Extended Micro-Raman Densimeter for CO_2 Applicable to Mantle-originated Fluid Inclusions

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Micro-Raman spectroscopy enables nondestructive analyses of CO_2 fluid density in a very small volume. For application of the method to CO_2 fluid inclusions in minerals originated from the deep Earth having widely various densities, we extended the relational expression between the density and Raman spectra of CO_2 up to the density corresponding to the boundary between liquid and solid.

Raman spectra of CO_2 contain useful information for characterizing its density. Several previous studies have documented the density-dependent band shifts in Raman spectra of CO_2. Raman spectra of CO_2 have two main peaks at 1388.0 (ν_+) and 1285.5 cm^{-1} (ν_-), which are split by the Fermi resonance (Figure 1). Bertrán found that the separation between those two bands ($\nu_+ - \nu_-$: Delta) is pressure-dependent.[1] That Delta value increases concomitant with pressure. The link between the Raman scale and density (pressure) of CO_2 fluid has also been demonstrated.[2–5]

The use of micro-Raman spectroscopy for determining the density of CO_2 fluid inclusions with several micrometers in diameter contained in minerals provides technical advantages over conventional methods.[6] In minerals derived from the uppermost part of the mantle (<ca. 100 km depth), carbon is commonly observed as a CO_2 fluid inclusion. The CO_2 fluid density reflects both conditions of temperature and pressure where the host mineral existed in the mantle. If the CO_2 density in the fluid inclusion is estimated, the depth (pressure) can be calculated using the equation of state of CO_2; the equilibration temperature can be estimated using the temperature-dependence of the partition of some elements between constituent minerals. Used in this manner, the CO_2 fluid density in mantle-derived minerals can serve as a new depth probe.

In general, the CO_2 fluid density in minerals is determined accurately by measuring the temperature at which liquid and vapor in two-phase CO_2 in minerals become homogenized to a single phase upon warming. This technique is called microthermometry. In the case of superdense CO_2 with density higher than 1.178 g/cm^3, it is extremely difficult to determine accurately the temperature of phase change between dry ice and liquid CO_2 because of the lack of gas phase in that entire temperature range. Recently, occurrences of superdense CO_2 fluid have been reported from fluid inclusions in mantle-derived silicate minerals.[7–9] Solid CO_2 inclusions were reported in natural diamond.[10] Kawakami et al. generated a dense CO_2 fluid by compressing CO_2 fluid in a high-pressure cell that was equipped with two sapphire windows up to 145 MPa.[11] They reported the relational-expression between the density and Delta using data with a wide range of densities (0.1–1.21 g/cm^3). However, only two data with superdense CO_2 were used for the relational expression. The accuracy of the relational expression in the range of superdense CO_2 was not clear. Hence, we have accumulated the Delta values of high-density CO_2 and have thereby extended the upper limit of the density range of the expression up to 1.24 g/cm^3 and 185 MPa.

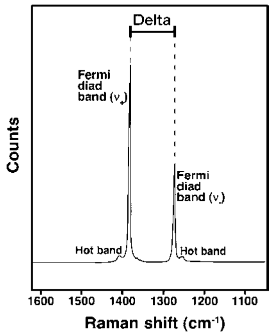

Figure 1. Representative Raman spectrum of CO_2. Delta designates the Fermi resonance split between the upper (ν_+) and lower (ν_-) bands.

The Raman spectra were obtained on a 30-cm single polychromator (250is; Chromex), equipped with an optical microscope (BX60; Olympus Optical Co., Ltd.), an Ar^+ ion laser (514.5 nm, 5500 A; Ion Laser Technology Inc.), and a CCD camera with 1024 × 256 pixels (DU-401-BR-DD SH; Andor Technology). The Rayleigh line was removed using a holographic supernotch filter (HIPF-514.5-1.0; Kaiser Optical Systems, Inc.). The Raman shift was calibrated with a standard sample of naphthalene. The spectral resolution was around 1.5 cm^{-1} per pixel; each CO_2 band was fitted to a Lorentzian curve to determine the accurate peak position. Applying this peak-fitting procedure reduces the effective spectral resolution to 0.03 cm^{-1} at signal counts higher than 500.[11]

Raman spectra of CO_2 with a wide range of densities were obtained using a high-pressure cell, which is the same cell as that used in Kawakami et al.[11] and Yamamoto et al.[12] The cell is equipped with two sapphire windows, a type-K thermocouple and a digital pressure transducer verified using a Bourdon tube pressure gauge. The cell was designed to generate fluid pressure up to 400 MPa,[13] but the maximum pressure for high-pressure experiments on CO_2 fluid was limited to 145 MPa because the mechanical hardness of stainless steel lines and a large vessel (piston cylinder) to pressurize CO_2 fluid constrained the achievable pressure. In this study, we improved the screws in the pressurizing vessel by changing the material from SUS316 to SUS630. We properly adjusted screws and gaskets of the pressure device. Because of these changes, the maximum achievable pressure for CO_2 was improved to 200 MPa in the present system. Pure CO_2 was introduced to the piston cylinder at room

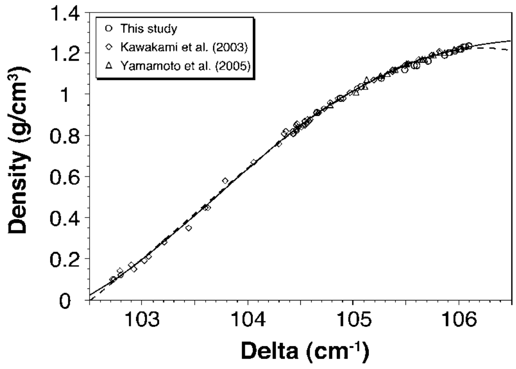

Figure 2. Plots of Delta vs. density of CO_2. Data are measured using CO_2 fluid in a high-pressure cell. The broken and solid lines correspond to the fitted expression of degree 3 and 8, respectively.

temperature, and the mixture of gas and liquid phases in the line was compressed to generate liquid CO_2 under high pressure. A hand pump was used to compress the fluid CO_2 to 185 MPa. Measurements were made at the undercritical condition in the range of 22.1–23.5 °C.

Figure 2 shows plots of Delta and CO_2 density in the cell. The density was estimated using the state equation of CO_2 from the measured pressure and temperature. Upon compression at 22.3 °C, the pressure of the CO_2 achieved a maximum pressure of 185 MPa. At that pressure, a part of liquid CO_2 began to transform to solid and the increase of pressure became a plateau. In the present study, we therefore obtained Raman spectra of CO_2 with densities of 0.91 up to 1.24 g/cm^3.

Garrabos et al. achieved a fit to their data of Delta and density of CO_2 using a second-order polynomial function in the density range of 0.1–1.18 g/cm^3 including supercritical fluid at 40 °C.[2,3] However, the scatter in their data produces obscurity of accuracy in fitting. Rosso and Bodnar[5] and Yamamoto et al.[14] inferred a linear relationship from limited data obtained at room temperature below the critical temperature. The present data were taken in liquid CO_2 below the critical temperature (31.1 °C) at approximately 23 °C, whereas the data of Kawakami et al.[11] were taken in part at 58–59 °C. Kawakami et al.[11] proposed that the relationship can be expressed as a cubic function from CO_2 with densities of 0.1–1.21 g/cm^3, including supercritical fluid at 58–59 °C. Figure 2 shows the density dependence of Delta determined from the present study, in comparison to data from other works.[11,12] The relationship is fitted to expressions of degree 3 and 8, respectively;

$\text{Density} = -0.01917{*}(\text{Delta} - 100)^3 + 0.1984{*}(\text{Delta} - 100)^2 - 0.2410{*}(\text{Delta} - 100) - 0.341$; $\text{Density} = -0.00111808{*}(\text{Delta} - 100)^8 + 0.04498451{*}(\text{Delta} - 100)^7 - 0.7727143{*}(\text{Delta} - 100)^6 + 7.4128146{*}(\text{Delta} - 100)^5 - 43.468301{*}(\text{Delta} - 100)^4 + 159.54433{*}(\text{Delta} - 100)^3 - 357.7651{*}(\text{Delta} - 100)^2 + 448.2404{*}(\text{Delta} - 100) - 240.461$

The deviation between those two fitting lines is considerably large for densities greater than 1.2 g/cm^3, which results from the fact that the correlation of the cubic function became convex upward on reaching the density of 1.198 g/cm^3. Any polynomial function with order between 3 and 7 fitted with the data having densities lower than 1.1 g/cm^3 did not predict the present experimental data with densities greater than 1.1 g/cm^3. By contrast, an 8th-order polynomial function can fit the data well and the extrapolated line coincides with the experimental values at higher pressure. Confining the density range used for fitting to less than 1.1 g/cm^3, data with density of more than 1.1 g/cm^3 are not fitted well with the cubic function fitted using data of less than 1.1 g/cm^3. Consequently, the correlation is preferably fitted by a polynomial equation with degree 8. The coefficient of determination of the fitting curve of Kawakami et al.[11] was 0.99883, whereas the coefficient of determination in Figure 2 is improved to 0.99947. The precision of Delta (0.03 cm^{-1}) corresponds to the precision in density of around 0.01 g/cm^3.

A Raman spectrum of CO_2 can be used to determine the density of the CO_2 in fluid inclusions derived from mantle. The pressure (depth) at which the mantle rock is entrained by the host magma is estimated from the combination of CO_2 density and the equilibrium temperature of the mantle rock. Natural examples of superdense CO_2 with a density of 1.21 g/cm^3 were identified in fluid inclusions in mantle-derived rocks[7] and in quartz.[8] Furthermore, Hirano et al.[9] predicted the occurrence of CO_2 fluid with a density of around 1.2 g/cm^3 in mantle-derived rock from the oceanic lithosphere. Therefore, we fully expect to find superdense CO_2 fluid with density of more than 1.21 g/cm^3 in the near future.

In the present study, we extended the upper limit of the density range of the relational expression between the density and Delta from 1.21 (145 MPa) up to 1.24 g/cm^3 (185 MPa). Assuming a mantle xenolith with equilibrium temperature of 1000 °C, the limitation to estimate the trapping pressure extended from 12,000 bar (39 km depth) to 13,500 bar (44 km depth) at a maximum. The present densimeter shows improved effectiveness as a depth probe.

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