taken to be unity (Helgeson, 1969; Helgeson et al., 1981; Tutolo et al., 2015). Model calculations were conducted at temperatures less than or equal to 200°C, largely in keeping with constraints imposed by the mineralogical and isotopic composition of dredged samples at or near the Lost City vent field, as well as the chemical and isotopic composition of the vent fluids. (Allen and Seyfried, 2004; Boschi et al., 2008; Foustoukos et al., 2008; Früh-Green et al., 2003; Proskurowski et al., 2008). All temperatures estimated from chemical and isotopic geothermometers exceed measured exit temperatures of the Lost City vents, which strongly suggests the fluids cool conductively on ascent to the seafloor (Allen and Seyfried, 2004), a characteristic in keeping with most other hydrothermal vent fluids at mid-ocean ridges (Pester et al., 2014; Pester et al., 2012). The subseafloor pressure at Lost City is difficult to constrain owing to fluid circulation pathways made possible by detachment related tectonics. However, the recent observation that fluid circulation is limited below 750 m within the Atlantis Massif (Blackman et al., 2014) may be used in the absence of other data to constrain total hydrostatic pressure to 150 bars, as was done here. Nevertheless, at low to moderate temperatures (e.g., 200°C) variation in pressure will not significantly affect results of phase equilibria calculations (Tutolo et al., 2014). Thus, even somewhat deeper circulation would not cause significant variability in the predicted composition of vent fluid chemistry at Lost City.

It is well known that olivine has no field of stability in aqueous fluids at low to moderate temperatures and pressures. Thus, given sufficient time, it will be replaced completely by serpentine (chrysotile) plus brucite, as follows:

Taking explicit account of constraints imposed by distribution of aqueous species calculations, the activity of dissolved silica can be calculated as a function of temperature assuming chrysotile-brucite coexistence (Fig. 9). As expected, dissolved silica concentrations are predicted to be extremely low at all

temperatures, and do not exceed 5 $\mu\text{mol/kg}$, even at 200°C. Furthermore, silica activity (in reference to Eq. 2) is unaffected by the potential stability of diopside at chemical and physical conditions relevant to the Lost City hydrothermal system (Allen and Seyfried, 2004), although this does affect pH (see below). The maximum silica concentration measured in the Beehive vent fluids, however, precludes definitively the participation of brucite in buffering aqueous silica, favoring instead an alteration assemblage more consistent with tremolite-chrysotile-diopside at approximately 180°C (Fig. 9). This temperature is broadly consistent with the predicted range of other chemical and isotopic geothermometers that have been applied to the Lost City vent fluids, including anhydrite-fluid equilibria (Allen and Seyfried, 2004; Lang et al., 2012) and serpentine-fluid oxygen isotope data (Foustoukos et al., 2008). Our more recent data for the Lost City vent fluids, in particular dissolved Ca and sulfate concentrations, while taking explicit account of recent revisions to thermodynamic data for aqueous species (Tutolo et al., 2014), suggests a temperature of ~180°C based on anhydrite-fluid equilibria (Fig. 9). In all cases, however, variation is still likely owing to existing uncertainties in analytical and thermodynamic data used for mineral solubility calculations, as well as the unsettled fractionation factors for oxygen isotope data for the serpentine-fluid system. It is for this reason that 200 $\pm$ 50°C is most often expressed for the temperature range of subseafloor reactions that contribute most directly to the formation of the Lost City vent fluid at present (Allen and Seyfried, 2003; Allen and Seyfried, 2004; Boschi et al., 2008; Boschi et al., 2006; Foustoukos et al., 2008).

As noted above, the instability of brucite in the subseafloor reaction zone at Lost City is best illustrated by plotting the Beehive endmember composition within an aqueous activity diagram (200°C and 150 bars), taking explicit account of the distribution of species in the CaO-MgO-SiO₂-NaCl-HCl-H₂O system. Fig. 10 thus shows $a\text{Ca}^{++}/a^2\text{H}^+$ as a function of dissolved silica ($a\text{SiO}_{2(\text{aq})}$) for these two limiting cases: one where chrysotile and diopside coexist with brucite; and the other, where chrysotile and diopside coexist with tremolite. The difference in $a\text{SiO}_{2(\text{aq})}$ for these two limiting conditions results in a change of approximately three orders of magnitude in $a\text{Ca}^{++}/a^2\text{H}^+$, with important implications for pH, at

both reaction zone conditions and when the fluids cool on ascent to the seafloor. For example, the pH (200°C) of fluid buffered by brucite-chrysotile-diopside and tremolite-chrysotile-diopside is 8.12 and 7.12 respectively. The 25°C equivalents of these fluids would also differ by approximately a full pH unit, such that the brucite bearing system could be expected to achieve measured pH values as high as ~11.5, while this would be ~10.5 for the tremolite bearing system (Fig 11). Foustoukos et al. (2008) performed similar calculations with similar results, but their lack of information about dissolved silica in Lost City vent fluids precluded consideration of a “brucite out” scenario.

The Si concentrations of the M6 (diffuse flow) fluids are virtually indistinguishable from local bottom seawater (~25 $\mu\text{mol/kg}$), but still in excess of that predicted for serpentine-brucite-diopside equilibria at all applicable temperatures (Fig. 9). If we assume these fluids were at one time also in equilibrium with the tremolite-chrysotile-diopside assemblage at a temperature similar to that indicated by Beehive, then it is clear the M6 vent fluids lost Si on ascent to the seafloor (see below). One process that might account for the loss of Si from M6 vent fluid could entail serpentinization of brucite in the chimney structure through which these fluids diffusively vent. If such were the case, however, serpentine would be abundantly present in these deposits, and this seems not to be the case (Ludwig et al., 2006), implicating reactions at greater depth beneath the seafloor.

4.2.1 Compositional controls on hydrothermal alteration reactions at the LCHF

The mechanism by which brucite is rendered unstable in the hydrothermal reaction zone at Lost City could be accounted for by interaction of mantle peridotite with fluids rich in silica from previous reaction with gabbro, the abundance of which is well known in and around the south wall of the Atlantis Massif (Boschi et al., 2008; Boschi et al., 2006). Indeed, based on careful studies of hydrothermally altered peridotite and gabbro, these investigators confirmed from major and trace element data that there potentially exists interaction between gabbroic and ultramafic rocks. Thus, a form of silica metasomatism could facilitate the replacement of a brucite bearing alteration assemblage by one containing tremolite. In a somewhat similar way, the composition of the putative peridotite in the subseafloor at Lost City may

not be typical of mantle rocks, and could contain zones of peridotite into which were intruded mafic melt lenses and/or chemically evolved gabbroic bodies. Abyssal peridotites cut by gabbro, for example, have often been reported in rocks dredged from mid-ocean ridges (Cannat et al., 2010; Cannat et al., 1997b; Constantin, 1999; Miller et al., 2004), with the peridotite and gabbro correspondingly modified in composition to an extent that reflects the chemical and physical conditions of melt/gabbro impregnation of the host peridotite. This same association has also been recognized for peridotite recovered from holes U1309B and U1309D at the Atlantis Massif, here referred to as “plagioclase peridotite” (Tamura et al., 2008). Somewhat similar associations have also been reported for lithologies recovered from the southern wall of the Atlantis Massif (Boschi et al., 2006), indicating that reaction of seawater with plagioclase (gabbro) bearing peridotite could be the key to the elimination of brucite, with silica mobility being an effect, not a cause.

To examine this possibility we conducted a simple reaction model in which unaltered seawater was incrementally added to 1 kg peridotite of harzburgite composition (Janecky and Seyfried, 1986; McCollom and Bach, 2009) at 200°C and 150 bars, while plagioclase (An₈₀) was simultaneously reacted. The GWB software package supported with thermodynamic data for minerals and aqueous species as described previously was used for the simulation (Fig. 12). As expected, the complete lack of stability of olivine and orthopyroxene at the conditions used for the model results in formation of serpentine (chrysotile) and brucite in amounts generally equivalent to the mass of the sum of olivine and orthopyroxene. Clinopyroxene (diopside), is stable throughout the simulation in a manner consistent with previous models of this sort (Allen and Seyfried, 2004; Foustoukos et al., 2008; Jøns et al., 2010; Klein et al., 2013; McCollom and Bach, 2009; Palandri and Reed, 2004). With the simultaneous addition of plagioclase into the system, however, chlorite forms from serpentine and brucite. When the addition of plagioclase achieves approximately 100 grams, which is roughly equivalent to 10% of the initial peridotite (Ol + OPx + CPx), brucite is eliminated as a component, being replaced by chlorite, anhydrite, and tremolite. Owing to mass balance constraints, Mg-alteration mineral products are dominated by

serpentine, but these also now include approximately 10% chlorite, and considerably lesser quantities of tremolite and diopside (Fig. 12a). Although tremolite and diopside are relatively minor in overall abundance, their formation is critical to pH buffering (Figs. 9-11).

The elimination of brucite with addition of plagioclase not only permits the formation of tremolite, but also allows silica to increase (Fig. 12b). With the increase in silica, Mg and Al are predicted to increase and decrease respectively, although both of these species are maintained by phase equilibria at similarly low concentrations. Owing to analytical/sampling limitations, such minor differences cannot be resolved in the vent fluid chemistry. The model results support the hypothesis that alteration of relatively small amounts of plagioclase which occurs simultaneously with serpentinization of olivine and orthopyroxene can account for the noteworthy concentrations of dissolved silica observed for the Lost City vent fluids by rendering brucite unstable, while Mg-chlorite and tremolite are predicted to form in its place. It is important to emphasize that our simple choice of An₈₀ plagioclase to represent any potential micro and macro-scale melt penetrations into peridotite will necessarily fail to produce the full range of variability observed in natural systems. If the gabbro crystallized from melts that had undergone variable degrees of fractional crystallization, this would then give rise to plagioclase with lower An content, while also being associated with relatively Si-rich pyroxene minerals (Cannat et al., 1997a). Rocks of such enriched composition would have an even greater capacity to eliminate brucite from altered peridotite host rocks during subsequent reaction with aqueous fluids.

The relatively high concentrations of trace alkali elements in Lost City vent fluids, especially Cs and Rb, similarly suggest alteration processes involving rocks other than mantle peridotite alone. Accordingly, alteration of plagioclase formed from melt possibly enriched in incompatible elements such as Cs and Rb might provide an explanation more suitable than alteration of residual peridotite at low fluid/rock mass ratio. As discussed earlier, the former scenario is all the more probable given the presence of such enriched protolith elsewhere along the MAR. This, furthermore, alleviates the need to reconcile

these alkali data in the vent fluids with the Sr isotopic constraints that otherwise predict alteration at a relatively high fluid/rock ratio (Boschi et al., 2008; Foustoukos et al., 2008; Ludwig et al., 2006).

Figure 12b, however, shows that the predicted dissolved silica concentration (~110 $\mu\text{m/kg}$) is slightly, but significantly, in excess of the maximum value measured for the Beehive vent fluid (Fig. 9). Part of this could be attributed to the modeled temperature being in excess of the “real temperature” in the subseafloor reaction zone at Lost City, although it is unlikely that this could account for more than ~20°C, based on constraints imposed by anhydrite-fluid equilibria on endmember dissolved Ca and sulfate concentrations measured for the 2008 vent fluids (Fig. 9). Thus, we need to consider the extent to which dissolved silica may be affected by precipitation/dissolution during ascent to the seafloor where a large thermal gradient is encountered.

4. 3 Reactive Transport Modeling of LCHF fluids

4.3.1 Model formulation

To account for the moderately high silica concentration of BH vent fluids at Lost City, tremolite-diopside-serpentine-fluid equilibria at approximately 180-200°C is proposed. That the measured temperature is approximately 100°C less than this temperature, however, has been interpreted as a result of conductive cooling (Allen and Seyfried, 2004; Foustoukos et al., 2008; Seyfried et al., 2007). Assuming this to be the case, it is important to consider additional modeling results that explicitly take into account rates of mineral precipitation and dissolution as a putative 200°C source fluid ascends from depth to the seafloor at Lost City. To accomplish this, we performed 1-dimensional reactive transport simulations with the PFLOTRAN reactive-transport code (Hammond et al., 2012). The depth of the 1-dimensional upflow model was set at 750 m below seafloor, in a manner consistent with constraints imposed by thermal observations from the Atlantis Massif (Blackman et al., 2014). Thus, the base of the system is given a fixed temperature and pressure of 200°C and 150 bar. No heat or fluid flow is allowed through the sides of the domain, and the thermal gradient along the flow pathway is fixed by the inferred source fluid temperature (200°C) and maximum measured BH vent temperature (116°C). The 200°C

fluid at the base of the modeled domain is less dense than the overlying fluid and therefore rises to the surface through buoyancy-driven flow. The upflowing fluid thereby evolves in both temperature and pressure as it travels upward through the domain, and, to account for this evolution, a thermodynamic database with equilibrium constants calculated along the steam saturation curve was employed for the PFLOTRAN simulations. Because the mineral-fluid and aqueous complexation equilibrium constants in this PFLOTRAN database are slightly different than those used in the calculations discussed above, slight (but insignificant) differences between the calculated pH and $\text{SiO}_2(\text{aq})$ concentrations are apparent within the calculated results.

As discussed above, fluids flowing through the Atlantis Massif and feeding the LCHF appear to be controlled by normal faults developed during uplift. Fluid flow within fractured rock tends to be dominated by flow within the fractures, which generally have considerably higher permeability than the unfractured matrix. Accordingly, measurements of permeability in igneous oceanic crust show a strong scale dependency, with larger-scale measurements generally giving higher permeability measurements due to their ability to capture these characteristic features (Becker and Davis, 2003). Discrete modeling of fluid flow within fractures is substantially more computationally intensive than standard continuum modeling and subject to considerable uncertainties due to the inability to characterize fracture spacing and geometry at the appropriate scales. Nonetheless, continuum models have been shown to effectively capture fluid flow, geochemical reactions, and solute fluxes within fractured media, provided that the right parameterizations are employed (Neuman, 1988; Pruess et al., 1990).

Recent 3D, continuum-scale numerical simulations of fluid flow in the Atlantis Massif and LCHF have constrained the permeability of the upflow zone feeding the LCHF to be on the order of 10^{-14} to 10^{-15} m^2 (Titarenko and McCaig, 2014). Three permeabilities spread over this range (1×10^{-15} , 5×10^{-15} , and $1 \times 10^{-14} \text{ m}^2$) were employed in the PFLOTRAN simulations. In all simulations, porosity was set to 0.02, which is consistent with values measured from drill cores sampled from the Atlantis Massif (Blackman et al., 2006). Two additional “end-member” simulations were run in order to examine the extent of

permeability and kinetic effects on observed fluid chemistry: 1) full fluid-mineral equilibration as the fluid flows upwards towards the surface, and 2) “conductive cooling,” wherein the fluid flows from the deep subsurface to the seafloor in the complete absence of mineral dissolution/precipitation processes. Both of these “end-member” simulations are independent of permeability (i.e. neither involve kinetic constraints), and only depend upon the thermal gradient of the upflow zone.

Kinetic parameters for minerals included in the reactive transport simulations were obtained from the literature (Table 3), and reactive surface area of all phases was set to $0.26 \text{ cm}^2/\text{g}$, which is consistent with the 0.7 m fracture spacing (Kelemen et al., 2011; Paukert et al., 2012). Due to a lack of appropriate parameterizations at the temperature, pressure, and pH conditions of our simulations, the pH dependence of mineral-fluid reaction rates (Lasaga, 1998) was not explicitly considered. To remain consistent with the mineral assemblage that we have inferred to buffer fluid chemistry (Fig. 10), the upflow zone was assumed to be comprised of equal parts diopside, chrysotile, and tremolite. The simulated results are insensitive to the modal abundance of these phases, and, regardless of their volume fraction, all minerals listed in Table 3 were allowed to dissolve or precipitate in all model runs. In addition, the saturation states of brucite and talc were monitored, but neither of these phases became supersaturated in any of the reported simulations. Fluids entering the bottom boundary were chemically equilibrated with the diopside-tremolite-chrysotile-anhydrite assemblage at 200°C , as discussed above (Sect. 4.2).

4.3.2 Results of reactive transport simulations

The results of the reactive transport simulations show that interaction of the upflowing fluid with the proposed Si-controlling diopside-tremolite-chrysotile buffer assemblage during ascent to the seafloor is consistent with the observed BH end-member fluid chemistry (Fig. 13). As expected, the lowest permeability simulations behave most similarly to the “full equilibrium” end-member, and the highest permeability simulations behave most similarly to the “conductive cooling” end member, due to the durations of fluid-rock interaction permitted by the assigned value of permeability. Accordingly, if the characteristic permeability of the upflow zone were lower than $1 \times 10^{-15} \text{ m}^2$ or higher than $1 \times 10^{-14} \text{ m}^2$, the

calculated chemistry would approach the “full equilibrium” and “conductive cooling” scenarios, respectively.

The simulated seafloor Si concentrations for all scenarios except pure conductive cooling are within the measured range (Table 1), and the permeability that produces Si concentrations that most closely match end-member BH Si concentrations is $5 \times 10^{-15} \text{ m}^2$. Together, these results strongly suggest that the fluids likely undergo at least some degree of fluid-rock interaction during ascent to the sea floor. Notably, the largest changes to Si concentration occur below ~200 mbsf, and the Si concentrations remain basically constant between that depth and the sea floor (Fig. 13C). The relative lack of Si-changing reactions above ~200 mbsf suggests that venting fluids are recording Si concentrations obtained at temperatures greater than ~140-150°C, and that below this temperature the kinetics of the fluid-mineral reactions are sufficiently slow to prevent significant changes in the Si concentrations observed at the seafloor.

The calculated pH of the vent fluids is subject to unique uncertainties relative to the Si concentration, particularly due to uncertainties attending the calculation of the pressure and temperature dependence of the aqueous complexation reactions. Although all calculated values of pH are generally quite similar, the end-member BH $\text{pH}_{25^\circ\text{C}}$ is most closely matched by the “full equilibration” scenario. This result, alongside that for Si above, implicates permeabilities on the lower end of those put forth by Titarenko and McCaig (2014). These pH values are generally quite high, which would tend to increase mineral-fluid reaction rate constants relative to near-neutral values.

Because some degree of uncertainty attends our inferred equilibration temperature and other researchers (Kelley et al., 2001; Kelley et al., 2005; Lang et al., 2012) have suggested somewhat lower temperatures of equilibration, it is important to discuss the potential implications of a lower-temperature equilibration on potential subseafloor flow properties at LCHF. The Si concentration of a fluid in equilibrium with the diopside-tremolite-chrysotile assemblage decreases from ~110 $\mu\text{mol/kg}$ to ~64 $\mu\text{mol/kg}$ between 200°C and 116°C (Fig. 13C). In our model, therefore, lower bottom boundary

“equilibration temperatures” would require a higher upflow zone permeability in order to preserve the relatively high end-member Si concentrations observed in the BH vent fluids. However, if the depth of the upflow zone is less than 750 m, or if the temperature of equilibration is at a temperature low enough for Si-depleting reactions to become sufficiently ineffective at removing Si from solution, lower up-flow zone permeability is possible.

The similarity of all components except Si between the BH and M6 end-member chemistries (Table 2) indicates that the two fluids are derived from a similar source at depth. The lower measured temperature, and the diffusive nature of the M6 fluids, are the only constraints we might use to hypothesize a reason for the lower silica concentrations. A number of reactions could potentially explain how ~50 $\mu\text{mol/kg}$ Si were removed from the M6 fluids without substantially affecting any other chemical components in the fluid. The simplest explanation would be partial or complete re-equilibration with the inferred chrysotile-diopside-tremolite buffer attending increased residence time in the upflow zone (Fig. 9). Another possible explanation noted earlier, is the reaction of previously formed brucite, which is known to exist in the chimney structures at LCHF (Ludwig et al., 2006). Both mechanisms nonetheless require the formation of a hydrous silicate phase, which is predicted to be kinetically prohibitive at temperatures below ~150 °C (Fig. 12). This is in spite of the fact that our calculations predict saturation maxima ($\log Q/K \sim 3-9$) for serpentine/tremolite around 80 -100 °C. Thus, barring any microbial involvement, it is possible the kinetic model does not sufficiently account for the unusually high pH of the Lost City vent fluids. Indeed, because insufficient data exist to include a pH dependency in our calculations of mineral-fluid reaction rates, the rates we calculate may be relatively slow compared to those expected at the relatively high pH associated with Lost City fluids. Renewed experimental effort into determining the pH dependency of the kinetics of diopside-chrysotile-tremolite reactions would help to place tighter constraints on reactive transport processes within the Atlantis Massif.

5. SUMMARY AND CONCLUSIONS

We report the chemistry of hydrothermal fluid issuing from two vent sites sampled at the Lost City hydrothermal field in 2008. In addition to extending time series observations, these data provide previously unreported information pertinent to the chemical evolution of this unique type of hydrothermal system. For previously measured components, the present dataset suggests little change, confirming the relative stability of heat and mass transport processes for the Lost City system. In general, the two vent sites studied show extensive overlap in the direction and magnitude of chemical changes relative to seawater, suggesting a common source fluid is feeding both sites. We also document previously unrecognized alteration processes affecting fluid chemistry issuing for both sites. Specifically:

1. Despite the clear influence of ultramafic lithologies, dissolved silica concentrations are considerably higher than predicted for equilibria involving serpentine-brucite coexistence at all reasonable temperatures. Geochemical modeling indicates these values are consistent with buffering by the following reaction:

We hypothesize that the silica for the Lost City vent fluids need not be provided from an external source, but rather can be derived directly by reaction of a gabbroic plagioclase component intruded into the peridotite host rocks, as observed here and elsewhere. Aluminum and silica released from plagioclase alteration renders brucite unstable, while enhancing formation of tremolite and chlorite. In addition to accounting for the silica in BH vent fluid, pH is also buffered at a value consistent with measurement (in-situ and at 25°C), when the activity of dissolved Ca is explicitly taken into account.

2. The dissolved concentration of Cl indicates a slight depletion relative to seawater. There are a number of processes that can account for this, including Cl uptake by serpentine and other hydrous alteration phases, as well as dehydration effects caused by the replacement of brucite by serpentine.
3. Assuming a depleted mantle protolith, dissolved concentrations of trace alkalis (Cs and Rb, in particular) predict an unusually low fluid/rock mass ratio, in contrast with constraints imposed by

other chemical and isotopic data. As with silica and pH buffering reactions, however, these data may also be accounted for by the localized presence and hydrothermal alteration of plagioclase in gabbro.

4. Reactive transport modeling taking explicit account of temperature dependent mineral reaction rates, and permeability values inferred for the Lost City hydrothermal field, suggest dissolved silica concentrations can be expected to decrease on ascent to the seafloor within a narrow range of temperature and permeability, and still account for the BH vent fluid chemistry and temperature. The relatively low dissolved silica concentrations observed for the M6 vent fluid, however, cannot be accounted for by changes in temperature or permeability. Partial re-equilibration attending increased cooling and residence time during upflow is still the best explanation, suggesting kinetic parameters do not sufficiently account for the high pH of the fluids.

The Lost City hydrothermal system likely represents one of many similar systems associated with hydrothermal alteration at slow spreading ridges, where tectonic processes permit seawater derived fluids to interact with lower crustal lithologies in the shallow footwall of detachment faults. It is only with continued discovery of such systems and application of quantitative tools and new modeling approaches that the origin and evolution of these and related system will become apparent.

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8. FIGURE CAPTIONS

Fig. 1. Lost City Hydrothermal Field (LCHF) adapted from Kelley et al. (2005) showing location on the southern wall of the Atlantis Massif (A) (Blackman et al., 2006; Blackman et al., 2014; Kelley et al., 2001; Kelley et al., 2005). The symbol “B” on this illustration marks the approximate location on the south wall of the Lost City vent system. Bathymetric map of the Lost City Hydrothermal Field showing vent locations (B). The symbols highlight vents 3, 6, C and Beehive (BH), located near the center of the field (“B”). Owing to overall cruise objectives, BH and M6 vent fluids were repeatedly sampled, providing a more complete measure of the effect of the full range of sampling related variability that can contribute to the reported concentrations of hydrothermal vent fluid chemistry at these two sites. The figure was kindly provided by Dr. Deborah Kelley.

Fig. 2. Hydrothermal vent fluid being sampled with isobaric gas tight samplers (Seewald et al., 2002) at Beehive structure, southern Atlantis Massif. This location (see Fig. 1) is one of the few areas of focused flow from which hydrothermal fluid could be effectively acquired owing to convenient access to the vent orifice. In many other areas, hydrothermal fluid vented more diffusively from carbonate-hosted structures, enhancing the likelihood of seawater entrainment. Vent fluid temperatures measured at this location were in the vicinity of $\sim 90^{\circ}\text{C}$, although temperature data for one sample recovered from this site indicated a temperature of 116°C .

Fig. 3. Dissolved sulfate (A) and chloride (B) in LC vent fluids plotted against dissolved Mg, which is an indicator of seawater entrainment. Thus, hydrothermal endmember for these and other components is calculated from the Y intercept of the regression line. Bottom seawater sampled at LC is indicated by the triangle (blue). One of the 2 samples at the “M vent site” (red circle) actually acquired seawater owing to an unfortunate offset separation of snorkel and the routinely attached thermocouple. Thus, we were measuring a fluid temperature different than that which was sampled. All of the hydrothermal vent fluids sampled at the beehive vent (black square) and the one other sample from M6 reveal very low concentrations of Mg and general agreement in the regressed endmember concentrations of dissolved

sulfate and chloride. Although low dissolved sulfate concentrations are typical of hydrothermal vent fluids at mid-ocean ridges, for the vents sampled, the endmember concentration is well above zero, in keeping with anhydrite buffering (see below). The depletion in dissolved Cl relative to seawater (B) is a more surprising discovery, and rarely encountered, especially in the absence of phase separation effects, which can be ruled out in this case (see text).

Fig. 4. Endmember concentrations of dissolved Na (A) and Ca (B) in Lost City hydrothermal vent fluids and local bottom seawater. See text and Fig. 3 for additional details.

Fig. 5. Endmember concentrations of Cs (A), Rb (B), Li (C) and Sr (D) in LC hydrothermal vent fluids and local bottom seawater. See text and Fig. 3 for additional details.

Fig. 6. Endmember concentration of dissolved boron in LC hydrothermal vent fluid and local seawater. See text and Fig. 3 for additional details.

Fig. 7. Endmember concentrations of dissolved silica in LC vent fluids and local seawater. Unlike other components, distinct differences exist between fluids at the two vent sites, apparently due to differential effects of cooling and reaction. The diffusively venting M6 site fluid conductively cools to temperatures near 50°C, apparently allowing the fluids to lose silica by reaction. This seems not to be the case for the beehive (BH) vent fluids, which are enriched in silica by a factor of approximately 3 relative to seawater and the M6 site vent fluids. See text and Fig. 3 for additional details. It is important to note that even the silica in seawater is well in excess of that predicted for brucite-serpentine equilibrium, suggesting sources of silica from lithologies other than peridotite. This is an important finding with implications for heat and mass transfer reactions at LCHF and other ultramafic-hosted hydrothermal systems.

Fig. 8. Endmember concentrations of H_2 (A) and CH_4 (B) in LC hydrothermal vent fluids and local bottom seawater (See text and Fig. 3 for additional details).

Fig. 9. Predicted concentrations of dissolved silica as a function of temperature for two reactions often implicated as a means of controlling Si in ultramafic-hosted hydrothermal vent fluid systems. The first reaction, which is capable of buffering silica at relatively high values, involves the coexistence of chrysotile-tremolite-diopside-fluid, while the second is more typical of peridotite-seawater interaction where olivine and orthopyroxene hydrolysis give rise to chrysotile-brucite-diopside. This reaction has long been recognized for low silica concentrations, as shown. For comparison, the maximum dissolved silica measured for BH vent fluid is shown suggesting control by the high-Si buffer reaction. Assuming this to be the case, the dissolved silica of the BH vent fluid suggests a subseafloor temperature of approximately 180°C , which is in good agreement with constraints imposed by anhydrite-fluid equilibria, as illustrated. Somewhat higher and lower temperatures are permissible when uncertainties in analytical and thermodynamic data are taken into account. Dissolved Si for M6 vent fluid is lower than 180°C , consistent with greater reaction on ascent to the seafloor at lower temperatures. Calculations were performed using GWB software ((Bethke and Yeakel, 2012) and thermodynamic data for minerals and aqueous fluids obtained from the SUPCRT92 database with revisions suggested by Tutlolo et al. (2014).

Fig. 10. Activity diagram in the $\text{CaO-MgO-SiO}_2\text{-NaCl-H}_2\text{O-HCl}$ system at 200°C and 150 bars (Bethke and Yeakel, 2012) using thermodynamic data described in section 4.2. Importantly, the relatively high $\log a_{\text{Ca}^{++}}/a_{\text{H}^+}^2$ ratio imposed by the coexistence of chrysotile-diopside-brucite and chrysotile-diopside-tremolite, respectively plays a key role in controlling dissolved silica in ultramafic-hosted hydrothermal systems. The latter mineral-fluid system likely accounts for the relatively high concentration of dissolved silica at Lost City.

Fig. 11. The effect of conductive cooling on pH from an inferred maximum temperature of 200°C to near ambient conditions when pH is buffered by chrysotile-diopside-brucite (black squares), and chrysotile-diopside-tremolite (red circle) – fluid systems, respectively. The measured pH at Lost City (star, and triangle) agree well with the latter chemical/mineralogical system, as does dissolved silica (Fig. 9, 10).

Fig. 12. Reaction path model that simulates the incremental addition of seawater (5 kg) to peridotite (1 kg) at 200°C and 150 bar. The peridotite has a composition consistent with that used by McCollom and Bach (2009) in their study modeling the effect of seawater-peridotite interaction on alteration mineral formation and H₂ generation at a range of temperatures. In contrast with this earlier study, however, mineral solid solutions of stable alteration mineral phases were not included here. Thus, our reference to solid solutions of unstable mineral reactants (e.g., olivine, orthopyroxene) simply serve the purpose of defining mineralogical and chemical mass balances. In addition to seawater, however, the present model allows the simultaneous addition of up to 200 grams of plagioclase (An₈₀). Data show that the reaction of plagioclase with completely serpentinized peridotite effectively removes brucite as an alteration product owing to replacement by chlorite and tremolite (A). Anhydrite, chrysotile, chlorite, tremolite and diopside are present at the end of the simulation. Thus, the reaction of even small amounts of plagioclase can provide sufficient aluminum to change the chemical system and preclude the existence of brucite as a constraint lowering dissolved silica (B). This is an important observation with implications for the interpretation of the chemical evolution of the relatively high silica, high pH Lost City vent fluids. Calculations were performed using GWB software (Bethke and Yeakel, 2012) and thermodynamic data for minerals and aqueous fluids obtained from the SUPCRT92 database with revisions suggested by Tutolo et al (2014).

Fig. 13. Results of 1-dimensional reactive transport simulations of the geochemical evolution of Beehive vent fluids as they ascend from the maximum observed depth of hydrothermal circulation in the Atlantis

Massif (750 m, Blackman et al., 2014) to the sea floor. The thermal profile was fixed as shown in panel A in order to simulate fluid flow between the inferred diopside-tremolite-chrysotile equilibration temperature (200°C) and the maximum observed vent temperature in the Beehive structure (116°C). The evolution of pH (B) and total dissolved silica (C) during fluid ascent to the seafloor was simulated for 5 different scenarios, including full mineral-fluid equilibration; permeabilities of 1×10^{-15} , 5×10^{-15} , 1×10^{-14} m² (representative of the likely range of LCHF upflow zone permeabilities reported by Titarenko and McCaig (2014)) ; and “conductive cooling” (i.e., fluid flow from the deep subsurface to the seafloor with no mineral dissolution/precipitation). It is important to note that the full equilibrium and “conductive cooling” results are independent of permeability and only dependent on the thermal gradient of the upflow zone. The calculated values of pH_{25°C} for each scenario are indicated above panel B, and the end-member silica concentration for the Beehive vent fluids (72.7 μmol/kg- see Table 2) is indicated above panel C. End-member (measured) pH_{25°C} for the Beehive vent fluids is 10.5 (Table 2).

Table 1

Table 1. Dissolved chemistry* of selected vent fluids from the Lost City Hydrothermal Field.

Vent	Sample	T°C	pH (25°)	Cl mm	Br µm	SO4 mm	Mg mm	Na mm	K mm	Ca mm	Sr µm	Li µm	B µm	Rb µm	Cs nm	Si µm	Fe µm	CH4 mm	H2 mm	H2S mm
M6**	J2-361 IGT8	53	7.57	554	831	27.2	52.8	483	10.5	10.9	91	25	415	1.5	5	25.8	-	-	-	-
M6	J2-362 IGT2	75	10.5	541	813	3.64	1.6	494	10.5	26.4	103	43	52	2.8	13	30.5	-	1.22	10.4	0.14
M6	J2-362 IGT4	78	10.5	541	803	3.51	1.3	494	10.5	26.6	102	43	51	2.8	17	24.2	-	1.18	9.9	0.22
BH	J2-360 IGT2	116	10.4	542	844	4.12	1.9	491	10.5	26.5	101	44	50	2.8	20	68.7	1.2	1.32	11.5	-
BH	J2-360 IGT6	90	10.6	541	912	3.46	0.1	485	10.3	26.9	99	44	39	2.8	14	73.3	1.1	-	-	-
BH	J2-360 CGTR	96	10.1	542	849	5.01	3.6	485	10.3	27.1	107	43	68	2.8	17	60.0	-	1.36	12	-
BH	J2-361 IGT5	90	10.5	541	850	3.99	1.4	495	10.5	26.9	102	43	51	2.8	13	60.5	0.6	1.23	10.5	0.07
BH	J2-361 IGT6	90	10.6	543	861	3.61	1.1	492	10.5	27.5	98	43	45	2.7	14	-	3.4	-	-	-
BH	J2-361 CGTB	85	10.2	543	818	6.16	6.6	490	10.4	25.2	101	41	80	2.7	14	67.4	1.9	1.11	9.4	0.21
BH	J2-361 CGT-Wu	94	10.5	543	820	4.24	2.4	493	10.5	26.5	101	42	52	2.7	14	92.1	1.7	1.25	10.5	-
	Seawater	2	8.0	554	857	28.7	53.3	475	10.3	10.4	92	24	412	1.4	2.3	25	0	0	0	0

*mm=mmol/kg; µm=µmol/kg; nm=nmol/kg, Seawater = LC bottom water, (-) = not analyzed

** Failed sample (see text)

Table 2. Endmember concentrations* of vent fluid chemistry from the Lost City Hydrothermal Field.

Vent	pH (25°)	Cl mm	Br um	SO ₄ mm	Na mm	Mg mm	K mm	Ca mm	Sr um	Li um	B um	Rb um	Cs nm	Si um	CH ₄ mm	H ₂ mm
M6**	10.5	541	815	3.5	494	1.3	10.5	26.6	102	43	51	2.8	17	24.2	1.20	9.9
BH	10.6	541	851	3.2	494	0.0	10.5	27.4	102	46	38	2.8	16	72.7	1.26	10.8
Seawater	8.0	554	857	28.2	475	53.3	10.3	10.4	92	24	412	1.4	2.3	25	0	0

* mm=mmol/kg; µm=µmol/kg; nm=nmol/kg, Seawater = LC bottom water

** Endmember defined as fluid with lowest measured Mg concentration (see Table 1).

Table 3. Kinetic parameters used in reactive transport simulations

Mineral	Surface Area (cm ² /g)	log(Rate Constant) (mol/cm ² /s)	Activation Energy (kJ/mol)	Reference
Chrysotile	0.26	-13.58	73.5	Palandri and Kharaka (2004)
Tremolite	0.26	-14.6	94.4	Murphy and Helgeson (1987); Pokrovsky and Schott (2000)
Diopside	0.26	-14.79	40.6	Knauss et al. (1993)
Anhydrite	0.26	-7.19	14.3	Palandri and Kharaka (2004)

Figure 1

Fig. 1.

Figure 2

Fig. 2.

Figure 3

Fig. 3

Figure 4

Fig. 4.

Fig. 5

Figure 6

Fig. 6

Figure 7

Fig. 7.

Figure 8

Fig. 8.

Figure 9

Fig. 9.

Figure 10

Fig. 10.

Figure 11

Fig. 11.

Figure 12

Fig. 12.

Figure 13

Fig. 13.