

Fate of sulfate in seafloor hydrothermal systems: Insights from *in situ* observation of the liquid–liquid phase separation in hydrothermal fluids

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Abstract

The ubiquitous hydrothermal circulation within the newly formed oceanic crust plays an important role in the transport of heat, water and chemical constituents in the earth-ocean-atmosphere system. One enigma during this process is whether seawater-derived sulfate participates in the deep hydrothermal circulation. Our results showed that homogeneous sulfate-bearing fluid separated to a sulfate-rich dense liquid phase and a sulfate-poor light liquid phase. The liquid–liquid phase separation (LLPS) temperature increased with rising fluid pressure but decreased with the addition of low dielectric constant (*D*) components. *In situ* Raman spectroscopic characterization revealed that the $\text{Zn}^{2+}\text{-SO}_4^{2-}$ association increased with the addition of low *D* components. All these observations confirmed our previous conclusions that strong ion complexation triggered the LLPS. The formation of a sulfate-rich dense liquid phase could postpone the precipitation of sulfate, resulting in the participation of seawater-derived sulfate in the deep hydrothermal circulation. Sulfate would be reduced to S^{2-} and mixed with that leached from the basalt, leading to the elevated $\delta^{34}\text{S}$ value of the sulfide precipitated on the seafloor.

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Keywords: *In situ* observation; Raman spectroscopy; Liquid–liquid phase separation; Sulfate; Seafloor hydrothermal system

1. Introduction

Based on sampling and analyses of the venting fluids exiting from ridge axes (e.g., Edmond et al., 1982; Butterfield and Massoth, 1994; Seyfried et al., 2003), mineralogical and chemical studies of hydrothermally altered basalts (e.g., Humphris and Thompson, 1978; Haymon and Kastner, 1986; Alt and Teagle, 2003), and experimental investigations of basalt–seawater interactions at elevated pressures and temperatures (e.g., Bischoff and Dickson, 1975; Seyfried and Bischoff, 1981; Seewald and Seyfried, 1990), it has been

confirmed that hydrothermal circulation is ubiquitous within the newly formed oceanic crust and plays an important role in the transport of heat, water and chemical constituents in the earth-ocean-atmosphere system (McDuff and Edmond, 1982; Elderfield and Schultz, 1996; Tivey, 2007; Zeng, 2011). Tivey (2007) summarized the generation of seafloor hydrothermal fluids, including (a) cold seawater infiltrates into the ocean crust in the recharge zone and is heated by deep magma or newly solidified hot rock; (b) after complex water–rock interactions, the resultant fluid leaches metals (e.g., Cu, Zn, Au) and S from the rock into the solution in the deep reaction zone; and (c) the hot and buoyant fluid ascends through the discharging zone to exit at the seafloor. There is no doubt that the circulation of seawater within seafloor basalts results in pervasive and significant variation in the chemistry and mineralogy of basalts and in chemistry of the ocean (Alt, 1995; Tivey, 2007; Zeng, 2011 and references therein).

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An obvious difference in the composition between seawater and hydrothermal venting fluids is the speciation and concentration of sulphur (S; e.g., McDuff and Edmond, 1982; Zeng, 2011). In seawater, dissolved sulfate is the dominant S species, with an average concentration of ~28 mM (Garrels and Thompson, 1962). On the contrary, the venting fluids is highly depleted in dissolved sulfate (~0 mM), but has H₂S concentrations ranging from several to more than one hundred mM (Zeng, 2011 and references therein). Geochemical analyses reveal elevated $\delta^{34}\text{S}$ values of the venting H₂S and sulfides (>1‰; 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; Tivey, 2007), compared with that of basaltic sulfide (~0‰; Sakai et al., 1984). Considering seawater sulfate is characterized by an obviously positive $\delta^{34}\text{S}$ value (20.9‰; Rees et al., 1978), aforementioned stable S isotopic studies indicate that seawater sulfate is an important S source for hydrothermal metal sulfides. However, mechanism for the involvement of seawater sulfate during the formation of seafloor metal sulfides has not been well addressed. During the circulation of seawater within the ocean crust, the precipitation of anhydrite removes most of sulfate from the fluids, preventing seawater-derived sulfate from participating in the deep S cycle (e.g., McDuff and Edmond, 1982; Tivey, 2007; Zeng, 2011). Therefore, the positive $\delta^{34}\text{S}$ value of some venting H₂S was interpreted as the isotope exchange between sulfide and sulfate during upflow through a shallow anhydrite-bearing zone at elevated temperatures (Ono et al., 2007).

Our previous studies showed that aqueous ZnSO₄ solution exhibits an intriguing liquid–liquid phase separation (LLPS) at $\geq 266.5^\circ\text{C}$ (Wang et al., 2016a); the homogeneously aqueous solution separated into a dense sulfate-rich liquid (L1) and a light sulfate-poor liquid (L2). The occurrence of LLPS was used to interpret the circulation and reduction of seawater sulfate in deep ocean crust (Wang et al., 2016a). Firstly, the formation of the L1 phase could postpone the precipitation of sulfate, favoring the penetration of seawater sulfate to deep ocean crust. Secondly, the complex Zn²⁺–SO₄^{2–} association within the L1 phase decreases the stability of the S–O bonds and promotes the reduction of sulfate in the presence of ferrous Fe of pyroxene or olivine. In addition, the formation of a sulfate-rich liquid phase can increase the rate of sulfate reduction. At last, the reduced S originated through sulfate-reduction mixes with that leached from basalt and vents to the seafloor to form metal sulfides. However, our previous experiments were carried out at vapor-saturation pressures, and the influence of low dielectric constant (*D*) components (e.g., H₂, H₂S, CO₂, CH₄ and other hydrocarbons), which are frequently discovered in venting fluids (e.g., Charlou et al., 2002; Konn et al., 2009; Zeng, 2011) was not well addressed.

In this study, *in situ* optical and Raman spectroscopic observations were conducted to investigate the implications of LLPS on the S cycle in the seafloor hydrothermal systems. Specifically, (a) LLPS of the system ZnSO₄–H₂O was investigated at elevated temperatures up to 300 °C and at

pressures from 5.10 to 44.34 MPa, (b) ethyl alcohol (C₂H₅OH) was selected as an example to investigate the effect of low *D* component on the occurrence of LLPS, and (c) *in situ* Raman spectroscopy was used to characterize the composition and structure of the fluids, further deciphering the mechanism of LLPS.

2. Samples and methods

2.1. Solution preparation

Aqueous ZnSO₄ solutions were prepared using Reagent-Plus grade zinc sulfate heptahydrate ($\geq 99\%$ purity, Sigma–Aldrich) and distilled deionized water. The concentration of ZnSO₄ was expressed in molality (mol/kg H₂O; *m*), i.e., 0.5 *m*, 1.0 *m*, and 2.0 *m* (Table 1). Ethyl alcohol ($\geq 99.7\%$ purity, Nanjing Chemical Reagent Co., LTD) was added to the aqueous ZnSO₄ solution, and the molar ratio between H₂O and C₂H₅OH (*m*H₂O/*m*C₂H₅OH) was used to describe the content of C₂H₅OH. In 0.5 and 1.0 *m* ZnSO₄, *m*H₂O/*m*C₂H₅OH ranges from 10 to 100 (Table 2). In 2.0 *m* ZnSO₄ solution, *m*H₂O/*m*C₂H₅OH was fixed at ~35 (Table 1).

As described in the introduction section, seafloor hydrothermal fluids are rich in low *D* components such as H₂, H₂S, CO₂, CH₄ and other hydrocarbons (e.g., Charlou et al., 2002; Konn et al., 2009; Zeng, 2011). Procedures of preparation of the gas-bearing solutions with a certain composition are complicated and time-consuming (Wang et al., 2020). In addition, hydrocarbon and water will react to form alcohols at $\geq 200^\circ\text{C}$ (Chou et al., 2008; Xu and Chou, 2017). Therefore, we chose ethyl alcohol as an example to explore the effect of low *D* components on the occurrence of LLPS.

2.2. Experimental design

The prepared solution was loaded into High-pressure Optical Cells (HPOCs; Chou et al., 2005; Wang et al., 2011). One end of about 20 cm long, rounded cross-sectioned fused silica tube [200 μm in inner diameter (ID), 600 μm in outer diameter

Table 1

The temperature (*T*) and pressure (*P*) conditions for the occurrence of LLPS in aqueous ZnSO₄ solution with and without additional C₂H₅OH.

0.5 <i>m</i> ZnSO ₄		1.0 <i>m</i> ZnSO ₄		2.0 <i>m</i> ZnSO ₄		2.0 <i>m</i> ZnSO ₄ ^a	
<i>P</i> (MPa)	<i>T</i> (°C)	<i>P</i> (MPa)	<i>T</i> (°C)	<i>P</i> (MPa)	<i>T</i> (°C)	<i>P</i> (MPa)	<i>T</i> (°C)
5.07	272.2	5.10	266.3	5.14	272.8	5.07	235.8
9.97	275.6	9.95	269.7	9.99	276.2	9.95	239.1
14.95	279.2	14.95	273.0	14.97	280.0	15.01	242.4
19.80	282.5	19.70	276.2	19.80	283.2	19.80	245.5
24.98	286	24.93	279.7	24.90	286.8	24.94	248.6
29.67	289.4	29.68	282.8	29.69	290.0	29.69	251.4
35.14	292.8	35.14	286.3	35.14	293.8	35.16	254.9
39.93	296.1	39.93	289.4	39.95	297.3	39.91	257.6
44.34	299.2	44.32	292.4	44.32	300.1	44.32	260.2
		49.26	295.5			49.35	263.1

^a Aqueous ZnSO₄–C₂H₅OH solution. The *m*H₂O/*m*C₂H₅OH ratio was fixed at ~35.

Table 2

The temperature (T) for the appearance of LLPS in 0.5 m and 1.0 m ZnSO_4 solutions with $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH}$ molar ratios ranging from 100 to 10.

$m\text{H}_2\text{O}/m\text{C}_2\text{H}_5\text{OH}$	100	76.92	50	25	10
T ($^{\circ}\text{C}$) ^a	263.0	262.5	257.7	247.7	215.6
T ($^{\circ}\text{C}$) ^b	259.3	257.7	255.8	245.5	216.8

^a 0.5 m ZnSO_4 .

^b 1.0 m ZnSO_4 .

(OD)] was sealed by fusion in oxyhydrogen flame. One end of another fused silica tube (~30 cm long, 50 μm ID and 150 μm OD) was epoxied inside the needle of a syringe (Fig. 1a). The sample solution was sucked into the syringe through the thinner silica tube. After inserting the thinner silica tube into the thick silica tube, the sample solution was loaded into the sealed end through squeezing the syringe (Fig. 1a). Similarly, a section of mercury was loaded into the thicker silica tube to separate the sample solution from the pressure medium (water in this study) (Fig. 1a).

The open end of the thicker tube was epoxied inside a stainless steel tube (4 cm long, 0.76 mm ID and 1.59 mm OD), and was connected to a pressurization system with a sleeve-gland assembly and a high-pressure valve (HiP. 15-15AF1, High Pressure Equipment Company) (see HPOC in Fig. 1b). The sample pressure was adjusted using a pressure generator. Pressure was measured by a Setra 204D digital pressure transducer with Datum 2000™ manometer (69 MPa full scale, accurate to $\pm 0.14\%$). The HPOC was fixed on a custom-designed stage (Fig. 1b). The sealed end of the HPOC was inserted into a Linkam CAP500 heating-cooling stage (Wan et al., 2015; Wang et al., 2016a), which was used to control the sample temperature. The temperature of the stage was calibrated by using the melting temperatures of n -hexadecane (18.17 $^{\circ}\text{C}$), sulfur (119 $^{\circ}\text{C}$), and NaNO_3 (306.8 $^{\circ}\text{C}$) (Wang et al., 2016a). The stage exhibits good thermal stability (± 0.1 $^{\circ}\text{C}$) with negligible temperature gradients (< 1 $^{\circ}\text{C}$ within 15 mm).

The heating-cooling stage, together with the HPOC were placed on the stage of an Olympus BX51 microscope equipped

with a QImaging MicroPublisher 3.3 RTV CCD and a $20\times$ long working distance objective. The phase behavior of the fluid sample was observed under the microscope and recorded using Linkam Linksys 32 software.

2.3. Acquisition and treatment of Raman spectra

In situ spectra of the fluid within an HPOC were collected using a LabRAM HR800 (JY/Horiba) Raman spectrometer. The excitation wavelength is 532.11 nm (air-cooled, frequency doubled Nd:YAG), and the laser power was adjustable from 0 to 500 mW. A 1800 groove/mm grating was applied, giving a spectral resolution of better than 1 cm^{-1} . A $50\times$ Olympus long-working distance objective with 0.5 numerical aperture provided a spatial resolution of a few μm . Before each experiment, the spectrometer was calibrated with the 520.7 cm^{-1} peak of silicon. The spectra were collected from 730 to 1320 cm^{-1} to cover the symmetric stretching vibration band of dissolved sulfate ($\nu_1(\text{SO}_4^{2-})$; Wang et al., 2013) and the C–O and C–C stretching vibration bands of ethanol (Corsetti et al., 2016), and from 2650 to 3780 cm^{-1} to cover the O–H symmetric stretching vibration band of water [ν_s (H_2O); Chen et al., 2004] and the C–H symmetric stretching vibration band of ethanol (Corsetti et al., 2016).

The spectra were corrected with a linear baseline. The wavenumber and the width of the $\nu_1(\text{SO}_4^{2-})$ bands were determined using a program operated on MATLAB R2015a (The MathWorks, Inc.) (Wang et al., 2017). Deconvolution of the $\nu_1(\text{SO}_4^{2-})$ bands were carried out using the Peakfit v. 4.0 program (AISN Software Inc.).

3. Results

3.1. Effect of pressure on the liquid–liquid phase separation

Fig. 2a shows the LLPS during a drop in fluid pressure in 0.5 m ZnSO_4 . When the fluid pressure decreased from 44.34 to 9.86 MPa at constant temperature of 299.2 $^{\circ}\text{C}$, abundant small

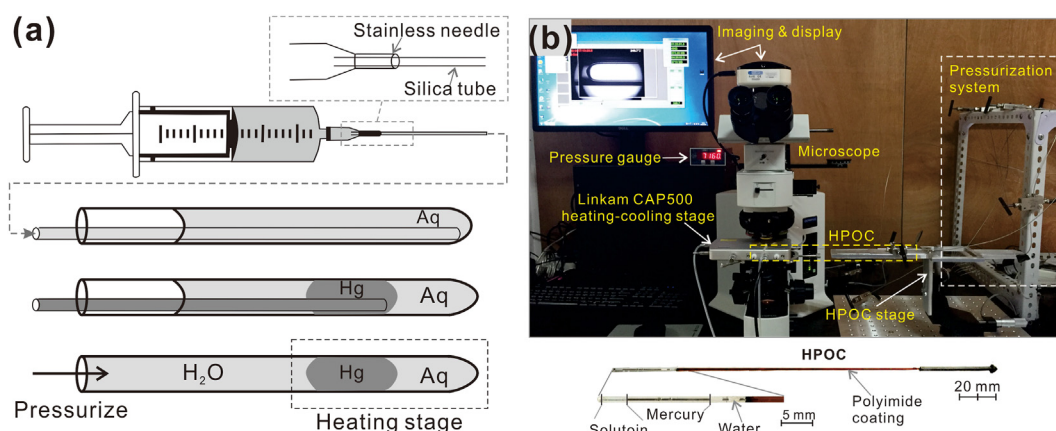


Fig. 1. (a) Sample loading procedures; (b) Experimental settings of *in situ* observations of the fluid phase behavior, and a prepared HPOC. Aq denotes aqueous solution.

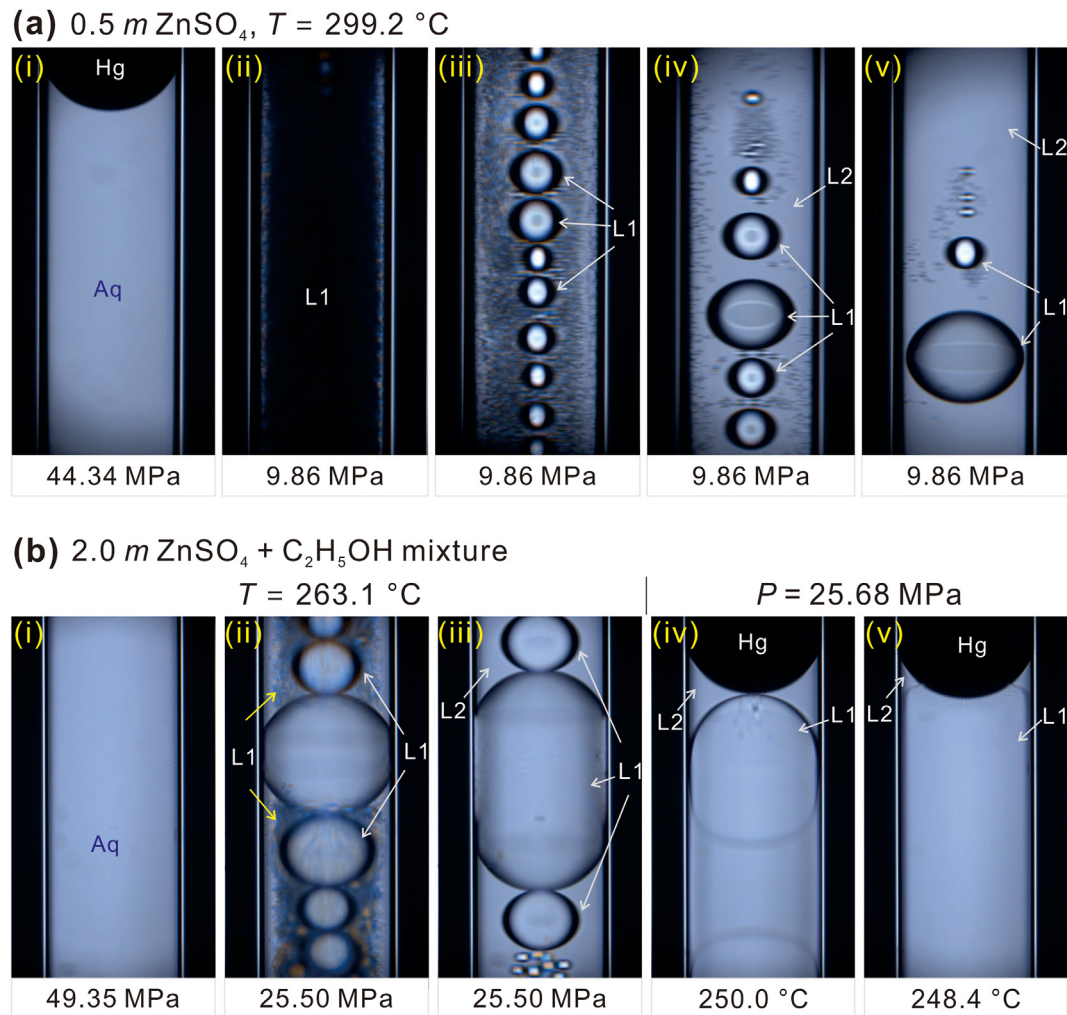


Fig. 2. LLPS in 0.5 m ZnSO₄ (a) and 2.0 m ZnSO₄ + C₂H₅OH (b) at elevated temperatures and pressures. (a) LLPS occurred during a drop of fluid pressure from 44.34 MPa to 9.86 MPa at constant temperature of 299.2 °C (i–v); (b) LLPS occurred when fluid pressure decreased from 49.35 MPa to 25.50 MPa at fixed temperature of 263.1 °C (i – iii). At 25.68 MPa, the L1-L2 phases homogenized during decrease in temperature (iv – v).

droplets emerged from the initially homogeneous aqueous phase. Due to the small size and large quantities of these droplets, the field of view was dark. As the experiment proceeded at a constant pressure, these small droplets coalesced to form larger droplets, and the field of view became clear again. Then, the 0.5 m ZnSO₄ was characterized by the coexistence of the L1 and L2 liquid phases under such temperature-pressure (T - P) conditions. Similar phenomenon can also be observed in the ZnSO₄–C₂H₅OH mixture. As shown in Fig. 2b, when the fluid pressure decreased from 49.35 MPa to 25.50 MPa, L1 droplets occur and merged to form the L1-L2 immiscibility in 2.0 m ZnSO₄ ($m\text{H}_2\text{O}/m\text{C}_2\text{H}_5\text{OH} = 35$) at constant temperature of 263.1 °C. At 25.68 MPa, the volume of L1 phase increased and the L1-L2 phase boundary faded away with decreasing temperature.

The T - P conditions for the occurrence of LLPS in aqueous ZnSO₄ and ZnSO₄–C₂H₅OH solutions were listed in Tables 2 and 3. Generally, the starting temperature of LLPS increases linearly with rising fluid pressure (Fig. 3a and b). For example, LLPS occurred at 272.2 °C and 5.07 MPa in 0.5 m ZnSO₄.

With rising fluid pressure, the starting temperature of the LLPS increased at a rate of 0.685 °C/MPa. Minor variation in the slope of the T - P curve can be identified in aqueous ZnSO₄ solutions with different concentrations (Fig. 3a). In the presence of C₂H₅OH, the starting temperature of LLPS also increased with rising fluid pressure (Fig. 3b).

3.2. Influence of ethanol on the liquid–liquid phase separation

As shown in Fig. 3b, the presence of C₂H₅OH lowered the starting temperature of LLPS at constant fluid pressure and ZnSO₄ concentration. For instance, when the fluid pressure was fixed at 9.95 MPa, the LLPS occurred at 271.7 °C in 2.0 m ZnSO₄ solution. In ZnSO₄ + C₂H₅OH solution with $m\text{H}_2\text{O}/m\text{C}_2\text{H}_5\text{OH}$ ratio of ~35, the starting temperature of LLPS was 32.6 °C lower than that for 2.0 m ZnSO₄ (Table 1; Fig. 3b). In addition, the slope for the T - P curve of the ZnSO₄–C₂H₅OH–H₂O system was slightly lower than that for the ZnSO₄–H₂O system (Fig. 3b).

Table 3

The wavenumber, peak width, and deconvolution results of the $\nu_1(\text{SO}_4^{2-})$ spectra of 1.0 *m* ZnSO_4 with additional $\text{C}_2\text{H}_5\text{OH}$ at 200 °C.

$m\text{H}_2\text{O}/m\text{C}_2\text{H}_5\text{OH}$	100	76.92	50	25	10
Wavenumber (cm^{-1})	978.28	978.74	978.79	979.25	980.16
FWHM (cm^{-1})	22.84	23.30	24.15	25.38	26.36
C_1 (cm^{-1}) ^a	978.92	978.41	977.79	977.91	978.46
C_2 (cm^{-1})	989.41	989.51	988.70	988.90	989.69
A_1 ^b	15878.51	18587.84	18661.22	12059.02	11790.27
A_2 ^b	6189.90	8877.78	11874.05	7760.04	8890.31
f_1 ^c	0.7195	0.6768	0.6111	0.6084	0.5701
f_2 ^c	0.2805	0.3232	0.3889	0.3916	0.4299

^a The peak position of the $\nu_1(\text{SO}_4^{2-})$ sub-bands at $\sim 980 \text{ cm}^{-1}$ (C_1) and $\sim 990 \text{ cm}^{-1}$ (C_2), respectively.

^b The peak area of the $\nu_1(\text{SO}_4^{2-})$ components at $\sim 980 \text{ cm}^{-1}$ (A_1) and $\sim 990 \text{ cm}^{-1}$ (A_2), respectively.

^c The peak area fraction of the $\nu_1(\text{SO}_4^{2-})$ components at $\sim 980 \text{ cm}^{-1}$ (f_1) and $\sim 990 \text{ cm}^{-1}$ (f_2), respectively.

Fig. 3c shows the starting temperature of LLPS at vapor-saturation pressure of 0.5 and 1.0 *m* ZnSO_4 with $m\text{H}_2\text{O}/m\text{C}_2\text{H}_5\text{OH}$ ratio ranging from 10 to 100. In general, the starting temperature of the LLPS increased with rising $m\text{H}_2\text{O}/m\text{C}_2\text{H}_5\text{OH}$ ratio at constant ZnSO_4 concentration. For example, in 0.5 *m* ZnSO_4 with $m\text{H}_2\text{O}/m\text{C}_2\text{H}_5\text{OH}$ ratio of 100, LLPS occurred at 263.0 °C. When the $m\text{H}_2\text{O}/m\text{C}_2\text{H}_5\text{OH}$ ratio decreased to 10, the starting temperature of LLPS decreased to 215.6 °C (Table 2; Fig. 3c).

3.3. Raman characterization of the $\text{ZnSO}_4\text{--H}_2\text{O--C}_2\text{H}_5\text{OH}$ mixtures

Fig. 4a shows the *in situ* Raman spectra of 1.0 *m* ZnSO_4 with $m\text{H}_2\text{O}/m\text{C}_2\text{H}_5\text{OH}$ ratio of 25. After LLPS, the $\nu_1(\text{SO}_4^{2-})$ band intensity was significantly increased in the L1 phase, whereas that for the L2 phase was obviously decreased. The bands of ethanol were marked with stars. Fig. 4b presents the $\nu_1(\text{SO}_4^{2-})$ spectra of the aqueous ($\leq 240 \text{ °C}$) and L1 ($\geq 250 \text{ °C}$) phases. Before LLPS, the intensity of the $\nu_1(\text{SO}_4^{2-})$ band decreased with rising temperature. In the L1 phase, $\nu_1(\text{SO}_4^{2-})$ band intensity increased with rising temperature. On the contrary, the $\nu_1(\text{SO}_4^{2-})$ band intensity decreased with increasing temperature in the L2 phase (Fig. 4c). It can be seen that the $\nu_1(\text{SO}_4^{2-})$ band position shifted slightly to higher wavenumber with rising temperature (Fig. 4b). Meanwhile, the asymmetry of the $\nu_1(\text{SO}_4^{2-})$ band could also be identified (Fig. 4b). In the aqueous phase, the symmetry of the $\nu_1(\text{SO}_4^{2-})$ band decreased with rising temperature, whereas it increased with rising temperature in the L1 phase (Fig. 4b).

In situ Raman spectra of 1 *m* ZnSO_4 with $m\text{H}_2\text{O}/m\text{C}_2\text{H}_5\text{OH}$ ratio ranging from 10 to 100 were collected at 200 °C (Fig. 5a). With decreasing $m\text{H}_2\text{O}/m\text{C}_2\text{H}_5\text{OH}$ ratio, the $\nu_1(\text{SO}_4^{2-})$ band slightly shifted to higher wavenumber. Meanwhile, the bandwidth (Full width at half maximum,

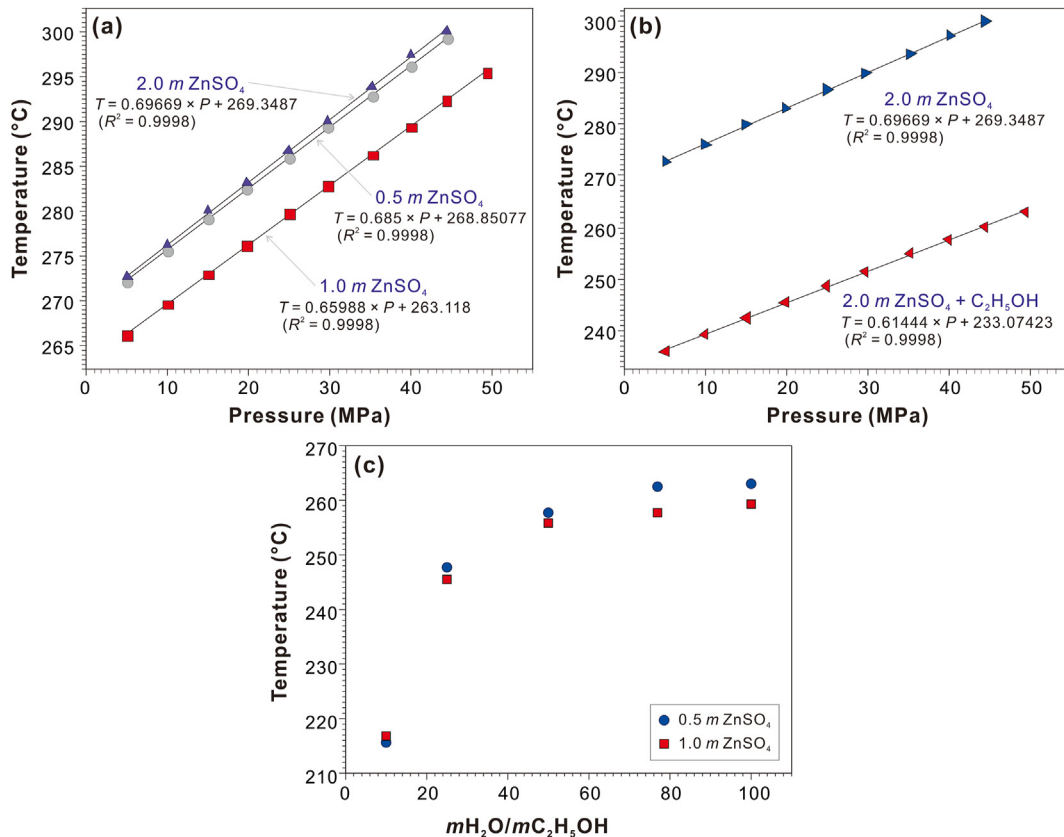


Fig. 3. Effects of pressure and low D component (i.e., $\text{C}_2\text{H}_5\text{OH}$) on the occurrence of LLPS. (a) *T-P* conditions for the occurrence of LLPS in 0.5 *m*, 1.0 *m* and 2.0 *m* ZnSO_4 solutions; (b) *T-P* conditions for the occurrence of LLPS in 2.0 *m* ZnSO_4 and 2.0 *m* $\text{ZnSO}_4 + \text{C}_2\text{H}_5\text{OH}$ solutions with $m\text{H}_2\text{O}/m\text{C}_2\text{H}_5\text{OH}$ ratio of ~ 35 ; (c) Starting temperatures of LLPS in 0.5 *m* and 1.0 *m* ZnSO_4 with $m\text{H}_2\text{O}/m\text{C}_2\text{H}_5\text{OH}$ ratio ranging from 10 to 100.

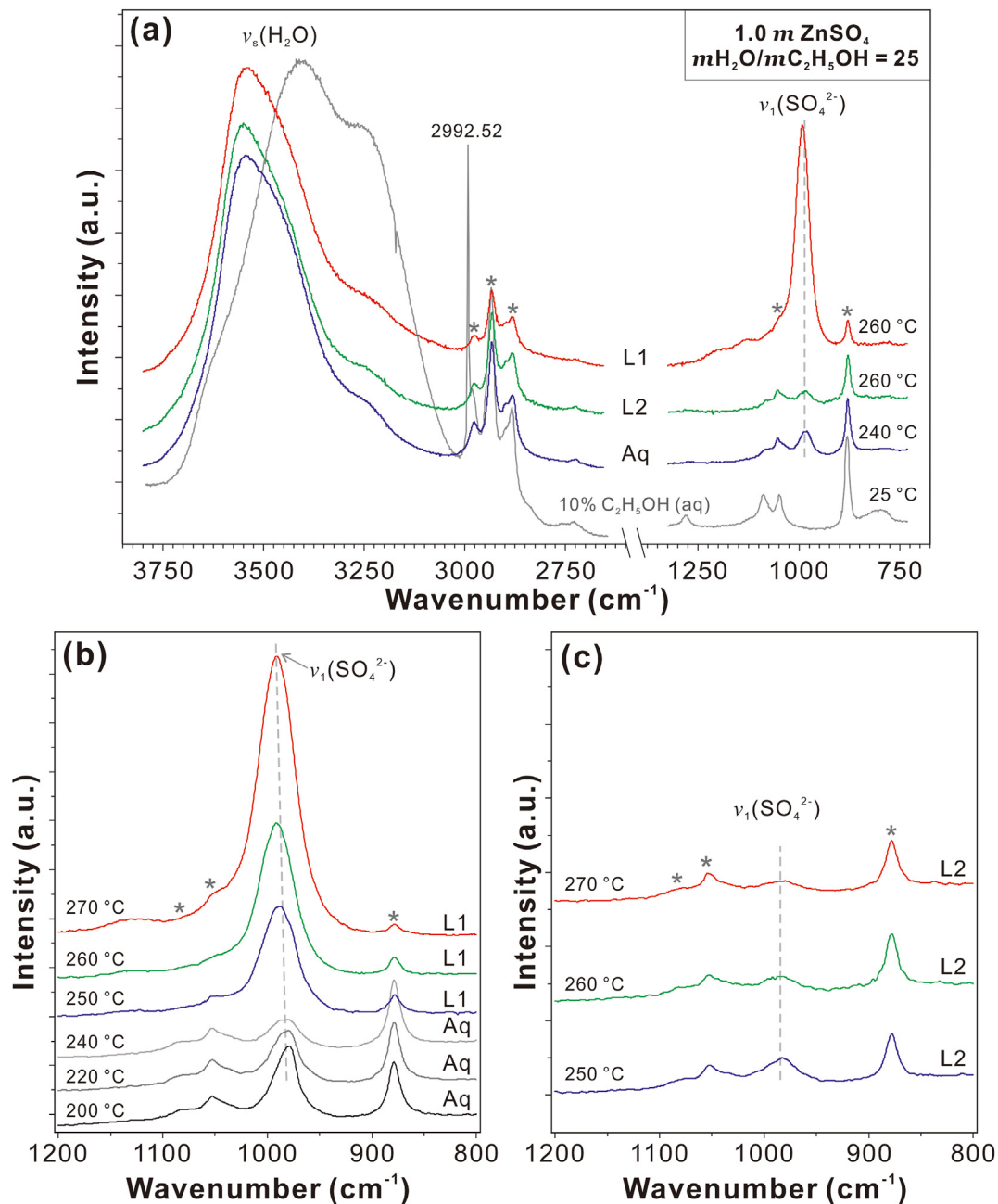


Fig. 4. *In situ* Raman spectra of 1.0 m ZnSO₄ with mH₂O/mC₂H₅OH ratio of 25. (a) Spectra for the homogeneous aqueous phase collected at 25 and 240 °C, and the immiscible L1 and L2 phases at 260 °C. The spectra of 10 vol.% ethanol solution was illustrated for comparison; (b) The ν₁(SO₄²⁻) spectra collected at 200–240 °C for the homogeneous aqueous phase, and at 250–270 °C for the L1 phase; (c) The ν₁(SO₄²⁻) spectra collected at 250–270 °C for the L2 phase. Stars indicate the signals of dissolved C₂H₅OH.

FWHM) increased from 22.8 cm⁻¹ to 26.4 cm⁻¹, when the mH₂O/mC₂H₅OH ratio decreased from 100 to 10 (Fig. 5b; Table 3). The ν₁(SO₄²⁻) band was fitted using two Gauss + Lorentz sub-bands at ~980 cm⁻¹ and 990 cm⁻¹ (Wang et al., 2016a). At constant temperature and fixed ZnSO₄ concentration, the peak area fraction of ~980 cm⁻¹ component decreased with decreasing mH₂O/mC₂H₅OH ratio, whereas that of the ~990 cm⁻¹ component increased (Fig. 5c).

4. Discussion

4.1. Origin of liquid–liquid phase separation

Secoy (1948, 1950) observed the LLPS in aqueous uranyl sulfate (UO₂SO₄) solutions at temperatures of ≥295 °C. Subsequently, William L. Marshall and his coworkers measured the compositions of the L1 and L2 phases, and investigated the effects of fluid pressure and composition on

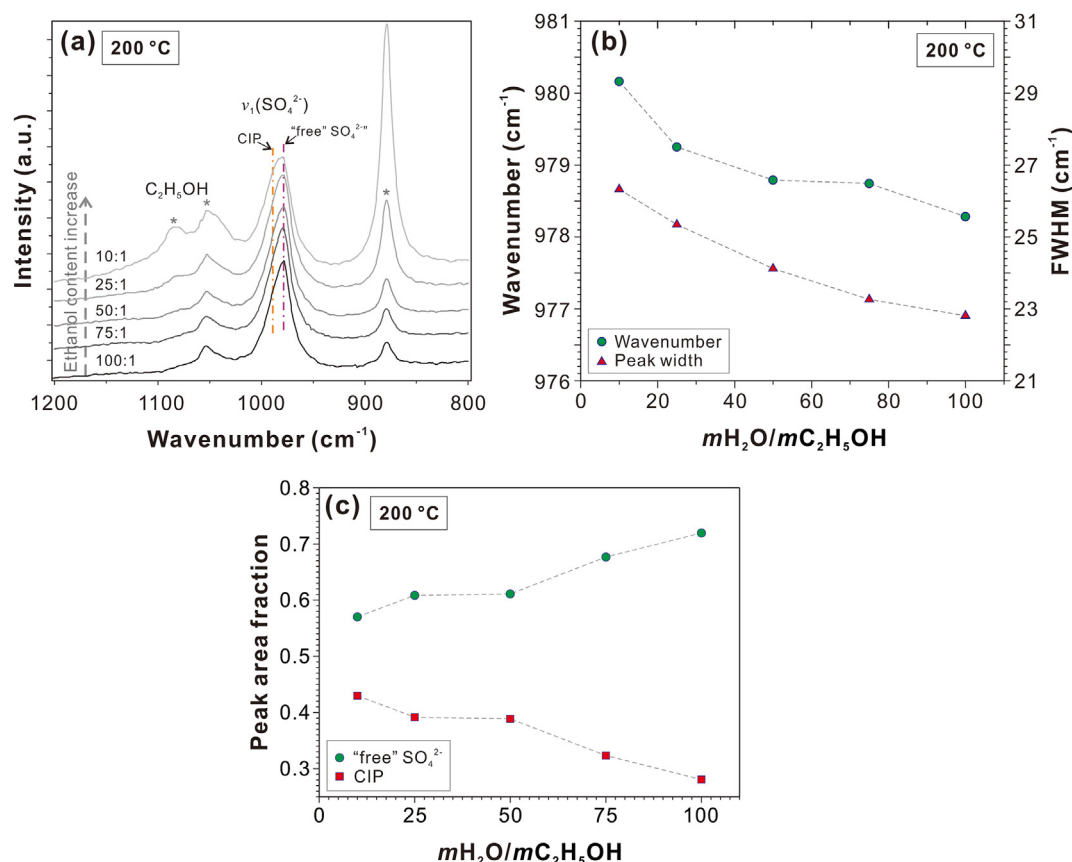


Fig. 5. *In situ* Raman spectra (a) and the spectral parameters (b, c) of 1.0 m ZnSO₄ with mH₂O/mC₂H₅OH ratio ranging from 10 to 100 at 200 °C. (b) Variations in wavenumber and peak width of the $\nu_1(\text{SO}_4^{2-})$ band with mH₂O/mC₂H₅OH ratio; (c) Dependence of the fractions of free SO₄²⁻ and CIP on the mH₂O/mC₂H₅OH ratio.

this intriguing phase behavior (e.g., Jones and Marshall, 1961; Marshall et al., 1962; Marshall and Gill, 1974). For the formation of LLPS, Marshall and Gill (1974) speculated that the strong association and polymerization of dissolved UO₂²⁺, SO₄²⁻, and UO₂SO₄ species at elevated temperatures might change the solution to a “pseudo organic-water” system. LLPS is relatively more common in organic-bearing solutions (e.g., Baltes et al., 1999; Paricaud et al., 2003; Gong et al., 2013). However, *in situ* characterization of the uranyl species in the L1 and L2 phase at elevated temperatures was limited, which weakened the reliability of Marshall’s conclusion. With the aid of a new optical cell constructed from fused silica capillary tube (Chou et al., 2008; Wang et al., 2011), the LLPS in aqueous MgSO₄ solutions was observed at temperatures of >259 °C (Wang et al., 2013). More importantly, this method allows *in situ* Raman spectroscopic analyses of the coexisting L1-L2 phases at temperatures of ≤500 °C. Analyses of the $\nu_1(\text{SO}_4^{2-})$ band indicated that contact ion pair (CIP), triple ion pair (TI), and a more complicated ion association (~1020 cm⁻¹) were the dominated sulfate species in the L1 phase (Wang et al., 2013). Interestingly, the newly discovered sulfate species with $\nu_1(\text{SO}_4^{2-})$ band at ~1020 cm⁻¹ was only detected in the L1 phase. Similar phenomena were also observed in aqueous UO₂SO₄ solutions. The UO₂²⁺-SO₄²⁻ association increased with rising temperature, and associated

UO₂²⁺ was the dominant uranyl species in the L1 phase (Wang et al., 2016b). It can be seen that *in situ* Raman spectroscopy can provide direct information of the fluid composition and structure, and strong ion association and polymerization caused the LLPS in aqueous sulfate solutions at elevated temperatures (Wang et al., 2013, 2016a, b, 2017; Wan et al., 2015, 2017). In this study, we will present more information on the mechanism of LLPS.

The restricted primitive model (RPM) can be used to predict the occurrence of LLPS in ionic solutions (Friedman and Larsen, 1979; Weingärtner et al., 1991). In this model, the fluid was simplified as a system of charged hard spheres of equal size in a dielectric continuum. We used the RPM model to investigate the effect of fluid pressure on the LLPS in aqueous CdSO₄ solution (Wan et al., 2017). Generally, the LLPS occurs at a near constant value of the product of the dielectric constant (*D*) of medium (i.e., water) and absolute temperature (*D* × *T*) for a given fluid system (Wan et al., 2017). Because the *D* value of water increases with rising pressure or decreasing temperature (Weingärtner et al., 1991), LLPS will occur at higher temperatures when the fluid pressure is increased, in order to maintain the constant *D* × *T* value. In this study, the onset temperature of LLPS in aqueous ZnSO₄ and ZnSO₄+C₂H₅OH solutions increased linearly with rising fluid pressure (Fig. 3a and b), confirming the RPM

calculating results. Increase in fluid pressure will increase the D value of water, suppressing the Zn^{2+} - SO_4^{2-} association. On the contrary, increase in fluid temperature can lower the D value of water, favoring the Zn^{2+} - SO_4^{2-} interaction. Therefore, the increase in the onset temperature of LLPS with rising fluid pressure implies that the ion association and/or polymerization caused the LLPS.

Our previous study showed that Zn^{2+} - SO_4^{2-} association increases with rising temperature (Wang et al., 2016a). The $\nu_1(\text{SO}_4^{2-})$ band shifted to lower wavenumber at $<200^\circ\text{C}$ but to higher wavenumber at $\geq 200^\circ\text{C}$ in 1.0 m ZnSO_4 (Fig. 6 in Wang et al., 2016a). The $\nu_1(\text{SO}_4^{2-})$ component at $\sim 980\text{ cm}^{-1}$ was assigned to Raman indistinguishable solvent separated ion pairs (2SIP), solvent shared ion pairs (SIP), and unassociated SO_4^{2-} , whereas the $\sim 990\text{ cm}^{-1}$ component was ascribed to contact ion pair (CIP) (Hayes et al., 1984; Kruus et al., 1985; Rudolph et al., 1999; Zhang and Chan, 2002; Wang et al., 2016a). Because the stabilities of 2SIP and SIP decrease with rising temperature, and only constitute minor sulfate fractions at 65°C (Akilan et al., 2006a, b), it's reasonable to infer that the $\sim 980\text{ cm}^{-1}$ component was ascribed to unassociated SO_4^{2-} at $\geq 65^\circ\text{C}$. The $\nu_1(\text{SO}_4^{2-})$ band of unassociated SO_4^{2-} was reported to shift to lower wavenumber with increasing temperature (Wang et al., 2013). Then, the $\nu_1(\text{SO}_4^{2-})$ band shifted to lower wavenumber with rising temperature at $\leq 220^\circ\text{C}$ in 1.0 m $\text{ZnSO}_4 + \text{C}_2\text{H}_5\text{OH}$ solution (Fig. 4b). At higher temperatures (e.g., $>220^\circ\text{C}$ in Fig. 4b), various contact ion pairs are the dominant sulfate species. The $\nu_1(\text{SO}_4^{2-})$ wavenumbers of these ion pair species are higher

than that of the unassociated SO_4^{2-} . In the L1 phase, the ion association is more complex than that in the aqueous phase; the $\nu_1(\text{SO}_4^{2-})$ band shifted to higher wavenumber with increasing length of the contact ion pair chains (Zhang et al., 2002; Jahn and Schmidt, 2010). Most importantly, the contact ion pair association increases with rising temperature (Jahn and Schmidt, 2010; Wang et al., 2013, 2016a). Therefore, in high temperature aqueous solution and L1 phase, the $\nu_1(\text{SO}_4^{2-})$ band shifted to higher wavenumber with rising temperature (Fig. 4b).

In the presence of ethanol, the $\nu_1(\text{SO}_4^{2-})$ shifted to higher wavenumber with decreasing $m\text{H}_2\text{O}/m\text{C}_2\text{H}_5\text{OH}$ ratio at 200°C (Fig. 5b). Meanwhile, the FWHM increased with decreasing $m\text{H}_2\text{O}/m\text{C}_2\text{H}_5\text{OH}$ ratio at constant temperature (Fig. 5b). These changes in the $\nu_1(\text{SO}_4^{2-})$ band can be ascribed to the increasing formation of CIP. As shown in Fig. 5c, the fraction of CIP increased with the addition of ethanol. The presence of alcohol can decrease the D of solution (Albright and Gosting, 1946; Mohsen-Nia et al., 2010), favoring the ion association (Tsierkezos and Molinou, 2000). As a result, the observed onset temperature for LLPS in ethanol-bearing solution under a specified pressure is lower than that in aqueous ZnSO_4 solution (Fig. 3b; Wang et al., 2016a).

4.2. Implications for the fates of seawater sulfate in seafloor hydrothermal systems

In seafloor hydrothermal systems, the penetration of seawater-derived sulfate to deep ocean crust was generally

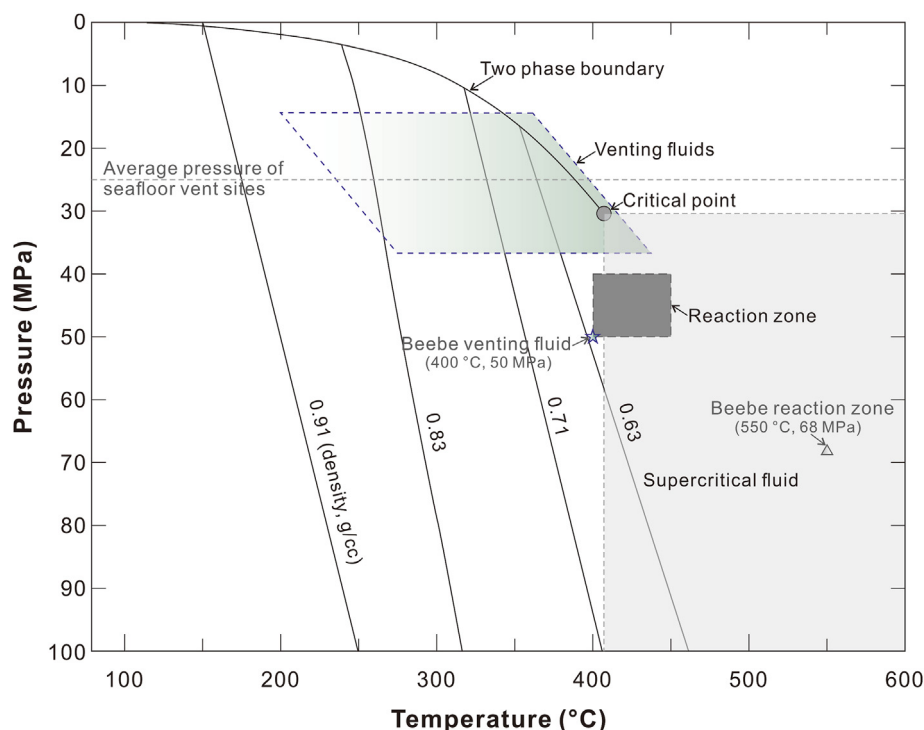


Fig. 6. T - P fields of typical seafloor venting fluids [modified after Bischoff and Rosenbauer (1985) and Tivey (2007)] and the reaction zone (cf., Tivey, 2007; Fontaine et al., 2007; Foustoukos and Seyfried, 2007; Zeng, 2011; Webber et al., 2015). Detailed T - P conditions of the global venting sites can be obtained freely from the InterRidge Vents Database (www.interridge.org/).

considered to be impossible (e.g., Zeng, 2011; Tivey, 2007). During the circulation of seawater within the ocean crust, about one-third of the sulfate was removed from the solution through the 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). Subsequent release of Ca^{2+} from the basalt resulted in further precipitation of anhydrite, which decreased the sulfate concentration to <1 mM (Bischoff and Dickson, 1975; Shanks, 2001). The aforementioned description of sulfate behavior was in accordance with most solubility experiment results, which showed that the solubility of CaSO_4 decrease with rising temperature (Blouinot and Dickson, 1969). However, the stable S isotope analyses of venting sulfide and H_2S indicated that seawater-derived sulfate might be involved in the deep circulation of seawater.

Fig. 6 shows the T - P field of typical venting fluids (cf., Bischoff and Rosenbauer, 1985; Tivey, 2007). The pressure of the venting fluid is generally less than 40 MPa, with an average of ~25 MPa. The temperature of the venting fluid ranges from ~200 to 450 °C. The reaction zone is characterized by higher pressure and higher temperature (e.g., >40 MPa, >400 °C; Fontaine et al., 2007; Foustoukos and Seyfried, 2007; Tivey, 2007; Zeng, 2011; Webber et al., 2015). Our experimental results showed that LLPS tends to occur in low pressure and high temperature fluids (Fig. 3a and b; Wang et al., 2013, 2016a, b, 2017; Wan et al., 2017). Apparently, T - P conditions of seafloor hydrothermal fluids favor the occurrence of LLPS. The formation of a sulfate-rich dense liquid phase is beneficial to the infiltration of seawater-derived sulfate to the deep ocean crust. At higher temperatures, the seawater-derived sulfate would be reduced to S^{2-} through thermochemical oxidation of Fe(II) in pyroxene or olivine or via the conversion of igneous pyrrhotite to pyrite in the basalt (Shanks et al., 1981; Janecky and Seyfried, 1986; Herzig et al., 1998; Kump and Seyfried, 2005). The reduced S mixed with that leached from the basalts, and ascended along the hydrothermal conduits. The venting hydrothermal fluid mixed with the cold seawater, resulting in the precipitation of metal sulfides. The involvement of LLPS during seafloor hydrothermal circulation could account for the elevated $\delta^{34}\text{S}$ value of venting sulfides; seawater sulfate is rich in ^{34}S , and the resultant reduced S through the thermochemical reduction of seawater sulfate is also characterized by high $\delta^{34}\text{S}$ value (Hoefs, 1997; Li et al., 2007).

In addition to LLPS, the elevated sulfate solubility in the presence of dissolved SiO_2 could also be used to interpret the involvement of seawater sulfate in the deep hydrothermal circulation. The solubility of Na_2SO_4 in binary Na_2SO_4 - H_2O system was suggested to decrease with rising temperature at >50 °C (cf., Shvarov and Bastrakov, 1999). However, recent experimental investigations showed that the solubility of Na_2SO_4 increased with increasing temperature at ≥ 313 °C in the presence of dissolved SiO_2 (Chou et al., 2005; Chen et al., 2020). For example, the solubility of

Na_2SO_4 is estimated to be 3.10 m at 388.2 °C in SiO_2 -saturated solutions (Chen et al., 2020), which is comparable with that in binary NaSO_4 - H_2O system at 50 °C (cf., Shvarov and Bastrakov, 1999). Considering that geofluids within the crust is generally SiO_2 -saturated, sulfate-rich hydrothermal fluids might participate in many geological and geochemical processes, such as the formation of seafloor metal sulfides.

5. Conclusion

LLPS in aqueous $\text{ZnSO}_4 + \text{C}_2\text{H}_5\text{OH}$ solutions was investigated at elevated temperatures up to 300 °C and at pressures from 5.10 to 44.34 MPa. The fluid composition and structure were characterized by using *in situ* Raman spectroscopy.

- (1) LLPS tends to occur in low pressure hydrothermal fluids. In 0.5 m ZnSO_4 solution, LLPS occurred at 272.2 °C when the fluid pressure was kept at 5.07 MPa. Then, the starting temperature for LLPS increased at a rate of 0.685 °C/MPa. The presence of low D components can decrease the starting temperature of LLPS.
- (2) Complex ion association triggers the LLPS in sulfate-bearing solutions. The RPM modeling indicates that LLPS occurs at a near constant value of the product of D of water and absolute temperature (T). D of water increases with rising pressure or decreasing temperature. The addition of low D components lowers the D of the solution. Decrease in D of water can promote the Zn^{2+} - SO_4^{2-} interaction, favoring the occurrence LLPS. *In situ* Raman spectroscopic characterization of the $\nu_1(\text{SO}_4^{2-})$ band also indicates that the addition of $\text{C}_2\text{H}_5\text{OH}$ strengthens the Zn^{2+} - SO_4^{2-} association.
- (3) The formation of a sulfate-rich dense liquid phase can interpret the elevated $\delta^{34}\text{S}$ value of seafloor venting sulfide. The occurrence of LLPS hinders the precipitation of sulfate during seafloor hydrothermal circulation, favoring the involvement of seawater-derived sulfate in deep hydrothermal cycle. At higher temperatures, sulfate was reduced to S^{2-} , which mixed with reduced S from basalt and ascended to the seafloor.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- Akilan, C., Hefter, G., Rohman, N., Buchner, R., 2006a. Ion association and hydration in aqueous solutions of copper(II) sulfate from 5 to 65 °C by dielectric spectroscopy. *J. Phys. Chem. B* 110 (30), 14961–14970.
- Akilan, C., Rohman, N., Hefter, G., Buchner, R., 2006b. Temperature effects on ion association and hydration in MgSO_4 by dielectric spectroscopy. *ChemPhysChem* 7, 2319–2330.
- Albright, P.S., Gosting, L.J., 1946. Dielectric constants of the methanol–water system from 5 to 55°. *J. Am. Chem. Soc.* 68 (6), 1061–1063.
- Alt, J.C., 1995. Subseafloor processes in mid-ocean ridge hydrothermal systems. In: Humphris, S.E., Zierenberg, R.A., Mullineaux, L.S., Thomson, R.E. (Eds.), *Seafloor Hydrothermal Systems: Physical, Chemical, Biological, and Geological Interaction*, vol. 91. *Geophysical Monograph*, pp. 88–114.
- Alt, J.C., Teagle, D.A.H., 2003. Hydrothermal alteration of upper oceanic crust formed at a fast-spreading ridge: mineral, chemical, and isotopic evidence from ODP Site 801. *Chem. Geol.* 201, 191–211.
- Baltes, T., Garret-Flaudy, F., Freitag, R., 1999. Investigation of the LCST of polyacrylamides as a function of molecular parameters and the solvent composition. *J. Polym. Sci. Polym. Chem.* 37, 2977–2989.
- Bischoff, J.L., Dickson, F.W., 1975. Seawater-basalt interaction at 200 °C and 500 bars: implications for origin of sea floor heavy metal deposits and regulation of seawater chemistry. *Earth Planet Sci. Lett.* 25, 385–397.
- Bischoff, J.L., Rosenbauer, R.J., 1985. An empirical equation of state for hydrothermal seawater (3.2 percent NaCl). *Am. J. Sci.* 285, 725–763.
- Bischoff, J.L., Seyfried Jr., W.E., 1978. Hydrothermal chemistry of seawater from 25° to 350 °C. *Am. J. Sci.* 278, 838–860.
- Blount, C.W., Dickson, F.W., 1969. The solubility of anhydrite (CaSO_4) in $\text{NaCl-H}_2\text{O}$ from 100 to 450 °C and 1 to 1000 bars. *Geochem. Cosmochim. Acta* 33 (2), 227–245.
- Bowers, T.S., 1989. Stable isotope signatures of water-rock interaction in mid-ocean ridge hydrothermal systems: sulfur, oxygen, and hydrogen. *J. Geophys. Res.* 94, 775–786.
- Butterfield, D.A., Massoth, G.J., 1994. Geochemistry of north Cleft segment vent fluids: temporal changes in chlorinity and their possible relation to recent volcanism. *J. Geophys. Res.* 99, 4951–4968.
- Charlou, J.L., Donval, J.P., Fouquet, Y., Jean-Baptiste, P., Holm, N., 2002. Geochemistry of high H_2 and CH_4 vent fluids issuing from ultramafic rocks at the Rainbow hydrothermal field (36°14'N, MAR). *Chem. Geol.* 191, 345–359.
- Chen, J., Zheng, H., Xiao, W., Zeng, Y., Weng, K., 2004. Raman spectroscopic study of CO_2 - $\text{NaCl-H}_2\text{O}$ mixtures in synthetic fluid inclusions at high temperatures. *Geochem. Cosmochim. Acta* 68, 1355–1360.
- Chen, H., Cui, H., Zhong, R., Xie, Y., Yu, C., Li, Z., Ling, Y., 2020. Solubility of Na_2SO_4 in silica-saturated solutions: implications for REE mineralization. *Am. Mineral.* <https://doi.org/10.2138/am-2020-7470>.
- Chou, I.-M., Burruss, R.C., Lu, W.J., 2005. A new optical cell for spectroscopic studies of geologic fluids at pressures up to 100 MPa. In: Chen, J., Wang, Y., Duffy, T.S., Shen, G., Dobrzhinetskaya, L.F. (Eds.), *Advances in High-Pressure Technology for Geophysical Applications*. Elsevier, Amsterdam, pp. 475–485.
- Chou, I.-M., Song, Y., Burruss, R.C., 2008. A new method for synthesizing fluid inclusions in fused silica capillaries containing organic and inorganic material. *Geochem. Cosmochim. Acta* 72, 5217–5231.
- Corsetti, S., McGloin, D., Kiefer, J., 2016. Comparison of Raman and IR spectroscopy for quantitative analysis of gasoline/ethanol blends. *Fuel* 166, 488–494.
- Edmond, J.M., Von Damm, K.L., McDuff, R.E., Measures, C.I., 1982. Chemistry of hot springs on the East Pacific Rise and their effluent dispersal. *Nature* 297, 187–191.
- Elderfield, H., Schultz, A., 1996. Mid-ocean ridge hydrothermal fluxes and the chemical composition of the ocean. *Annu. Rev. Earth Planet Sci.* 24, 191–224.
- Fontaine, F.J., Wilcock, W.S.D., Butterfield, D.A., 2007. Physical controls on the salinity of mid-ocean ridge hydrothermal vent fluids. *Earth Planet Sci. Lett.* 257, 132–145.
- Foustoukos, D.I., Seyfried Jr., W.E., 2007. Quartz solubility in the two-phase and critical region of the $\text{NaCl-KCl-H}_2\text{O}$ system: implications for submarine hydrothermal vent systems at 9°50'N East Pacific Rise. *Geochem. Cosmochim. Acta* 71, 186–201.
- Friedman, H.L., Larsen, B., 1979. Corresponding states for ionic fluids. *J. Chem. Phys.* 70 (1), 92–100.
- Gamo, T., Chiba, H., Yamanaka, T., Okudaira, T., Hashimoto, J., Tsuchida, S., Ishibashi, J., Kataoka, S., Tsunogai, U., Okamura, K., Sano, Y., Shinjo, R., 2001. Chemical characteristics of newly discovered black smoker fluids and associated hydrothermal plumes at the Rodriguez Triple Junction, Central Indian Ridge. *Earth Planet Sci. Lett.* 193, 371–379.
- Garrels, R.M., Thompson, M.E., 1962. A chemical model for sea water at 25 degrees C and one atmosphere total pressure. *Am. J. Sci.* 260, 57–66.
- Gong, K., Marshall, B.D., Chapman, W.G., 2013. Modeling lower critical solution temperature behavior of associating polymer brushes with classical density functional theory. *J. Chem. Phys.* 139, 094904.
- Hannington, M.D., Scott, S.D., 1988. Mineralogy and geochemistry of a hydrothermal silica-sulfide-sulfate spire in the caldera of Axial-Seamount, Juan de Fuca Ridge. *Can. Mineral.* 26, 603–625.
- Hayes, A.C., Kruus, P., Adams, W.A., 1984. Raman spectroscopic study of aqueous $(\text{NH}_4)_2\text{SO}_4$ and ZnSO_4 solutions. *J. Solut. Chem.* 13, 61–75.
- Haymon, R.M., Kastner, M., 1986. The formation of high temperature clay minerals from basalt alteration during hydrothermal discharge on the East Pacific Rise axis at 21 °N. *Geochem. Cosmochim. Acta* 50 (9), 1933–1939.
- Herzig, P.M., Hannington, M.D., Arribas Jr., A., 1998. Sulfur isotopic composition of hydrothermal precipitates from the Lau back-arc: implications for magmatic contributions to seafloor hydrothermal systems. *Miner. Deposita* 33, 226–237.
- Hoefs, J., 1997. *Stable Isotope Geochemistry*, fourth ed. Springer-Verlag, Berlin, p. 201.
- Humphris, S.E., Thompson, C., 1978. Hydrothermal alteration of oceanic basalts by seawater. *Geochem. Cosmochim. Acta* 42, 107–125.
- InterRidge Vents Database. Available from: www.interridge.org/ (accessed 9.12.2020).
- Jahn, S., Schmidt, C., 2010. Speciation in aqueous MgSO_4 fluids at high pressures and high temperatures from ab Initio molecular dynamics and Raman spectroscopy. *J. Phys. Chem. B* 114, 15565–15572.
- Janecky, D.R., Seyfried Jr., W.E., 1986. Hydrothermal serpentinization of peridotite within the oceanic crust: experimental investigations of mineralogy and major element chemistry. *Geochem. Cosmochim. Acta* 50, 1357–1378.
- Janecky, D.R., Shanks III, W.C., 1988. Computational modelling of chemical and isotopic reaction processes in seafloor hydrothermal systems: chimneys, massive sulfides, and subjacent alteration zones. *Can. Mineral.* 26, 805–825.
- Jones, E.V., Marshall, W.L., 1961. Aqueous systems at high temperature-IV: compositions of light- and heavy-liquid phases in the systems $\text{UO}_3\text{-SO}_3\text{-H}_2\text{O}$ and $\text{UO}_3\text{-SO}_3\text{-D}_2\text{O}$. *J. Inorg. Nucl. Chem.* 23, 287–293.
- Knott, R., Fallick, A.E., Rickard, D., Baecker, H., 1995. Mineralogy and sulphur isotope characteristics of a massive sulphide boulder, Galapagos Rift, 85°55'W. In: Parson, L.M., Walker, C.L., Dixon, D.R. (Eds.), *Hydrothermal Vents and Processes*, vol. 87. *Geol. Soc. Spec. Pub.*, pp. 207–222.
- Konn, C., Charlou, J.L., Donval, J.P., Holm, N.G., Dehairs, F., Bouillon, S., 2009. Hydrocarbons and oxidized organic compounds in hydrothermal fluids from Rainbow and Lost City ultramafic hosted vents. *Chem. Geol.* 258, 299–314.
- Kruus, P., Hayes, A.C., Adams, W.A., 1985. Determination of ratios of sulfate to bisulfate ions in aqueous solutions by Raman spectroscopy. *J. Solut. Chem.* 14, 117–128.
- Kump, L.P., Seyfried Jr., W.E., 2005. Hydrothermal Fe fluxes during the Precambrian: effect of low oceanic sulfate concentrations and low hydrostatic pressure on the composition of black smokers. *Earth Planet Sci. Lett.* 235, 654–662.
- Li, W., Huang, Z., Yin, M., 2007. Isotope geochemistry of the Huize Zn-Pb ore field, Yunnan Province, southwestern China: implications for the sources of ore fluid and metals. *Geochem. J.* 41, 65–81.

- Marshall, W.L., Gill, J.S., 1974. Effects of pressure on liquid–liquid immiscibility of high temperature aqueous solution mixtures of uranyl sulfate and sulfuric acid, 280–450 °C, 75–1800 bars. *J. Inorg. Nucl. Chem.* 36, 2303–2312.
- Marshall, W.L., Jones, E.V., Hebert, G.M., Smith, F.J., 1962. Aqueous systems at high temperature-VII: liquid–liquid immiscibility and critical phenomena in the systems $\text{UO}_3\text{--SO}_3\text{--H}_2\text{O}$, $\text{UO}_3\text{--SO}_3\text{--D}_2\text{O}$ and $\text{CuO--SO}_3\text{--D}_2\text{O}$, 270–430 °C. *J. Inorg. Nucl. Chem.* 24, 995–1000.
- McDuff, R.E., Edmond, J.M., 1982. On the fate of sulfate during hydrothermal circulation at mid-ocean ridges. *Earth Planet Sci. Lett.* 57, 117–132.
- Mohsen-Nia, M., Amiri, H., Jazi, B., 2010. Dielectric constants of water, methanol, ethanol, butanol and acetone: measurement and computational study. *J. Solut. Chem.* 39 (5), 701–708.
- Monnin, C., Balleur, S., Goffe, B., 2003. A thermodynamic investigation of barium and calcium sulfate stability in sediments at an oceanic ridge axis (Juan de Fuca, ODP legs 139 and 169). *Geochem. Cosmochim. Acta* 67, 2965–2976.
- Ono, S., Shanks III, W.C., Rouxel, O.J., Rumble, D., 2007. S-33 constraints on the seawater sulfate contribution in modern seafloor hydrothermal vent sulfides. *Geochem. Cosmochim. Acta* 71, 1170–1182.
- Paricaud, P., Galindo, A., Jackson, G., 2003. Understanding liquid–liquid immiscibility and LCST behaviour in polymer solutions with a Wertheim TPT1 description. *Mol. Phys.* 101 (16), 2575–2600.
- Rees, C.E., Jenkins, W.J., Monster, J., 1978. The sulfur isotopic composition of ocean water sulfate. *Geochem. Cosmochim. Acta* 42, 377–381.
- Rudolph, W.W., Brooker, M.H., Tremaine, P.R., 1999. Raman spectroscopy of aqueous ZnSO_4 solutions under hydrothermal conditions: solubility, hydrolysis, and sulfate ion pairing. *J. Solut. Chem.* 28 (5), 621–630.
- Sakai, H., des Marais, D.J., Ueda, A., Moore, J.G., 1984. Concentrations and isotope ratios of carbon, nitrogen and sulfur in ocean-floor basalts. *Geochem. Cosmochim. Acta* 48, 2433–2441.
- Secoy, C., 1948. The system uranyl sulfate–water. I. Temperature–concentration relationships below 300 °C. *J. Am. Chem. Soc.* 70, 3450–3452.
- Secoy, C.H., 1950. The system uranyl–sulfate–water. II. temperature–concentration relationships above 250 °C. *J. Am. Chem. Soc.* 72, 3343–3345.
- Seewald, J.S., Seyfried Jr., W.E., 1990. The effect of temperature on metal mobility in subseafloor hydrothermal systems: constraints from basalt alteration experiments. *Geochem. Cosmochim. Acta* 101, 388–403.
- Seyfried Jr., W.E., Bischoff, J.L., 1981. Experimental seawater–basalt interaction at 300 °C, 500 bars, chemical exchange, secondary mineral formation and implications for the transport of heavy metals. *Geochem. Cosmochim. Acta* 45, 135–147.
- Seyfried Jr., W.E., Seewald, J.S., Berndt, M.E., Ding, K., Foustoukos, D.I., 2003. Chemistry of hydrothermal vent fluids from the Main Endeavour Field, northern Juan de Fuca Ridge: geochemical controls in the aftermath of June 1999 seismic events. *J. Geophys. Res.* 108 (B9), 1–23.
- Shanks III, W.C., 2001. Stable isotopes in seafloor hydrothermal systems: vent fluids, hydrothermal deposits, hydrothermal alteration, and microbial processes. *Rev. Mineral. Geochem.* 43, 469–525.
- Shanks III, W.C., Seyfried Jr., W.E., 1987. Stable isotope studies of vent fluids and chimney minerals, southern Juan de Fuca Ridge: sodium metasomatism and seawater sulfate reduction. *J. Geophys. Res.* 92 (B11), 11387–11399.
- Shanks III, W.C., Bischoff, J.L., Rosenbauer, R.J., 1981. Seawater sulfate reduction and sulfur isotope fractionation in basaltic systems: interaction of seawater with fayalite and magnetite at 200 ± 350 °C. *Geochem. Cosmochim. Acta* 45, 1977–1995.
- Shvarov, Y.V., Bastrakov, E.N., 1999. HCh: a software package for geochemical equilibrium modelling. In: User's Guide (Australian Geological Survey Organization, 518 Canberra, 1999). Record 199/25.
- Tivey, M.K., 2007. Generation of seafloor hydrothermal vent fluids and associated mineral deposits. *Oceanography* 20, 50–65.
- Tsierkezos, N.G., Molinou, I.E., 2000. Limiting molar conductances and thermodynamic association constants for nickel (II), cadmium (II), magnesium (II), and copper (II) sulfates in mixtures of methanol and water at 293.15 K. *J. Chem. Eng. Data* 45 (5), 819–822.
- Wan, Y., Wang, X., Hu, W., Chou, I.-M., 2015. Raman spectroscopic observations of the ion association between Mg^{2+} and SO_4^{2-} in MgSO_4 -saturated droplets at temperatures of ≤ 380 °C. *J. Phys. Chem.* 119 (34), 9027–9036.
- Wan, Y., Wang, X., Hu, W., Chou, I.-M., Wang, X., Chen, Y., Xu, Z., 2017. *In situ* optical and Raman spectroscopic observations of the effects of pressure and fluid composition on liquid–liquid phase separation in aqueous cadmium sulfate solutions (≤ 400 °C, 50 MPa) with geological and geochemical implications. *Geochem. Cosmochim. Acta* 211, 133–152.
- Wang, X., Chou, I.-M., Hu, W., Burruss, R.C., Sun, Q., Song, Y., 2011. Raman spectroscopic measurements of CO_2 density: experimental calibration with high-pressure optical cell (HPOC) and fused silica capillary capsule (FSCC) with application to fluid inclusion observations. *Geochem. Cosmochim. Acta* 75, 4080–4093.
- Wang, X., Chou, I.-M., Hu, W., Burruss, R.C., 2013. *In situ* observations of liquid–liquid phase separation in aqueous MgSO_4 solutions: geological and geochemical Implications. *Geochem. Cosmochim. Acta* 103, 1–10.
- Wang, X., Wan, Y., Hu, W., Chou, I.-M., Cao, J., Wang, X., Wang, M., Li, Z., 2016a. *In situ* observations of liquid–liquid phase separation in aqueous ZnSO_4 solutions at temperatures up to 400 °C: implications for $\text{Zn}^{2+}\text{--SO}_4^{2-}$ association and evolution of submarine hydrothermal fluids. *Geochem. Cosmochim. Acta* 181, 126–143.
- Wang, X., Wan, Y., Hu, W., Chou, I.-M., Cai, S., Lin, N., Zhu, Q., Li, Z., 2016b. Visual and *in situ* Raman spectroscopic observations of the liquid–liquid immiscibility in aqueous uranyl sulfate solutions at temperatures up to 420 °C. *J. Supercrit. Fluids* 112, 95–102.
- Wang, X., Wang, X., Chou, I.-M., Hu, W., Wan, Y., Li, Z., 2017. Properties of lithium under hydrothermal conditions revealed by *in situ* Raman spectroscopic characterization of $\text{Li}_2\text{O--SO}_3\text{--H}_2\text{O}$ (D_2O) systems at temperatures up to 420 °C. *Chem. Geol.* 451, 104–115.
- Wang, X., Qiu, Y., Lu, J., Chou, I.-M., Zhang, W., Li, G., Hu, W., Li, Z., Zhong, R., 2020. *In situ* Raman spectroscopic investigation of the hydrothermal speciation of tungsten: implications for the ore-forming process. *Chem. Geol.* 532, 119299.
- Webber, A.P., Roberts, S., Murton, B.J., Hodgkinson, M.R.S., 2015. Geology, sulfide geochemistry and supercritical venting at the Beebe hydrothermal vent field, Cayman Trough. *G-cubed* 16, 2661–2678.
- Weingartner, H., Merkel, T., Maurer, U., Conzen, J.P., Glasbrenner, H., Kshammer, S., 1991. On coulombic and solvophobic liquid–liquid phase–separation in electrolyte solutions. *Ber. Bunsen. Phys. Chem.* 95 (12), 1579–1586.
- Woodruff, L.G., Shanks III, W.C., 1988. Sulfur isotope study of chimney minerals and vent fluids from 21°N, East Pacific Rise: hydrothermal sulfur sources and disequilibrium sulfate reduction. *J. Geophys. Res.* 93 (B5), 4562–4572.
- Xu, X., Chou, I.-M., 2017. Raman spectroscopic study of cracking and hydrolysis of propane in fused silica capillary capsules between 300 and 400 °C. *J. Raman Spectrosc.* 48 (11), 1420–1425.
- Zeng, Z., 2011. Submarine Hydrothermal Geology. Science Press, Beijing, pp. 1–567 (in Chinese).
- Zhang, Y.-H., Chan, C.-K., 2002. Understanding the hygroscopic properties of supersaturated droplets of metal and ammonium sulfate solutions using Raman spectroscopy. *J. Phys. Chem.* 106, 285–292.
- Zhang, X., Zhang, Y., Li, Q., 2002. Ab initio studies on the chain of contact ion pairs of magnesium sulfate in supersaturated state of aqueous solution. *J. Mol. Struct.* 594, 19–30.