**Temperature dependence of a Raman CO2 densimeter from 23 to 200°C and 7.2 to 248.7 MPa:** **Evaluation of density underestimation by laser heating**

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**1. Criteria to select the earlier studies for use in comparison**

To raise the accuracy of discussion related to the temperature-dependence of Δ, the differences of measurement conditions among earlier studies such as spectral resolution, pressure measurement accuracy, temperature range, and fluid composition must be clarified. Then published data suitable for comparison with this study must be selected strictly. Therefore, we used the following three criteria to select the earlier studies for use in comparison.

The first is the wavenumber resolution when measuring the Raman spectrum of CO2. Bondarenko[1] used HPOC to obtain pure CO2 Raman spectra at temperatures between 20 and 600°C and pressures of 50 and 100 MPa. That study compared the data with those obtained by Garrabos et al.[2] at room temperature, producing the inference that Δ decreases concomitantly with increasing temperature at constant density, at least at densities of 0.27–1.05 g/cm3 (Figure 2b of Bondarenko[1]). However, Bondarenko[1] did not adequately describe the wavenumber resolution. That study measured Δ of CO2 with densities of 0.819 g/cm3 at 100°C and 0.811 g/cm3 at 200°C. The difference between the two Δ values is 0.70 cm–1. Because this value is significantly different from 0.18 cm–1, which is the value calculated using our Equation (2), we infer that the measurement precision of Δ of Bondarenko[1] was worse than that of the present Raman system. Chen et al.[3] examined the temperature-dependence of Δ using synthetic CO2–H2O±NaCl fluid inclusions with compositions of 5 and 10 mass% CO2. They concluded that the variations of Δ are small at lower temperatures (< 200°C), whereas, with increasing temperature, Δ clearly decreases, which is apparently consistent with the results reported by Bondarenko[1]. However, Chen et al.[3] investigated a wide wavenumber region (1000–4000 cm–1) to measure the H2O and CO2 peaks simultaneously, implying that the wavenumber resolution was worse than that of the present study. This implication is also apparent from the CO2 spectrum of Figure 3 of Chen et al.[3]. Kawakami et al.[4] examined the temperature-dependence of Δ at 20–200°C using a CO2 fluid inclusion in orthopyroxene with density of 1.163 g/cm3. They measured the Δ of the inclusions three times at room temperature, and they showed a large variation of up to approx. 0.2 cm–1 (see their Figure 10). It is necessary to have a wavenumber resolution comparable to that in the present study to evaluate slight differences in the temperature-dependence of the Δ–*ρ* relations. We therefore excluded data reported by Bondarenko[1], Chen et al.[3], and Kawakami et al.[4] from the discussion.

The second criterion is pressure measurement accuracy. Yuan et al.[5] used HDAC to investigate characteristics of the Raman spectrum of CO2–H2O±CH4±NaCl fluid at 22–400°C and 5–1200 MPa. They reported the relation among ΔD, temperature, and pressure, where ΔD represents the wavenumber shifts of measured Δ relative to the reference values measured at 23°C and 6 MPa. However, the densimeter reported by Yuan et al.[5] differs considerably from the densimeter described in other published reports.[4,6–10] The main cause for these discrepancies between the report by Yuan et al.[5] and earlier reports appears to be a large pressure uncertainty (± 40 MPa) because Yuan et al.[5] used the peak shift of quartz at 464 cm–1, whereas others used the digital pressure transducer. This uncertainty of ± 40 MPa is extremely large at around our experimental pressure condition (7.2–248.7 MPa). It is necessary to have pressure accuracy comparable to that of the present study to evaluate slight differences in the temperature-dependence of the Δ–*ρ* relations. We therefore excluded results reported by Yuan et al.[5] from the discussion.

The third criterion is the fluid temperature during measurement. Fall et al.[8] reported the temperature-dependence of Δ–*ρ* relations below room temperatures of –10 to 35°C and pressures of 1.0 to 30.0 MPa using a HPOC. Because our experimental temperatures are higher than 23°C, data measured at 35°C are the only data which can be compared with our own. However, it is difficult to discuss the temperature-dependence of Δ from such a small temperature variation. In fact, we cannot identify the temperature-dependence of the Δ–*ρ* relations from their data. All data appear to be shown on a single monotonically increasing curve (Figure 4b of Fall et al.[8]). Therefore, because a sufficient temperature difference is necessary to discuss the temperature-dependence of Δ, we excluded results reported by Fall et al.[8] from the discussion.

As illustrated by the reasons presented above, data of earlier studies that might be compared with our results are limited to those reported by Sublett et al.[11], Wang et al.[12], and Wang et al.[6], but they engender mutually contradictory results related to the density-dependence of |(∂Δ/∂*T*)*ρ*|.

**2. Effect of density on ∂Δ/∂*T* at density lower than 0.6 g/cm3**

Figure S1 shows the density dependence of |(∂Δ/∂*T*)*ρ*| below 0.6 g/cm3 calculated by Equation (8) in Sublett et al.[11] and Equation (3) in Wang et al.[12]. In both results, the value of |(∂Δ/∂*T*)*ρ*| increases as the density increases from 0.01 to 0.6 g/cm3. In combination with the results of previous studies, it is suggested that there exists a density around 0.6–0.7g/cm3 where the sign of *d*|(∂Δ/∂*T*)*ρ*|/*dρ* is reversed.



Figure S 1 Δ change relative to initial Δ obtained at 24°C as a function of temperature. Solid lines are temperature dependence of Δ at constant density calculated using a) Equation (3) of Wang et al.[12] and b) Equation (8) of Sublett et al.[11]. The dotted line shows the extrapolation of the Δ-*T*-*ρ* relation derived in each study to the *P*-*T* region where no experimental calibration has been performed. Colored solid lines are isochores at 0.01, 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 g/cm3.

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