Extended Micro-Raman Densimeter for CO₂ Applicable to Mantle-originated Fluid Inclusions

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Micro-Raman spectroscopy enables nondestructive analyses of CO₂ fluid density in a very small volume. For application of the method to CO₂ 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 CO₂ up to the density corresponding to the boundary between liquid and solid.

Raman spectra of CO₂ contain useful information for characterizing its density. Several previous studies have documented the density-dependent band shifts in Raman spectra of CO₂ characterizing its density. Several previous studies have documented the method to CO₂ fluid inclusions in minerals originated from the uppermost part of the mantle (<ca. 100 km depth), carbon is commonly observed as a CO₂ fluid inclusion. The CO₂ fluid density reflects both conditions of temperature and pressure where the host mineral existed in the mantle. If the CO₂ density in the fluid inclusion is estimated, the depth (pressure) can be calculated using the equation of state of CO₂; the equilibration temperature can be estimated using the temperature-dependence of the partition coefficient contained in minerals provides technical advantages over conventional methods. In minerals derived from the uppermost part of the mantle (<ca. 100 km depth), carbon is commonly observed as a CO₂ fluid inclusion. The CO₂ fluid density reflects both conditions of temperature and pressure where the host mineral existed in the mantle. If the CO₂ density in the fluid inclusion is estimated, the depth (pressure) can be calculated using the equation of state of CO₂; the equilibration temperature can be estimated using the temperature-dependence of the partition of some elements between constituent minerals. Used in this manner, the CO₂ fluid density in mantle-derived minerals can serve as a new depth probe.

In general, the CO₂ fluid density in minerals is determined accurately by measuring the temperature at which liquid and vapor in two-phase CO₂ in minerals become homogenized to a single phase upon warming. This technique is called microthermometry. In the case of superdense CO₂ with density higher than 1.178 g/cm³, it is extremely difficult to determine accurately the temperature of phase change between dry ice and liquid CO₂ because of the lack of gas phase in that entire temperature range. Recently, occurrences of superdense CO₂ fluid have been reported from fluid inclusions in mantle-derived silicate minerals. Solid CO₂ inclusions were reported in natural diamond. Kawakami et al. generated a dense CO₂ fluid by compressing CO₂ fluid in a high-pressure cell that was equipped with two sapphire windows up to 145 MPa. They reported the relational-expression between the density and Delta using data with a wide range of densities (0.1–1.21 g/cm³). However, only two data with superdense CO₂ were used for the relational expression. The accuracy of the relational expression in the range of superdense CO₂ was not clear. Hence, we have accumulated the Delta values of high-density CO₂ and have thereby extended the upper limit of the density range of the expression up to 1.24 g/cm³ and 185 MPa.

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⁺ laser (514.5 nm, 5500 A; Ion Laser Technology Inc.), and a CCD camera with 1024 × 256 pixels (DU-401-BR-DD SH; Andor Technologies). The Rayleigh line was removed using a holographic supernoitch 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 CO₂ 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.

Raman spectra of CO₂ 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. and Yamamoto et al. 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, but the maximum pressure for high-pressure experiments on CO₂ fluid was limited to 145 MPa because the mechanical hardness of stainless steel lines and a large vessel (piston cylinder) to pressurize CO₂ fluid constrained the achievable pressure. In this study, we improved the screws in the pressurizing vessel by changing the material from SUS316 to SUS360. We properly adjusted screws and gaskets of the pressure device. Because of these changes, the maximum achievable pressure for CO₂ was improved to 200 MPa in the present system. Pure CO₂ was introduced to the piston cylinder at room temperature. The maximum pressure for CO₂ was improved to 200 MPa in the present system. Pure CO₂ was introduced to the piston cylinder at room temperature.
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 trans-
form 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. However, the scatter in their data produces ob-
scurity of accuracy in fitting. Rosso and Bodnar and Yamamoto
et al. 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. were taken in part at 58–59°C. Kawakami et al. 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 super-
critical fluid at 58–59°C. Figure 2 shows the density dependence of
Delta determined from the present study, in comparison to da-
ta from other works. The relationship is fitted to expressions
of degree 3 and 8, respectively;

\[
\text{Density} = -0.01917^*(\Delta - 100)^3 + 0.1984^*(\Delta - 100)^2 - 0.2410^*(\Delta - 100) - 0.341; \quad \text{Density} = -0.00111808^*(\Delta - 100)^3 + 0.04498451^*(\Delta - 100)^2 - 0.7727143^*(\Delta - 100)^1 + 7.4128146^*(\Delta - 100) - 43.468301^*(\Delta - 100)^1 + 159.54433^*(\Delta - 100)^1 - 357.7651^*(\Delta - 100)^1 + 448.2404^*(\Delta - 100) = 240.461
\]

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 up-
ward 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 exper-
imental data with densities greater than 1.1 g/cm$^3$. By contrast,
an 8th-order polynomial function can fit the data well and the ex-
trapolated 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 fit-
ted 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 determi-
nation of the fitting curve of Kawakami et al. was 0.99983,
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$_2$ den-
sity 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 and in
quartz. Furthermore, Hirano et al. 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 den-
sity range of the relational expression between the density and
Delta from 1.21 (145 MPa) up to 1.24 g/cm$^3$ (185 MPa). Assum-
ing 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 max-
imum. The present densimeter shows improved effectiveness as
a depth probe.

References