In situ observations of liquid–liquid phase separation in aqueous ZnSO$_4$ solutions at temperatures up to 400 °C: Implications for Zn$^{2+}$–SO$_4^{2-}$ association and evolution of submarine hydrothermal fluids

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Abstract

Liquid–liquid immiscibility is gaining recognition as an important process in hydrothermal fluid activity. However, studies of this complex process are relatively limited. We examined liquid–liquid immiscibility in aqueous ZnSO$_4$ solutions at temperatures above ~266.5 °C and at vapor-saturation pressures. The homogeneous aqueous ZnSO$_4$ solution separated into ZnSO$_4$-rich (L$_1$) and ZnSO$_4$-poor (L$_2$) liquid phases coexisting with the vapor phase. The L$_1$–L$_2$ phase separation temperature decreased with increasing ZnSO$_4$ concentration up to 1.0 mol/kg, and then increased at greater ZnSO$_4$ concentrations, showing a typical lower critical solution temperature (LCST) of ~266.5 °C. Gunningite (ZnSO$_4$.H$_2$O) precipitated in 2.0 mol/kg ZnSO$_4$ solution at 360 °C. The L$_1$–L$_2$ phase separation resulted mainly from the strong Zn$^{2+}$–SO$_4^{2-}$ association at high temperatures. The major results of this study are: (1) the discovery of the LCST in these systems, a macroscale property associated with polymeric mixtures; (2) analyses of the peak area ratios of the $v_1$(SO$_4^{2-}$) and OH stretching bands, which suggest that the sulfate concentration increases with increasing temperature in L$_1$, especially above 375 °C; (3) a new Raman $v_1$(SO$_4^{2-}$) mode at ~1005 cm$^{-1}$ observed only in the L$_1$ phase, whose fraction increases with increasing temperature; and (4) the shape of the OH Raman stretching band, which indicates that water molecules and solute interact much more strongly in L$_1$ than in the coexisting L$_2$ phase, suggesting that water molecules fit into the framework formed by various Zn$^{2+}$–SO$_4^{2-}$ pairs and chain structures in L$_1$. These results have potential implications for understanding transport and reduction of seawater-derived sulfate in submarine hydrothermal systems. The formation of an immiscible sulfate-rich liquid phase can favor the circulation of sulfate within mid-ocean ridge basalt because the sulfate-rich liquid density is higher than that of the coexisting fluid. The reduction of sulfate could also be accelerated because sulfate is locally concentrated and strong Zn$^{2+}$–SO$_4^{2-}$ association increases the reactivity of sulfate.

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1. INTRODUCTION

Hydrothermal activities at the plate spreading centers of mid-ocean ridges, back-arc basins, and hot-spot volcanoes have attracted much attention since the direct observation in 1977 of submarine hydrothermal vents on the Galapagos Rift in the eastern equatorial Pacific by the Alvin submersible (Corliss et al., 1979; Williams et al., 1979). The formation of sulfides in modern seafloor hydrothermal systems provides a possible analogue to the formation of ore deposits (e.g., Herzeg and Hannington, 1995; Halbach et al., 1997; Herzig, 1999; Tivey, 2007; Zeng, 2011; and references therein). The hydrothermal fluids precipitating seafloor metal sulfides result from interactions between seawater and the ocean crust at conditions near the critical point of seawater (e.g., Kump and Seyfried, 2005; Tivey, 2007).

Sulfate is the second most abundant solute in seawater (~28 mM, Garrels and Thompson, 1962) and is important to the formation of metal sulfides (Shanks and Seyfried, 1987; Herzeg et al., 1998; Ono et al., 2007; Tivey, 2007).

The even well-documented stable sulfur isotopic compositions of the mid-ocean ridge basalts and seawater (δ34S = ±0‰ and 20.9‰, respectively; Rees et al., 1978; Sakai et al., 1984) make stable sulfur isotope analysis useful for investigating the contribution of seawater-derived sulfide to the formation of metal sulfides in seafloor hydrothermal systems (e.g., Shanks and Seyfried, 1987; Hannington and Scott, 1988; Woodruff and Shanks, 1988; Knott et al., 1995; Herzig et al., 1998; Gamo et al., 2001; Shanks, 2001; Ono et al., 2007). For example, combined δ34S and δ18O systematics have revealed that 73–89% of vent sulfides are derived from the leaching of basaltic sulfide, with the remainder coming from seawater-derived sulfide (Ono et al., 2007). Sulfate can form various contact ion pairs (CIPs) with many divalent and trivalent cations (e.g., Mg2+, Fe2+, Cu2+, Ni2+, Cd2+, and Al3+) (Rudolph and Irmer, 1994; Rudolph et al., 1997, 2003; Rudolph and Mason, 2001; Zhang and Chan, 2002; Chen et al., 2005; Papangelakis, 2005). For the Zn2+-SO42- association (e.g., Hayes et al., 1984; Kruus et al., 1985; Rudolph et al., 1999; Zhang and Chan, 2002), and the technique has shown that Zn2+ and SO42- can form a monodentate CIP (ZnSO4) at high temperatures (up to 256 °C); the corresponding t1(SO42-) mode is at ~897–992 cm−1. Nevertheless, experimental investigation of the Zn2+-SO42- interaction under submarine hydrothermal conditions remains limited.

This paper presents a previously unknown low-temperature (~267 °C) liquid–liquid phase separation in aqueous ZnSO4 solutions at vapor-saturation pressures, and discusses the implications for Zn2+-SO42- complexation, sulfate transport, and the corresponding formation of metal sulfides in sub-seafloor hydrothermal systems. The main objectives of this work include: (1) describing the liquid–liquid phase separation at temperatures up to 400 °C and documenting the T-x conditions for the appearance of the second liquid phase in the ZnSO4-H2O system; (2) analyzing the compositions of the immiscible liquid phases with in situ Raman spectroscopy; (3) investigating Zn2+-SO42- association at high temperatures, especially in the immiscible sulfate-rich liquid, and the formation mechanism for the liquid–liquid phase separation; and (4) discussing the implications for the transport and reduction of seawater-derived sulfate in submarine hydrothermal systems.

that a homogeneous aqueous MgSO4 solution separates into MgSO4-rich and MgSO4-depleted liquid phases at temperatures above 260 °C and at vapor-saturation pressures (Wang et al., 2013a). However, seawater Mg is removed from the fluid through the precipitation of clays (i.e., Mg-rich smectite and chlorite) at temperatures above 150 °C during the penetration of seawater into basalt (Alt, 1995; Tivey, 2007). This limits the applicability of current studies on the phase behavior and Mg2+-SO42- association in the MgSO4-H2O system to interpreting the evolution of submarine hydrothermal fluids.

Zinc is a common metallic element in the venting fluids leached from basalt, and zinc sulfide constitutes a major ore mineral in vent deposits (e.g., Von Damm and Bischoff, 1987; Butterfield and Massoth, 1994; Charloiu et al., 1996; Seyfried et al., 2003; Houghton et al., 2004; Tivey, 2007). Therefore, the phase behavior of the ZnSO4-H2O system might aid the investigation of the mass transport and origin of metal sulfides in submarine hydrothermal systems. However, phase equilibrium data for the ZnSO4-H2O system have mainly been recorded at low temperatures (i.e., <100 °C; Linke and Seidell, 1958; Jambor et al., 2000; Chou and Seal, 2005), with only a few works considering temperatures up to 256 °C (Rudolph et al., 1999; Liu and Papangelakis, 2005). For the Zn2+-SO42- association, classical measurements (e.g., freezing point, osmotic coefficient, electrical conductivity, and solubility) can predict the formation of ion pairs through observed macrophysical bulk properties of solutions; however, they do not provide direct information about the ion pairs at the molecular level (e.g., Brown and Prue, 1955; Katayama, 1976; Libus et al., 1980; Hinatsu et al., 1992; Beuster-Rogač, 2008). Raman spectroscopy is a powerful tool for investigating Zn2+-SO42- association (e.g., Hayes et al., 1984; Kruus et al., 1985; Rudolph et al., 1999; Zhang and Chan, 2002), and the technique has shown that Zn2+ and SO42- can form a monodentate CIP (ZnSO4) at high temperatures (up to 256 °C); the corresponding t1(SO42-) mode is at ~897–992 cm−1. Nevertheless, experimental investigation of the Zn2+-SO42- interaction under submarine hydrothermal conditions remains limited.
2. MATERIALS AND METHODS

2.1. Construction of optical cells

All experiments used either square or round cross-sectioned fused silica capillary capsules (FSCCs; Polymicro Technologies) as high P-T optical cells (Chou et al., 2008). Three types of round cross-sectioned tubes were used: 0.05 mm inner diameter (ID) and 0.3 mm outer diameter (OD), 0.1 mm ID and 0.3 mm OD, and 0.3 mm ID and 0.6 mm OD. The square cross-sectioned tubes had internal edge lengths of 0.1 mm and external edge lengths of 0.3 mm. The detailed procedures for the preparation of the FSCCs were reported elsewhere (e.g., Chou et al., 2008; Wang et al., 2011; Wang et al., 2013a,b,c; Caumon et al., 2013). The lengths of the prepared FSCCs were generally 10–20 mm.

Aqueous ZnSO₄ solutions were prepared at 0.1, 0.3, 0.4, 0.5, 1.0, 1.5, 2.0, 2.5, and 3.3 mol/kg from ReagentPlus grade zinc sulfate heptahydrate (>99%, Sigma–Aldrich) and distilled deionized water (>18.2 kΩ). FSCCs containing these various solutions were placed on a heating–cooling stage (CAP500, Linkam) to control the sample temperature (Chou, 2012; Dargent et al., 2013; Wan et al., 2015). The temperature of the stage was calibrated by using the melting temperatures of n-hexadecane (18.17°C), sulfur (119°C), and NaNO₃ (306.8°C). The stage provided good thermal stability (±0.1°C) with negligible temperature gradients (<1°C within 15 mm) (Pokrovski and Dubessy, 2015).

2.2. In situ visual observation and acquisition of Raman spectra

FSCCs containing the solutions were heated to set temperatures up to 400°C. Most were heated to less than 350°C along the liquid–vapor curve at 5°C/min below 200°C and at 0.5°C/min above 200°C. A FSCC containing 1.0 mol/kg ZnSO₄ solution was heated to the homogenization temperature of 372°C along the liquid–vapor curve, and then was heated further to 400°C approximately along an isochore, neglecting the thermal expansion of the FSCC (Chou et al., 2008). The phase behavior of the ZnSO₄–H₂O system was observed under a microscope with 10× and 20× Olympus objectives. To ensure the reproducibility of the phase behavior of ZnSO₄–H₂O system, each sample was visually observed 2–5 times.

The components of this system (aqueous, liquid, and solid phases) were analyzed in situ with a Raman spectrometer (LabRAM HR800, Horiba) equipped with a charge coupled device (CCD) detector (1024 × 256 pixel, air-cooled to −70°C). Raman spectra were acquired using 532.11 nm (air-cooled, frequency-doubled Nd:YAG) laser excitation, a 50× Olympus objective, a 1800 groove/mm grating with a spectral resolution of about 1 cm⁻¹. Laser light (9.5 mW) was focused on the horizontal central level of the tube during the spectra measurements. For the v₁(SO₄²⁻) band of silicon at 520.2 cm⁻¹ and the v₁(H₂O) band of water at 1638.2 cm⁻¹, one can observe the symmetric stretching mode of aqueous H₂SiO₄ (Schmidt, 2009, 2014). Spectra were collected from 2600 to 4000 cm⁻¹ for the OH stretching band [v₁(H₂O)], and from 100 to 1500 cm⁻¹ for the solid phase. The spectrometer was calibrated with the v₁ band of silicon at 520.2 cm⁻¹ (Parker et al., 1967). To minimize uncertainty in the spectra fitting, spectra were acquired for 60–300 s with three acquisitions per spectrum.

2.3. Processing the collected spectra

Sulfate concentrations were investigated by using the method of Wopenka and Pasteris (1986), which examines the peak area ratios between the v₁(SO₄²⁻) and v₁(H₂O) bands as an indicator of the sulfate concentration, as supported by the experimental work of Dubessy et al. (1983). The peak areas of these bands were calculated with Labspec 5.58.25 software using integration ranges of 880–1100 cm⁻¹ for the v₁(SO₄²⁻) band and 2800–3800 cm⁻¹ for the v₁(H₂O) band. This also covers spectra of HSO₄⁻ (~1050 cm⁻¹, Rudolph, 1996).

The spectra of the v₁(SO₄²⁻) bands were fitted by PeakFit v4.0 (AISN Software Inc.) using the Gaussian + Lorentzian function. Linear baseline correction and 0.5% smoothing were applied to all the spectra. The integrated areas from the Gauss + Lorentz fits were used as the integrated intensities of each v₁(SO₄²⁻) band component. The Raman shift and the full width at half maximum (FWHM) of the v₁(SO₄²⁻) and v₁(H₂O) bands were analyzed by Labspec 5.58.25 software.

3. RESULTS

3.1. Phase behavior

The ZnSO₄–H₂O system showed a distinctive high-temperature liquid–liquid phase separation. Fig. 1a–h show the phase behavior of 2.0 mol/kg ZnSO₄ sealed in a round cross-sectioned FSCC (0.1 mm ID and 0.3 mm OD). Heating the FSCC to 270.2°C along the liquid–vapor curve induced the homogeneous aqueous solution to separate into two liquid phases (red arrow, Fig. 1b), which coexisted with the vapor phase. Immiscible droplets formed, and subsequently coalesced with further heating (Fig. 1c, d). We term the droplets as liquid phase 1 (L1) and the other liquid phase as liquid phase 2 (L2). The volume of L1 increased upon cooling (Fig. 1e, f), and the phase boundary between the two phases faded away (Fig. 1g, h) to form a homogeneous aqueous phase at ~270.2°C, showing typical critical liquid–liquid homogenization. Critical L1–L2 homogenizations were also observed in ZnSO₄ solutions at higher concentrations (Table 1). The L2–vapor homogenization in the FSCC containing 1.0 mol/kg ZnSO₄ occurred at ~373°C, and then the liquid phases L1 and L2 (supercritical fluid at ≥374°C) coexisted at temperatures up to 400°C. Fig. S1 shows the phase behavior of 3.3 mol/kg ZnSO₄ solution at temperatures up to 400°C (APPENDIX A).

Compared with the previously reported liquid–liquid phase separation in MgSO₄–H₂O systems (Wang et al., 2013a), the immiscible liquid phases L1 and L2 were more stable, and coexisted up to 360°C before a solid phase formed in 2.0 mol/kg ZnSO₄ (Fig. 2). In addition to forming in...
Fig. 1. Liquid–liquid phase separation in aqueous ZnSO₄ solutions at temperatures above 267 °C and at vapor-saturation pressures. (a)–(h) show the liquid–liquid phase separation phenomena in 2.0 mol/kg ZnSO₄ solution. The fused silica capillary tube has 0.05 mm ID and 0.30 mm OD with round cross-section. During heating, the homogeneous aqueous phase (Aq) started to separate into two immiscible liquid phases, liquid 1 (L₁) and liquid 2 (L₂), coexisting with a vapor phase (V) at ~270 °C (a–c). L₁ is composed of small droplets, which coalesced during subsequent heating (d). During cooling, the volume of L₁ increased (e, f) and the phase boundary between L₁ and L₂ faded away to form a homogeneous aqueous phase at ~270 °C (g, h); (i) shows the liquid-liquid immiscibility in 0.1 mol/kg ZnSO₄ at 325 °C. The tube is square cross-sectioned and the inner cross-section area is 0.1 mm x 0.1 mm; (j) and (k) show the liquid-liquid immiscibility in 1.0 mol/kg ZnSO₄ at 267 and 268 °C, respectively. The tubes are round cross-sectioned and the inner diameter is 0.1 mm and 0.3 mm, respectively; (l) shows the liquid-liquid immiscibility in 3.3 mol/kg ZnSO₄ sealed in a round cross-sectioned FSCC with 0.1 mm ID.
2.0 mol/kg ZnSO$_4$, the immiscible liquid phases appeared in the 0.1, 1.0, and 3.3 mol/kg ZnSO$_4$ solutions (Fig. 1i–l). Note that the FSCCs used for these solutions were of different types, with the square cross-sectioned type used in Fig. 1i, and the round cross-sectioned FSCCs in Fig. 1j–l with IDs of 0.1, 0.3, and 0.1 mm, respectively. These results suggest that the liquid–liquid phase separation occurred in all the different FSCCs, thus precluding the capillary effect on the phase separation.

High-temperature phase equilibria data for the ZnSO$_4$–H$_2$O system are limited. In this study, we modified the high-temperature part (>266°C) of the phase diagram of this system (Fig. 2). The ZnSO$_4$ solubility data in Fig. 2 are cited from Rudolph et al. (1999). The stable field of the solid phases is summarized from those reported in Rudolph et al. (1999) and Jambor et al. (2000). The upper part of Fig. 2 shows that the phase separation temperature decreased with increasing ZnSO$_4$ concentration up to 1.0 mol/kg, before increasing at higher concentrations. The lowest temperature at which liquid–liquid phase separation occurs is known as the lower critical solution temperature (LCST). Our results identify the LCST in the ZnSO$_4$–H$_2$O system as 266.5°C (Table 1, Fig. 2). The pressures at which phase separation occurred were approximated by the vapor pressures of MgCl$_2$ solutions of equivalent compositions (Duan et al., 2006, Table 1).

### 3.2. Raman spectroscopic characterization

#### 3.2.1. Sulfate concentrations of L$_1$ and L$_2$

Fig. 3 shows the Raman spectra of the $v_1$(SO$_4^{2-}$) and $v_3$(H$_2$O) bands of the coexisting L$_1$ and L$_2$ phases in 1.0 mol/kg ZnSO$_4$ solution at 280, 350, and 400°C. The $v_3$(H$_2$O) intensity-normalized Raman spectra of L$_1$ are characterized by a strong $v_1$(SO$_4^{2-}$) band, whereas those of L$_2$ appear weak, indicating that L$_1$ was sulfate-rich and L$_2$ was sulfate-poor. This is a similar finding to previous observations for the MgSO$_4$–H$_2$O system (Wang et al., 2013a).

In situ spectra of L$_1$, L$_2$ and vapor phases in 1.0 mol/kg ZnSO$_4$ solution were shown in Fig. S2 (APPENDIX A). The vapor phase is characterized by a narrow $v_3$(H$_2$O) band, whereas those in liquid L$_1$ and L$_2$ phases are broader. Based on Placzek’s ratio method (e.g., Dubessy et al., 1983; Wopenka and Pasteris, 1986), we used the integrated Raman intensity ratios of the $v_1$(SO$_4^{2-}$) and $v_3$(H$_2$O) bands ($A_{sulfate}/A_{water}$) to investigate

### Table 1

Pressure–temperature conditions for the appearance of liquid-liquid phase separation for 0.1–3.3 mol/kg ZnSO$_4$ solutions.

<table>
<thead>
<tr>
<th>ZnSO$_4$ (mol/kg)</th>
<th>0.1</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>1.0</th>
<th>1.5</th>
<th>2.0</th>
<th>2.5</th>
<th>3.3</th>
</tr>
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<tr>
<td>Temperature (°C)</td>
<td>284</td>
<td>279</td>
<td>269</td>
<td>267</td>
<td>266.5</td>
<td>266.6*</td>
<td>270.4*</td>
<td>272.8*</td>
<td>275*</td>
</tr>
<tr>
<td>Pressure* (MPa)</td>
<td>6.66</td>
<td>6.16</td>
<td>5.36</td>
<td>5.36</td>
<td>5.08</td>
<td>4.94</td>
<td>5.07</td>
<td>5.01</td>
<td>4.72</td>
</tr>
</tbody>
</table>

* Shows near critical L$_1$–L$_2$ homogenization phenomenon during cooling.

* The vapor pressures of ZnSO$_4$ solutions were estimated from aqueous MgCl$_2$ solutions with equivalent concentrations (Duan et al., 2006).

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Fig. 2. The phase diagram of ZnSO$_4$–H$_2$O system. In the upper part, the liquid-liquid phase separation temperature decreases with increasing ZnSO$_4$ concentration up to 1.0 mol/kg and then starts to increase with increasing ZnSO$_4$ concentration, showing a typical lower critical solution temperature (LCST) phenomenon. In 1.5–3.3 mol/kg ZnSO$_4$ solutions, the homogenization between L$_1$ and L$_2$ is characterized by the fading away of the phase boundary. Solid phase was identified in 2 mol/kg ZnSO$_4$ solution at 360°C and dissolved during subsequent cooling. Data plotted are from Table 1 and those reported by Rudolph et al. (1999) and Jambor et al. (2000).
the changes in the sulfate concentrations of the L1 and L2 phases during heating.

The \( A_{\text{sulfate}}/A_{\text{water}} \) ratio generally increased with increasing temperature in L1, but decreased in L2 upon heating, approaching zero above 375 °C (Fig. 4, Table S1 in APPENDIX B). The two phases contained different sulfate species. The Raman spectra of the \( v_1(\text{SO}_4^{2-}) \) bands of the 1.0 mol/kg solution from 25 to 400 °C (Fig. 5) showed that the main sulfate species in L2 above 320 °C was \( \text{HSO}_4^- \) (Fig. 5b), a hydrolysis product of \( \text{Zn}^{2+} \) (Rudolph et al., 1999). However, the Raman signal of \( \text{HSO}_4^- \) in L1 was weak, especially above 320 °C (Fig. 5a).

![Raman spectra of coexisting L1 and L2 phases](image)

Fig. 3. \( v_1(\text{H}_2\text{O}) \) intensity-normalized Raman spectra of the coexisting L1 and L2 in 1.0 mol/kg ZnSO_4 solution at 280, 350, and 400 °C. They show that L1 is characterized by a strong \( v_1(\text{SO}_4^{2-}) \) band, whereas that band in L2 is very weak. The spectra of \( \text{HSO}_4^- \) at ~1050 cm\(^{-1}\) was also identified (Rudolph, 1996). Two additional bands at ~1130 cm\(^{-1}\) and ~1215 cm\(^{-1}\) were also detected (question marks). In addition, the \( v_1(\text{H}_2\text{O}) \) band of L1 is relatively broader and less symmetric than that in L2. With increasing temperature, the \( v_1(\text{H}_2\text{O}) \) bands in L1 and L2 shift to higher wavenumber, especially in L2. Inserted picture shows the \textit{in situ} Raman analyzing spots for the coexisting L1 and L2 phases.

![Peak area ratio](image)

Fig. 4. The peak area ratio between the \( v_1(\text{SO}_4^{2-}) \) and \( v_1(\text{H}_2\text{O}) \) bands (\( A_{\text{sulfate}}/A_{\text{water}} \)) of L1 and L2 in 1.0 mol/kg ZnSO_4 solution as a function of temperature. It shows that the \( A_{\text{sulfate}}/A_{\text{water}} \) Ratio increases with increasing temperature in L1 while decreases with increasing temperature in L2. Data plotted are those listed in Table S1 (APPENDIX B).
3.2.2. $v_1$(SO$_4^{2-}$) bands

The Raman spectrum of the $v_1$(SO$_4^{2-}$) band in 1.0 mol/kg ZnSO$_4$ solution was symmetric at 25 °C (Fig. 5a). Heating shifted this band to higher wavenumber and broadened it. The symmetry of the $v_1$(SO$_4^{2-}$) band decreased upon heating. The Raman signals of the $v_1$(SO$_4^{2-}$) band in L2 were weak (Figs. 3 and 5b), and are not discussed further. Fig. 6 shows the quantitative variation of the peak position and peak width of the $v_1$(SO$_4^{2-}$) band. In aqueous solution, the band shifted from 981.3 cm$^{-1}$ at 25 °C to 978.1 cm$^{-1}$ at 200 °C, but shifted to a higher wavenumber of 982.2 cm$^{-1}$ at 250 °C. After the liquid–liquid phase separation, the $v_1$(SO$_4^{2-}$) band shifted from 989.9 cm$^{-1}$ at 280 °C to 1001.8 cm$^{-1}$ at 400 °C (Fig. 6a, Table S1 in APPENDIX B). The band’s FWHM increased slightly from 8.2 to 10.3 cm$^{-1}$ upon heating from 25 to 100 °C, and then increased significantly with increasing temperature in both the aqueous and L1 phases (Fig. 6b, Table S1 in APPENDIX B). Comparing the Raman spectra of the $v_1$(SO$_4^{2-}$) band in L1 and 1.0 mol/kg (NH$_4$)$_2$SO$_4$ solution at 350 °C (Fig. 5c) shows that in L1 the band shifted to a higher wavenumber and was much broader than that observed in aqueous (NH$_4$)$_2$SO$_4$ solution.

Below 250 °C, this band in aqueous solution was described accurately with two Gaussian + Lorentzian components centered at ~980 and ~990 cm$^{-1}$ (Fig. 7a, b, Table S2 in APPENDIX B). The ~980 cm$^{-1}$ component (C$_{980}$) was ascribed to Raman indistinguishable solvent separated ion pairs (2SIP), solvent shared ion pairs (SIP), and unassociated SO$_4^{2-}$, whereas the ~990 cm$^{-1}$ component (C$_{990}$) mainly arose from the formation of CIPs (ZnSO$_4$) (Hayes et al., 1984; Kruus et al., 1985; Rudolph et al., 1999; Zhang and Chan, 2002). 2SIP and SIP are not stable at higher temperatures (Akilan et al., 2006a,b), and only contributed minor sulfate fractions at 65 °C, with the fractions continuing to decrease with increasing temperature in aqueous MgSO$_4$ solution. Therefore, at higher temperatures (>200 °C), the C$_{980}$ component mainly resulted from

![Fig. 5. (a) $v_1$(SO$_4^{2-}$) spectra of aqueous and L1 phases in 1.0 mol/kg ZnSO$_4$ solution at 25–250 °C and 280–400 °C, respectively; (b) $v_1$(SO$_4^{2-}$) spectra of coexisting L2 at 280–400 °C; (c) Upper part shows the $v_1$(SO$_4^{2-}$) spectra of L1 for 1.0 mol/kg ZnSO$_4$ solution at 350 °C and of 1.0 mol/kg (NH$_4$)$_2$SO$_4$ solution at 300 and 350 °C. Lower part is the spectrum of the solid phase identified in 2.0 mol/kg ZnSO$_4$ solution at 360 °C. Inserted is a picture of gunningite (ZnSO$_4$.H$_2$O) precipitated at 354.2 °C coexisting with L1 and L2. The reference spectrum of gunningite was cited from an open data base hosted in the Department of Geosciences at University of Arizona, USA (RRUFF™ Project, http://rruff.info/).]
unassociated $\text{SO}_4^{2-}$. However, after the liquid–liquid phase separation, large fitting residuals were present in the high-wavenumber region of the $v_1(\text{SO}_4^{2-}/C_0)$ band in L1. Interestingly, excellent fitting resulted from adding a third Gaussian + Lorentzian component centered at $\sim 1005$ cm$^{-1}$ ($C_{1005}$) (Fig. 7c, d, Table S2 in APPENDIX B). This new $v_1(\text{SO}_4^{2-})$ mode has not been reported previously.

Two Raman bands also emerged at $\sim 1130$ and $\sim 1215$ cm$^{-1}$ in the L1 phase (Fig. 3). The former might be associated with the $v_3(\text{SO}_4^{2-})$ modes (1104 cm$^{-1}$, Dong et al., 2007) or the bidentate $\text{Zn}^{2+}–\text{SO}_4^{2-}$ complex ($\sim 1140$ cm$^{-1}$, Rudolph et al., 1999). It has been suggested that the latter band is associated closely with unreported sulfate complex species (Rudolph et al., 1999). These new bands could not be assigned; however, our results suggest that they do not arise from the fused silica background because they were not observed in the L2 phase (Figs. 3 and 5b).

3.2.3. OH stretching bands

The Raman spectrum of liquid water is characterized by a complex profile of several broad, overlapping bands in the OH stretching region (2800–3800 cm$^{-1}$) with a bending mode at $\sim 1630$ cm$^{-1}$ (Furić et al., 2000). Owing to the low intensity of the bending mode, we only considered the OH stretching bands, $v_s(\text{H}_2\text{O})$. Fig. 3 shows that heating sharpened the band and shifted it to higher wavenumbers in both L1 and L2. Its symmetry also increased upon heating. This band was sharper, more symmetric, and at higher wavenumber in L2 than in the coexisting L1 at the same temperature.

Fig. 8 shows the Raman shift and width of the $v_s(\text{H}_2\text{O})$ band. The band shifted to higher wavenumber and its FWHM decreased with increasing temperature in the aqueous and L2 phases. The peak position of the band at maximum intensity shifted from 3414 cm$^{-1}$ at 25 °C to 3543 cm$^{-1}$ at 250 °C in aqueous solution, and then further shifted from 3553 cm$^{-1}$ at 280 °C to 3590 cm$^{-1}$ at 400 °C in L2. However, this band in L1 only shifted from 3539 cm$^{-1}$ at 280 °C to 3543 cm$^{-1}$ at 400 °C (Table S1 in APPENDIX B). The band’s FWHM decreased from 406 cm$^{-1}$ at 25 °C to 226 cm$^{-1}$ at 250 °C in aqueous solution, and then continued to decrease from 200 cm$^{-1}$ at 280 °C to 101 cm$^{-1}$ at 400 °C in L2. In contrast, in L1 the FWHM decreased from...
229 cm\(^{-1}\) at 280 °C to 201 cm\(^{-1}\) at 400 °C (Table S1 in Appendix B). The differences in the Raman shifts and bandwidths between the phases L1 and L2 increased with increasing temperature (right, Fig. 8).

4. DISCUSSION

4.1. Relationship between the L1–L2 phase separation and Zn\(^{2+}\)–SO\(_4^{2-}\) interaction

4.1.1. Macroscale properties

Liquid–liquid phase separation is a common feature of organic-bearing solutions (e.g., Marshall and Gill, 1974; Baltes et al., 1999; Paricaud et al., 2003; Gong et al., 2013), whereas it has been rarely reported in aqueous inorganic electrolyte solutions (Marshall and Begun, 1989; Valyashko, 1997, 2008). Liquid–liquid phase separations in aqueous inorganic electrolyte solutions have been observed below 300 °C only in the following systems: UO\(_2\)SO\(_4–\)H\(_2\)O, MgSO\(_4–\)H\(_2\)O/H\(_2\)SO\(_4\), Na\(_2\)B\(_4\)O\(_7–\)H\(_2\)O, and Na\(_2\)HPO\(_4–\)H\(_2\)O (Secoy, 1950; Clark et al., 1959; Marshall et al., 1962; Marshall, 1982; Marshall and Begun, 1989; Valyashko, 1997; Wang et al., 2013a; Wan et al., 2015). To the best of our knowledge, such phase separation or L–L immiscibility in aqueous ZnSO\(_4\) solution has not been reported. Given that the solubility of ZnSO\(_4\) decreases upon heating above 50 °C (Linke and Seidell, 1958; Rudolph et al., 1999; Jambor et al., 2000), the three-phase immiscibility (L1–L2–vapor) in the ZnSO\(_4–\)H\(_2\)O system may be unstable (Valyashko, 1997, 2008), as has been suggested for the MgSO\(_4–\)H\(_2\)O system (Wang et al., 2013a). For example, Rudolph et al. (1999) observed the precipitation of gunnige (ZnSO\(_4–\)H\(_2\)O) and zincosite (ZnSO\(_4\)) at 210 and 244 °C, respectively. However, we did not observe solid phases at these temperatures. The absence of a solid phase before the L1–L2 phase separation suggests that the structure of the solution might have changed, preventing the formation of precipitates. This change might be ascribed to the strong, complex Zn\(^{2+}\)–SO\(_4^{2-}\) association. In 2.0 mol/kg ZnSO\(_4\) solution, a solid phase was observed at 360 °C after the liquid–liquid phase separation (Fig. 5c); it formed from the L1 phase, and thus was accompanied by a decrease in the volume of L1. Note that the in situ Raman spectrum of the solid phase matches that for gunningite in Fig. 4 reported by Rudolph et al. (1999). Our results show that the stable solid phase of this system at temperatures above 350 °C should be gunningite rather than zincosite. In addition, the liquid–liquid immiscibility appears more stable than that in the MgSO\(_4–\)H\(_2\)O system. For example, kieserite precipitated at ~306 °C from the immiscible MgSO\(_4\)-rich phase of the 2.0 mol/kg MgSO\(_4–\)H\(_2\)O system, which was 33 °C higher than the L1–L2 phase separation temperature (Wang et al., 2013a), whereas gunningite formed in the 2.0 mol/kg ZnSO\(_4\) solution at ~90 °C above the L1–L2 phase separation temperature.

Like previously reported systems of UO\(_2\)SO\(_4–\)H\(_2\)O, MgSO\(_4–\)H\(_2\)O/H\(_2\)SO\(_4\), and Na\(_2\)HPO\(_4–\)H\(_2\)O (e.g., Clark et al., 1959; Marshall, 1982; Wang et al., 2013a; Wan et al., 2015), the L1–L2 phase separation in the ZnSO\(_4–\)H\(_2\)O system is also characterized by a LCST, which is a macroscale chemical property of polymeric mixtures (e.g.,
Therefore, the LCST in the ZnSO₄–H₂O system supports the formation of inorganic Zn²⁺–SO₄²⁻ polymer(s), as suggested by the behavior of the MgSO₄–H₂O system with or without excess H₂SO₄ (Wang et al., 2013a; Wan et al., 2015). The interaction between cations and anions is favored at elevated temperatures (e.g., Marshall and Gill, 1974; Marshall and Begun, 1989; Neuefeind et al., 2004), because the dielectric constants of water and electrolyte solutions decrease upon heating (e.g., Wasserman et al., 1995; Filimonova et al., 2002; Maribo-Mogensen et al., 2013; Lyashchenko et al., 2014). However, almost all the sulfate accumulated in the L1 phase, especially above 320°C (Figs. 4 and 5b). The H₂O/ZnSO₄ molar ratio in the L1 phase was not obtained accurately here, but in the UO₂SO₄–H₂O system, the water/solute molar ratio in the immiscible UO₂SO₄-rich phase above 350°C was estimated to be 5–6 (Jones and Marshall, 1961). Therefore, ZnSO₄ was probably highly concentrated in the L1 phase. Both Zn²⁺ and SO₄²⁻ are highly hydrated in aqueous solutions (e.g., Ohtaki et al., 1976; Licheri et al., 1982; Kuzmin et al., 1997; Rudolph and Pye, 1999; Chillemi et al., 2002; Vchirawongkwin et al., 2007). The inner coordination shell of Zn²⁺ is composed of six water molecules, and the coordination number of SO₄²⁻ is up to 12. As a result, in the concentrated L1 phase, the remaining water molecules may not be able to isolate the Zn²⁺ and SO₄²⁻ ions, allowing the ions to associate strongly with each other. As postulated by Marshall and Gill (1974) for the UO₂SO₄–H₂O system, the L1–L2 immiscibility in the ZnSO₄–H₂O system might
also result from increasing association and polymerization of dissolved Zn$^{2+}$, SO$_4^{2-}$, and simple CIPs with increasing temperature, and the system at high temperatures may even be termed a pseudo organic–water system.

The possibility that SiO$_2$ in the silica capillary tubes dissolved and affected the L1–L2 phase separation should be considered, because silica shows increasing solubility in aqueous solutions upon heating (e.g., Siever, 1962; Newton and Manning, 2000; Schmidt, 2014). However, field emission scanning electron microscopy observations of the inner surfaces of the quenched optical cell suggested negligible dissolution of silica in the ZnSO$_4$–H$_2$O system at high temperatures. As shown in Fig. 10a, the inner surface of the quenched cell for the ZnSO$_4$–H$_2$O system (350 °C) appeared smooth with no etch pits or grooves. In contrast, the quenched cell for the ZnSO$_4$–H$_2$O system (400 °C) showed etch pits and grooves (red and blue arrows, respectively, Fig. 10b), indicating significant dissolution of SiO$_2$. Previous experiments have suggested that the dissolution of SiO$_2$ is favored in high-pH solutions (e.g., Alexander et al., 1954; Knauss and Wolery, 1988). Therefore, the weak dissolution of SiO$_2$ in the ZnSO$_4$–H$_2$O system may be ascribed to the acidic conditions created by the hydrolysis of Zn$^{2+}$. The relatively strong dissolution of SiO$_2$ in the Na$_2$SO$_4$–H$_2$O system might indicate a basic pH, as supported by the higher SiO$_2$ solubility in aqueous Na$_2$CO$_3$ solutions than in pure water at temperatures up to 600 °C (Schmidt, 2014). The dissolution of SiO$_2$ in hot Na$_2$SO$_4$ solutions can also be increased by the formation of Si(OH)$_4$SO$_4^{2-}$ (Marshall and Chen, 1982; Schmidt, 2009).

4.1.2. Spectroscopic evidence

The shape and wavenumber of the $v_1$(SO$_4^{2-}$) band in aqueous ZnSO$_4$ solutions can provide information about interactions between the Zn$^{2+}$ and SO$_4^{2-}$ ions (e.g., Hayes et al., 1984; Kruus et al., 1985; Rudolph et al., 1999; Zhang and Chan, 2002). In aqueous (NH$_4$)$_2$SO$_4$ solutions, NH$_4^+$ and SO$_4^{2-}$ are fully unassociated (Rudolph et al., 2003), and the $v_1$(SO$_4^{2-}$) spectrum in aqueous (NH$_4$)$_2$SO$_4$ solution can be used as a reference for unassociated SO$_4^{2-}$. This band remains symmetrical at temperatures up to 200 °C in aqueous (NH$_4$)$_2$SO$_4$ solution (Hayes et al., 1984; Rudolph et al., 2003). We found that the symmetry of this band in (NH$_4$)$_2$SO$_4$ solution was preserved to 350 °C (Fig. 5c). However, in the ZnSO$_4$–H$_2$O system, the $v_1$(SO$_4^{2-}$) band in the L1 phase at the same temperature was less symmetric, broader, and shifted to a higher frequency (Fig. 5c). These differences can be ascribed to the ion association between Zn$^{2+}$ and SO$_4^{2-}$. In addition, the $v_1$(SO$_4^{2-}$) spectrum of the L1 phase showed differing peak position and width from gunitite at a similar temperature (Fig. 5c), indicating that the $v_1$(SO$_4^{2-}$) bands represented liquid species favored at elevated temperatures.

The documented $v_1$(SO$_4^{2-}$) band of aqueous ZnSO$_4$ solutions at temperatures from 20 to 244 °C can be described by two $v_1$(SO$_4^{2-}$) components at ~980 and ~990 cm$^{-1}$, although the exact wavenumbers differed slightly (Hayes et al., 1984; Rudolph et al., 1999; Zhang and Chan, 2002). As mentioned in the Results section, these two $v_1$(SO$_4^{2-}$) components can be assigned to unassociated SO$_4^{2-}$ and CIPs (ZnSO$_4$), respectively. In addition to the C$_{980}$ and C$_{990}$ components, a new $v_1$(SO$_4^{2-}$) component emerged at ~1005 cm$^{-1}$ in L1 (Fig. 7c, d), whose detailed assignment is constrained by a lack of relevant reports. However, if we compare the investigated $v_1$(SO$_4^{2-}$) bands with those reported for MgSO$_4$–H$_2$O system, it can be speculated that the C$_{1005}$ component should arise from the transformation of more complex ion pairs, including multiple ion pairs and/or Zn$^{2+}$–SO$_4^{2-}$ chain structures. This is because experimental and Raman spectroscopic investigations have suggested that the Raman shift of the $v_1$(SO$_4^{2-}$) band in aqueous MgSO$_4$ solution is shifted to higher wavenumbers as the length of the CIP chain increases (e.g., Zhang et al., 2002; Jahn and Schmidt, 2010; Wang et al., 2013a; Wan et al., 2015).

The assignment of the C$_{1005}$ component can be supported by analyses of the changes of the fractions of these three $v_1$(SO$_4^{2-}$) components. Previous studies have suggested that the fractions of each $v_1$(SO$_4^{2-}$) component can be described using the peak area fractions while assuming equal scattering coefficients for complexed and unassociated sulfate (Rudolph et al., 1999; Jahn and Schmidt, 2010). Fig. 9 shows the peak area fraction of the $v_1$(SO$_4^{2-}$) components at ~980, 990, and 1005 cm$^{-1}$ in 1.0 mol/kg ZnSO$_4$ solution. The minor band component at ~1050 cm$^{-1}$ (Fig. 7) was not included in the peak area calculations. The fraction of the C$_{990}$ component decreased from 0.95 at 50 °C to 0.49 at 250 °C in aqueous solution, and then from 0.30 at 280 °C to 0.02 at 350 °C in L1 phase. The C$_{980}$ component could not be identified at ≥375 °C. The fraction of CIP (f$_{990}$) increased from 0.05 at 50 °C to 0.52 at 250 °C, and reached its maximum of 0.52 at 280 °C in the L1 phase, before decreasing to ~0.3 with increasing temperature. Unlike f$_{990}$, the fraction of the C$_{1005}$ component generally increased with increasing temperature. Like those observed in the MgSO$_4$–H$_2$O system, the decreases of f$_{990}$ and f$_{990}$ in the L1 phase imply the transformation of unassociated sulfate and CIPs to more complex ion pairs, probably chain structures (Jahn and Schmidt, 2010; Wang et al., 2013a). The detailed fractions of these $v_1$(SO$_4^{2-}$) components are listed in Table S2 (APPENDIX B).

In aqueous ZnSO$_4$ solution, the appearance of HSO$_4^-$ indicates the hydrolysis of Zn$^{2+}$ (Figs. 3 and 5a, b) (Rudolph et al., 1999):

$$\text{Zn}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Zn(OH)}^+ + \text{H}_3\text{O}^+$$  \hspace{1cm} (1)

$$\text{H}_3\text{O}^+ + \text{SO}_4^{2-} \rightleftharpoons \text{HSO}_4^- + \text{H}_2\text{O}$$  \hspace{1cm} (2)

The hydrolysis of Zn$^{2+}$ increases with increasing temperature (Rudolph et al., 1999), as suggested by the increasing Raman intensity of the HSO$_4^-$ band at ~1050 cm$^{-1}$ (Fig. 5a). Interestingly, HSO$_4^-$ tends to accumulate in the L2 phase, whereas the Raman signal of HSO$_4^-$ is weak in L1 and absent above 320 °C (Fig. 5a, b). The hydrolysis of Zn$^{2+}$ is strongly influenced by the formation of Zn$^{2+}$–SO$_4^{2-}$ ion pairs (Rudolph et al., 1999). HSO$_4^-$ is generally considered to be a non-complexing anion at high temperature (Rudolph, 1996; Rudolph et al., 1999; Rudolph and...
Mason, 2001); therefore, its high concentration in L2 indicates that the ion association in L1 was stronger than that in L2. With increasing temperature, the $\text{Zn}^{2+}$–$\text{SO}_4^{2-}$ association became stronger and favored the transformation of $\text{HSO}_4^-$ to $\text{SO}_4^{2-}$, which formed complexes with $\text{Zn}^{2+}$ or $\text{Zn}^{2+}$–$\text{SO}_4^{2-}$ ion pairs.

Besides the $v_1(\text{SO}_4^{2-})$ band, the shape and wavenumber of the OH stretching band [$v_3(\text{H}_2\text{O})$] can also be used to investigate the interactions between ions and water molecules (Dong et al., 2007; Wan et al., 2015). Given that the $v_3(\text{H}_2\text{O})$ band is broad and complex, the hydrogen bonding and structure of water is often studied by deconvolution with Gaussian functions (e.g., Walrafen and Chu, 1995; Carey and Korenowski, 1998; Crupi et al., 2005, 2008; Li et al., 2009). However, due to the complexity in the Gaussian analysis, researchers often use the peak position at maximum intensity and the peak width to indicate the variation of the hydrogen bonding in aqueous solutions (e.g., Frantz et al., 1993; Ikushima et al., 1998; Dubessy et al., 1999; Chen et al., 2004); a high-wavenumber shift and a decrease in the FWHM of the $v_3(\text{H}_2\text{O})$ band indicate a decrease in the hydrogen bonding. As shown in Fig. 8, the hydrogen bonding in aqueous ZnSO$_4$ solution decreased with increasing temperature. However, the
v3(H2O) band shape in L1 changed less than that in L2; under the same pressure and temperature, the band shifted to a lower wavenumber and was broader in L1 than in L2, in accordance with previous observations of the MgSO4–H2SO4–H2O system (Wan et al., 2015). It has been suggested that Zn2+ and SO42− are hydrated in aqueous solutions and are structure makers, because the hydrogen bonding between the ions and the surrounding water molecules is stronger than that between water molecules in the bulk solvent (Rudolph and Pye, 1999; Vchirawongkwin et al., 2007). As temperature increases, the probability of collision of water molecules with Zn2+ and SO42− ion pairs and ion pair chain(s), as observed in supersaturated (NH4)2SO4 and MgSO4 droplets (Dong et al., 2007; Wan et al., 2015).

The above discussions indicate that the L1–L2 phase separation in aqueous ZnSO4 solution should be closely associated with the strong (inner sphere) ion pairing between Zn2+ and SO42−. Zhang and Chan (2002) suggested that the covalent nature of the CIPs of Zn2+–SO42− is stronger than that of Mg2+–SO42−. The main evidence for this includes: (1) Zn2+–SO42− CIPs formed in droplets with higher water–solute ratios than did Mg2+–SO42− CIPs; (2) the frequency of the Zn2+–SO42−(H2O)x stretching vibration at 275 cm−1 was much higher than that of Mg (245 cm−1); and (3) the spherically filled 18-e electron cloud of Zn2+ was more easily polarized by anions than the 8-e shell of Mg2+. This is supported by the simulation results of Matthews and Naidoo (2010), which show that the association constant for Zn2+–SO42− is higher than that for Mg2+–SO42−. These results account for the more stable liquid–liquid immiscibility in the ZnSO4–H2O system compared with that in the MgSO4–H2O system.

4.2. Implications for the evolution of submarine hydrothermal fluids

Submarine hydrothermal fluids in vent fields are derived from the circulation of seawater within the oceanic crust at spreading centers (Tivey, 2007; Zeng, 2011 and references therein). Experimental and computational investigations have shown that the circulation of seawater within the ocean crust results in the removal of sulfate by precipitation of anhydrite at temperatures above 150 °C (Bischoff and Seyfried, 1978; Shanks et al., 1981; Janecky and Shanks, 1988; Bowers, 1989; Monnin et al., 2003). The precipitation removes all the Ca from seawater and about one-third of the sulfate (Herzig et al., 1998; Tivey, 2007). Subsequent precipitation of anhydrite accompanied by the release of Ca from basalt decreases the seawater sulfate to less than 1 mM (Bischoff and Dickson, 1975; Shanks, 2001). However, low concentrations of seawater sulfate can persist in seawater–rock interactions, and their contribution to the formation of metal sulfides cannot be neglected, as demonstrated by stable sulfur isotope analyses of metal sulfides (e.g., Shanks and Seyfried, 1987; Hannington and Scott, 1988; Woodruff and Shanks, 1988; Knott et al., 1995; Herzig et al., 1998; Shanks, 2001; Ono et al., 2007).

Seawater-derived fluids infiltrating deeper basalts are heated by deep magma or newly solidified hot rock (Tivey, 2007). The submarine hydrothermal fluid often contains components with low dielectric constants (i.e., H2, H2S, CH4, CO2; Ishibashi et al., 1995; Gamo et al., 2001; Fu et al., 2007; Seyfried et al., 2007; Klein et al., 2009; McCollom and Bach, 2009) that lower the dielectric constant of a solution (e.g., Harvey and Prausnitz, 1987; Moriyoishi et al., 1990; Wang and Anderko, 2001), favoring ion complexation (e.g., Marshall and Gill, 1974; Neufeld et al., 2004; Reimer et al., 2015). As discussed previously, the liquid–liquid phase separation in aqueous sulfate solution results from strong metal–sulfate association at high temperatures, and thus could occur in sub-seafloor hydrothermal fluid, despite its low sulfate concentration. Given that sulfates (ZnSO4) accumulate in the newly formed liquid phase, the transport of metal sulfates will accelerate because their density is higher than the ambient fluid. In addition, our observation shows that Zn2+ and SO42− are strongly associated at high temperatures, especially in the immiscible ZnSO4-rich phase. Previous studies have shown that the transport of metal sulfates in aqueous solutions is favored by the formation of ion pairs (Leaist and Lyons, 1981; Brady et al., 1996). For example, the diffusion coefficient of ion pairs is about 40% higher than that of dissociated salt (Leaist and Lyons, 1981). The strong Zn2+–SO42− association and the occurrence of the liquid–liquid phase separation might prevent the precipitation of sulfate minerals (cf. Rudolph et al., 1999), favoring the transport of metal sulfate in the circulation of seawater-derived fluid within basalt.

Experimental simulation and analyses of vent fluids have suggested that basalt–seawater interactions can create reducing conditions (e.g., Frost, 1985; Berndt et al., 1996; Ding et al., 2001; Charlou et al., 2002; Allen and Seyfried, 2004; Seyfried et al., 2007; Klein et al., 2009; McCollom and Bach, 2009), and even form abiogenic hydrocarbons through the reduction of CO2 (e.g., Foustoukos and Seyfried, 2004; Fu et al., 2007). The remaining seawater sulfate can be reduced to sulfide via the oxidation of ferrous Fe in pyroxene or olivine or through the conversion of igneous pyrrhotite to pyrite in the basalt at elevated temperatures (250–400 °C) (e.g., Shanks et al., 1981; Janecky and Seyfried, 1986; Herzig et al., 1998; Kump and Seyfried, 2005). Experimental investigations have suggested a slow rate of sulfate reduction in peridotite-bearing systems at temperatures as high as 300 °C (Seyfried and Dibble, 1980; Janecky and Seyfried, 1986). However, the formation of liquid–liquid immiscibility will increase the rate of sulfate reduction owing to the high concentration of sulfate in one of the liquid phases. Based on theoretical calculations, Ma et al. (2008) investigated the reactivity of different sulfate species in aqueous solutions. Their results indicate that a fully water-solvated “free” SO42− is highly stable due to its symmetrical tetrahedral molecular structure, whereas the formation of a metal-sulfate contact ion pair (i.e., Mg2+SO42−) can increase the polarity of sulfate and
decrease the strength of some S–O bonds, favoring the reduction of sulfate. The interaction between Zn$^{2+}$ and SO$_4^{2-}$ in the contact ion pairs was suggested to be stronger than that between Mg$^{2+}$ and SO$_4^{2-}$ (Zhang and Chan, 2002). Considering the polarization effect of Zn$^{2+}$, the stability of the S–O bonds in Zn$^{2+}$–SO$_4^{2-}$ complexes should be decreased compared with that of “free” SO$_4^{2-}$. Therefore, the strong Zn$^{2+}$–SO$_4^{2-}$ association can also promote the reduction of sulfate under hydrothermal conditions.

The high-temperature submarine hydrothermal fluids are often characterized by low pH (e.g., Charlou et al., 2002; Douville et al., 2002; Ding et al., 2005; Seyfried et al., 2011; Zeng, 2011), which allows the formation of HSO$_4^-$. Interestingly, our results show that HSO$_4^-$ tends to accumulate in the sulfate-poor fluid owing to the strong ion association in the immiscible sulfate-rich fluid (Fig. 5a, b). As a result, the sulfate-poor fluid should be more acidic than the sulfate-rich fluid, and may leach metals from the host rocks, thus helping to accumulate metals (i.e., Zn, Cu) in the hydrothermal fluid, forming metal sulfides during venting near the seafloor.

The mixing of seawater sulfate and venting fluid, for example at porous chimneys (e.g., Shanks and Seyfried, 1987; Woodruff and Shanks, 1988; Kim et al., 2006), might allow liquid–liquid phase separation to occur, because: (1) the sulfate concentration is higher than in deep hydrothermal fluid; (2) there are more low-dielectric components (H$_2$, H$_2$S, CO$_2$, CH$_4$, and other light hydrocarbons; Charlou et al., 2002; Fu et al., 2007; Konn et al., 2009; Zeng, 2011 and references therein); and (3) the pressure is low (Marshall and Gill, 1974). As described earlier in this section, the strong metal–sulfate association and liquid–liquid phase separation accelerates the reduction of seawater sulfate to generate heavy S isotopic metal sulfides and H$_2$S, as has been documented in some hydrothermal vents (e.g., Shanks and Seyfried, 1987; Woodruff and Shanks, 1988; Kim et al., 2006).

5. CONCLUSIONS

The phase behavior of 0.1–3.3 mol/kg ZnSO$_4$ solutions in FSCCs were investigated by microscopy and in situ Raman spectroscopy at temperatures up to 400 °C. We observed a previously unknown liquid–liquid phase separation in aqueous ZnSO$_4$ at temperatures above 266.5 °C. At vapor-saturation pressures, the homogenous aqueous solutions separated into the sulfate-rich L1 phase and the sulfate-poor L2 phase, which coexisted with the vapor phase.

We attributed the liquid–liquid phase separation to strong Zn$^{2+}$–SO$_4^{2-}$ association at elevated temperatures for the following four reasons. (1) The phase-separation temperature decreased with increasing ZnSO$_4$ concentration up to 1.0 mol/kg, and then increased further, showing typical LCST behavior, which is a macroscale property of polymeric mixtures. (2) The sulfate mainly accumulated in the L1 phase. The decrease in the water/solute ratio in this phase with increasing temperature indicated that the hydration of Zn$^{2+}$ and SO$_4^{2-}$ could not be maintained, favoring the inner sphere ion interaction between Zn$^{2+}$ and SO$_4^{2-}$. (3) In addition to the v$_1$(SO$_4^{2-}$) component of unassociated SO$_4^{2-}$ and Zn$^{2+}$–SO$_4^{2-}$ CIPs at ~980 and 990 cm$^{-1}$, respectively, a new v$_1$(SO$_4^{2-}$) component at ~1005 cm$^{-1}$ was identified in the L1 phase. The fractions of unassociated SO$_4^{2-}$ and CIPs in L1 decreased with heating, whereas the fraction of the ~1005 cm$^{-1}$ component increased, indicating the transformation of SO$_4^{2-}$ and simple ion pair(s) to more complex Zn$^{2+}$–SO$_4^{2-}$ ion associations. This result supports the assignment of the ~1005 cm$^{-1}$ component to Zn$^{2+}$–SO$_4^{2-}$ chain structures or polymer(s). (4) The stronger solvent–solute interactions in phase L1 than in L2 indicated that water molecules fitted into the framework formed by various Zn$^{2+}$–SO$_4^{2-}$ ion pairs and polymeric structures. These observations are consistent with the proposed strong ion association in aqueous solutions at high temperatures owing to the decrease in the dielectric constant of water with increasing temperature. Accordingly, we predict that liquid–liquid phase separation can also occur in other metal sulfate solutions with metal–sulfate associations stronger than those between Mg$^{2+}$ or Zn$^{2+}$ and SO$_4^{2-}$. We also suggest that the high-temperature (~350 °C) solid phase of the ZnSO$_4$–H$_2$O system is gunnite rather than zincoite. Any dissolution of silica from the sample tubes negligibly affected the development of liquid–liquid immiscibility.

The liquid–liquid immiscibility explored here may aid our understanding of element transport under hydrothermal conditions. In sub-seafloor hydrothermal systems, seawater-derived sulfate may accumulate in an immiscible sulfate-rich liquid phase when it is heated by deep magma or newly solidified rocks. The formation of liquid–liquid immiscibility would facilitate the transport of sulfate because its density is higher than the ambient fluid. Sulfate reduction can also be favored in immiscible sulfate-rich liquid phase because sulfate is locally concentrated and the strong Zn$^{2+}$–SO$_4^{2-}$ association increases the reactivity of sulfate. Therefore, if sulfate-related liquid–liquid immiscibility occurs, it will help to promote the transport and reduction of sulfate. These observations will also help us to understand the behavior of sulfate deep in the Earth and the corresponding mineralization processes.

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APPENDICES A AND B. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2016.03.001.
REFERENCES


Konn C., Charlou J. L., Donval J. P., Holm N. G., Dehairs F. and Bouillon S. (2009) Hydrocarbons and oxidized organic com-
pounds in hydrothermal fluids from Rainbow and Lost City ultramafic hosted vents. Chem. Geol. 258, 299–314.


Liu H. and Papangelakis V. G. (2005) Thermodynamic equilibrium of the O_{2}–ZnSO_{4}–H_{2}SO_{4}–H_{2}O system from 25 to 250 °C. Fluid Phase Equilib. 234, 122–130.


