Hydrothermal Vapor-Phase Fluids on the Seafloor: Evidence From In Situ Observations

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Abstract

Subseafloor phase separation is a common and significant process in hydrothermal systems and may result in a large of fluid composition differences. The temperatures of hydrothermal fluids are generally considered to be below the associated fluid boiling temperature due to mixing with ambient seawater and the phase separation process. However, we report here shimmering water with temperatures up to 383.3 °C observed in a hot overturned lake at the Yokosuka site, Okinawa Trough, East China Sea, where in situ Raman spectra suggest the presence of a superheated vapor phase. Hydrothermal vents similar to the low-density hydrothermal system found at the Yokosuka site have also been observed in many other regions. Therefore, much more attention should be given to the impacts of low-density hydrothermal fluid emanations on marine environments and resource distributions.

Plain Language Summary

Hydrothermal systems characterized by the emanations of supercritical- and vapor-phase fluids associated with igneous activities have been observed on mid-ocean ridges. Here, we report a newly found hydrothermal system dominated by low-density vapor-phase fluids at the Yokosuka site, a hydrothermal field located in a backarc basin spreading center. Multiple methods, including in situ Raman spectroscopy measurements, thermocouple sensor measurements, and gas-tight sampling, were used to investigate this vapor-phase hydrothermal emanation. In situ observations suggest that the highest temperature (383.3 °C) of the hydrothermal fluids at the Yokosuka site is above the two-phase boundary of seawater at a depth of 2,180 m (378.1 °C) and in situ Raman spectra indicate the fluid of the hot overturned lake features a layered structure. Hydrothermal systems with low-density emanations are likely to be widespread throughout various tectonic settings since similar phenomena have been observed in other hydrothermal fields with conditions close to the phase separation boundary.

1. Introduction

Since the discovery of deep sea hydrothermal systems in 1977 (Corliss et al., 1979; Weiss et al., 1977), hydrothermal circulation has been considered one of the significant factors affecting seawater compositions (Hein et al., 2003; Humphris et al., 1995). Hydrothermal activities play an important role in energy and material exchange between the lithosphere and the hydrosphere and are responsible for the formation of a large number of valuable metal-rich sulfide deposits (Hannington et al., 2010, 2011; Rona, 2003). When the temperature of hydrothermal fluid is above the boiling point of seawater at a given depth, a low-density, gas-rich, and Cl-depleted vapor phase separates from the brine phase (Coumou et al., 2009). Subcritical/supercritical phase separation (i.e., boiling) can occur under conditions close to or above the critical point (CP) of seawater (298 bar/407 °C) (Bischoff & Rosenbauer, 1984). For example, in the hydrothermal sites of the Brandon, Bastille, Sisters Peak, and Turtle Pits, the low-density supercritical- and vapor-phase fluids emanate intermittently from chimneys (Koschinsky et al., 2008; Von Damm et al., 1995, 2003). Significant impacts on the mineralization process and element behavior of superheated vapor and supercritical emanations have been observed (Schmidt et al., 2010, 2017). The superheated gas produced by phase separation in the subseafloor is quickly cooled by ambient seawater in the orifice (Von Damm, 1995). Therefore, it is extremely difficult to recover supercritical- and vapor-phase hydrothermal fluids, which severely hinders further research on such hydrothermal systems dominated by low-density emanations (Koschinsky et al., 2008; Von Damm et al., 1995).

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A special hydrothermal phenomenon involving numerous inverted lakes filled with shimmering water has been observed and surveyed at the Yokosuka site in our recent cruises of the research vessel (R.V.) Kexue (Figure 1) (Movies S1 in the supporting information). The mushroom cap structures above the hydrothermal orifice impede direct contact between seawater and the hot fluids. The heat preservation effect of the cap structures allows the superheated gas phase to exist above the seafloor. Similar phenomena have also been observed at the Lion and Iheya North hydrothermal sites (Figure S1). The widespread distribution of the mushroom cap structures at the Yokosuka site results from the unique hydrothermal fluid temperature and pressure conditions and is likely associated with a previously undescribed emanation mode for hydrothermal systems with conditions near the phase separation.

The Yokosuka site is the deepest (2,180 m) and hottest (364 °C) hydrothermal field among those found in the Okinawa Trough (Miyazaki et al., 2017). Large chimneys with flanged extensions are the most prominent features of the Yokosuka site. The upward view of a camera on the remotely operated vehicle (ROV) captured the shimmering water trapped by the mushroom cap structures, indicating the presence of a strong reflective layer (Figure 1c) (Movies S1). In the 2018 cruises of R.V. Kexue, in situ temperature and Raman measurements and gas-tight sampling were used to perform measurements of these so-called overturned lakes (Movies S2). The measurement results of the shimmering water revealed a special reaction process and fluid stratification under the mushroom cap structures.

2. Methods

A K-type Omega thermocouple (TJ100-CA316SS-316 U-20-SMPW-M) with an upper range limit of 650 °C and a precision of 0.75% was used to measure the temperature of the hydrothermal fluids under the mushroom cap (Movies S2). The thermocouple sensor was calibrated using multipoint temperature data before each measurement. To ensure the reliability of the temperature measurements, the thermocouple sensor was held as stationary as possible.

In this study, in situ Raman measurements were conducted using the Raman insertion probe (RiP) system (Movies S2) (Zhang, Du, Luan, et al., 2017; Zhang, Du, Zheng, et al., 2017), which has been successfully applied in the Manus Basin hydrothermal fields and cold seeps in the South China Sea (Du, Zhang, Luan, et al., 2018; Du, Zhang, Xi, et al., 2018; Li et al., 2018a; Xi et al., 2018; Zhang, Du, Luan, et al., 2017). The RiP system was developed on the basis of the Deep Ocean Raman In Situ Spectrometer (DORISS) (Brewer et al., 2004), and it inherits the main hardware components and spectral parameters of DORISS (Brewer et al., 2004; Zhang et al., 2010, 2012). The RiP system has a spectral resolution of 1 cm$^{-1}$ and uses a custom-designed N-RXNE-532-RA-SP spectrometer (Kaiser Optical Systems, Inc., Ann Arbor, USA), a frequency-doubled Nd:YAG laser (532 nm) (Kaiser Optical Systems, Inc., Ann Arbor, USA) with an output power of 150 mW and a DU-440A-BV-136 charge-coupled device (CCD) (Andor Technology, Inc., South Windsor, CT, USA) with 2,048 × 512 pixels and a 27.6 × 6.9 mm image area. Before the deployment of the RiP system, the spectral intensity and wave number were calibrated using halogen and neon lamps (Li et al., 2018b, 2018c; Zhang et al., 2020).

The hydrothermal fluids of the Yokosuka site were sampled using a custom-designed gas-tight sampler (Movies S2) (Li et al., 2018a). The gas-tight samples were processed immediately after the ROV returned to the ship (less than 24 hr). The compositions of gases were determined using a gas chromatograph with thermal conductivity detection (GC-TCD) (Thermo Scientific Corp., Ltd, USA), and the δ$^{13}$C values of CH$_4$ and CO$_2$ were determined using a continuous-flow isotope ratio mass spectrometer (IRMS) (Trace GC Ultra/Delta V Advantage, Thermo Scientific Corp., Ltd, USA) with an analytical error of 0.5‰, applying a modified method at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (Huang et al., 2016; Pan et al., 2006).

3. Results

3.1. The Geochemistry of the Hydrothermal Fluids at the Yokosuka Site

The temperatures of the hydrothermal fluids at the Yokosuka site were measured during dive 197 of ROV Faxian. The temperature recorded by the thermocouple sensor increased rapidly from 4 to 383.3 °C (Figure 2a). The endmember Cl concentration of the hydrothermal fluids at the Yokosuka site (132 mM)
is much lower than that of the surrounding seawater (~560 mM) because of phase separation below the seafloor (Table S2) (Miyazaki et al., 2017). The shimmering water trapped by the mushroom cap displayed strong light reflection, which indicates significant temperature and density differences with the surrounding seawater (Figure 3a). The densities of liquid and supercritical water as a function of temperature are shown in Figure 2b. At the pressure of 223 bar, the density of pure water decreases from 0.50 to 0.16 g/ml as the temperature increases from 370 to 383 °C.

The Raman insertion probe for the hydrothermal vent (RiP-Hv) was inserted into the shimmering water to different depths (Li et al., 2018a; Zhang, Du, Zheng, et al., 2017). According to the characteristics of the Raman spectra (Figure 2c), the liquid trapped in the inverted lake can be divided into three layers (Figure 3b). The bottom layer is normal seawater with the lowest temperature and largest density. Heat, metal ions, and dissolved gaseous species are transported by the flowing seawater from this layer to the ambient environment. The spectrum of the fluid in the middle layer indicates a low concentration of SO$_4^{2-}$ (Figure 2c) (Hayes et al., 1984), which suggests that this layer is likely a mixture of hydrothermal fluid and seawater. In this layer, the condensation and evaporation of seawater occur simultaneously. Raman peaks of CO$_2$ (~1,385 cm$^{-1}$) (Wright & Wang, 1973), H$_2$S (~2,595 cm$^{-1}$) (Peltzer et al., 2016), and CH$_4$ (~2,910 cm$^{-1}$) (Lu et al., 2007) are obvious in the spectrum of this layer, and the in situ concentrations of
CO₂, CH₄, and H₂S were calculated to be 121.5, 8.4, and 9.6 mmol/kg, respectively (Table S1) (Li et al., 2018a; Zhang et al., 2011). According to the Raman spectrum of the fluid in the top layer, the OH stretching band has an obvious weak hydrogen bond (HBW) (~3,570 cm⁻¹), and the strong hydrogen bond (HBS) (~3,240 cm⁻¹) is nearly invisible, indicating that the top layer is a high-temperature vapor phase (Sun et al., 2010; Walrafen et al., 1999; Wu et al., 2017).

Gas-tight samples from the Yokosuka site were collected during dive 196 of ROV Faxian. Approximately 400 ml of gas and less than 20 ml of liquid were recovered from one of the gas-tight samples with the best quality (150 ml volume bottle). The analytical results of the gas-tight samples indicate that CO₂ (98.76%) is the main component of the hydrothermal gas species of the Yokosuka site, whereas the proportions of

Figure 2. Temperatures and Raman spectra of hydrothermal fluids measured at the Yokosuka site. (a) Temperature data were measured during dive 197 using a thermocouple sensor (Data Set S1). (b) Densities of liquid and supercritical water as a function of temperature between 370 °C and 383 °C at 223 bar. (c) In situ Raman spectra of hydrothermal fluids under the mushroom cap collected by the RiP system (Data Set S2).
CH₄ and H₂S in the gas are only 0.63% and 0.60%, respectively (Table S2). H₂ was not detected in this study, which is quite different from the findings of previous studies (Miyazaki et al., 2017), indicating significant variations in the geochemical characteristics of the hydrothermal fluids emanating from different chimneys. The values of δ¹³C-CH₄ and δ¹³C-CO₂ are −23.26‰ ± 0.5‰ and −7.21‰ ± 0.5‰, respectively, suggesting a thermogenic origin for the methane and an abiotic origin for the carbon dioxide (Seewald et al., 1994; Whiticar, 1999).

3.2. Formation Model of the Mushroom Cap Structures

Hydrothermal minerals precipitate rapidly when high-temperature metal-rich fluids mix with cold ambient seawater. The effects of cold ambient seawater and bottom currents promote lateral chimney growth (Figure 3b). A severe phase separation process occurs below the seafloor at the Yokosuka site, as deduced from the depletion of Cl⁻ (132 mM) (Table S2). The superheated vapor phase emanating from the chimney vaporizes the seawater and forms the uppermost layer of inverted lake. The vapor-phase fluids move upward along the chimney due to density differences, and rapid cooling and precipitation occur at the chimney head. Once the mushroom cap is formed, the direct contact between the hydrothermal fluid and seawater is blocked (Figure 3b). The hot fluids meet cold seawater only at the edge of the flange structure; therefore, the interface between the hydrothermal fluid and the seawater under the mushroom cap controls the growth of this structure. This finding may account for the flat edge of the flange structure and horizontal growth lines in the mushroom cap’s interior.

4. Discussion

4.1. Hydrothermal Regions Similar to the Yokosuka Site Around the World

Temperature and pressure (depth) are crucial factors controlling the state of hydrothermal emanations. A vapor phase can exist when the temperature is above the two-phase boundary at a given depth. Supercritical fluids can also exist as long as both temperature and pressure exceed the CPhydrothermal fluids conditions. The highest temperature measured at the Yokosuka site was 383.3 °C (Figure 2a), which is lower than the critical temperature of seawater (407 °C) but is above the two-phase boundary of seawater at a depth of 2,180 m (378.1 °C) (Figure 4) (Bischoff & Pitzer, 1985). The depth of the Yokosuka site also does not reach the critical pressure for low-salinity hydrothermal fluids (the calculated critical pressures for a solution with 100 to 300 mM NaCl range from 244 to 272 bar) (Driesner & Heinrich, 2007). Given the temperature fluctuation of hydrothermal emanations, the emanating liquid probably alternates between liquid and vapor phases at the Yokosuka site.

Unlike the temporary superhot emanations of hydrothermal fields on the East Pacific Rise (Von Damm et al., 1995) and at 5°S on the Mid-Atlantic Ridge (Koschinsky et al., 2008) that result from igneous activities and tectonic events, the mushroom cap structures at the Yokosuka site provide stable conditions for vapor-phase emanations. Similar flange structures have also been found in the Endeavour Segment of the Juan de Fuca Ridge (Delaney et al., 1992) and the East Scotia Ridge (James et al., 2014) (Figure S1). The temperature and depth conditions for all these hydrothermal fields are close to or at the phase separation boundary (Figure 4a). The temperatures of the fluids under the mushroom cap are probably above the two-phase boundary of seawater or low-Cl hydrothermal fluids (Bischoff & Rosenbauer, 1984) (Figure 4b). Supercritical fluid can also exist if the temperature and pressure conditions are above the CP of low-Cl hydrothermal fluids (Von Damm et al., 1995). At sites in the Southern Trough of Guaymas Basin (Lonsdale & Becker, 1985) and Pescadero Basin, Gulf of California (Goffredi et al., 2017; Paduan et al., 2018), similar phenomena were also observed, although the fluid temperatures are lower than those of the phase separation.
condition (Figure S1). In these hydrothermal fields, the highest temperature of the hydrothermal fluids may not have been achieved yet due to the unfavorable measurement conditions.

High hydrothermal fluid temperatures and high levels of dissolved components are favorable for rapid sulfide accumulation in the orifice (Reed & Palandri, 2006). Vapor-phase emanations have a high ability to hydrate ions, resulting in strong selectivity and propensity of metal transformation (Pokrovski et al., 2005). There are obvious differences between the fluid chemical evolution of vapor hydrothermal systems and normal hydrothermal systems (Schmidt et al., 2010, 2017); thus, the inverted lake with shimmering water at the Yokosuka site is a natural laboratory for studying hydrothermal systems dominated by low-density emanations.
The relatively moderate emanations at the Yokosuka site result in hydrothermal minerals tending to precipitate at the edge of the mushroom cap. Fewer metal ions and sulfides are taken away by surrounding seawater, which would weaken the hydrothermal activity’s influences on the marine environments. The relatively concentrated precipitation highlights the potential of such hydrothermal activities to form massive sulfide deposits and provides new insights into the exploration of hydrothermal sulfide deposits (Hannington et al., 2011).

4.2. Geological Implications for the New Emanation Mode of the Yokosuka Site

The flange structures at the Yokosuka site prevent the direct contact of the hydrothermal fluids with seawater, which is favorable for the formation and emanation of superheated hydrothermal fluid. According to the hydrothermal database, more than 650 confirmed and unconfirmed active hydrothermal sites have been reported (Figure S1) (http://www.interridge.org/). The temperatures and depths of all the confirmed active hydrothermal sites (180) are displayed in Figure 4c. Among these hydrothermal sites, approximately 23 fields (12.8%) are near the two-phase separation boundary line (Figure 4c). Given the difficulties and technological limitations in performing in situ measurements, there is likely to be a discrepancy between the true maximum temperature and the reported value. If there is a 5 to 10 °C error between the field-observed value and the true maximum temperature, the proportion of hydrothermal sites close to or above the two-phase boundary ranges from 15.6% to 18.8% (the red shaded area in Figure 4c). Many hydrothermal sites close to the two-phase boundary probably intermittently emanate supercritical- or vapor-phase fluids because of temporal variations in the venting fluid temperature (Koschinsky et al., 2008). Fluid density controls the solubility, mobilization, transportation, and fractionation of metals and thus affects hydrothermal mineralization processes (Pokrovski et al., 2005; Schmidt et al., 2010, 2017). The metal solubility of low-density vapor-phase fluids is commonly lower than that of dense-phase fluids (except for Au and Cu) (Pokrovski et al., 2005; Williams-Jones & Heinrich, 2005). Therefore, compared with hydrothermal systems dominated by higher-density emanations, hydrothermal systems with high temperature and low density supercritical- and vapor-phase fluids usually exhibit large-scale precipitation at the top of the fluid conduit or at the vent orifice due to reduction in solubility.

5. Conclusions

As shown in Figure 4c, hydrothermal sites with vapor-phase and supercritical emanations have been observed in mid-ocean ridge areas with fast (Brandon) (Von Damm et al., 2003), intermediate (Bastille) (Von Damm et al., 1995), and slow (Sisters Peak and Turtle Pits) (Koschinsky et al., 2008) spreading rates; in arc volcano regions (Kick’em Jenny volcano) (Carey et al., 2014); and in backarc spreading centers (Yokosuka site). Hence, this type of hydrothermal system is broadly distributed in diverse tectonic settings. Although no such hydrothermal system has been observed on superfast or ultraslow spreading ridges, approximately 800 mid-ocean ridge hydrothermal sites remain to be discovered according to a statistical prediction (Beaulieu et al., 2015). Given the wide distribution of hydrothermal systems characterized by supercritical- and vapor-phase fluids, the influence of low-density hydrothermal emanations on processes such as mineralization in deep sea hydrothermal systems should be paid more attention.

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