Properties of lithium under hydrothermal conditions revealed by in situ Raman spectroscopic characterization of Li$_2$O-SO$_3$-H$_2$O (D$_2$O) systems at temperatures up to 420 °C

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ABSTRACT

Lithium (Li) is an important component of hydrothermal fluids, especially submarine hydrothermal fluids. Investigation of the species and ion complexation of Li$^+$ at elevated temperature and pressure can improve our knowledge on the behavior of Li under hydrothermal conditions. In this study, in situ optical and Raman spectroscopic experiments were conducted on the Li$_2$SO$_4$-H$_2$SO$_4$-H$_2$O system and its D$_2$O analogue at temperatures ≥ 420 °C. An unexpected liquid-liquid phase separation (immiscibility) was observed at temperatures above 336.5 °C; the aqueous phase was separated into a sulfate-rich heavy liquid phase and a sulfate-poor light liquid phase at vapor-saturation pressures. The liquid-liquid phase separation temperature decreased as the Li$_2$SO$_4$ concentration increased in dilute solutions (≤ 1.25 m), increased as the Li$_2$SO$_4$ concentration increased in concentrated solutions (> 1.25 m), and exhibited a lower critical solution temperature (LCST) at ~ 336.5 °C. The presence of excess H$_2$SO$_4$ (or D$_2$SO$_4$) increased the liquid-liquid phase separation temperature at a constant Li$_2$SO$_4$ concentration. Liquid-liquid phase separation is common in organic-bearing solutions, and LCST is considered to be a macroscopic scale property of polymer solutions, indicating complicated ion pairing between Li$^+$ and SO$_4^{2−}$. Liquid-liquid phase separation can be summarized as (1) strong and various Li$^+$-SO$_4^{2−}$ association increased with increasing temperature at a constant Li$_2$SO$_4$ concentration, and (2) continued growth on the surface of early formed solid phase. Submarine hydrothermal fluids can play important roles in the precipitation of sulfates and other minerals.

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1. Introduction

Submarine hydrothermal activity at mid-ocean ridges plays an important role in the transport of heat, water and chemical constituents in the earth-ocean-atmosphere system (Elderfield and Schultz, 1996). Cold seawater enters the ocean crust and is heated by deep magma or newly solidified hot rock (Tivey, 2007). The circulation of seawater within seafloor basalt results in pervasive and significant variation in the chemistry and mineralogy of basalt and in chemistry of the ocean (Alt, 1995; Tivey, 2007; Zeng, 2011 and references therein). Lithium (Li) has been considered an effective indicator of sub-marine temperatures due to its uptake into secondary minerals (Li) has been considered an effective indicator of sub-marine temperatures (e.g., Seyfried et al., 1984; Chan et al., 1993, 2002; James et al., 2003; Tomascak, 2004; Misra and Froelich, 2012). As a result, studies have partitioning between solubility, mass transport, electrical conductivity and element distributions of venting fluids has been suggested to be an effective tool to study the complexation between Li⁺ and Cl⁻ using conventional Raman spectroscopy because (1) only Raman-active species can be detected by Raman spectroscopy, whereas “free” Li⁺ and Cl⁻ are Raman-inactive, and (2) the signal of the Li-Cl symmetric vibration mode of associated Li⁺-Cl⁻ species is very weak (~380 cm⁻¹, Rudolph et al., 1995). Sulfate is the second most abundant solute in seawater (~28 mM, Garrels and Thompson, 1962) and is also an important component of submarine hydrothermal fluids (e.g., Douville et al., 1999; Wang et al., 2016a). Although most sulfate is removed from seawater via the precipitation of anhydrite during the circulation of seawater within the ocean crust (Bischoff and Dickson, 1975; Bischoff and Seyfried, 1978; Shanks et al., 1981; Janecky and Shanks, 1988; Bowers, 1989; Shanks, 2001; Monnin et al., 2003), seawater sulfate can still persist in seawater-rock interactions, 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; Herzeg et al., 1998, Shanks, 2001; Ono et al., 2007); combined δ³⁴S and Δ³³S systematics have revealed that 73–89% of vent sulfides are derived from the leaching of basaltic sulfide, with the remainder coming from seawater-derived sulfate (Ono et al., 2007). In addition, dissolved sulfate is Raman-active, and it exhibits a strong symmetric mode (ν₁) at ~980 cm⁻¹ (e.g., Zhang and Chan, 2000; Rudolph et al., 2003). The ν₁(SO₄²⁻) band is sensitive to the molecular environment. For example, the contact ion pairing between Mg²⁺ and SO₄²⁻ can change the shape and wavenumber of the ν₁(SO₄²⁻) band (e.g., Zhang and Chan, 2000, 2002; Rudolph et al., 2003; Buchner et al., 2004, 2006; Jahn and Schmidt, 2010). Therefore, a detailed description and interpretation of the ν₁(SO₄²⁻) band can be used to investigate the species and ion association in aqueous sulfate solutions (e.g., Rudolph and Irner, 1994; Rudolph et al., 1997, 2003; Rudolph and Mason, 2001; Zhang and Chan, 2002; Chen et al., 2005; Akilan et al., 2006a,b; Schrödle et al., 2007; Schröder et al., 2011; Jahn and Schmidt, 2010; Wang et al., 2013, 2016a).

In this study, we present an unusual liquid-liquid phase separation in an aqueous Li₂SO₄ solution at temperatures > 336 °C, and we discuss the implications for the species and transport of Li⁺ in hydrothermal fluids. Liquid-liquid phase separation may play important roles in the precipitation of sulfates under hydrothermal conditions. Specifically, the objectives of this work were to (1) describe the liquid-liquid phase separation and subsequent precipitation of Li₂SO₄ at temperatures up to 420 °C; (2) document in situ Raman spectra of the aqueous phase, two immiscible liquid phases and the solid phase; and (3) investigate the speciation and ion associations in aqueous Li₂SO₄ solutions at high temperatures.

2. Experimental section

2.1. Sample preparation

Li₂SO₄·H₂O (≥99% purity, Sigma-Aldrich) and distilled deionized water (~18.2 kΩ) were used to prepare aqueous Li₂SO₄ solutions with the following molality (mol/kg, m): 0.1, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75 and 2.0 m. To prevent the corrosion of silica tube in basic solutions at high temperatures, excess H₂SO₄ (0.5 mol/L, Dongguan Sibo Electronic Material Co., LTD) was added to the aqueous Li₂SO₄ solutions to adjust the molar Li₂SO₄/H₂SO₄ ratio to 10 and 5 (Wang et al., 2016a). Anhydrous Li₂SO₄ (≥98.5% purity, Sigma-Aldrich) and deuterium oxide (99.8 atom% D, TCI Shanghai) were used to prepare Li₂SO₄·D₂O solution with a concentration of 1.0 m. Excess D₂SO₄ (99.5 atom% D, Sigma-Aldrich) was added to the Li₂SO₄·D₂O solution to adjust the molar Li₂SO₄/D₂SO₄ ratio to 10. (NH₄)₂SO₄ (≥98.5% purity, Sigma-
Aldrich) and deionized water were used to prepare 1.0 \( m \) (NH\(_4\))\(_2\)SO\(_4\) solution.

Fused silica capillary capsules (FSCCs, Chou et al., 2008) were used as optical and spectroscopic cells containing these solutions. About 8 cm long fused silica tubing (Polymicro Technologies, LLC) with 100 \( \mu \)m inner diameter and 300 \( \mu \)m outer diameter was chosen to construct a FSCC. Firstly, the polyimide coating on the tubing was burned out in hydrogen flame and one open end was sealed by fusion in oxyhydrogen flame. Secondly, salt solution was loaded into the tubing and was centrifuged to the sealed end. Thirdly, the open end was connected to the vacuum line and the solution-bearing section of the tubing was immersed in cool water (or liquid nitrogen) to avoid boiling of solution in the tubing. At last, the tubing was vacuumed and the open end was sealed by fusion in oxyhydrogen flame. The length of a prepared FSCC is about 1.5–2.0 cm.

2.2. In situ optical and Raman spectroscopic observations

The temperature of the sample was controlled in a Linkam CAP500 heating-cooling stage. The temperature difference in the sample slot is <0.2 °C within 3 cm in the temperature range of 100–300 °C. At temperatures from 300 to 450 °C, the temperature difference is <0.5 °C within 3 cm. The temperature of the stage was calibrated with a Type-K thermocouple, which was calibrated using the melting (0 °C) and boiling (100 °C) temperatures of water. The FSCC containing prepared solutions was heated from 25 to ~350 °C at vapor-saturated pressures (along liquid-vapor curve). Then, the vapor phase homogenized into the aqueous phase and the sample was further heated to 420 °C along an isochoric fluid-vapor curve. Then, the vapor phase was homogenized into the aqueous phase rather quickly and could not grow into ordered crystals in a short period of time. With the prolonged experimental duration, the latter formed crystal gradually grew at the expense of the \( S_{\text{rich}} \) phase (Fig. 1f). The early formed solid phase was characterized by a strong (010) band, whereas this band was weak in the light \( S_{\text{poor}} \) phase (Fig. 1e). The early formed solid phase was characterized by a strong (010) band, whereas this band was weak in the light \( S_{\text{poor}} \) phase.

3. Results

3.1. Phase behavior

As shown in Fig. 1a–d, a second liquid phase was observed in homogeneous 1.0 \( m \) Li\(_2\)SO\(_4\)-0.1 \( m \) H\(_2\)SO\(_4\) solution at 341.7 °C. In other words, the aqueous phase separated into two immiscible liquid phases, coexisting with the vapor phase at elevated temperatures. Similar to previously reported liquid-liquid phase separation in other sulfate solutions (e.g., UO\(_2\)SO\(_4\), CuSO\(_4\), MgSO\(_4\), ZnSO\(_4\); Secoy, 1950; Marshall et al., 1962; Marshall and Gill, 1974; Wang et al., 2013, 2016a; Wan et al., 2015), the second liquid phase was rich in sulfate (\( S_{\text{rich}} \)), whereas the remaining aqueous phase was depleted in sulfate (\( S_{\text{poor}} \) (Fig. S1). The separated \( S_{\text{rich}} \) phase was a liquid phase rather than a solid phase because (1) the OH stretching band of liquid water was identified (Fig. S1), and (2) the Raman characterization showed that the signals of the Li\(^{+}\)-SO\(_4^{2-}\) association increased as the temperature increased in the \( S_{\text{rich}} \) phase, which will be discussed in detail in the next section. No solid phase was observed, even when the sample was heated to 420 °C. During cooling, the volume of the \( S_{\text{rich}} \) phase decreased as the temperature decreased and homogenized into the remaining aqueous phase (Fig. 1c and d). In concentrated solutions (e.g., 2 \( m \) Li\(_2\)SO\(_4\)), the phase boundary between \( S_{\text{rich}} \) and \( S_{\text{poor}} \) phases faded away during cooling, indicating a critical homogenization phenomenon (Table 1).

Liquid-liquid phase separation was also observed in an aqueous Li\(_2\)SO\(_4\) solution without excess H\(_2\)SO\(_4\) (1 \( m \) Li\(_2\)SO\(_4\), Fig. 1e). However, obvious corrosion of the tube was observed at temperatures above 350 °C (Fig. S2); the inner surface of the tube was full of dissolution pits. The addition of excess H\(_2\)SO\(_4\) can prevent the corrosion of the tubes because the dissolution of SiO\(_2\) is favored in high-pH solutions (e.g., Alexander et al., 1954; Knauß and Wolery, 1988). Solid precipitated from the \( S_{\text{rich}} \) phase during subsequent heating (Fig. 1f). The early formed solid phase was poorly crystallized (lower part in Fig. 1f), whereas the late formed solid was characterized by a nice crystal face (upper part in Fig. 1f). Since the \( S_{\text{rich}} \) phase was supersaturated, the solid precipitated from the \( S_{\text{rich}} \) phase rather quickly and could not grow into ordered crystals in a short period of time.

In aqueous Li\(_2\)SO\(_4\) or Li\(_2\)SO\(_4\)-H\(_2\)SO\(_4\) solutions, the liquid-liquid phase separation temperature decreased as the Li\(_2\)SO\(_4\) concentration increased in diluted solutions and increased as the Li\(_2\)SO\(_4\) concentration increased in concentrated solutions (Fig. 2 and Table 1), exhibiting a typical lower critical solution temperature (LCST) phenomenon. For example, the LCST of the Li\(_2\)SO\(_4\)-H\(_2\)O system was ~336 °C. The presence of excess H\(_2\)SO\(_4\) generally increased the liquid-liquid phase separation temperature at constant Li\(_2\)SO\(_4\) concentration; the LCSTs were ~339.5 and 342.2 °C for solutions having molar Li\(_2\)SO\(_4\)/H\(_2\)SO\(_4\) ratios of 10 and 5, respectively (Table 1). In addition, the liquid-liquid phase separation temperature in Li\(_2\)SO\(_4\) heavy water solution was lower than that in light water solution. For instance, the temperature for the appearance of the second liquid phase in the 1 \( m \) Li\(_2\)SO\(_4\)-0.1 \( m \) H\(_2\)SO\(_4\)-H\(_2\)O system was 341.7 °C, whereas the liquid-liquid phase separation temperature in the 1\( m \) Li\(_2\)SO\(_4\)-0.1 \( m \) D\(_2\)SO\(_4\)-D\(_2\)O system was ~336 °C.

2.3. Raman spectral characterization

Effects of instrument response factor, wavenumber and temperature on the intensity of the collected spectra were calibrated by the procedures described by Rudolph (1996) and Applegarth et al. (2015) (S1). Then, the spectra were corrected using a linear baseline. The wavenumber and width of the \( v_1(\text{SO}_4^{2-}) \) bands were determined using a program operated on MATLAB R2015a (The MathWorks, Inc.) (S1). Spectra of the \( v_1(\text{SO}_4^{2-}) \) band were treated with 0.5% smoothing and then fitted with Lorentz model (Rull and Ohtaki, 1997) using PeakFit v. 4.0 program (AISN Software Inc.).
separation, the $v_1(SO_4^{2-})$ band showed a dramatically high-wavenumber shift compared with that observed in the aqueous phase; it shifted from 977.0 cm$^{-1}$ at 338 °C in the aqueous phase to 987.6 cm$^{-1}$ at 355 °C in the Srich phase (Figs. 3 and 4, Table S1). In the Srich phase, the $v_1(SO_4^{2-})$ band kept shifting to a higher wavenumber as the temperature increased (Figs. 3 and 4). Unlike in the Li$_2$SO$_4$-H$_2$SO$_4$ solution, the $v_1(SO_4^{2-})$ band in the 1 m (NH$_4$)$_2$SO$_4$ solution shifted to lower wavenumbers monotonically when the temperature was increased to 320 °C (Fig. 4a, Table S1). In addition, the Raman shift of the $v_1(SO_4^{2-})$ band in the Li$_2$SO$_4$-H$_2$SO$_4$ solution was higher than that in the (NH$_4$)$_2$SO$_4$ solution at the same temperature. As to the peak width, the full width at half maximum (fwhm) of the $v_1(SO_4^{2-})$ band in the 1 m (NH$_4$)$_2$SO$_4$ solution was separated into two immiscible liquid phases that coexist with a vapor phase at temperatures above 342 °C (a, b). During subsequent cooling, the volume of sulfate-rich (Srich) droplets decreased and would homogenize into the sulfate-poor (Spoor) phase (c–d). In the 1.5 m Li$_2$SO$_4$ solution, the solid phase was formed from the Srich phase at ~360 °C (e, f). Then, the crystallization of the solid phase was accompanied by a decrease in the volume of the remaining Srich droplets (g–h).

**Table 1**

<table>
<thead>
<tr>
<th>Investigated systems</th>
<th>Li$_2$SO$_4$ molality</th>
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<tr>
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<td>0.1</td>
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<tr>
<td>Li$_2$SO$_4$-H$_2$O</td>
<td>352</td>
</tr>
<tr>
<td>mLi$_2$SO$_4$/mH$_2$SO$_4$ = 10$^a$</td>
<td>353</td>
</tr>
<tr>
<td>mLi$_2$SO$_4$/mH$_2$SO$_4$ = 5$^b$</td>
<td>353.6</td>
</tr>
<tr>
<td>mLi$_2$SO$_4$/mD$_2$SO$_4$ = 10$^c$</td>
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$^a$ Indicates the molar ratio between Li$_2$SO$_4$ and H$_2$SO$_4$ in aqueous solutions.

$^b$ Indicates the molar ratio between Li$_2$SO$_4$ and D$_2$SO$_4$ in D$_2$O solutions.

$^c$ Represents near critical Srich-Spoor homogenization phenomenon during cooling.
m Li2SO4–0.1 m H2SO4–H2O system increased with increasing temperature before liquid-liquid phase separation (Fig. 4b, Table S1). However, the fwhm remained fairly stable in the Srich phase, although it was larger than that in the aqueous phase. The fwhm of the 1 m (NH4)2SO4 solution also increased upon heating; however, the increase was smaller than that observed in the Li2SO4–H2SO4 solution at a constant temperature.

The v1(SO42−) band of the 1 m Li2SO4–0.1 m H2SO4 solution at 25 °C could be described by two Lorentzian components at ~981 (C1) and 987 cm−1 (C2) (Table S2). The former v1(SO42−) component was ascribed to the contribution of “free” SO42−, whereas the latter v1(SO42−) component was in close association with Li+–SO42− complexes (i.e., LiSO4, Tomišić and Simeon, 2000). Both v1(SO42−) components shifted to a lower wavenumber as the temperature increased (Table S2). For example, as the temperature increased to 175 °C, components C1 and C2 shifted to 977.5 and 982.9 cm−1, respectively. At temperatures of ≥200 °C, the v1(SO42−) band could not be well fitted with two Lorentzian components due to large fitting residuals in the high-wavenumber region; a third v1(SO42−) component (C3) at 987.3 cm−1 was identified at 200 °C in the aqueous phase (Fig. 5a, Table S2). In line with the low-wavenumber shift of the v1(SO42−) band, these three v1(SO42−) components all shifted to a lower wavenumber as the temperature increased. After the liquid-liquid phase separation, an additional v1(SO42−) component (C4) was identified at ~997.3 cm−1 at 350 °C (Fig. 5b, Table S2). Meanwhile, the signal of C1 could not be detected after the liquid-liquid phase separation. It should be noted that, the deconvolution of the v1(SO42−) band was not significantly influenced by the solvent composition in this study (i.e., H2O versus D2O; Fig. 5). The v1(SO42−) spectrum in the Spoor phase was weak, and no detailed deconvolution was completed.

The HSO4− spectrum at ~1050 cm−1 (Rudolph, 1996) was stronger in the Spoor phase than in the Srich phase at a constant temperature (Fig. 3). Fig. 6 shows the v1(SO42−)-intensity-normalized spectra of the immiscible Srich and Spoor phases of the 1 m Li2SO4–0.1 m H2SO4–H2O system. It further demonstrated that the HSO4− signal was much stronger in the Spoor phase than in the Srich phase. The v1(SO42−) band in the Srich phase shifted to a higher wavenumber than that in the Spoor phase at the same temperature.

4. Discussion

4.1. Contact ion pairing between Li+ and SO42−

Valyashko (1997) reviewed the liquid-liquid immiscibility in binary and ternary water-salt systems and noted that liquid-liquid phase separation occurred in the Li2SO4–H2O system at temperatures above 395 °C (cf. Fig. 1b in this reference). However, liquid-liquid phase separation was not observed in the Li2SO4–H2SO4–H2O system and its D2O
analogue even at temperatures up to 470 °C (Marshall et al., 1963). In this study, liquid-liquid phase separation was confirmed to occur in aqueous Li$_2$SO$_4$ solutions but at a much lower temperature (i.e., ≥ 336 °C) compared with the one given by Valyashko (1997). Since the phase behavior could be observed in situ under a microscope and the CAP500 heating stage exhibited good thermal stability (Pokrovski and Dubessy, 2015), the liquid-liquid phase separation temperature reported here should be reliable. In aqueous Na$_2$SO$_4$ solutions, SO$_4^{2−}$ was reported to form an Si(OH)$_4$·SO$_4^{2−}$ complex with SiO$_2$ at high temperatures (Marshall and Chen, 1982; Schmidt, 2009). However, the effect of dissolved SiO$_2$ on the liquid-liquid phase separation in aqueous Li$_2$SO$_4$ solutions was not obvious, because the dissolution of SiO$_2$ in aqueous Li$_2$SO$_4$ solution was weak at ≤ 350 °C, especially in the presence of excess H$_2$SO$_4$ (Fig. S2). Liquid-liquid phase separation was rarely documented in inorganic solutions (Marshall and Begun, 1989; Valyashko, 1997, 2008), although it is a common feature in organic-bearing solutions (Baltes et al., 1999; Paricaud et al., 2003; Gong et al., 2013). In addition, the liquid-liquid phase separation in Li$_2$SO$_4$ solutions with or without excess H$_2$SO$_4$ was characterized by the LCST phenomenon, as reported in other inorganic solutions (e.g., UO$_2$SO$_4$/CuSO$_4$·H$_2$O, MgSO$_4$·H$_2$O/H$_2$SO$_4$, Na$_2$B$_4$O$_7$·H$_2$O, Na$_2$HPO$_4$·H$_2$O, ZnSO$_4$·H$_2$O; Secoy, 1950; Clark et al., 1959; Marshall et al., 1962; Marshall, 1982; Marshall and Begun, 1989; Valyashko, 1997; Wang et al., 2013, 2016a; Wan et al., 2015). The presence of LCST in the aqueous Li$_2$SO$_4$ solution indicates that poly-ion associations occurred in this system because LCST was considered to be a macro-scale property of polymer solutions (e.g., Baltes et al., 1999; Paricaud et al., 2003; Gong et al., 2013). 2SIPs and SIPs are weak association complexes formed mainly by electrostatic forces, whereas CIPs are strong association complexes of Li$^+$ and SO$_4^{2−}$ formed by covalent bonds (c.f. Zhang and Chan, 2000). Moreover, the stability of 2SIPs and SIPs generally decreased as temperatures increased (e.g., Akilan et al., 2006a,b). For example, dielectric spectroscopic investigations showed that the concentrations of 2SIP and SIP significantly decreased as temperature increased in aqueous MgSO$_4$ solutions (e.g., 0.5 m, 5–65 °C); however, the concentration of CIP increased as temperature increased (Akilan et al., 2006b). Therefore, it can be concluded that strong contact ion pairing triggered liquid-liquid phase separation in the aqueous Li$_2$SO$_4$ solution at elevated temperatures. In addition, the Li$^+$·SO$_4^{2−}$ association may also benefit from the capillary effect: intermolecular interactions are increased to hinder the movements of molecules in the thin capillary (Vladimir M. Valyashko, personal communications).

The liquid-liquid phase separation temperature is above the solubility curve of the Li$_2$SO$_4$·H$_2$O system at constant Li$_2$SO$_4$ concentration (Marshall et al., 1963). The appearance of a second liquid phase instead of a solid phase indicates that the structure of the solution must have changed. The hydration numbers of Li$^+$ and SO$_4^{2−}$ were reported to be 4 and 12, respectively (Rudolph et al., 1995; Egorov et al., 2003; Vchirawongkwin et al., 2007; Yamaguchi et al., 2010). In the supersaturated S-rich phase, the remaining water molecules could not completely isolate the Li$^+$ and SO$_4^{2−}$ ions, indicating inner-sphere ion pairing between Li$^+$ and SO$_4^{2−}$. It should be noted that the liquid-liquid phase separation temperature of the Li$_2$SO$_4$·H$_2$O system was much higher than what was observed in the other reported sulfate solutions (Marshall et al., 1962; Wang et al., 2013, 2016a,b). For example, liquid-liquid phase separation in the aqueous MgSO$_4$ solution was reported to occur at ≥260 °C (Wang et al., 2013), which is ~73 °C lower than that observed in the aqueous Li$_2$SO$_4$ solution. This result can be partly ascribed to the relatively weaker contact ion pairing between Li$^+$ and SO$_4^{2−}$ than the pairing between Mg$^{2+}$ (or Zn$^{2+}$) and SO$_4^{2−}$ (c.f. Gilligan and Atkinson, 1980; Zhang and Chan, 2002).

4.1.2. $ν_1(SO_4^{2−})$ spectral evidence

Interpretation of the $ν_1(SO_4^{2−})$ spectra in an aqueous Li$_2$SO$_4$ solution is still debated. Some researchers have argued that Li$^+$ and SO$_4^{2−}$ cannot form CIPs in aqueous solutions, and the variation in the shape and wavenumber of the $ν_1(SO_4^{2−})$ spectra is ascribed to changes in the dynamics of the water molecules around the anion perturbed by the cations (e.g., Rull et al., 1995; Rull and Ohtaki, 1997; Matsumoto et al., 2009). Other researchers have suggested that the $ν_1(SO_4^{2−})$ spectra can be used to investigate Li$^+$·SO$_4^{2−}$ inner-sphere association (e.g., Rull, 1995; Tomišić and Simeon, 2000; Matsumoto et al., 2009). If the changes of the $ν_1(SO_4^{2−})$ spectra in an aqueous solution mainly arise from the hydrogen bond fluctuations of the water molecules in the first hydration shell of SO$_4^{2−}$, then the $ν_1(SO_4^{2−})$ spectra in light water and heavy water solutions should be different under the same conditions (i.e., temperature, pressure, composition; Rudolph et al., 2003).
However, our results show that the Raman shift and the peak width exhibited high consistency between the Li₂SO₄-D₂SO₄-D₂O and Li₂SO₄-D₂SO₄-D₂O systems at the same temperatures (Fig. 4). Moreover, deconvolution of the ν₁(SO₄²⁻) spectra yielded similar ν₁(SO₄²⁻) components for light water and heavy water solutions (Fig. 5). These observations indicate that the changes of the ν₁(SO₄²⁻) spectra in this study cannot be explained in the context of the dynamics of water molecules.

NH₄⁺ and SO₄²⁻ were suggested to be fully isolated in aqueous solutions (Rudolph et al., 2003). As a result, the ν₁(SO₄²⁻) spectra in aqueous (NH₄)₂SO₄ solutions can be used as a reference for unassociated SO₄²⁻ (e.g., Rudolph et al., 2003; Wang et al., 2016a). As shown in Fig. 4, the ν₁(SO₄²⁻) spectra of the aqueous (NH₄)₂SO₄ solution shifted to a lower wavenumber and were narrower than those observed in the Li₂SO₄-D₂O solution at a given temperature. The broadening of the ν₁(SO₄²⁻) band was considered to be the result of the distribution of CIPs (Zhang and Chan, 2000). Considering 2SIPs and SIPs are Raman indistinguishable (e.g., Rull, 1995; Rudolph et al., 2003; Buchner et al., 2004; Schmidt, 2009), the differences of the ν₁(SO₄²⁻) spectra between (NH₄)₂SO₄ and Li₂SO₄-D₂O solutions should be ascribed to the presence of inner-sphere Li⁺-SO₄²⁻ association.

The Raman peak area fraction was used to describe the fraction of each ν₁(SO₄²⁻) component, assuming that the scattering coefficients are equal for “free” and associated sulfate species (e.g., Rudolph et al., 1999; Jahn and Schmidt, 2010). The equation was described as follows:

$$f_i(\%) = A_i/A_{total} \times 100$$

where $f_i$ and $A_i$, respectively, denote the fraction and peak area of the ν₁(SO₄²⁻) component of C₁–C₄. $A_{total}$ represents the peak area of all ν₁(SO₄²⁻) components. Fig. 7 and Table S2 show the variation of the fractions of ν₁(SO₄²⁻) components in the 1.0 m Li₂SO₄-0.1 m D₂SO₄-D₂O solution. The fraction of the C₁ component decreased as temperature increased and approached 0 during liquid-liquid phase separation. The fraction of C₂ component increased as temperature increased up to 334 °C in the aqueous phase and then decreased as temperature increased in the Sₙrst phase. A C₃ component was identified at ≥ 260 °C, and its fraction ($f_3$) generally increased as temperature increased. If components C₁ and C₂ could be assigned to “free” SO₄²⁻ and LiSO₄, respectively (Rull, 1995; Tomišić and Simeon, 2000), then components C₃ and C₄ must be contributed from poly-ion Li⁺-SO₄²⁻ ion associations because “free” SO₄²⁻ and LiSO₄ transformed to C₃ and C₄ at higher temperatures. This conclusion is also consistent with previous speculations that complicated ion association is favored at elevated temperatures (Marshall and Gill, 1974; Marshall and Begun, 1989; Neuheide et al., 2004) due to the decreasing dielectric constant of water and electrolyte solutions as temperature increases (Wasserman et al., 1995; Filimonova et al., 2002; Maribo-Mogensen et al., 2013; Lyaschenko et al., 2014). According to the two-step Li⁺-SO₄²⁻ association pathway proposed by Rull (1995), component C₄ can be assigned to Li₂SO₄. Measurements of electrical conductance of the aqueous Li₂SO₄ solution also indicated that LiSO₄ and Li₂SO₄ are the dominant Li⁺-SO₄²⁻ complexes at temperatures from 250 to 380 °C (Sharygin et al., 2006). The assignment of component C₄ cannot be achieved in this study, but it should result from stronger and more complicated ion associations than component C₃ because (1) C₄ was identified only in concentrated Sₙrst phase, and (2) the fraction of component C₄ increased at the expense of the fraction of component C₃ upon heating. In fact, poly-ion Li⁺-SO₄²⁻ ion association, such as Li₆(SO₄)₆, was predicted to be present in aqueous solutions at temperatures above 400 °C (Sharygin et al., 2006).

The presence of hot band can also affect the Raman band profile (e.g., Holzer et al., 1970; Hochhenleicher and Schrött, 1971; Rosso and Bodnar, 1995). A hot band will be observed if a significant fraction of the number of molecules is in a vibrationally excited state. The Raman intensity of the hot band increases as temperature increases. Additional hot bands can form at higher temperatures (e.g., CO₂ hot bands; Wang et al., 2011) because the vibrational transition of a molecule does not only start in the ground state, but in any other vibrational level which is thermally populated (Hochhenleicher and Schrött, 1971). If the anharmonic oscillator model is applicable, the hot bands occur at lower wavenumbers than the fundamentals (e.g., Hochhenleicher and Schrött, 1971; Bernjo et al., 2001; C. Schmidt, personal communication). However, in the aqueous Li₂SO₄ solution, compared with the ν₁(SO₄²⁻) component of “free” sulfate, additional ν₁(SO₄²⁻) components of associated sulfate appeared in the higher wavenumber region in order. In addition, if the ν₁(SO₄²⁻) hot bands form, these phenomena should be observed in other aqueous sulfate solutions under hydrothermal conditions. In fact, these phenomena were not observed in aqueous (NH₄)₂SO₄ solutions; the ν₁(SO₄²⁻) spectrum is symmetric at temperatures even above 300 °C. Therefore, the variation in the ν₁(SO₄²⁻) band profile cannot be ascribed to the vibrational transition.

### 4.2. Behavior of Li⁺ in hydrothermal fluids

Since the hydration of Li⁺ is strong in aqueous solutions, contact ion pairing was suggested to be negligible in aqueous solutions (e.g., Rull et al., 1995; Rull and Ohtaki, 1997; Wachter et al., 2007). Although contact ion pairing was predicted by electrical conductivity measurements and molecular dynamics simulations (e.g., Accascina et al., 1967; Sverjensky et al., 1997; Chialvo and Simonson, 2006; Sharygin et al., 2006; Harashny and Pusztai, 2012), direct evidence for the formation of CIPs between Li⁺ and anions is still quite limited (e.g., Rull, 1995; Tomišić and Simeon, 2000). In this study, we confirmed that, on a molecular level, Li⁺ could form CIPs with ligands at elevated temperatures.

In submarine hydrothermal activity areas, the behavior of Li can be classified into two types: high temperature leaching (≥ 200 °C) and low temperature precipitation (< 150 °C; e.g., Seyfried et al., 1984; Chan et al., 1993, 2002; James et al., 2003; Tomascak, 2004; Misra and Froelich, 2012). At high temperatures, Li was leached from wall rocks into hydrothermal fluids because hydrothermal fluids, compared with seawater, were reported to be enriched in Li (e.g., Seyfried et al., 1984; Von Damm, 1988; Butterfield et al., 1990; Chan et al., 1993; Elderfield and Schulz, 1996; James et al., 2003; Brant et al., 2012). However, low-temperature alteration (or weathering) of basaltic near the seafloor leads to the uptake of Li from hydrothermal fluids and seawater into secondary minerals; the Li concentration of altered basalt was found to increase with increasing exposure time on the seafloor (e.g., Chan et al., 1992, 2002; Tomascak, 2004). According to the results of this study, various CIPs are the major Li species during the leaching of Li.

![Figure 7](image-url)

**Figure 7.** Peak area fractions of the ν₁(SO₄²⁻) components of the 1 m Li₂SO₄-0.1 m D₂SO₄-D₂O system from 25 to 420 °C. The dashed line indicates the liquid-liquid phase separation temperature (336 °C) in this system. The data plotted are those listed in Table S2.
from basalt into hydrothermal fluids at high temperatures. Complexation between Li and ligands can retain high solubility of Li and increase the overall mobility and thermodynamic driving forces for Li diffusion (e.g., Seyfried and Janecky, 1985; Leist and Goldik, 2001; Tagirov et al., 2005; Sander and Koschinsky, 2011). Therefore, the strong complexation of Li\(^+\) at high temperatures can enhance the efficiency of Li leaching. During the low-temperature uptake of Li into secondary minerals (e.g., clay minerals), hydrated Li\(^+\) and various 2SiPs and SLPs should be the dominant Li species. Recently, Brant et al. (2012) proposed that low-temperature hydrothermal fluid (50–125 °C) could also leach Li\(^+\) from the lavas without changing the mineral composition of the primary igneous rocks; Li diffuses out of minerals into warm hydrothermal fluids. However, the leaching of Li at low temperature was less effective than that occurring at high temperatures (Brant et al., 2012).

Previous studies have suggested that obvious fractionation of Li-isotopes occurs during water-rock interaction in submarine hydrothermal systems (e.g., Chan et al., 1993; Elderfield and Schultz, 1996; Tomascak, 2004; Brant et al., 2012). Analyses of the \(^6\)Li compositions can be used to trace the hydrothermal circulation. It was reported that \(^7\)Li was preferentially leached from the basalts at high temperatures, whereas \(^6\)Li tended to be incorporated into secondary minerals during low-temperature water-rock interaction (e.g., Chan et al., 1992, 1993, 2002; Seyfried et al., 1998; Tomascak, 2004; Vigier et al., 2008; Brant et al., 2012). During the low-temperature leaching of Li, Li\(^+\) diffused faster than Li, based on mass difference between \(^6\)Li and \(^7\)Li, and experimental results at high-temperatures (e.g., Richter et al., 2003; Döhlen et al., 2010). Further study of the species of Li is important to better understand the fractionation of Li-isotopes under hydrothermal conditions. For example, theoretical and experimental modeling showed that the Mg\(^2+\)-association with ligands exhibited significant influence on the Mg-isotopic composition of natural fluids and precipitated Mg-bearing minerals (Schott et al., 2016); different ligands preferentially associated different Mg isotopes (i.e., \(^{24}\)Mg and \(^{25}\)Mg).

Investigating the species of Li under hydrothermal conditions can also help us better understand the hydrothermal alteration of Li-bearing minerals. For example, Charoy et al. (2001) observed the replacement of spodumene by eucryptite at 200–300 °C in Li-rich aplite-pegmatite dykes from Northern Portugal. London and Burt (1982) investigated the alteration of spodumene, montebrasia and lithiophilite in pegmatites of the White Picacho District in Arizona. They suggested that these Li-rich minerals were altered by postmagmatic fluids and that secondary minerals including eucryptite and mica formed during this process. Therefore, Li\(^+\) can be leached from Li-bearing minerals into hydrothermal fluids, existing as various CIPs. In addition, zabuyelite (Li\(_2\)CO\(_3\)) is a common daughter mineral in crystal-rich inclusion (CI) hosted in spodumene in pegmatite deposits (e.g., Anderson et al., 2001; Li and Chou, 2016). The formation of zabuyelite in CIs was interpreted to be either a primary trapping or a secondary alteration of the host mineral spodumene (e.g., Anderson et al., 2001; Li and Chou, 2016). Regardless of the argument surrounding its origin, the formation temperature of zabuyelite was generally reported to be higher than 300 °C. At such high temperatures, Li\(^+\) should exist as various CIPs, favoring quick precipitation of zabuyelite in hydrothermal fluids. It can be predicted that CIPs and more complicated ion associations of Li\(^+\) should be the dominate Li species during the precipitation of Li-bearing minerals at high temperatures, especially for those formed in pegmatite (e.g., >400 °C; London, 1984; Ackerman et al., 2007; London and Kontak, 2012). Recent experimental work showed that large spodumene crystals can directly crystallize from aqueous fluids at elevated temperatures and pressures ranging from 570 to 710 °C and from 320 to 520 MPa, respectively (Li et al., 2013). Li et al. (2013) reported that the growth rate of spodumene can reach 4.7 × 10\(^{-7}\)–3.6 × 10\(^{-5}\) cm s\(^{-1}\). It can be inferred that the formation of Li\(^+\) complexes can maintain Li high solubility and promote the transport of Li in high-P-T aqueous fluids, favoring fast growth of spodumene.

4.3. Precipitation of sulfates in hydrothermal fluids

Based on classical nucleation and crystallization models, crystals should form through the monomer-by-monomer addition of simple chemical species in solution (Burton et al., 1951; Kashchiev, 2003). In contrast to classical models, recent field and laboratory observations have shown that crystals can form by the addition and attachment of particles, a process termed crystallization by particle attachment (CPA; De Yoreo et al., 2015). The particles include high-ordered species ranging from multi-ion complexes to fully formed nanocrystals (e.g., Gower and Odom, 2000; Beniash et al., 2009; Demichelis et al., 2011; Li et al., 2012; Habraken et al., 2013; De Yoreo et al., 2015). Among these particles, an immiscible dense liquid phase was suggested to be in close association with the formation of calcite at room temperature (e.g., Bewernitz et al., 2012; Wallace et al., 2013; Nielsen et al., 2014; De Yoreo et al., 2015). The mechanism for the transformation from a dense liquid phase to a crystalline phase is largely unknown (De Yoreo et al., 2015). Possible processes of the liquid-liquid phase separation-induced precipitation of calcite include (1) the transition of dense liquid into amorphous calcium carbonate (ACC), and (2) the transformation of ACC into crystalline calcite (e.g., Bewernitz et al., 2012; De Yoreo et al., 2015). However, the effect of liquid-liquid phase separation on the precipitation of crystals under hydrothermal conditions has not been well documented.

According to the phase diagram of the Li\(_2\)SO\(_4\)-H\(_2\)O system, the precipitation of anhydrous Li\(_2\)SO\(_4\) can be predicted in 1.5 m Li\(_2\)SO\(_4\) solutions at −288 °C (Marshall et al., 1963). However, no solid phase was observed in this Li\(_2\)SO\(_4\) solution at temperatures up to 359 °C (Fig. 1e). Instead, an unexpected dense liquid phase separated from the aqueous phase at ~337.7 °C and at vapor-saturated pressure (Fig. 2, Table 1). At 360 °C, the precipitation of anhydrous Li\(_2\)SO\(_4\) was observed within the dense liquid phase (Fig. 1f). As previously discussed, the liquid-liquid phase separation in the aqueous Li\(_2\)SO\(_4\) solution was induced by strong and complicated Li\(^+\)-SO\(_4\)\(^{2-}\) associations. At elevated temperatures, especially in the N\(_{seal}\) phase, Li\(^+\) and SO\(_4\)\(^{2-}\) could form more complicated ion associations than Li\(_2\)SO\(_4\) such as Li\(_{16}\)(SO\(_4\))\(_{15}\) (Sharygin et al., 2006). Therefore, the processes for the precipitation of Li\(_2\)SO\(_4\) induced by liquid-liquid phase separation may be summarized as follows: (1) strong and complicated Li\(^+\)-SO\(_4\)\(^{2-}\) associations lead to the presence of a dense liquid phase (Fig. 1a–e), (2) precipitation of Li\(_2\)SO\(_4\) within the dense liquid phase (might be amorphous; Fig. 1f), and (3) growth of crystalline Li\(_2\)SO\(_4\) on the surface of the early formed Li\(_2\)SO\(_4\) (Fig. 1f–h). Due to the relatively low optical and spectral resolution in this study (c.f. Rieger et al., 2014; De Yoreo et al., 2015 and references therein), a detailed mechanism for the precipitation of Li\(_2\)SO\(_4\) in the presence of the immiscible dense liquid phase is unclear. Nevertheless, our observations confirmed that liquid-liquid phase separation-induced CPA could be an important pathway for the precipitation of sulfates (and other minerals) in hydrothermal fluids.

In submarine hydrothermal fluids, all Ca\(^{2+}\) and one third of sulfate were removed from seawater at temperatures of >150 °C (e.g., Herzig et al., 1998; Tivey, 2007). The release of Ca\(^{2+}\) from basalt and the subsequent precipitation of anhydrite decreased the seawater sulfate to <1 mM (Bischoff and Dickson, 1975; Shanks, 2001). Ca\(^{2+}\) and SO\(_4\)\(^{2-}\) were suggested to form contact ion pairs at elevated temperatures (Ma et al., 2008). Low-D components were frequently observed in submarine hydrothermal fluids (e.g., H\(_2\), H\(_2\)S, CH\(_4\), CO\(_2\); Ishibashi et al., 1995; Gamo et al., 2001; Fu et al., 2007; Seyfried et al., 2007; Klein et al., 2009; McCollom and Bach, 2009). The presence of a low-D component can decrease the D value of the submarine hydrothermal fluids (c.f. Harvey and Prausnitz, 1987; Moriyoshi et al., 1990; Wang and Anderko, 2001). Therefore, ion-association-induced liquid-liquid
phase separation may occur during the precipitation of anhydrites in submarine hydrothermal fluids. In high-temperature venting fluids, especially for those chimneys with high porosity and permeability (e.g., Shanks and Seyfried, 1987; Woodruff and Shanks, 1988; Kim et al., 2006), the liquid-liquid phase separation is more likely to occur during the mixing of seawater and high-temperature venting fluids due to the high sulfate concentrations and a relatively low pressure (Marshall and Gill, 1974; Jahn and Wunder, 2009; Wang et al., 2016a). The presence of the liquid-liquid phase separation can, on one hand, serve as a precursor for the precipitation of anhydrite. On the other hand, it also accelerates the reduction of sulfate (e.g., Wang et al., 2013, 2016a). In summary, the observed liquid-liquid phase separation sheds new light on the nucleation and crystallization of minerals in hydrothermal fluids.

5. Conclusion

Fused silica capillary capsules (FSCCs) were used to prepare optical and spectroscopic cells containing 0.1–2.0 m Li2SO4 in light and heavy water solutions with and without excess H2SO4 (or D2SO4). The samples were placed in a Linkam CAP500 heating-cooling stage, and in situ Raman spectra of the samples were acquired at temperatures up to 420 °C. Although Li+ was reported to be strongly hydrated in aqueous solutions, our results show that Li+ can form various inner-sphere ion pairs with ligands in hydrothermal fluids, as evidenced by the following results: (1) Liquid-liquid phase separation with a lower critical solution temperature (LCST) at ~336.5 °C was observed in aqueous Li2SO4 solutions at vapor-saturation temperature. Since LCST was considered to be a macro-scale property of polymer solutions, poly-ion Li+−SO4−2 association can be predicted at high temperatures. In addition, the temperature for the occurrence of a second liquid phase in the aqueous Li2SO4 solution was significantly lower than previously documented (i.e., ~395 °C, Vyalashko, 1997). (2) In situ Raman spectra of the v1(SO4−2) band provided direct evidence of contact Li+−SO4−2 ion association at the molecular level. The results showed that the changes of the v1(SO4−2) spectra of the aqueous Li2SO4 solution upon heating were mainly ascribed to the Li+−SO4−2 association instead of to the hydrogen bond fluctuations of the water molecules in the first hydration shell of SO4−2. Further deconvolutions of the v1(SO4−2) spectra confirmed the presence of LiSO4, possible Li2SO4 and other poly-ion Li+−SO4−2 associations at high temperatures, as predicted by electrical conductivity measurement (Sharygin et al., 2006). The results also showed that the Li+−SO4−2 association increased as the temperature increased at a constant Li2SO4 concentration. For example, “free” SO4−2, LiSO4, Li2SO4 were the major sulfate species in the 1.0 m Li2SO4-0.1 m H2SO4 solution at 200 °C. However, the fraction of “free” SO4−2 was negligible and nearly all Li+ and SO4−2 were strongly associated at >350 °C.

In submarine hydrothermal systems, contact ion pairs of Li+ should be the major Li species during high temperature leaching of Li from basalts (e.g., >200 °C). The contact ion pairing between Li+ and ligands can promote the leaching of Li because the mobility and diffusion of a Li+−SO4−2 complex has been reported to be stronger than that of “free” ions. However, “free” Li+ and outer-sphere ion pairs are the dominant Li+ species during the low-temperature (e.g., <150 °C) uptake of Li+ into secondary minerals (e.g., clays). Various contact ion pairs of Li+ can also play important roles during the hydrothermal alteration/pre- precipitation of Li-rich minerals in pegmatite systems. Further study of the species of Li+ in hydrothermal fluids is important to better understand the fractionation of Li-isotope, as reported for the effect of Mg2+−association on the Mg-isotopic composition of natural fluids and precipitated Mg-bearing minerals (Schott et al., 2016).

In addition, anhydrous Li2SO4 was observed to precipitate within the dense immiscible liquid phase at ≥ 360 °C in 1.5 m Li2SO4. Compared with the classical nucleation and crystallization model, our observations indicate that liquid-liquid phase separation can play important roles in the formation of sulfates in hydrothermal fluids, serving as an important complement for the reported crystallization by particle attachment at low temperatures. Possible processes for the crystalization after the liquid-liquid phase separation are that (1) liquid-liquid phase separation results from strong and complicated ion association; (2) nucleation and crystallization occur within the dense liquid phase; and (3) crystals continue to grow on the surface of early formed solid phase. Liquid-liquid phase separation and the corresponding precipitation of sulfates and other minerals possibly occur in submarine hydrothermal fluids because strong and complicated ion associations are available due to high temperature, low pressure and the presence of low-dielectric components (e.g., CH4).

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Appendix A. Supplementary data

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References


