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In Situ Observation of Gypsum-Anhydrite Transition at High Pressure and High Temperature *

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An in-situ Raman spectroscopic study of gypsum-anhydrite transition under a saturated water condition at high pressure and high temperature is performed using a hydrothermal diamond anvil cell (HDAC). The experimental results show that gypsum dissolves in water at ambient temperature and above 496 MPa. With increasing temperature, the anhydrite (CaSO₄) phase precipitates at 250–320°C in the pressure range of 1.0–1.5 GPa, indicating that under a saturated water condition, both stable conditions of pressure and temperature and high levels of Ca and SO₄ ion concentrations in aqueous solution are essential for the formation of anhydrite. A linear relationship between the pressure and temperature for the precipitation of anhydrite is established as $P(\text{GPa}) = 0.0068T - 0.7126$ ($250^\circ\text{C} \leq T \leq 320^\circ\text{C}$). Anhydrite remained stable during rapid cooling of the sample chamber, showing that the gypsum-anhydrite transition involving both dissolution and precipitation processes is irreversible at high pressure and high temperature.

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Among the hundreds of minerals existing naturally on Earth and other planetary bodies, many are hydrous minerals that contain molecular H₂O, OH groups, or both in their crystal structures.^[1] In the interior of the Earth, the dehydration of these hydrous minerals controls some geodynamic processes of great importance, for example, magmatism in the subduction zone, palintectic earthquakes in the mantle and interactions between the plate boundary.^[2]

Calcium sulfate occurs naturally as the mineral gypsum (CaSO₄·2H₂O) and is the most common hydrous sulfate mineral in the Earth's crust. Gypsum often occurs in sedimentary deposits associated with limestone, shales, marls and clays,^[3–5] massive anhydrite beds.^[6] In recent years, with the development of high-temperature and high-pressure experimental techniques and the applications of analytical instruments such as x-ray diffraction, nuclear magnetic resonance, infrared spectroscopy, Raman spectroscopy and neutron diffraction, many investigations on gypsum in relation to its phase transition and thermal behavior have been extensively carried out. Zhou *et al.*^[7] observed the dehydration process of gypsum to anhydrite in aqueous solution at 16–200°C and pressures to 840 MPa. Sarma *et al.*^[8] and conducted a study of phase transitions in natural gypsum up to 550 K at ambient pressure using Raman spectroscopy, indicating the temperatures for the appearance of bassanite (CaSO₄·0.5H₂O) and anhydrite(CaSO₄) were at around 388 ± 5 K and 448 ± 5 K, respectively. A recent powder x-ray diffraction and Raman study has revealed polymorphic transitions of gypsum in the pressure range of 5–10 GPa.^[9] Knittle *et al.*^[10] confirmed discontinuities in the behavior of gypsum at high pressure through infrared and Raman spectroscopy, suggesting that a pressure-

induced phase transition in gypsum occurred in the vicinity of 5–6 GPa. Mirwald^[11] determined the dehydration boundaries in the gypsum-bassanite-anhydrite system by differential pressure analysis (DPA). Also, the stabilities of gypsum, bassanite and anhydrite up to 3 GPa have been studied by Yamamoto and Kennedy^[12] and Kennedy.^[13]

Although the stability and behavior of gypsum under high pressure and high temperature conditions have been widely studied, the dissolution and precipitation behaviors of gypsum in saturated water under high pressure and high temperature have not been reported since they are important for understanding of geologic processes in the presence of water. In this Letter, we present the studies on gypsum by using Raman spectroscopic measurements in a hydrothermal diamond anvil cell (HDAC). A gypsum-anhydrite transition relating to both dissolution and precipitation is observed under high pressure and high temperature.

All experiments were conducted using a Bassett-type hydrothermal diamond anvil cell.^[14] The diamond anvils were supported by tungsten carbide seats which housed the heating components of the cell. The transparency of the diamonds to light allows direct observations of the sample and the aqueous medium under a microscope. Inconel alloy wires were wrapped around the seats and externally heated the diamonds by applying electrical current. The temperature inside the sample chamber, accurate to within $\pm 1^\circ\text{C}$, was measured by a *K*-type (NiCr-NiSi) thermocouple attached to the diamond anvil. Temperature calibration was achieved by the melting points of stearic acid ($T_m = 69^\circ\text{C}$) and phenothalin ($T_m = 262^\circ\text{C}$) inside the HDAC.

The diamond anvils have a culet diameter of

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0.8 mm. The stainless steel gasket, which separated the anvils, has a thickness of 250 μm and with a 300 μm hole in the center. A natural gypsum sample was used in this study. Heavy oxygen water with a concentration of 98% served as the solvent and the pressure-transmitting medium. The internal pressure of the system was determined by the relationship between the pressure and the 464 cm^{-1} Raman shift of quartz,^[15] as described in Eq. (1).

$$P(\text{MPa}) = 0.36079 \cdot [(\Delta\nu_p)_{464}]^2 + 110.86 \cdot (\Delta\nu_p)_{464}, \quad (1)$$

where $(\Delta\nu_p)_{464}$ is the difference of Raman shifts at high pressure and ambient pressure ($0 < (\Delta\nu_p)_{464} \leq 20 \text{ cm}^{-1}$). The pressure determined by this method is within an uncertainty of $\pm 50 \text{ MPa}$. With respect to the determination of pressure in the case of heating, the Raman shift needed to be calibrated according to the following expression:

$$\begin{aligned} (\Delta\nu_p)_{464} = & 2.50136 \cdot 10^{-11} \cdot T^4 + 1.46454 \cdot 10^{-8} \cdot T^3 \\ & - 1.801 \cdot 10^{-5} \cdot T^2 - 0.01216 \cdot T + 0.29 \\ & (-196^\circ\text{C} \leq T \leq 560^\circ\text{C}). \end{aligned} \quad (2)$$

The solid sample gypsum, together with quartz single crystal, was loaded into the chamber, and then the fluid injected into the sample chamber was quickly sealed by compressing the gasket with screws.

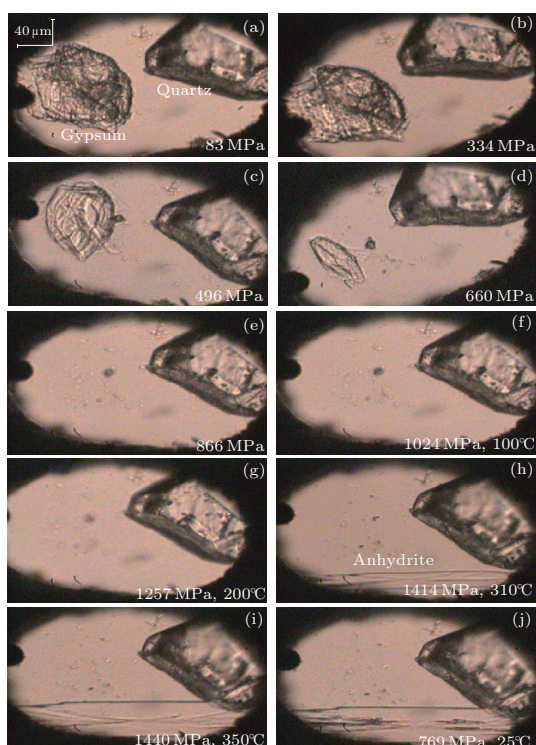


Fig. 1. (a)–(e) The progression of dissolution of gypsum at different pressures and room temperature. (f)–(j) The progression of precipitation of anhydrite at different pressures and temperatures.

Raman spectra were recorded using a confocal micro-Raman system Renishaw 1000. The excitation was performed using an Ar^+ laser with a wavelength

of 514.5 nm and a power of 50 mW. The spectra in the range 50–4000 cm^{-1} were collected with a counting time of 10 s, 1 accumulation, a slit of 50 μm and a Leica 20 \times long working distance objective. The spectral resolution was $\pm 1 \text{ cm}^{-1}$. The Raman peak positions were determined by fitting the spectra using the JANDEL SCIENTIFIC PEAKFIT V4.04 computer program.

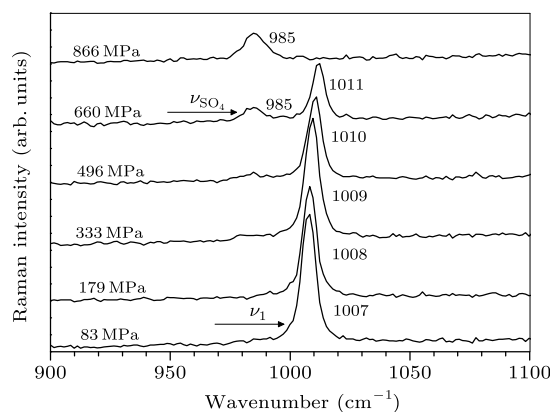


Fig. 2. Raman spectra of the $\nu_1(\text{SO}_4)$ mode of gypsum and the ν_{SO_4} mode of CaSO_4 -bearing solution measured at 25°C and different pressures.

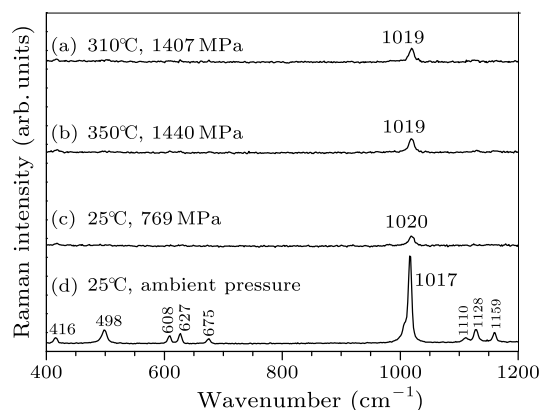


Fig. 3. (a) and (b) Raman spectra of the new phase measured at 310°C and 350°C, respectively. (c) Raman spectrum measured at 769 MPa and room temperature. (d) Raman spectrum measured at 25°C and ambient pressure.

Six experiments were performed with the HDAC at high pressure and high temperature. During each experiment, the pressure of the sample was first applied at room temperature and maintained for 5 min before the Raman spectrum was collected in order to attain an equilibrium condition for the system. Then, the sample in the chamber was heated after the gypsum completely dissolved in aqueous solution with increasing pressure, and the Raman measurement was carried out at a stable P - T condition during heating. The digital images were taken at various P - T conditions throughout the experiment.

Gypsum is a mineral with a layered structure, which can completely dissolve in water under high pressure and recrystallize with decreasing pressure.^[16] Pressure-induced variations of gypsum in

aqueous solution at room temperature are displayed in Figs. 1(a)–1(e). The initial pressure of the experiment was 83 MPa and there was no obvious change in the pressure below 334 MPa. It was noticed that, at a pressure of about 496 MPa, the gypsum began to partly dissolve. The degree of solubility showed a strong increase at around 660 MPa, as proposed by Wang *et al.*,^[16] simultaneously leading to a continuous rise in the concentration of sulfate solution. Finally, the solid sample disappeared in aqueous solution at a pressure up to 866 MPa. Figures 1(f)–1(j) show a progression of new mineral precipitation at different pressures and temperatures. In the initial stage of heating, no precipitations appeared at a temperature of 100°C and 200°C. However, needle-shaped crystals began to precipitate from CaSO₄-bearing supersaturated solution at approximately 310°C. As the temperature was increased to 350°C, the crystals grew up gradually (Fig. 1(i)). Then, the sample chamber was rapidly cooled to the ambient temperature (Fig. 1(j)) and the crystals retained the preceding state.

The observed vibrational bands of gypsum under

ambient conditions and well documented values are listed in Table 1. In this study, the most intense ν_1 Raman mode is devoted to probing the phase transition. Figure 2 clearly indicates the presence of spectrum characteristic of SO₄ ion in aqueous solution even though the ν_{SO_4} mode appears to be relatively weak at a pressure of 496 MPa. In particular, the spectrum at 866 MPa is quite different from those at lower pressures, showing that the ν_1 mode of gypsum abruptly disappears, whereas the ν_{SO_4} Raman mode indicating sulfate solution concentration strengthens.

Table 1. Wave numbers ($\tilde{\nu}$) of Raman bands in gypsum recorded under ambient conditions.

$\tilde{\nu}$ (cm ⁻¹) (This work)	$\tilde{\nu}$ (cm ⁻¹) (Ref. [8])	$\tilde{\nu}$ (cm ⁻¹) (Ref. [10])	$\tilde{\nu}$ (cm ⁻¹) (Ref. [17])	$\tilde{\nu}$ (cm ⁻¹) (Ref. [18])	Assignment
1008	1008	1008	1008	1007	$\nu_1(\text{SO}_4)$
415	420	415	415	416	$\nu_2(\text{SO}_4)$
494	494	495	495	491	$\nu_2(\text{SO}_4)$
1139	1139	1136	1140	1136	$\nu_3(\text{SO}_4)$
619	623	619	623	618	$\nu_4(\text{SO}_4)$
3406	3345	3405	3405	3406	$\nu_1(\text{H}_2\text{O})$
3484	3452	3489	3490	3492	$\nu_3(\text{H}_2\text{O})$

Table 2. Wavenumbers (ν) of Raman bands in anhydrite recorded under ambient conditions.

ν (cm ⁻¹) (This work)	ν (cm ⁻¹) (Ref. [8])	ν (cm ⁻¹) (Ref. [19])	ν (cm ⁻¹) (Ref. [20])	ν (cm ⁻¹) (Ref. [21])	ν (cm ⁻¹) (Ref. [22])	ν (cm ⁻¹) (Ref. [23])	Assignment
416		417		416		416	$\nu_2(\text{SO}_4)$
498	490	498	490	498		498	$\nu_2(\text{SO}_4)$
608		608		608	615	608	$\nu_4(\text{SO}_4)$
627		627		627		626	$\nu_4(\text{SO}_4)$
675	670	675	673	675	676	674	$\nu_4(\text{SO}_4)$
1017	1016	1018	1023	1016	1014	1016	$\nu_1(\text{SO}_4)$
1110				1110		1111	$\nu_3(\text{SO}_4)$
1128		1129		1128	1124	1128	$\nu_3(\text{SO}_4)$
1159	1163	1160	1159	1159	1157	1159	$\nu_3(\text{SO}_4)$

Table 3. The onset temperature and pressure of the precipitation of anhydrite at each experiment.

	No 1	No 2	No 3	No 4	No 5	No 6
Temperature (°C)	280	260	310	250	320	290
Pressure (MPa)	1145	1038	1414	1019	1462	1256

Raman spectra of the new mineral phase obtained under various conditions are shown in Fig. 3. Figure 3(a) displays the Raman spectrum of the new phase at 310°C, of which the $\nu_1(\text{SO}_4)$ mode centers at 1019 cm⁻¹. In Fig. 3(c), we achieve the Raman spectrum of the new mineral phase after the sample was cooled to room temperature. As can be seen, the $\nu_1(\text{SO}_4)$ mode at about 1020 cm⁻¹ persists all through the cooling cycle, although the peak intensity becomes weaker compared to those in Figs. 3(a) and 3(b). Moreover, strong diamond fluorescence appears at high temperatures so that the detection of other Raman modes including ν_2 , ν_3 and ν_4 fails, as shown in Figs. 3(a)–3(c). We kept the new crystal inside the sample chamber after the pressure was completely released. It is clear from Fig. 3(d) that a Raman spectrum corresponding to anhydrite becomes prominent under ambient conditions.

Under ambient conditions the observed Raman bands belonging to anhydrite at 416, 498, 608,

627, 675, 1017, 1110, 1128 and 1159 cm⁻¹ are in good agreement with those reported in the literature,^[8,19–23] as listed in Table 2. In addition, gypsum is not recoverable by rapidly cooling the sample system and releasing the pressure, suggesting that the gypsum-anhydrite transition under high P and T conditions is irreversible. It is concluded that all these observations indicate structural changes involving the rearrangement of sulphate ions during the transition process at the onset temperature of around 310°C.

Figure 4 shows the phase relations of gypsum-bassanite-anhydrite determined by previous studies,^[11–13] and the data points obtained in our study are also included. We can see that the new mineral existing in our experiments is in the stability field of anhydrite, which convincingly demonstrates that the mineral phase coincides with previous studies. Furthermore, the onset temperature for the formation of anhydrite in Mirwald's study is about 85–110°C lower than that acquired by dissolution and precipitation processes. Taking into account this case, it is likely that the SO₄ ion has undergone considerable changes in its crystallographic environment during the two disparate transition processes.

In this series of experiments, the pressure increases

with increasing temperature due to the enclosed environment inside the sample chamber. Also, it can be seen that the higher the pressure of gypsum dissolution, the higher the temperature of anhydrite precipitation. Table 3 lists the P and T conditions for the precipitation of anhydrite obtained in the pressure and temperature ranges of 1.0–1.5 GPa and 250–320°C, respectively. It is important to note, however, that there is a good linear relationship between the onset temperature and pressure for the precipitation of anhydrite phase (Fig. 4). By the linear fitting method, the dissolution-precipitation boundary of $\text{CaSO}_4(l)$ -anhydrite transition yields a positive dP/dT slope of 6.8 MPa/K, as expressed by

$$P(\text{GPa}) = 0.0068T - 0.7126 \quad (250^\circ\text{C} \leq T \leq 320^\circ\text{C}),$$

$$R^2 = 0.9787. \quad (3)$$

Kinsman^[24] proposed the dissolution-precipitation mechanism controlling the genesis of several anhydrite deposits in geological environments. It was thought that the early formed gypsum was first dissolved in fluid, and that Ca and SO_4 ions were carried and precipitated to form anhydrite. For the formation of the anhydrite phase under high P and T conditions, a stable range of pressure and temperature conditions is indispensable. On the other hand, the Ca and SO_4 ion concentrations in aqueous solution must reach supersaturation. More importantly, the change in dielectric constant of water has a positive effect on the precipitation of anhydrite. It is known that the dielectric constant will decrease with increasing temperature, causing a decreasing solubility of mineral in water. Thus, the precipitation of anhydrite occurs with the rise of temperature.

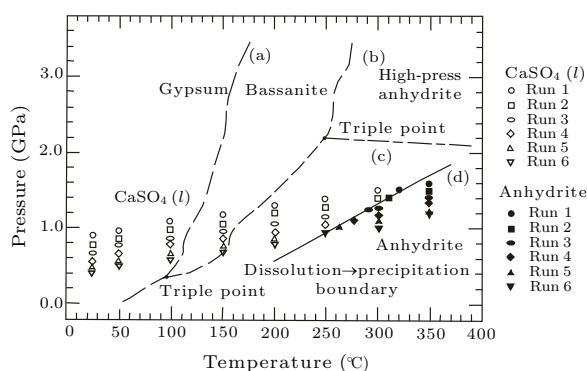


Fig. 4. Phase relations of gypsum-bassanite-anhydrite (from Mirwald^[11] and Kennedy *et al.*^[12,13]) The dashed lines (a) and (b) are the phase boundaries of gypsum-bassanite and bassanite-anhydrite. The dashed line (c) is the stable and metastable high pressure transition boundary of CaSO_4 . The empty and solid symbols represent the $\text{CaSO}_4(l)$ and anhydrite phase in this study, respectively. The solid line (d) is the boundary line of $\text{CaSO}_4(l)$ and anhydrite.

As seen in Fig. 4, anhydrite exists on the right region of the dissolution-precipitation boundary, and it would precipitate at higher temperature or lower pressure. In addition, the different pressures for gypsum dissolution prove that the water-mineral ratios

are different for each experimental run, thus leading to different precipitation temperatures of anhydrite. This inconsistency of water-mineral ratio is predominately caused by the initial nonuniformity of systems or various reaction kinetic mechanisms.^[25] In our opinion, the precipitation of anhydrite phase from CaSO_4 -bearing supersaturated solution is likely to take place so long as the P - T conditions in the system correspond to the dissolution-precipitation boundary obtained in our experiments (Eq. (3)). Further work is still needed to establish whether this conclusion is appropriate for a wider P - T range.

In summary, we have discussed the dissolution and precipitation behaviors of gypsum-anhydrite transition through hydrothermal diamond anvil cell and Raman spectroscopy. It is shown that the solubility of gypsum strongly increases with pressure, and the gypsum entirely dissolves in aqueous solution at a pressure of around 866 MPa. The precipitation of anhydrite occurs at 250–320°C and the pressure range of 1.0–1.5 GPa, respectively. A linear relationship between the onset pressure and temperature for the precipitation of anhydrite phase has also been established as $P(\text{GPa}) = 0.0068T - 0.7126$ ($250^\circ\text{C} \leq T \leq 320^\circ\text{C}$). Both a stable range of pressure and temperature conditions and supersaturation of Ca and SO_4 ion concentrations in aqueous solution are essential for the formation of anhydrite. In addition, the gypsum-anhydrite transition involving both dissolution and precipitation processes is irreversible.

References

- [1] Comodi P *et al* 2008 *Am. Mineral.* **93** 1530
- [2] Popp T and Kern H 1993 *Earth Planet. Sci. Lett.* **120** 43
- [3] Ibarra J V, Palacios J M and Andres A M 1989 *Fuel* **68** 861
- [4] Shatkay M and Magaritz M 1987 *Geochim. Cosmochim. Acta* **51** 1135
- [5] Lakatos B *et al* 1979 *Acta Agron. Hung.* **28** 335
- [6] Bath A H *et al* 1987 *Geochim. Cosmochim. Acta* **51** 3113
- [7] Zhou X Z *et al* 2006 *Acta Petrol. Sin.* **22** 3047
- [8] Sarma L P *et al* 1998 *J. Raman Spectrosc.* **29** 851
- [9] Huang E *et al* 2000 *High Press Res.* **17** 57
- [10] Knittle E *et al* 2001 *Phys. Chem. Miner.* **28** 630
- [11] Mirwald P W 2008 *J. Chem. Phys.* **128** 074502
- [12] Yamamoto H and Kennedy G C 1969 *Am. J. Sci.* **267A** 550
- [13] Kennedy G C 1961 *Adv. Geophys.* **7** 303
- [14] Bassett W A *et al* 1993 *Rev. Sci. Instrum.* **64** 2340
- [15] Schmidt C and Ziemann M A 2000 *Am. Mineral.* **85** 1725
- [16] Wang S X and Zheng H F 2008 *Chin. J. High Press. Phys.* **22** 429
- [17] Krishnamurthy N and Soots V 1971 *Can. J. Phys.* **49** 885
- [18] Ma Y P, Liu Y M, Zhang Y F and Cui Q L 2009 *Analyt. Instrum.* **6** 45
- [19] Yang Y P and Zheng H F 2005 *Acta Mineral. Sin.* **25** 299
- [20] Lishi K 1979 *Phys. Chem. Miner.* **4** 341
- [21] Chen C C, Liu L G, Lin C C and Yang Y J 2001 *J. Phys. Chem. Solids.* **62** 1293
- [22] Prasad P S R, Chaitanya V K, Prasad K S and Rao D N 2005 *Am. Mineral.* **90** 672
- [23] Ma Y M, Zhou Q, He Z, Li F F, Yang K F, Cui Q L and Zou G T 2007 *J. Phys. : Condens. Matter.* **19** 425221
- [24] Kinsman D J J 1974 *Fourth Symposium on Salt*, Northern Ohio Geological Society 343
- [25] Deng H L, Tu G C, Li C Y and Liu C Q 1999 *Acta Mineral Sin.* **19** 267