



Determination of pressure from measured Raman frequency shifts of anhydrite and its application in fluid inclusions and HDAC experiments

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Abstract

A new geobarometry was derived from the quantified relationships among Raman vibrational frequencies of anhydrite, pressure and temperature, as determined from in-situ micro-Raman spectroscopy of natural anhydrite crystals measured at p – T conditions up to 560 °C and 1400 MPa by using a hydrothermal diamond anvil cell (HDAC). With this geobarometry, the pressure in HDAC experiments and in anhydrite-bearing fluid inclusions can be determined directly from the ν_1 , ν_{1016} , $\nu_{3, 1128}$ and $\nu_{3, 1160}$ Raman frequency shifts of anhydrite at high p – T conditions relative to their values measured at ambient conditions. The pressure can be determined to an accuracy of better than 30 MPa based on the attainable accuracy of $\pm 0.1 \text{ cm}^{-1}$ for the fitted ν_1 Raman peak positions, provided the measured spectra are calibrated using the emission peak of an external fluorescent light source. The feasibility and reliability of this geobarometry were verified by rebuilding the p – T history of two fluid inclusions from the ν_1 frequency shifts of anhydrite daughter minerals from room to high temperatures, and by measuring the phase-transition pressures of calcite– $\text{CaCO}_3(\text{II})$ – $\text{CaCO}_3(\text{III})$ sequence at ambient temperature in a HDAC experiment using anhydrite as a Raman pressure sensor.

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1. INTRODUCTION

Anhydrite (CaSO_4) is one of the most abundant sulfates in the Earth's crust and occurs in various environments such as magmatic, hydrothermal and evaporitic deposits. Three different anhydrite phases, i.e., a high temperature AI or α - CaSO_4 , a moderately soluble AII or β - CaSO_4 and a low temperature and totally soluble AIII or γ - CaSO_4 , have been documented, but only AII occurs in nature (Gay, 1965; Bezou et al., 1995; Freyer and Voigt,

2003; Dantas et al., 2007; Albis et al., 2008; Christensen et al., 2008; Prieto-Taboada et al., 2014, 2015). Extensive experimental studies have been made on the dissolution and precipitation of CaSO_4 (Dickson et al., 1963; Marshall et al., 1964; Blounot and Dickson, 1969; Carlberg, 1973; Newton and Manning, 2005; Ossorio et al., 2014) and on the phase transitions of anhydrite under various p – T conditions (Borg and Smith, 1975; Chen et al., 2001; Ma et al., 2007; Mirwald, 2008; Bradbury and Williams, 2009). The results from these studies show that natural anhydrite is structurally stable over a wide p – T range, until it was observed to transit to a monoclinic

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monazite structure at about 2 GPa and to new unknown phases after being heated to higher than 1000 °C.

The Raman bands of natural anhydrite (AII) have been measured and interpreted (Berenblut et al., 1973; Sarma et al., 1998; Prasad et al., 2001; Ma et al., 2007; Buzgar et al., 2009; Liu et al., 2009): The intense peak at approximately 1016 cm⁻¹ represents the ν_1 symmetric stretching vibration of the SO₄ tetrahedra, whereas the symmetric bending vibration (ν_2), the anti-symmetric stretching vibration (ν_3) and the anti-symmetric bending vibration (ν_4) of the SO₄ tetrahedra are split into 8 peaks: ν_2 occurs at 418 and 498 cm⁻¹, ν_3 occurs at 1112, 1128 and 1160 cm⁻¹, and ν_4 occurs at 608, 627 and 675 cm⁻¹; the weak peaks observed between 50 and 300 cm⁻¹ are assigned to the Ca²⁺-SO₄²⁻ rotational and translational vibrations. Several pressure-dependent Raman scattering studies of natural anhydrite (Chen et al., 2001; Yang and Zheng, 2005; Ma et al., 2007) have indicated systematic shifts of peak positions to higher frequencies at varying $\partial\nu/\partial p$ rates with increasing pressure, thereby exhibiting potential usefulness of the anhydrite Raman peak positions as a geobarometer for the study of anhydrite-containing mineral assemblages in HDAC experiments or anhydrite-bearing fluid inclusions. However, there is substantial disagreement in the $\partial\nu/\partial p$ rates among the reported studies (e.g., from 2.7 cm⁻¹/GPa by Ma et al. (2007) to 5.3 cm⁻¹/GPa by Yang and Zheng (2005) for the ν_1 band). Furthermore, to our knowledge no Raman studies of anhydrite at high temperatures, or of the anhydrite + water system to simultaneously high p - T conditions, have been reported. In this paper we present an in-situ Raman spectroscopic investigation of natural anhydrite in water at high p - T conditions using a HDAC. We have derived a new geobarometry from the fitted Raman peak positions as a function of pressure and temperature, and have applied the geobarometry for the determination of internal pressures in natural anhydrite-bearing fluid inclusions at elevated temperatures, and of the calcite-CaCO₃(II)-CaCO₃(III) phase transition pressures at ambient temperature, from the fitted ν_1 frequency shifts of anhydrite relative to the values measured at reference conditions.

2. EXPERIMENTAL APPARATUS AND PROCEDURES

2.1. Hydrothermal diamond anvil cell and anhydrite samples

Our experiments were carried out using a Bassett-type hydrothermal diamond anvil cell (Bassett et al., 1993). Two opposed low-fluorescence diamond anvils with 800 μ m diameter culets, supported by tungsten carbide seats and heated resistively using two molybdenum heaters wound around the seats, were used to subject the samples to high p - T conditions. The sample chamber was assembled by sealing the diamond anvils against a 400 μ m diameter hole in the center of a 125 μ m thick rhenium gasket. Temperature of the sample was measured using two K -type thermocouples attached to each of the diamond anvils, calibrated by measuring the melting temperatures of ice (0 °C), sodium nitrate (307 °C) and anhydrous copper

chloride (498 °C) at room pressure, to an accuracy of ± 1 and ± 2 °C from the set point at temperatures below and above 300 °C, respectively. Pressure at a given temperature was determined by the 464 cm⁻¹ Raman frequency shift of quartz from the value measured at ambient conditions (Schmidt and Ziemann, 2000):

$$p(\text{MPa}) = 0.036079 \times (v_{p,T} - v_{0,T})^2 + 110.86 \times (v_{p,T} - v_{0,T}); \quad (1a)$$

$$v_{0,T}(\text{cm}^{-1}) = v_{0,23^\circ\text{C}} + 2.50136 \times 10^{-11} \times T^4 + 1.46454 \times 10^{-8} \times T^3 - 1.801 \times 10^{-5} \times T^2 - 0.01216 \times T + 0.29. \quad (1b)$$

The reported pressure uncertainty (Schmidt and Ziemann, 2000) was about ± 50 MPa based on the attainable accuracy of the fitted Raman peak position of ± 0.2 cm⁻¹.

In-situ high p - T Raman scattering experiments were performed with natural anhydrite crystals from Chihuahua, Mexico. A 250 \times 70 \times 50 μ m anhydrite chip was loaded into the sample chamber at ambient temperature, together with a quartz chip measuring approximately 150 \times 70 \times 40 μ m for pressure calibration, and HPLC water as a pressure transmitting medium (Fig. 1a). Our high-pressure experiments started at a sealing pressure of ~ 6 MPa, and by slightly advancing the platen screws of the HDAC, the pressure in the sample chamber was increased stepwise to 1133 MPa. After reloading the pressure transmitting medium, high-temperature runs were carried out with starting pressures ranging from ~ 4 to 631 MPa, and temperature was raised from room temperature to 560 °C or to a maximum pressure of 1400 MPa, at intervals of 50 °C. Slight dissolution of quartz at high temperatures and of anhydrite at high pressures were observed from their flatter surfaces and smoother edges, and minor amounts of acicular anhydrite crystals precipitated and redissolved during the repeated heating and cooling runs (Fig. 1b and c). Several small, transparent and unknown minerals crystallized at temperatures above 550 °C and were kept stable thereafter (Figs. 1b and c), which demands further studies. Fortunately, the major portions of the quartz and anhydrite chips remained stable and we were able to acquire the Raman spectra from these minerals throughout the entire experiment. After all of the high p - T Raman measurements of both minerals were made, the sample chamber was opened and Raman spectra of the same (dry) anhydrite sample were collected in the 23–560 °C temperature range and at ambient pressure.

2.2. Raman spectrometer and spectral calibration

The unpolarized Raman spectra were acquired using a HORIBA Jobin Yvon confocal LabRAM HR800 micro-Raman system installed at Missouri State University. The system was equipped with a frequency doubled Nd:YAG green laser (532.06 nm), a Mitutoyo M Plan Apo NIR 20 \times long-working distance objective with 0.40 numerical aperture ($f = 200$), and a stigmatic 800 mm spectrometer with a 2400 groove/mm grating. The confocal hole was

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