



HOKKAIDO UNIVERSITY

Title	Evaluation of factors controlling laser heating phenomena of inclusions during Raman spectroscopy and their influence on quantitative analysis
Author(s)	萩原, 雄貴
Degree Grantor	北海道大学
Degree Name	博士(理学)
Dissertation Number	甲第14792号
Issue Date	2022-03-24
DOI	https://doi.org/10.14943/doctoral.k14792
Doc URL	https://hdl.handle.net/2115/85921
Type	doctoral thesis
File Information	Yuuki_Hagiwara.pdf



Doctoral Dissertation

Evaluation of factors controlling laser heating phenomena of inclusions
during Raman spectroscopy and their influence on quantitative analysis
(ラマン分光法における包有物のレーザー加熱現象の制御因子とそ
の定量分析への影響の評価)

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2022, March

Abstract

Chapter1: Effect of experimental, optical, and geometrical parameters on laser heating of inclusions during Raman spectroscopic analysis

Raman spectroscopy for fluid, melt, and mineral inclusions provides direct insight into the physicochemical conditions of the environment surrounding the host mineral at the time of trapping. However, the obtained Raman spectral characteristics such as peak position are modified because of local temperature enhancement of the inclusions by the excitation laser, which might engender systematic errors and incorrect conclusions if the effect is not corrected. Despite the potentially non-negligible effects of laser heating, the laser heating coefficient (B) ($^{\circ}\text{C}/\text{mW}$) of inclusions has remained unsolved. For this study, I found B from experiments and heat transport simulation to evaluate how various parameters such as experimental conditions, mineral properties, and inclusion geometry affect B of inclusions. To assess the parameters influencing laser heating, I measured B of a total of 19 CO_2 -rich fluid inclusions hosted in olivine, orthopyroxene, clinopyroxene, spinel, and quartz. My results revealed that the measured B of fluid inclusions in spinel is highest (approx. $6^{\circ}\text{C}/\text{mW}$) and that of quartz is lowest (approx. $1 \times 10^{-2}^{\circ}\text{C}/\text{mW}$), consistent with earlier inferences. My simulation results show that the absorption coefficient of the host mineral is correlated linearly with B . It is the most influential parameter when the absorption coefficient of the host mineral (α_h) is larger than that of an inclusion (α_{inc}). Furthermore, although my results indicate that both the inclusion size and depth have little effect on B if $\alpha_h > \alpha_{inc}$, the thickness and radius of the host mineral slightly influence B . These results suggest that the choice of inclusion size and depth to be analyzed in a given sample do not cause any systematic error in the Raman data because of laser heating, but the host radius and thickness, which can be adjusted to some degree at the time of sample preparation, can cause systematic errors between samples.

My results demonstrate that, even with laser power of 10 mW, which is typical for inclusion analysis, the inclusion temperature rises to tens or hundreds of degrees during the analysis, depending especially on the host mineral geometry and optical properties. Therefore, correction of the heating effects will be necessary to obtain reliable data from Raman spectroscopic analysis of inclusions. This paper presents some correction methods for non-negligible effects of laser heating.

Chapter2: Temperature dependence of a Raman CO_2 densimeter from 23 to 200°C and 7.2 to 248.7 MPa: Evaluation of density underestimation by laser heating

Unintended local temperature enhancement by excitation laser might change Raman

spectral features and potentially lead to misinterpretation of the data. To evaluate robustness of Raman CO₂ densimeters in the presence of laser heating, I investigate the relation between temperature (T , °C), density (ρ , g/cm³), and Fermi diad split (Δ , cm⁻¹) using a high-pressure optical cell at 23–200°C and 7.2–248.7 MPa. Results indicate that Δ decreases concomitantly with increasing temperature for a constant density in all density regions investigated. This result suggests that the density estimated based on Δ might be underestimated if the fluid is heated locally by the laser. Combining results of earlier studies with those of the present study indicates that the temperature dependence of Δ ($|\partial\Delta/\partial T|_\rho$) has a maximum value around 0.6–0.7 g/cm³. Consequently, at very high densities such as 1.1–1.2 g/cm³, $|\partial\Delta/\partial T|_\rho$ is small. Thus, Δ at such densities is less affected by laser heating. However, at densities below approximately 0.7 g/cm³, although $|\partial\Delta/\partial T|_\rho$ becomes smaller at lower densities, the relative density decrease becomes larger even for a small density decrease because the density itself becomes smaller. Therefore, at such densities, a density decrease of more than 10% was observed for some fluid inclusions, even at typical laser powers for inclusion analysis. Finally, to accurately estimate the density even in the presence of laser heating, I show that it is effective to estimate the intercept Δ from the correlation between Δ and laser power, and substitute it into Δ - ρ relations.

Chapter3: Why CO₂ fluid inclusions in mantle xenolith have different densities depending on mineral species and inclusion size: Evaluation of laser heating effect on measured density

The density of fluid inclusions in mantle xenoliths has been used to estimate the depth provenance rocks. However, since the density of fluid inclusions depends on the mineral species and the inclusion diameter, the depth estimated depends on which inclusion density is used as an indicator of the depth provenance. However, such dependence may be artificially introduced by the properties of the measurement technique itself. For example, when CO₂ density is estimated using microthermometry, heating of inclusions by transmitted light may homogenize the gas phase into the liquid phase at a lower temperature than the true temperature, resulting in an overestimation of density. On the other hand, in the case of density estimation by Raman CO₂ densimeter, the density may be underestimated due to laser heating.

In this study, to prove that the size-dependence and mineral species-dependence of the density of fluid inclusions are not caused by the properties of the measurement technique itself, we investigated the size-dependence of the density of fluid inclusions with diameters ranging from less than 1 μ m to several tens of μ m in olivine, orthopyroxene, orthopyroxene, clinopyroxene, and Cr

spinel. To measure the density of fluids above 1.179 g/cm^3 and submicron fluid inclusions, the density was measured using a Raman CO_2 densitometer rather than microthermometry in this study.

Among the inclusions that escaped decrepitation, the density of inclusions in Cr-spinel was the highest, the density of inclusions in orthopyroxene and clinopyroxene was almost the same, and the density of inclusions in olivine was the lowest. This is consistent with previous studies. The size dependence of the density of inclusions in the olivine was also consistent with previous studies, with smaller inclusions having higher density. However, the size dependence of the density of inclusions in orthopyroxene, clinopyroxene, and Cr-spinel was lower for smaller inclusions, a trend that has never been reported before. The effect of laser heating on the results was evaluated by combining the laser power during the analysis, the temperature dependence of the Raman CO_2 densitometer, and the temperature increase per unit laser power of the inclusions. The results showed that laser heating had little effect on the results under the analysis conditions in this study. Therefore, the mineral species and size dependence of the inclusion densities found in this study are not due to systematic errors caused by the analytical method, but reflect the results of natural physicochemical processes.

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General Introduction

1. General context of the thesis

1.1 Significance of CO₂ density for fluid and melt inclusions in various geological environments

CO₂-bearing fluids are very common in many geological environments, widely distributed in metamorphic (Newton et al., 1980; Touret, 2001; Lamadrid et al., 2014a) and mantle-derived rocks (Roedder, 1965; Roedder, 1983; Andersen et al., 1984; Roedder, 1984; De Vivo et al., 1988; De Vivo et al., 1990; Hansteen et al., 1991; Frezzotti et al., 1992; Neumann et al., 1995; Hansteen et al., 1998; Andersen and Neumann, 2001; Yamamoto et al., 2004; Sapienza et al., 2005; Yamamoto et al., 2007; Hansteen and Klugel, 2008; Berkesi et al., 2012; Frezzotti et al., 2012a; Yamamoto et al., 2012), volcanic fumaroles (Giggenbach, 1996; Chiodini et al., 1998; Fischer, 2008; Mitchell et al., 2010), hydrothermal vent (Li et al., 2018; Li et al., 2020), sedimentary geological environment (Lammers et al., 2015) and many ore-forming systems (Roedder, 1984; Klein and Fuzikawa, 2010; Bodnar et al., 2014).

Since fluid and melt inclusions in minerals grown in the above geological environments are thought to capture and preserve past crustal and mantle CO₂ fluids, the density of CO₂ fluids in such inclusions has been used to estimate the CO₂ concentration and pressure in the surrounding environment at the time of trapping. Specific examples of how CO₂ density of inclusions has been used to interpret geoscientific phenomena are listed below.

[1]. Estimation of the amount of volatile in pre-eruptive magma.

Volcanic eruption is driven by the buoyancy of volatiles dissociated from magma. Although the volatile content of magma is an essential factor in the interpretation of eruptions, it is difficult to measure the volatile content of magma because volatiles exsolve and escape as magma rises and decompresses. The best-preserved information on pre-eruption magma is in melt inclusions, which are trapped in crystals growing deep in the magma plumbing system. Since the melt inclusion is isolated from the surrounding magma by the crystal host, the composition and volatile content of the magma can be preserved when the effects of re-equilibration are negligible. In melt inclusion, the shrinking bubble often accommodates more CO₂ than the glass because of the low solubility of CO₂ in the melt (Steele-macinnis et al., 2011; Moore et al., 2015; Wallace et al., 2015). The CO₂ density in the bubble phase is quantified using Raman spectroscopy, and previous estimates of the CO₂ density in shrinking bubbles using Raman CO₂ densimeters have been about 0.02-0.4 g/cm³, which corresponds to the single-phase gas to vapor-liquid equilibrium region at

room temperature (Esposito et al., 2011; Hartley et al., 2014; Moore et al., 2015; Aster et al., 2016; Hanyu et al., 2020; Mironov et al., 2020; Allison et al., 2021).

[2]. Tracking structure of magma plumbing system.

An understanding of the internal structure of active volcanoes is a major objective of igneous petrology and volcanology. To investigate the structure of the magma plumbing system, the density of CO₂ fluid inclusions in olivine phenocryst has been used (Zanon and Frezzotti, 2013; Levresse et al., 2016; Oglialoro et al., 2017). This is because fluid inclusions and mineral geothermobarometry can provide information on the depth of magma ponding and crystallization (Andersen and Neumann, 2001; Hansteen and Klugel, 2008). Fluid inclusions record pressures of fluid entrapment and changes in fluid density in response to magma pressure variations over short time scales (Peccerillo et al., 2006). They are therefore sensitive records of discrete magma storage regions. In this type of study, the density of CO₂ in fluid inclusions conserves a very wide range of densities, from single gas phase to single liquid phase at room temperature.

[3]. Estimating depth provenance of the rocks and the formation depth of the deposit.

The density (or molar volume) and composition of fluid inclusions define the isochoric P-T path and provides thus a major constraint to evaluate the pressure or depth of mineral and ore deposit formation (Roedder, 1965; Roedder, 1983; Andersen et al., 1984; De Vivo et al., 1988; De Vivo et al., 1990; Hansteen et al., 1991; Frezzotti et al., 1992; Schiano and Clocchiatti, 1994; Andersen et al., 1995; Andersen and Neumann, 2001; Sapienza et al., 2005; Peccerillo et al., 2006; Frezzotti and Peccerillo, 2007; Yamamoto et al., 2007; Bali et al., 2008; Chi et al., 2009; Klein and Fuzikawa, 2010; Yamamoto et al., 2012; Zanon and Frezzotti, 2013; Yamamoto et al., 2014; Levresse et al., 2016; Oglialoro et al., 2017; Zanon et al., 2020). Especially in the case of fluid inclusions in mantle xenoliths, fluid inclusions are formed under pressures of several GPa, and fluid inclusions become very dense. In fact, a superdense fluid inclusion with a density of 1.21 g/cm³ has been reported so far (Frezzotti et al., 1992; Frezzotti and Peccerillo, 2007).

From the above examples, a wide range of densities from the low-density (approx. 0.0 g/cm³) to the high-density region (approx. 1.2 g/cm³) have been the subject of various studies. Therefore, accurate and precise estimation of the density of CO₂ fluids is important. In the following, I introduce the methods used to estimate the density of CO₂ and their advantages and disadvantages.

1.2 Methods for estimating CO₂ density of inclusions

Currently, the primary method for estimating the pressure of a CO₂ fluid inclusion is

microthermometry, which is based on the measurement of the phase transition temperature (homogenization temperature of liquid-vapor CO₂) upon heating and the use of a known equation of state for CO₂ (Pitzer and Sterner, 1994; Span and Wagner, 1996). While this method is valid in some cases, it has some limitations:

- [1]. Inclusions must be sufficiently large to effectively observe phase transitions with optical microscopy (Rosso and Bodnar, 1995). For CO₂ inclusions with a diameter of less than 3 μm , it is difficult to measure CO₂ density by microthermometry (Kobayashi et al., 2012). Furthermore, even if the inclusion size is larger than 5 μm , it may be difficult to observe the phase transition temperature if the host mineral has a large absorption coefficient.
- [2]. If the density is higher than 1.179 g/cm³, homogenization occurs when the solid dissolves into a liquid at a temperature higher than the triple point. However, due to the large difference in refractive index between the host mineral and the low-density vapor, it is difficult to accurately measure the homogenization temperature because small amounts of CO₂ solids are hidden in optically dark regions (Hurai et al., 2015). Superdense CO₂ can be found in the crust and mantle at low temperatures, where the thermal gradient is lower than ~23 °C/km (Urban et al., 2006). Also, superdense CO₂ inclusions with $\rho > 1.2 \text{ g/cm}^3$ were described from upper-mantle xenoliths (Frezzotti et al., 1992; Frezzotti and Peccerillo, 2007). In addition, densities of up to 1.21 g/cm³ are recorded in amphibolite-facies migmatites of the Colorado Front Range, which are probably related to a secondary tectonic squeezing of the host quartz (van den Kerkhof and Olsen, 1990). Densities as high as 1.197 g/cm³ in hydrothermal sulfidic veins in low-grade volcanic-sedimentary rocks of Western Carpathians (Urban et al., 2006) are to the best of my knowledge probably the highest densities of tectonically unmodified CO₂ inclusions recorded so far in the Earth's crust. Therefore, microthermometry is not suitable for density measurement of such superdense CO₂ fluid.
- [3]. For densities in the range of 0.013 to 0.468 g/cm³, homogenization occurs by diminishing infinitesimal liquid phase in the range of -56.6 to 31.1°C. Therefore, it is necessary to measure the temperature at which the infinitesimal liquid phase that wets the inclusion walls evaporates. Due to the large refractive index difference between the host mineral and the low-density vapor, a small amount of CO₂ liquid is hidden in the optically dark region, making it difficult to measure the exact homogenization temperature. Therefore, microthermometry cannot be applied to density estimation of shrinkage bubble in melt inclusions because reported densities so far in melt inclusions are ranging from approx. 0.0 to 0.4 g/cm³.

In summary, the accuracy is reduced at low and high density and microthermometry can be applied only to the CO₂ inclusions whose density range from around 0.65 to 1.18 g/cm³ (Kobayashi et al., 2012).

Raman spectroscopy is used as an alternative or complementary technique to estimate CO₂ fluid density when estimating fluid density by microthermometry is difficult. The method is applicable to a wide density range of 0.001–1.24 g/cm³ and to small inclusions down to sub-micrometer size and to inclusions in colored minerals, where the homogenization temperature is difficult to measure, as long as Raman scattering photons with a sufficient number for quantitative analysis reach the detector.

2. Problems

The fluid density is estimated using the density-dependence of the wavenumber difference of the two large peaks ($\nu_{F,D}^+$ and $\nu_{F,D}^-$) of the CO₂ Raman spectrum. Raman-based CO₂ densimetry uses the relation between CO₂ fluid density (ρ) and Fermi diad splitting ($\Delta = \nu_{F,D}^+ - \nu_{F,D}^-$). Although Raman CO₂ densimeter is useful, some caution is necessary for application of this method to density measurements of natural fluid inclusions: 1) Effect of intermolecular interactions between CO₂ and trace molecules other than CO₂ on the spectral properties of CO₂ (Seitz et al., 1996; Chen et al., 2004; Wang et al., 2011; Yuan et al., 2017; Lamadrid et al., 2018; Le et al., 2019; Wang et al., 2019; Hagiwara et al., 2020; Le et al., 2020; Sublett et al., 2020b), 2) discrepancy in the Δ – ρ relations derived in earlier studies (Lamadrid et al., 2017; Hagiwara et al., 2020), and 3) apparent density reduction because of the local temperature rise caused by excitation lasers (Hagiwara et al., 2021).

Regarding the first problem, this method has been improved vigorously to quantify the fluid pressure in inclusions with various P – V – T – x properties. Its applicability is now expanding to include the CO₂±N₂±CH₄ (Seitz et al., 1996; Hacura, 1997; Wang et al., 2011; Lamadrid et al., 2018; Le et al., 2020; Sublett et al., 2020b) and CO₂–H₂O±NaCl systems (Chen et al., 2004; Wang et al., 2011; Yuan et al., 2017; Wang et al., 2019; Hagiwara et al., 2020). The second difficulty can be resolved by adding to the measured Δ a correction term δ , which can be found by optimizing the residual sum of squares between the density estimated by any Δ – ρ relation from the Δ values of several standard fluid inclusions and the known density to the minimum (Hagiwara et al., 2020). Alternatively, in the region where the Δ – ρ relation can be approximated linearly, it is also effective to derive an original Δ – ρ relation applicable to the Raman system to be used, using two standard fluid inclusions with known density (Lamadrid et al., 2017). For the third one, because $(\partial\Delta/\partial T)_\rho$ is

always negative, at least in the density range investigated by earlier studies (Wang et al., 2019; Sublett et al., 2020b), the density estimated from the measured Δ might be underestimated if the excitation laser causes unintended heating. Nevertheless, few examples exist to verify the conditions and the extent to which it affects the measurement accuracy.

Problems 1) and 2) above have been discussed in many papers, whereas for problem 3), it is not even known to what extent laser heating occurs. Therefore, if laser heating affects the density measurement of fluid inclusions, different data may be obtained from different laboratories, or even from the same laboratory on different analytical conditions, even when the same sample is measured. The following problems need to be solved to enable high quality density measurements that can be compared between laboratories:

1. To what extent are inclusions heated by the excitation laser when analyzing them using Raman spectroscopy?
2. What procedures and environments should be used for analysis to reduce the effects of laser heating to the greatest extent possible?
3. How can we accurately measure fluid density even in the presence of laser heating?

Although the effects of laser heating on sample damage and measurement results that can occur during Raman spectroscopy have been discussed in many review articles and books, there has been no comprehensive study of this issue for about 40 years since Raman spectroscopy was first used for inclusion research. Therefore, this problem is not limited to the specific case of density measurement of CO₂ by Raman spectroscopy, but will spill over to the general problem of quantitative analysis of inclusions by Raman spectroscopy.

3. Organization of the manuscript

In the introduction of this paper, (i) the geological implications of measuring the density of CO₂ fluid inclusions, (ii) methodological issues, and (iii) the purpose and approach of this paper are presented in succession, followed by a detailed discussion in the following three chapters:

In chapter 1, the heating effect of inclusions during Raman spectroscopic analysis is quantified by three-dimensional heat conduction simulation and two independent experiments. To evaluate the effect of laser heating, the laser heating coefficient (°C/mW), defined as the temperature rise per unit laser power, is introduced. Finite element simulations are used to investigate the effect of variations in all possible experimental, optical, heat transport, and geometrical parameters on the laser heating coefficient in inclusion studies. On the contrary, laser heating coefficient are measured using

two independent experiments: hot band thermometer and homogenization measurements. Then, by combining experimental and simulation results, I discuss the effects of the respective parameters on the laser heating of inclusions. Finally, I propose favorable analytical procedures under which results obtained from Raman spectroscopy are reliable even in the presence of laser heating. Parts of the content of this chapter was published on 5 January 2021 in the journal *Chemical Geology* (Hagiwara et al., 2021).

In Chapter 2, I investigate the extent to which laser heating of inclusions during Raman spectroscopy, as revealed in Chapter 1, leads to uncertainties in the actual quantitative analysis. In this chapter, I investigate the temperature dependence of Raman CO₂ densitometer using a high-pressure optical cell from 23–200 °C and 7.2–258.7 MPa. Then, using CO₂ fluid inclusions of various densities, I evaluate the specific effect of laser heating on the results in actual density measurements. The content of this chapter was accepted in the journal *Journal of Raman Spectroscopy* (Hagiwara et al., in press).

In Chapter 3, to prove that the size-dependence and mineral species-dependence of the density of fluid inclusions are not caused by the properties of the measurement technique itself, I investigated the size-dependence of the density of fluid inclusions with diameters ranging from less than 1 µm to several tens of µm in olivine, orthopyroxene, orthopyroxene, clinopyroxene, and Cr spinel. In this chapter, I show that the observed dependence is not caused by laser heating, based on the insights obtained in Chapters 1 and 2.

The manuscript will conclude with a general conclusion highlighting all my findings and prospects for future developments that may potentially be of interest to the scientific community.

Chapter1: Effect of experimental, optical, and geometrical parameters on laser heating of inclusions during Raman spectroscopic analysis

1. Introduction

Raman spectroscopy is now well established as a versatile tool for inclusion research because of its non-invasive analysis and high spatial resolution. This method has been applied to various fields of inclusion studies: ascertaining the depth provenance of rocks from mineral inclusions (Kohn, 2014), estimation of peak metamorphic temperatures from graphite inclusions (Beyssac et al., 2002), determination of the pre-eruptive volatile contents of magmas from melt inclusions (Moore et al., 2015), and characterization of paleo crust-mantle fluid activities from fluid inclusions (Frezzotti et al., 2012b). To extract the physicochemical properties of unknown inclusions from the measured Raman spectra, experimental calibrations related to spectral features to the P – V – T – X properties of fluids or the strains and crystal orientations of minerals have been the subject of many studies (e.g., Burke, 2001; Angel et al., 2019). Furthermore, the combined technique of microthermometry and Raman spectroscopy enables accurate estimation of the temperatures of phase transition in situ, even for phases that are difficult to assess under optical observation (e.g., Bakker, 2004). Typically, to obtain Raman spectra of an inclusion having a sufficient signal-to-noise ratio for quantitative analysis, laser power of tens to hundreds of milliwatts is necessary, thereby necessitating focal intensities as high as several gigawatts per square centimeter. Even for analysis of transparent geomaterials, such high excitation energy can lead to non-negligible temperature increments at the focal position because of light absorption by host minerals or inclusions themselves. Such undesired heating at the focus will change Raman spectral features and might engender misinterpretation of the data. However, this important experimental parameter, temperature, has been difficult to control and estimate during Raman spectroscopic analysis because local temperatures behave intricately depending on the sample geometry, experimental conditions, and sample optical and heat transport properties. To interpret the inclusion data obtained by Raman spectroscopy correctly, one must ascertain the temperature of inclusion under the analysis and clarify how the temperature is governed as functions of experimental, geometrical, and optical parameters.

Although the thermal damage caused by the excitation laser to samples has been a concern especially in the field of bioengineering (e.g., Català et al., 2017), no comprehensive work assessing laser heating effects of small objects hosted in a solid phase, i.e., inclusions, during Raman spectroscopic analysis has been reported to date. Fall et al. (2011) observed the phase transition of

CO₂ fluid after laser irradiation. In their experiments, the CO₂-bearing inclusions, for which homogenization temperatures are slightly higher than the ambient temperature, are heated by an excitation laser, being not homogenized during the experiment. Therefore, the effect of laser heating might be negligible (less than <1 °C), at least under their experimental conditions and when using minerals with very small visible light absorption coefficients, such as quartz. However, the absolute value of the temperature rises at a certain laser power (laser heating coefficient (B); °C/mW) has persisted as an open problem for inclusion in representative rock-forming minerals, including quartz.

In the field of Earth science, laser-heating effects on the sample are evaluated especially with respect to Raman spectroscopy of a carbonaceous material (RSCM) thermometer that is used widely for estimating peak metamorphic temperatures. Kagi et al. (1994) reported that an appreciable local temperature increase occurs because of absorption of the incident laser by graphite. According to data reported by Kagi et al. (1994), B is approx. 1×10^2 °C/mW. In addition, Umeda and Enami (2014) reported that laser power higher than 2 mW would enhance the graphitization of CM and would provide apparently high peak metamorphic temperature by the RSCM thermometer. Similar warming effects by transmitted light have been reported for near-infrared microthermometry for fluid inclusions in opaque to translucent minerals (e.g., Casanova et al., 2018). Therefore, depending on the experimental, geometrical, and optical parameters, the inclusions are heated by the laser during Raman spectroscopic analysis. Their local heating alters the Raman spectral properties. Nevertheless, little is known about which parameters strongly affect laser heating.

To ascertain a correct physical picture of laser heating in inclusion, I perform heat transport simulations of an inclusion hosted by a solid phase (mineral) using finite element method, taking special care of the effects of spherical aberration at the air-sample boundary and the entire three-dimensional spatial profile of the focused beam. Based on the model, the effects of various parameters were evaluated. I also report the experimentally determined value of B of CO₂-rich fluid inclusions hosted by representative mantle minerals and quartz. Actually, B was measured using two independent experiments: hot band thermometer and homogenization measurements. Finally, by combining experimental and simulation results, I discuss the effects of the respective parameters on the laser heating of inclusions. Goals of this paper are to ascertain the most influential parameters on the laser heating of inclusions, and to propose favorable analytical procedures under which results obtained from Raman spectroscopy are reliable.

2. Literature review

Other research fields for which B has already been determined provide some examples. A field showing particular progress is optical tweezers for microscopic particle manipulation (e.g., Liu et al., 1995). Earlier studies measured temperatures surrounding optically trapped microspheres in water or glycerol during near infrared irradiation. Reportedly, temperature increases are 0.008–0.099 °C/mW. In most cases, determination of local temperature in an optical trap is based on measurement of the viscosity of the liquid (e.g., water) surrounding an optically trapped bead (e.g., silica) rather than a bead itself. By contrast, my target is a fluid inclusion (liquid CO₂) itself, located at the focal point of the laser, which is surrounded by a solid phase (host mineral).

According to earlier studies, one parameter that strongly influences laser heating is the absorption coefficient of the host phase, not of the trapped particle (Liu et al., 1995; Celliers and Conia, 2000; Peterman et al., 2003; Mao et al., 2005; Català et al., 2017). Because the absorption coefficient depends on the wavelength, it also depends on the laser wavelength (Haro-González et al., 2013). Regarding the bead size, two opposing results have been reported: Peterman et al. (2003) asserted that size has no effect on B . Also, Català et al. (2017) reported that larger particles suppress laser heating. The distance between the bead and the boundary of solvent and surrounding material, i.e. glass, also affects B . In fact, B becomes small only when the bead is close to the interface with the glass (Peterman et al., 2003; Català et al., 2017). Based on the model proposed by Mao et al. (2005), B is expected to show logarithmic growth with increasing sample thickness. In addition, B is correlated linearly with the reciprocal of the thermal conductivity of the liquid (Celliers and Conia, 2000; Peterman et al., 2003; Mao et al., 2005; Català et al., 2017). The specific B and measurement methods used for earlier studies are presented in Table S2 of the report by Català et al. (2017).

3. Model: Three-dimensional heat transport simulation using finite element method

To clarify the temperature distribution within and around an inclusion when illuminated by excitation laser, I performed heat-transfer simulation by finite element method using a software package: COMSOL Multiphysics. Fig. 1-1 depicts a laser beam transmitted through the objective lens towards the inclusion. I assumed symmetric disc shape for the host mineral. The disc has H_h thickness and R_h radius. A spherical inclusion with radius of r_{inc} exists at z_{inc} below the top surface of the disc. The actual focal position (= inclusion depth) is given as $z_{inc} = (n_h/n_a)z_1$, where z_1 is the nominal focal position below the sample surface and where n_a and n_h respectively denote the refractive indices of the air and host mineral.

Temperature is in general terms governed by the heat equation

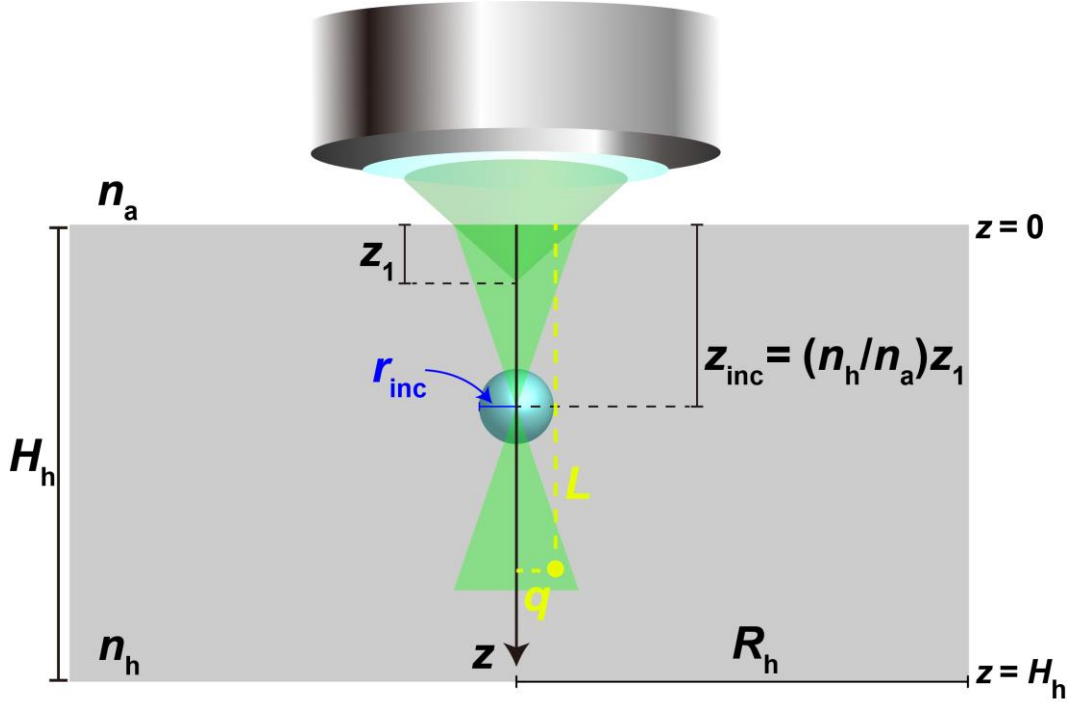


Figure1-1 Schematic of the simulation situation considered in the model. Refractive indices of the host mineral and air are presented respectively as n_h and n_a . The surface (i.e., air–host mineral boundary) of the host mineral is defined as the $z = 0$ plane. The focus position of a transmitted beam shifts from an intended position at $z = z_1$ to $z = (n_h/n_a)z_1$. A blue sphere represents an inclusion with radius of r_{inc} and depth of z_{inc} . q is the radial distance from the optical axis of an illuminated point and L denotes the depth of an illuminated point. The host mineral shape is assumed to be a disc with radius R_h and height H_h .

$$\nabla^2 T = \frac{1}{k_h} \frac{\partial T}{\partial t} - \frac{\alpha_h I_{ill}}{K_h}, \quad (1-1)$$

where k_h (m^2/s) stands for the thermal diffusivity, K_h (W/mK) expresses the thermal conductivity, and α_h denotes the absorption coefficient of host mineral ($1/m$). Also, I_{ill} (W/m^2) represents the spatial distribution of the focused intensity inside the sample as (e.g., Maruyama and Kanematsu, 2011)

$$I_{ill}(q, L, z_1) = I_0 \left\{ \frac{w_0}{w(L, z_1)} \right\}^2 \exp \left\{ -\frac{2q^2}{w^2(L, z_1)} \right\}, \quad (1-2)$$

where q (m) represents the radial distance from the optical axis of an illuminated point, L (m) denotes the depth of an illuminated point, and w_0 (m) corresponds to the waist-radius of the laser-beam, where the laser-beam diameter converges to a minimum. The value of w_0 was estimated directly from the

Raman instruments used for the measurements. The bitmap image of the laser spot reflected from the silicon wafer surface is used. The estimated w_0 was 1.46 μm for LU Plan $\times 50$ (used at Hokkaido University) and 1.0 μm for TU Plan $\times 50$ (used at Japan Agency for Marine–Earth Science and Technology (JAMSTEC)). Detailed procedures for estimating w_0 are presented in Supplementary information S1-3. Also, I_0 (W/m^2) and $w(L, z_1)$ respectively represent the laser intensity at the center of the beam waist and the beam-waist radius at the axial position, given as

$$I_0 = \frac{2P_{\text{ill}}}{\pi w_0^2}, \quad (1-3)$$

$$w(L, z_1) = w_0 \sqrt{1 + \left(\frac{L - (n_h/n_a)z_1}{n_h z_0} \right)^2}, \quad (1-4)$$

where P_{ill} represents the laser power at the sample surface (W) and $z_0 = \pi w_0^2/\lambda$ (m) is the Rayleigh range. Also, λ denotes the excitation laser wavelength.

In an earlier model, the boundary condition which determines heat flux at the interface was the Dirichlet condition (i.e., $T = \text{const.}$ at boundaries), but in this study, in addition to the Dirichlet condition, I also performed simulations under convective heat flux boundary condition that is defined

Table1-1 Optical and thermal transfer properties of host mineral.

	α_h at 532 nm ^{a, b}	K_h at ~ 300 K ^{c, d}	k_h at ~ 300 K ^{c, d}	n_h ^e
	cm^{-1}	W/mK	mm^2/s	-
olivine	1.14	5.50	2.05	1.65
orthopyroxene	9.60	5.85	2.17	1.66
clinopyroxene	3.07	6.21	2.40	1.65
spinel	20.30	5.50	1.79	1.72
quartz	0.02	9.00	5.19	1.55

^a The compositions of each mineral are $\text{Mg}_{1.880}\text{Fe}_{0.106}\text{Ca}_{0.002}\text{Mn}_{0.006}\text{Si}_{1.002}\text{O}_4$, $(\text{Mg}_{1.63}\text{Fe}_{0.27}\text{Ca}_{0.04}\text{Al}_{0.02})\text{Si}_{1.97}\text{Al}_{0.03}\text{O}_6$, $(\text{Ca}_{0.948}, \text{Fe}_{0.056}, \text{Na}_{0.040})_{1.044}(\text{Ti}_{0.003}, \text{Mg}_{0.941}, \text{Cr}_{0.024}, \text{Al}_{0.004})_{0.972}\text{Si}_{1.993}\text{O}_6$, $\text{Mg}_{1.01}\text{Fe}^{3+}_{0.01}\text{Al}_{1.99}\text{Cr}_{<0.01}\text{O}_4$, and quartz glass, respectively.

^b α_h are compiled from Taran and Matsyuk (2013) for olivine, Taran and Langer (2001) for orthopyroxene, Taran et al. (2011) for clinopyroxene, Taran et al. (2014) for spinel, and Khashan and Nassif (2001) for quartz.

^c The compositions of each mineral are Fo93, En89, Diopside, $\text{Mg}_{0.5}\text{Fe}_{0.5}\text{AlO}_4$, and SiO_2 , respectively.

^d K_h and k_h are compiled from Osako et al. (2004) for olivine, Hofmeister (2012) for orthopyroxene, Wang et al. (2014) for clinopyroxene, Hofmeister (2001) for spinel, and Branlund and Hofmeister (2007) for quartz.

by $h(T_{\text{ext}} - T)$ at the glass-sample and air-sample interfaces. At the air-sample boundary, the convective heat transfer coefficient ($h_{\text{a/s}}$) was fixed to be 5 W/m²K at $z = 0$ plane and $q = R_{\text{h}}$ curved surface, assuming heat transfer by free convection (Whitelaw, 1997). In case of the boundary between the sample and the plate on which the sample is placed ($z = H_{\text{h}}$), it is difficult to settle the style of heat transport because it is affected by many parameters such as surface conditions, optical and heat transport properties of the plate, and the temperature distribution below the sample. Therefore, I considered the heat transport coefficient at the glass-sample interface ($h_{\text{g/s}}$) as a variable. Both the ambient (T_{ext}) and initial sample temperature (T_{sample}) are equal. Of the parameters throughout Eqs. 1-1 to 1-4, α_{h} , k_{h} , K_{h} , and n_{h} are optical and physical properties unique to the host mineral and are shown in Table 1. The influence of reflection and crystal orientation dependence of α_{h} , k_{h} , K_{h} , and n_{h} on the laser heating effect was not considered here.

No report of the relevant literature describes a study of the absorption coefficient of CO₂ at the specific conditions of my simulation, i.e. 532 nm and approx. 7 MPa. Thompson et al. (1963) estimated that absorption coefficient of CO₂ at 198 nm is 10⁻⁵ cm⁻¹. According to Hansen (1997), absorption coefficient of solid CO₂ at 532 nm is about 10⁻⁴ cm⁻¹. In both studies, the absorption coefficient decreases as the wavelength increases from approx. 180 nm. The absorption coefficient of CO₂ at 532 nm is so small compared to the host mineral (for the smallest case, e.g., 0.02 cm⁻¹ for quartz) that it was regarded as negligible in the present model. Therefore, I assumed it to be 0 (see section 7.1 for details). Thermal diffusivity of CO₂ is 0.02 mm²/s at the conditions of 0.7 g/cm³ and 25 °C based on the NIST Chemistry WebBook. The simulated inclusion temperature and B are an average over an inclusion domain in 3D models.

All the parameters used for this study are presented in Table 2. Hereinafter, I use an abbreviation for each parameter. As described in section 2, earlier studies have experimentally or theoretically examined the effects of λ , w_0 , α_{inc} , z_{inc} , r_{inc} , K_{inc} , K_{h} , α_{h} , H_{h} , and R_{h} on B . In addition to these parameters, I investigated the effects of n_{h} , which can change the temperature distribution around the inclusion, k_{h} , which affects the time to reach the steady state, and $h_{\text{a/s}}$ and $h_{\text{g/s}}$, which determine the heat flow rate at the boundary, on B .

Table1-2 List of parameters, their abbreviations and units.

Symbol	Parameter and unit
B	Laser heating coefficient [$^{\circ}\text{C}/\text{mW}$]
B_{Raman}	Laser heating coefficient determined by hot band thermometer [$^{\circ}\text{C}/\text{mW}$]
$h_{\text{a/s}}$	Heat transfer coefficient at air–sample boundary [$\text{W}/\text{m}^2\text{K}$]
$h_{\text{g/s}}$	Heat transfer coefficient at glass–sample boundary [$\text{W}/\text{m}^2\text{K}$]
H_{h}	Host mineral thickness [μm]
$\left(\frac{I_{\text{HB}}^+ + I_{\text{HB}}}{I_{\text{FD}}^+ + I_{\text{FD}}}\right)^{\text{calc}}$	Hot bands to the Fermi diad intensity ratio calculated by substituting density and temperature into Eq. 1-5 [-]
$\left(\frac{I_{\text{HB}}^+ + I_{\text{HB}}}{I_{\text{FD}}^+ + I_{\text{FD}}}\right)^{\text{calib Eq. S1}}$	Calibrated hot bands to the Fermi diad intensity ratio defined as $\left(\frac{I_{\text{HB}}^+ + I_{\text{HB}}}{I_{\text{FD}}^+ + I_{\text{FD}}}\right)^{\text{sens. calib, ave}} + \delta_{\text{HB/FD}}$ [-]
$\left(\frac{I_{\text{HB}}^+ + I_{\text{HB}}}{I_{\text{FD}}^+ + I_{\text{FD}}}\right)^{\text{sens. calib, ave}}$	Average of sensitivity calibrated hot bands to the Fermi diad intensity ratio at each measurement condition [-]
I_0	Laser intensity at the center of the beam-waist [W/m^2]
I_{ill}	Spatial distribution of the focused laser intensity [W/m^2]
K_{h}	Thermal conductivity of host mineral [W/mK]
k_{h}	Thermal diffusivity of host mineral [m^2/s]
K_{inc}	Thermal conductivity of inclusion [W/mK]
k_{inc}	Thermal diffusivity of inclusion [m^2/s]
L	Depth of an illuminated point [m]
n_{a}	Refractive index of air [-]
n_{h}	Refractive index of host mineral [-]
q	Radial distance from the optical axis of an illuminated point [m]
R_{h}	Equivalent circle radius of projected area of host mineral [μm]
r_{inc}	Equivalent circle radius of projected area of inclusion [μm]
T_{sample}	Initial temperature of the sample [$^{\circ}\text{C}$]
$t_{N-2, 31.7\%}$	Two-tailed t -distribution at $N-2$ degrees of freedom (confidence level is 68.3%) [-]
$t_{0.9}$	Time required for temperature reaches 90% of its steady-state value [s]
T_{h}	Homogenization temperature [$^{\circ}\text{C}$]
w_0	Waist-radius [μm]
$w(L, z_1)$	Beam waist radius at the axial position defined by Eq. 1-4 [μm]
z_0	Rayleigh range [μm]
z_1	Nominal focal position [μm]
z_{inc}	Inclusion depth from sample surface [μm]
α_{h}	Absorption coefficient of host mineral [cm^{-1}]
α_{inc}	Absorption coefficient of inclusion [cm^{-1}]
$\delta_{\text{HB/FD}}$	Correction term for hot bands to the Fermi diad intensity ratio [-]
δ_{Δ}	Correction term for Fermi diad splits [cm^{-1}]
$\Delta^{\text{Ne calib}}$	Distance of Fermi diad splits calibrated by using distances between the Ne lines [cm^{-1}]
$\Delta^{\text{Ne \& Qtz calib}}$	Distance of Fermi diad splits calibrated by using both Ne lines and a standard fluid inclusion in quartz [cm^{-1}]
Δ	Distance of Fermi diad splits [cm^{-1}]
λ	Wavelength of excitation laser [nm]
ρ	Density of a fluid inclusion [g/cm^3]
ρ_{Raman}	Density estimated from distance of Fermi diad splits [g/cm^3]
ρ_{Th}	Density estimated from homogenization temperature [g/cm^3]
$\sigma_{B_{\text{Raman}}}$	Standard errors of laser heating coefficient determined by hot band thermometer [$^{\circ}\text{C}/\text{mW}$]
$\sigma_{P_{\text{ill}}}$	Uncertainty of the laser power defined as $\sigma_{P_{\text{ill}}} = 0.03 \times P_{\text{ill}}$ [mW]

4. Samples

I selected a total of 19 CO₂-rich fluid inclusions hosted in mineral separates of five species; olivine, orthopyroxene, clinopyroxene, spinel, and colorless quartz (Fig. 1-2). Fluid inclusions in olivine, orthopyroxene, clinopyroxene, and spinel are derived from a mantle xenolith designated as “En2A” from Ennokentiev, Sikhote-Alin, Far Eastern Russia. Petrological descriptions were presented by Yamamoto et al. (2012). Quartz-hosted fluid inclusions are derived from pegmatites of Kadugannawa Complex from Owala-Kaikawala area, Matale, Sri Lanka. Seven mineral grains were selected and made into doubly polished chips. The fluid inclusion compositions are investigated using Raman spectroscopic analysis; volatile species other than CO₂ and H₂O are not detected. Although no H₂O liquid phase was visible under microscopic observation, trace amounts of H₂O were confirmed in Raman spectra from some inclusions. Therefore, the composition of the fluid inclusions used for this study is approximately binary CO₂–H₂O. The CO₂ homogenization temperatures are measured using a heating–cooling stage (THMS600; Linkam Scientific Instruments Ltd.) at Hokkaido University. The instrument was calibrated using the melting points of H₂O (0.0 °C) in synthetic pure H₂O fluid inclusions. Homogenization were recorded at the heating rate of 0.1 °C/min. Fluid densities are calculated as described by Span and Wagner (1996), as shown

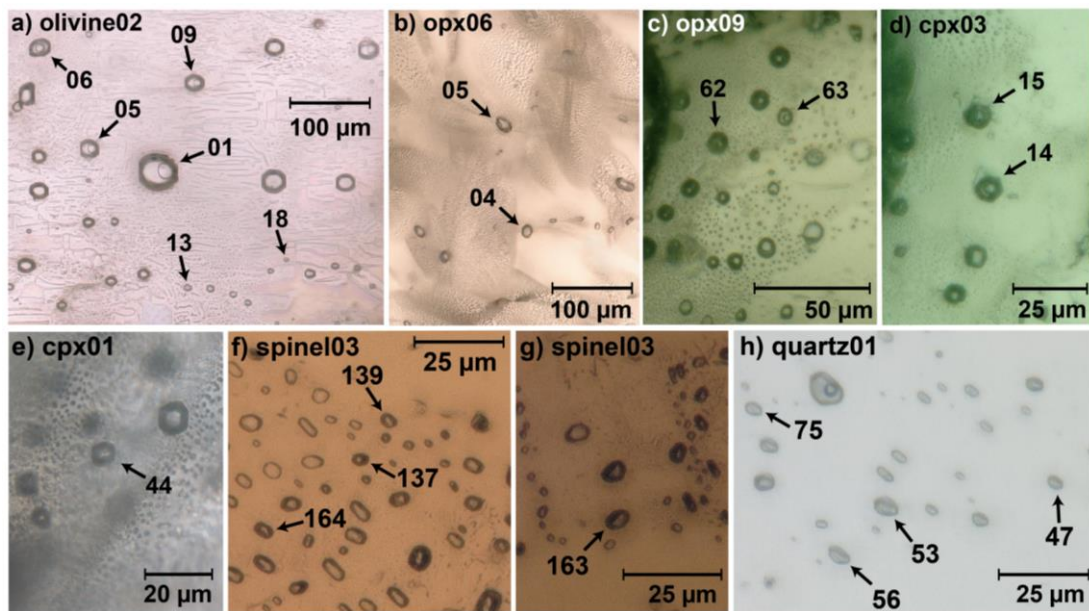


Figure1-2 Photomicrographs of studied fluid inclusions hosted in olivine (a), orthopyroxene (b and c), clinopyroxene (d and e), spinel (f and g), and quartz (h) in transmitted light. A total of 21 fluid inclusions are selected for determination of laser heating coefficient. To increase the depth of field in their photomicrographs, multi-focus (“stacking”) techniques were applied except for Fig. 1-2e.

in Table 3.

The respective sizes and depths of the fluid inclusions were measured using a 2000× objective (VH-ZST; Keyence Co.) with a digital microscope (VHX-5000; Keyence Co.). The projected area of fluid inclusions was measured automatically by identifying the outline of a fluid inclusion using the brightness contrast. The inclusion radius (r_{inc}) was defined by the equivalent

Table1-3 Microthermometric data and geometric properties of fluid inclusions and host minerals.

	T_h^a °C	ρ_{Th} g/cm ³	r_{inc} μm	z_{inc} μm	H_h μm	R_h μm
En2A oli02 fi01	26.4	0.687	22.2	75.4	497	1548
En2A oli02 fi05	26.7	0.682	11.2	47.5	497	1548
En2A oli02 fi06	26.2	0.691	11.5	59.9	497	1548
En2A oli02 fi09	25.6	0.701	10.9	96.4	497	1548
En2A oli02 fi13	25.8	0.698	4.5	42.9	497	1548
En2A opx06 fi04	26.2	0.691	7.4	73.7	461	1191
En2A opx06 fi05	25.6	0.701	9.3	50.5	461	1191
En2A opx09 fi62	26.4	0.687	4.8	12.5	270	1084
En2A opx09 fi63	26.4	0.687	3.7	7.0	270	1084
En2A cpx03 fi14	27	0.676	4.6	2.6	252	841
En2A cpx03 fi15	26.9	0.678	4.5	3.3	252	841
En2A cpx01 fi44	25.2	0.707	3.4	25.5	189	807
En2A sp03 fi137	26.1	0.693	2.0	8.6	42	534
En2A sp03 fi139	25.6	0.701	2.0	2.6	42	534
En2A sp03 fi163	26	0.694	2.8	5.7	42	534
Quartz 01 fi 47	19.6	0.778	2.0	8.2	743	5645
Quartz 01 fi 53	18.8	0.786	2.9	14.6	743	5645
Quartz 01 fi 56	18.8	0.786	2.6	4.5	743	5645
Quartz 01 fi 75	18.7	0.787	2.0	44.8	743	5645

^a Temperature of partial homogenization of the carbonic phase to liquid.

circle radius of the obtained projected area. I also measured the equivalent circle radius of projected area of host mineral (R_h). I calculated the depth of the inclusion from the distance between the mechanical position for focus at the top of the host mineral and at a position where I obtained a sharp image of a fluid inclusion. The actual depth (z_{inc}) is calculated approximately by the simple expression of $z_{inc} = \text{refractive index of host mineral } (n_h) \times \text{measured depth}$. As shown in Table 1, the

values of n_h of olivine, orthopyroxene, clinopyroxene, spinel, and quartz are, respectively, 1.65, 1.66, 1.65, 1.72, and 1.55 (Lucey, 1998; Palik, 1998; Ghosh, 1999). In addition to z_{inc} , the host mineral thickness (H_h), which is defined by the distance between the mechanical position for focus at the surface of the host mineral and top of the slide glass, is shown in Table 3.

5. Experimental procedures

Actual measurements of laser heating coefficient were taken for inclusions as described above using two independent experiments: in-situ measurement of the temperature using Raman spectra, and based on phase transition observations.

5.1. Laser heating coefficient estimation by Raman based thermometer

5.1.1. Overview of the hot band to Fermi diad intensity ratio thermometer

The CO₂ fluid temperature can be estimated using Raman spectra: a so-called hot band thermometer was developed using a high pressure optical cell (HPOC) (Rosso and Bodnar, 1995; Arakawa et al., 2008; Hagiwara et al., 2018). The experimental calibrations of earlier studies do not cover the P – T conditions of my interest. Therefore, I expanded the applicable P – T range using newly measured Raman spectra of CO₂ from 23 to 200 °C in approximately 20 °C increments under 10 temperature conditions (Fig. S1-1). Specific temperature, pressure, and density conditions are presented in Table S1-1. Details of the experimental apparatuses and procedures are provided in online Supplementary materials S1.

Fig. 1-3 shows the hot band to Fermi diad intensity ratio ($[I_{H.B.}^+ + I_{H.B.}^-] / [I_{F.D.}^+ + I_{F.D.}^-]$) versus the density of CO₂ fluid at temperatures of 23–200 °C. I proposed a new equation relating $[I_{H.B.}^+ + I_{H.B.}^-] / [I_{F.D.}^+ + I_{F.D.}^-]$, temperature (T ; °C), and density (ρ ; g/cm³) as

$$T = a + b\rho + c\rho^2 + d\rho^3 + e \left(\frac{I_{H.B.}^+ + I_{H.B.}^-}{I_{F.D.}^+ + I_{F.D.}^-} \right) + f \left(\frac{I_{H.B.}^+ + I_{H.B.}^-}{I_{F.D.}^+ + I_{F.D.}^-} \right)^2 + g \left(\frac{I_{H.B.}^+ + I_{H.B.}^-}{I_{F.D.}^+ + I_{F.D.}^-} \right)^3 + h\rho \left(\frac{I_{H.B.}^+ + I_{H.B.}^-}{I_{F.D.}^+ + I_{F.D.}^-} \right), \quad (1-5)$$

where a through h represent fitting parameters ($a = -472.925$, $b = 1074.306$, $c = -985.102$, $d = 325.905$, $e = 3855.1$, $f = -17374.6$, $g = 44140.7$, and $h = -385.88$). Also, Eq. 1-5 is useful at $0.6 < \rho < 1.2$ g/cm³ and $23 < T < 200$ °C. The maximum absolute value of residual errors for all 131 measurements was 9.5 °C. The average of the absolute value of residual errors was 2.0 °C. Applicability of this thermometer for natural fluid inclusions was confirmed from natural fluid inclusions in quartz, which are shown as square (temperature increasing cycle) and triangle (decreasing cycle) symbols in Fig. 1-3. This test experiments were performed with a laser power of 7.7 mW because my experiments show that the hot band to Fermi diad intensity ratio of a CO₂ inclusion in quartz does not change for

laser powers up to at least 15 mW (Fig. S1-2 and Table S1-2).

5.1.2. Raman setup

To determine B , Raman spectra of fluid inclusions were measured using P_{ill} ranging from 4.2 to 14.2 mW along both laser increasing and decreasing cycles. The values of P_{ill} during the experiments were measured using a laser power meter (PD300-ROHS; Ophir Optronics Ltd.). The uncertainty of the measured P_{ill} is $\pm 3\%$. During the measurement, T_{sample} was controlled by the room temperature, which was controlled by an air conditioner. The sample was placed on the Linkam stage. The actual T_{sample} was monitored by the thermocouple of the Linkam stage. In this study, measurements are performed without a silver lid so that the sample and the ambient air can quickly reach thermal equilibrium. Measurements were performed five times at each P_{ill} . Measured $[I_{\text{H.B.}}^+ + I_{\text{H.B.}}^-]/[I_{\text{F.D.}}^+ + I_{\text{F.D.}}^-]$ were converted to the temperature using Eq. 1-5. Table S1-2 presents the T_{sample} and average fluid temperatures of five measurements and their standard deviation (1σ) at each P_{ill} . The duration of every

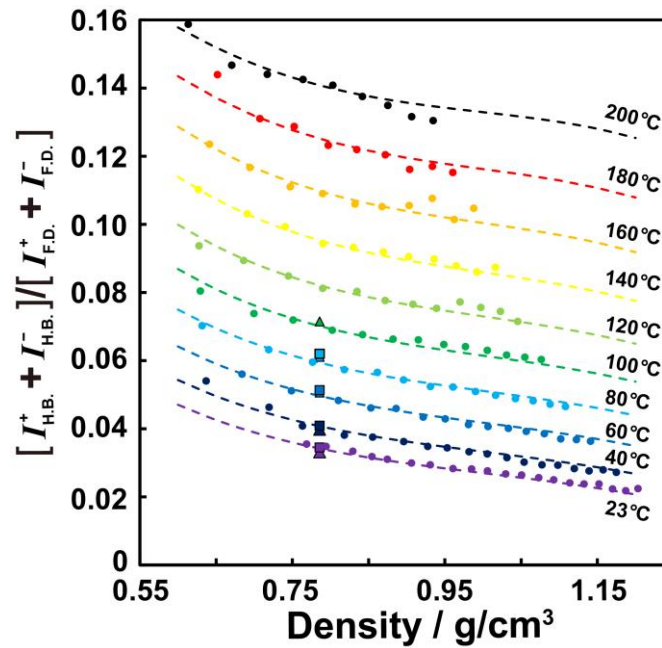


Figure1-3 Effects of density and temperature on the hot band to the Fermi diad intensity ratio of CO_2 . Circles represent data obtained from high-pressure optical cell experiments and data are presented in Table S1-1. The dashed lines represent the best fit to data. The calibrated hot band to Fermi diad intensity ratio (i.e., $[I_{\text{H.B.}}^+ + I_{\text{H.B.}}^-]/[I_{\text{F.D.}}^+ + I_{\text{F.D.}}^-]^{\text{sens. calib}} + \delta_{\text{HB/FD}}$) and density obtained from a natural fluid inclusion at 26, 40, 60, 80, and 100 °C are plotted as square and triangle symbols, which are measured respectively along the temperature increasing and decreasing cycle (Table S1-4). $\delta_{\text{HB/FD}}$ was calculated as -0.0075 (Table S1-4).

Raman analysis is 300 or 600 s.

Raman spectra of the CO₂ fluid were obtained using a micro-Raman spectrum analysis system set up at the Hokkaido University Museum, with 1,200 grooves/mm grating. Raman spectra were acquired using diode-pumped solid-state laser (532 nm, Gem 532; Laser Quantum) excitation, a spectrometer with 75 cm focal length (Acton SP-2750; Princeton Instruments, Inc.), and a CCD camera (1650 × 200 pixels, 16-μm width, iVac; Andor Technology). A Nikon microscope (ECLIPSE E600-POL) with a ×50 (N.A. = 0.8, LU Plan; Nikon Corp.) objective was used to focus on the samples.

Spectra were collected in a single window between 656 and 1,481 cm⁻¹. In the case of fluid inclusions in quartz, which requires higher P_{ill} for accurate determination of B , almost identical measurements were performed using a micro-Raman spectrum analysis system (RAMANtouch VIS-HP-MAST; Nanophoton) at JAMSTEC. The laser output was 1500–4000 mW at the source. Using neutral-density filters with variable transmission, I adjusted P_{ill} at the sample surface from 5 to 351 mW. Raman spectra were acquired using semiconductor laser (532 nm) excitation, a 1,200 grooves/mm grating, and a CCD camera (1340 × 400 pixels). In this experiment, the sample was placed on a slide glass, not on a Linkam stage. Therefore, T_{sample} is not measured directly. The ambient temperature during the measurement was monitored using a thermometer (TR-73U; T&D Corp.) placed next to a microscope and was almost constant at the range of 20.2–22.1 °C. A Nikon objective (N.A. = 0.8, TU Plan ×50) was used to focus on the samples. The duration of every Raman analysis is 30 to 300 s. Spectra were collected in a single window between 559 and 1,780 cm⁻¹. Sensitivity calibration, spectra fitting, and data correction procedures are described in Supplementary material S1 and Tables S1-3 and S1-4. The average of the sensitivity calibrated hot band to Fermi diad intensity ratio at each P_{ill} ($[I_{H.B.}^+ + I_{H.B.}] / [I_{F.D.}^+ + I_{F.D.}]^{\text{sens. calib, avg}}$) is presented in Table S1-2.

5.1.3. Specific procedures for laser heating coefficient determination and error analysis

Earlier reports have described linear correlation between sample temperature and P_{ill} (Kagi et al., 1994; Liu et al., 1995; Haro-González et al., 2013; Català et al., 2017). Therefore, I can also expect the linear increase of inclusion temperature with P_{ill} . Figure 1-4 presents relations between P_{ill} and the inclusion temperature obtained from simulations. Actual data obtained from spinel03 fi139 are also presented as an example. The open symbols show the simulated relation between P_{ill} and inclusion temperature calculated using finite element method. Parameters used for the simulation are almost identical to the actual experimental conditions and listed in the caption of Fig. 1-4. The boundary conditions are calculated with varying $h_{\text{g/s}}$ from 5 to 50 W/m²K. As all measured results show the linear relation between inclusion temperature and P_{ill} (Fig. 1-4 for an example), I define B as the slope

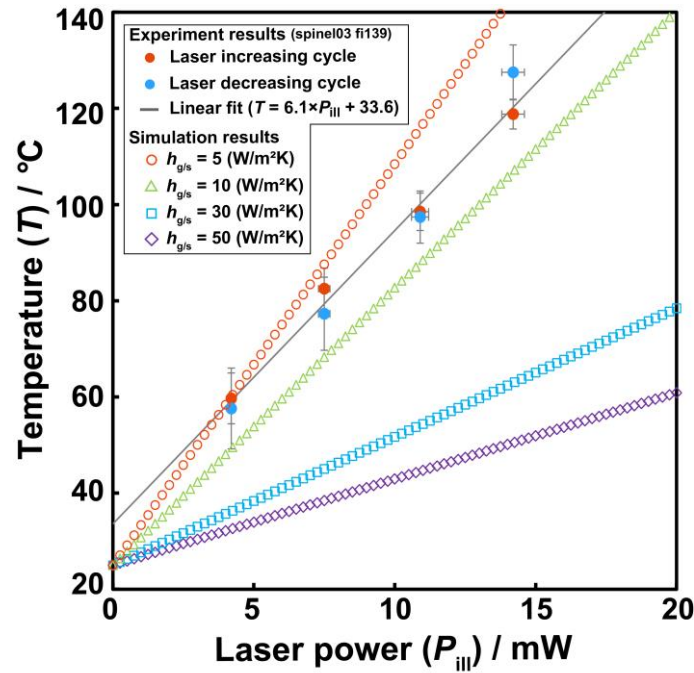


Figure1-4 Measured and simulated inclusion temperature as a function of laser power. Red and blue filled circles represent the data obtained from the fluid inclusion in spinel (spinel03 fi139) and measured respectively along the laser increasing and decreasing cycles. Error bars for temperature show the standard deviation ($n = 5$). Those for laser power are 3%. These data are presented in Table S1-3. A solid line shows the linear fit (York method) to eight data points. The laser heating coefficient determined from the linear fit is 6.1 ± 0.6 °C/mW. Open symbols show the simulated relations between inclusion temperature and laser power. Parameters used for simulation are the following: $T_{\text{sample}} = 25$ °C, $\lambda = 532$ nm, $P_{\text{ill}} = 0\text{--}20$ mW, $w_0 = 1.46$ μm , $\alpha_{\text{inc}} = 0$ m⁻¹, $z_{\text{inc}} = 2.6$ μm , $r_{\text{inc}} = 2.0$ μm , $K_{\text{inc}} = 0.08$ W/mK, $k_{\text{inc}} = 0.02$ mm²/s, $H_{\text{h}} = 42$ μm , $R_{\text{h}} = 0.534$ mm, $K_{\text{h}} = 5.5$ W/mK, $k_{\text{h}} = 1.79$ mm²/s, $\alpha_{\text{h}} = 2030$ m⁻¹, $n_{\text{h}} = 1.72$, $h_{\text{a/s}} = 5$ W/m²K, and $h_{\text{g/s}} = 5\text{--}50$ W/m²K.

of the linear fit of the measured values. The red and blue circles respectively present the measured data obtained from laser increasing and decreasing cycles. For estimating the best fit straight line to data, I applied bivariate least squares fitting method (York method) using OriginPro9.0 (solid line in Fig. 1-4). In this case, I obtained the slopes (B_{Raman}) and those of errors as 6.1 ± 0.6 °C/mW. To construct 68.3% confidence intervals around the calculated slopes, I used the two-tailed t -distribution at $N - 2$ degrees of freedom ($t_{N-2, 31.7\%}$) and the standard errors of the slopes ($\sigma_{B_{\text{Raman}}}$). Estimated slopes and those of 68.3% confidence intervals ($\sigma_{B_{\text{Raman}}} \times t_{N-2, 31.7\%}$) are presented in Table 5.

5.2 Laser heating coefficient estimation based on homogenization observations after laser irradiation

By ascertaining the minimum P_{ill} required to homogenize the fluid inclusion for which the homogenization temperature (T_{h}) is slightly higher than room temperature ($T_{\text{h}} = T_{\text{room}} + \Delta T$), B can be estimated. Once CO₂ liquid and vapor homogenize to the liquid phase upon heating (point **B** in Fig. 1-5), supersaturated conditions are necessary on cooling to re-nucleate the gas phase. Therefore, under the conditions in which ΔT is lower than temperature difference required for re-nucleation of the bubble, even if the sample temperature is cooled to room temperature after laser irradiation, the fluid inclusion remains homogenized (point **C** in Fig. 1-5). Consequently, selection of inclusions with favorable T_{h} is crucially important for these measurements. Observations were made as follows: 1) Set the room and sample temperature to the target temperature ($T_{\text{sample}} = T_{\text{room}} = T_{\text{h}} - \Delta T$) (point **A** in Fig. 1-5) and focus on the target fluid inclusion. 2) Iterative irradiation was performed for 30 s on the inclusion, with increasing laser power, until homogenization was observed. After each irradiation, a cool-down period of 30 s was taken. During iterative irradiation, I can obtain both the minimum laser power required for homogenization (P_1) and maximum laser power to avoid homogenization (P_0). 3) Repeat step 2) again to confirm reproducibility. Finally, B is obtainable from measured P_0 and P_1 and the known ΔT . The laser power necessary to homogenize the fluid is approximated as the average of P_0 and P_1 . The laser heating coefficient $B_{T_{\text{h}}}$ is calculated as $B_{T_{\text{h}}} = \Delta T / (P_0 + P_1) / 2$. The uncertainty of $B_{T_{\text{h}}}$ ($\sigma_{B_{T_{\text{h}}}}$) was calculated from the uncertainty of the ΔT ($\sigma_{\Delta T} = 0.07$ °C) and the laser power ($\sigma_{(P_0+P_1)/2} = (((P_1 - P_0)/2)^2 + (0.03 \times 0.5(P_1 + P_0))^2)^{0.5}$) as

$$\sigma_{B_{T_{\text{h}}}} = \sqrt{\left\{ \frac{\sigma_{\Delta T}}{0.5(P_0 + P_1)} \right\}^2 + \left\{ \frac{\Delta T \times \sigma_{(P_0+P_1)/2}}{[0.5(P_0 + P_1)]^2} \right\}^2} . \quad (6)$$

The measured $B_{T_{\text{h}}}$ and errors are shown in Table 5.

Generally, because it takes more than several tens of seconds to obtain sufficient Raman scattering signal for quantitative analysis from an inclusion, it is difficult to use Raman spectra to track heating processes that occur in a short time (< 10 s). However, this method enables me to track heating that occurs during such a short time. The heating processes are highly sensitive to boundary condition, which enables one to infer the boundary condition. Section 6.2.2 presents additional details. Therefore, additional experiments were performed following the procedure described above: 4) Set the laser power to a certain power, P_i ($i = 2, 3, 4$), above P_1 , and measure the maximum time without homogenization ($t_{\max}$) and the minimum time necessary for homogenization ($t_{\min}$) at that laser power. 5) Repeat step 4) again to confirm the reproducibility. I defined the times necessary to homogenize fluid inclusions at a certain laser power as $(t_{\max} + t_{\min})/2$. Figure 1-6b shows the results.

Table1-4 Laser heating coefficients and errors obtained from two independent experiments.

Sample	Homogenization observation						Hot band thermometer		
	ΔT °C	$\sigma_{\Delta T}$ °C	P_0 mW	P_1 mW	$\sigma_{(P_0+P_1)/2}$ mW	B_{Th} °C/mW	$\sigma_{B_{Th}}$ °C/mW	B_{Raman} °C/mW	$\sigma_{B_{Raman}} \times t_N - 2, 31.7\%$ °C/mW
En2A oli02 fi01	0.3	0.07	4.3	4.4	0.14	0.07	0.02	1.0	0.3
En2A oli02 fi05	0.3	0.07	2.7	2.9	0.13	0.11	0.03	0.5	0.4
En2A oli02 fi06	0.3	0.07	2.2	2.4	0.12	0.13	0.03	0.02	0.2
En2A oli02 fi09	0.3	0.07	4.7	4.8	0.15	0.06	0.02	0.4	0.4
En2A oli02 fi13	0.3	0.07	3.2	3.3	0.11	0.09	0.02	0.6	0.3
En2A oli02 fi18	0.3	0.07	4.1	4.5	0.24	0.07	0.02	n.d.	n.d.
En2A opx06 fi04	0.8	0.07	1.7	1.8	0.07	0.46	0.04	0.8	0.3
En2A opx06 fi05	0.8	0.07	2.2	2.3	0.08	0.36	0.03	0.5	0.2
En2A opx09 fi62	0.8	0.07	0.9	1.1	0.10	0.80	0.11	1.2	0.2
En2A opx09 fi63	0.8	0.07	1.5	1.7	0.11	0.50	0.06	0.7	0.3
En2A cpx03 fi14	0.8	0.07	1.5	1.6	0.07	0.52	0.05	0.6	0.2
En2A cpx03 fi15	0.8	0.07	1.1	1.2	0.06	0.70	0.07	0.7	0.2
En2A cpx01 fi44	0.8	0.07	1.5	1.6	0.07	0.52	0.05	1.3	1.4
En2A sp03 fi137	0.4	0.07	0.08	0.11	0.02	4.2	1.0	5.2	0.9
En2A sp03 fi139	0.4	0.07	0.14	0.16	0.01	2.7	0.5	6.1	0.6
En2A sp03 fi163	0.4	0.07	0.08	0.11	0.02	4.2	1.0	6.4	1.1
En2A sp03 fi164	0.3	0.07	0.05	0.08	0.02	4.6	1.5	n.d.	n.d.
Quartz 01 fi 47					n.d.			0.014	0.002
Quartz 01 fi 53					n.d.			0.012	0.001

These experiments were done using an optical microscope, excitation laser, and objective set up at the Hokkaido University Museum, which are the same as those described in section 5.1.2. The laser exposure time can be set to any time interval up to 100 s in 0.1 s intervals by a mechanically controlled shutter. During the measurement, T_{sample} was monitored constantly by a Linkam stage similarly to section 5.1.2. The value of T_{sample} during the experiment was maintained so that the deviation from the target temperature was less than 0.1 °C. Measured P_0 , P_1 , P_i , t_{max} , and t_{min} are shown in Table S1-5 and Fig. 1-6.

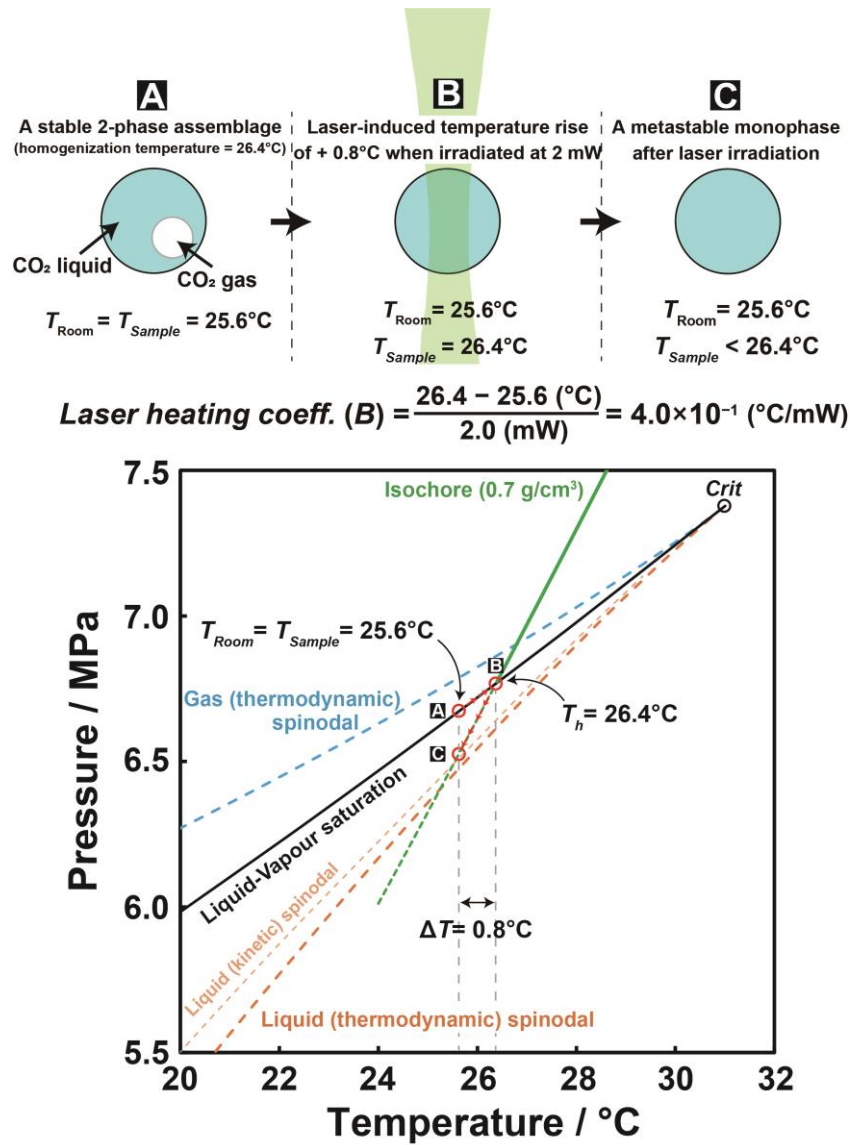


Figure1-5 Schematic procedures for estimation of laser heating coefficients based on the homogenization observation after the laser irradiation. Temperature–pressure diagram of a pure CO₂ is calculated according to Bakker (2012) and Pitzer and Sterner (1994).

6. Results

6.1. Finite element method

6.1.1. Simulation of temperature distribution inside the host mineral

In Fig. 1-7, I present a typical q - z section of the stationary temperature distribution around the inclusion (parameters are those of spinel03 fi139). I set $h_{g/s}$ as 10 W/m²K. Similarly to earlier studies, the radial temperature distribution from the optical axis at the laser focus showed logarithmic

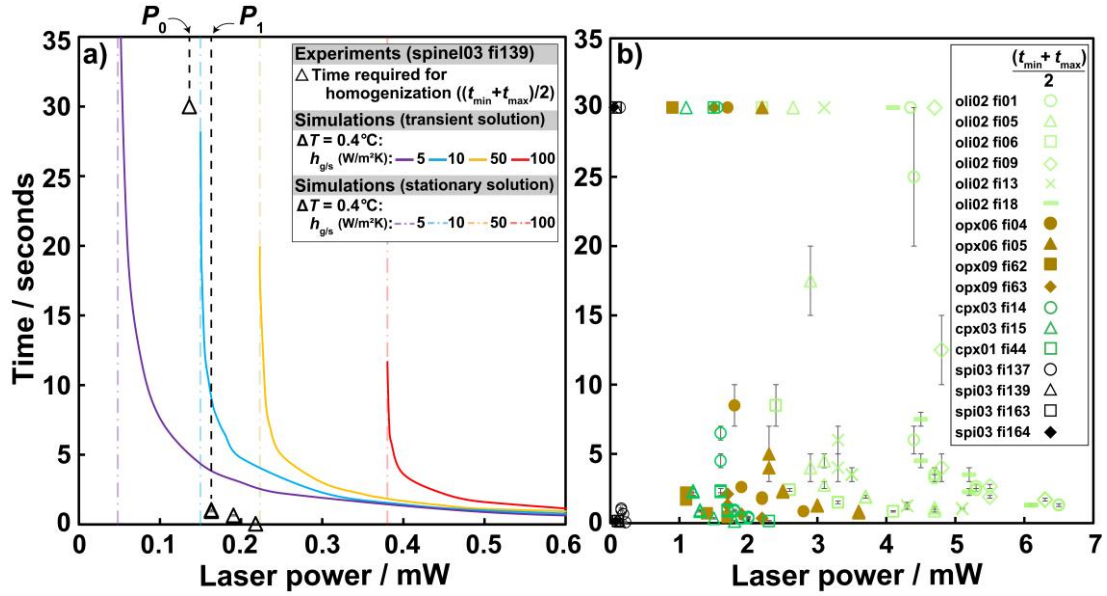


Figure1-6 a) Measured and simulated relations between laser power and time required for temperature increase of 0.4 °C for fluid inclusion in spinel (spinel03 fi139). Black triangles represent the measured time required for homogenization at a certain laser power defined as $(t_{\min} + t_{\max})/2$. Black dashed vertical lines are measured maximum laser power without homogenization after 30 s irradiation ($P_0 = 0.14$ mW) and minimum laser power necessary to homogenize the fluid ($P_1 = 0.16$ mW). Solid lines show the simulated relations between the laser power and the time necessary for the temperature increase of 0.4 °C under various glass–sample boundary conditions ($h_{g/s} = 5$ to 100 W/m²K). Dashed–dotted lines represent the laser power necessary for the 0.4 °C rise obtained by solving the stationary solution for each boundary condition. Parameters used for simulations are the following: $T_{\text{sample}} = 25.2$ °C, $\lambda = 532$ nm, $w_0 = 1.46$ μm , $\alpha_{\text{inc}} = 0$ m⁻¹, $z_{\text{inc}} = 2.6$ μm , $r_{\text{inc}} = 2.0$ μm , $K_{\text{inc}} = 0.08$ W/mK, $k_{\text{inc}} = 0.02$ mm²/s, $H_h = 42$ μm , $R_h = 0.534$ mm, $K_h = 5.5$ W/mK, $k_h = 1.79$ mm²/s, $\alpha_h = 2030$ m⁻¹, $n_h = 1.72$, $h_{a/s} = 5$ W/m²K, and $h_{g/s} = 5$ –100 W/m²K. b) Measured time required for homogenization $((t_{\min} + t_{\max})/2)$ at a certain laser power. The error bars represent $(t_{\min} - t_{\max})/2$. Data are listed in Table S1-5.

distance dependence (upper inset of Fig. 1-7) (Celliers and Conia, 2000; Mao et al., 2005; Haro-González et al., 2013; Català et al., 2017). In addition, reports of earlier studies described that the temperature distribution along the optical axis also shows logarithmic decay (Català et al., 2017). However, my simulation results do not follow such a monotonic decrease (right inset of Fig. 1-7). Compared to results of earlier studies, my simulated temperature distributions along the optical axis show complex behavior: temperatures take a minimum value at $z \sim z_{\text{inc}}$; the temperature decreases gradually after taking a maximum value at $z > z_{\text{inc}}$.

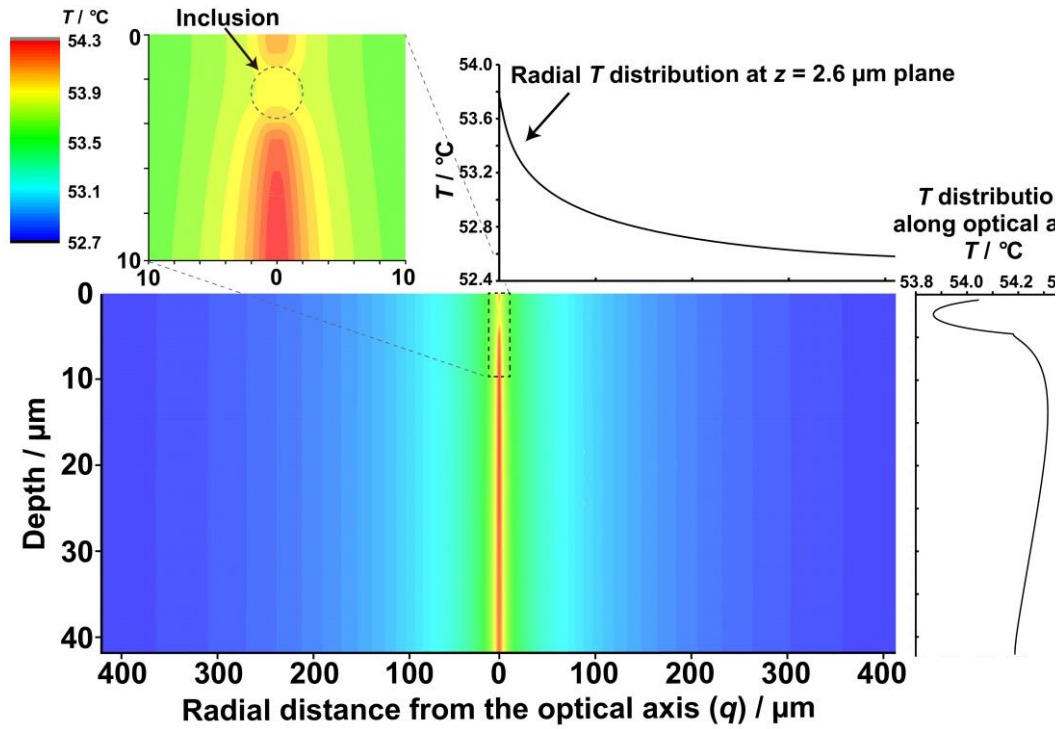


Figure1-7 Simulation of stationary temperature distribution inside the host mineral containing inclusion at $z_{\text{inc}} = 2.6 \mu\text{m}$. Radial temperature distributions at the $z_{\text{inc}} = 2.6 \mu\text{m}$ plane following the $\ln(1/q)$ decay (upper inset graph). The temperature along the optical axis becomes minimum at $z = 2.3 \mu\text{m}$ (right inset graph). The inset schematic shown at upper left is an enlarged view of the temperature distribution around and within a fluid inclusion. Parameters used for simulations are the following: $T_{\text{sample}} = 25 \text{ }^{\circ}\text{C}$, $\lambda = 532 \text{ nm}$, $P_{\text{ill}} = 5 \text{ mW}$, $w_0 = 1.46 \mu\text{m}$, $\alpha_{\text{inc}} = 0 \text{ m}^{-1}$, $z_{\text{inc}} = 2.6 \mu\text{m}$, $r_{\text{inc}} = 2.0 \mu\text{m}$, $K_{\text{inc}} = 0.08 \text{ W/mK}$, $k_{\text{inc}} = 0.02 \text{ mm}^2/\text{s}$, $H_{\text{h}} = 42 \mu\text{m}$, $R_{\text{h}} = 0.534 \text{ mm}$, $K_{\text{h}} = 5.5 \text{ W/mK}$, $k_{\text{h}} = 1.79 \text{ mm}^2/\text{s}$, $\alpha_{\text{h}} = 2030 \text{ m}^{-1}$, $n_{\text{h}} = 1.72$, $h_{\text{a/s}} = 5 \text{ W/m}^2\text{K}$, and $h_{\text{g/s}} = 10 \text{ W/m}^2\text{K}$. It is noteworthy that, although simulations were performed assuming $R_{\text{h}} = 0.534 \text{ mm}$, this schematic depicts the radial distance up to around 0.42 mm because the isotherm farthest from the optical axis existed at around $q = 0.42 \text{ mm}$.

6.1.2. Laser heating coefficient as functions of experimental, geometrical, and optical variables

In Fig. 1-8, I present simulation of the effect of each variable on B by changing each parameter within the range that can occur in the study of inclusions. The parameters used in the simulation are presented in the caption in Fig. 1-8.

My simulation results showed a linear relation between B and α_h (Fig. 1-8a). Although B and H_h have a positive relation throughout whole simulated H_h , it almost reaches a plateau when H_h was greater than 200 μm (Fig. 1-8b). For $H_h < 100 \mu\text{m}$, B decreases rapidly as H_h decreases (Fig. 1-8b). Although R_h and B show negative correlation, B remains nearly constant even as R_h increases when R_h exceeds 4 mm (Fig. 1-8c). The negative correlation between B and K_h was confirmed by my simulations (Fig. 1-8d). k_h and n_h did not influence B (Figs. 1-8e and 1-8f). I investigated the r_{inc} dependence of B over $r_{\text{inc}} = 0.1\text{--}10 \mu\text{m}$ at $z_{\text{inc}} = 10 \mu\text{m}$, which revealed that B decreases slightly, concomitantly with increasing r_{inc} (inset in Fig. 1-8g). Additionally, I simulated the size dependence of B at $z_{\text{inc}} = 100 \mu\text{m}$ from $r_{\text{inc}} = 0.1\text{--}50 \mu\text{m}$. As a result, the relation between B and r_{inc} was completely the same as that at $z_{\text{inc}} = 10 \mu\text{m}$ when $r_{\text{inc}} \leq 10 \mu\text{m}$, but the amount of change increased dramatically at $r_{\text{inc}} > 10 \mu\text{m}$ (inset in Fig. 1-8g). My simulation results show an exponential decrease (i.e., $B \propto \exp(-r_{\text{inc}})$), whereas those of Català et al. (2017) show logarithmic decay (i.e., $B \propto -\log(r_{\text{inc}})$). By contrast, in the case of $\alpha_{\text{inc}} > \alpha_h$, B clearly increases concomitantly with increasing r_{inc} at constant w_0 (Figs. 1-8i and 1-9), probably because the inclusions generate heat more efficiently than the host minerals when $\alpha_{\text{inc}} > \alpha_h$. I investigated z_{inc} dependence of B . It decreases near both the air-sample and glass-sample boundaries. However, the variation of B was very slight (Fig. 1-8h). I investigated variations of B by changing α_{inc} from 10^{-4} to 10^2 cm^{-1} and r_{inc} from 0.1 to 2.5 μm while maintaining $\alpha_h = 1.14 \text{ cm}^{-1}$ (Fig. 1-8i). As a result, the effect of α_{inc} on B is negligible when $\alpha_{\text{inc}} < \text{approx. } 0.1\text{--}1 \text{ cm}^{-1}$, but it cannot be negligible when $\alpha_{\text{inc}} > \text{approx. } 0.1\text{--}1 \text{ cm}^{-1}$. The transition of the effect of α_{inc} on B occurs around $\alpha_{\text{inc}} = 1 \text{ cm}^{-1}$, which is comparable to α_h (1.14 cm^{-1}). Therefore, the impact of α_{inc} on B cannot be negligible when $\alpha_{\text{inc}} > \alpha_h$ (Fig. 1-8i). Fig. 1-8j presents evaluation of the effect of λ dependence of Rayleigh length on B , assuming constant α_h ($= 1.14 \text{ cm}^{-1}$). As a result, the difference in λ did not affect B between 300 and 1100 nm. Negative correlation between B and w_0 was observed when α_{inc} is 100 and 1 cm^{-1} (Fig. 1-8k). However, B was constant when α_{inc} is 0 and 0.01 cm^{-1} , irrespective of w_0 . If $\alpha_{\text{inc}} < \alpha_h$ and if r_{inc} is constant (each solid line in Fig. 1-9), then B is constant because heat generation is ineffective at the focus, which has the highest energy density and the highest

potential for heat generation. The larger $h_{a/s}$ (or $h_{g/s}$) becomes, the smaller B is (Figs. 1-8l and S1-3).

Among the parameters used for the simulations, α_h , H_h , R_h , α_{inc} , $h_{a/s}$, and $h_{g/s}$ strongly affected B . In fact, B changed about one order of magnitude or more in the investigated range. However, k_h , n_h , z_{inc} , and λ do not affect B . In addition, K_h , r_{inc} , and w_0 slightly affect B .

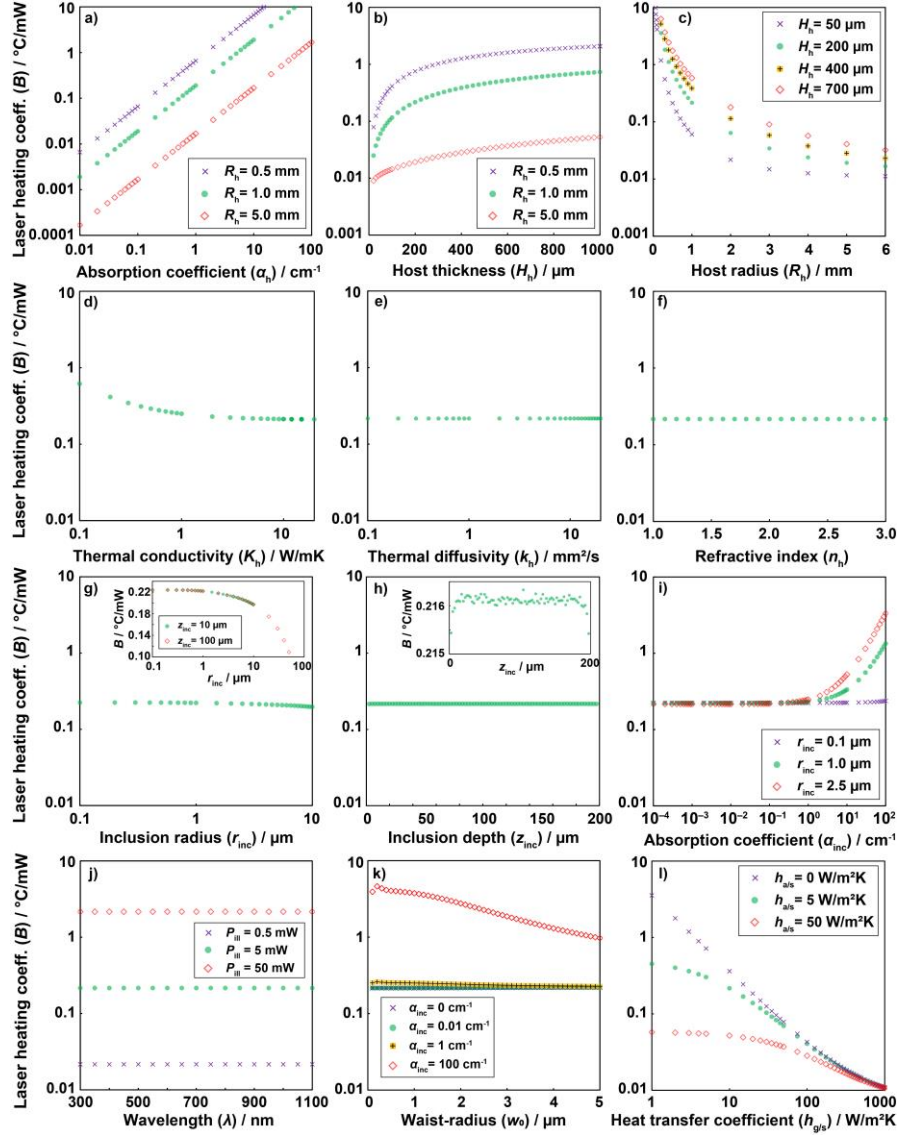


Figure1-8 Simulated laser heating coefficient as functions of a–f) host mineral, g–i) inclusion, and j–l) experimental parameters. Parameters used for simulations are fundamentally the following otherwise used as variables in each figure: $T_{\text{sample}} = 25\text{ }^{\circ}\text{C}$, $\lambda = 532\text{ nm}$, $P_{\text{ill}} = 5\text{ mW}$, $w_0 = 1.46\text{ }\mu\text{m}$, $\alpha_{\text{inc}} = 0\text{ m}^{-1}$, $z_{\text{inc}} = 10\text{ }\mu\text{m}$, $r_{\text{inc}} = 2.5\text{ }\mu\text{m}$, $K_{\text{inc}} = 0.08\text{ W/mK}$, $k_{\text{inc}} = 0.02\text{ mm}^2/\text{s}$, $H_h = 200\text{ }\mu\text{m}$, $R_h = 1\text{ mm}$, $K_h = 5.5\text{ W/mK}$, $k_h = 2.05\text{ mm}^2/\text{s}$, $\alpha_h = 114\text{ m}^{-1}$, $n_h = 1.65$, $h_{a/s} = 5\text{ W/m}^2\text{K}$, and $h_{g/s} = 10\text{ W/m}^2\text{K}$.

6.1.3. Temporal evolution of temperature distribution

I simulated the temporal evolution of the inclusion temperature when the inclusions were irradiated with 0.5, 5, and 50 mW excitation laser, and found that the inclusion temperature approached the steady-state value asymptotically with time (Fig. 1-10). Simulations were performed by assuming geometrical and material parameters the same as those of spinel03 fi139. Details of parameters are described in the caption of Fig. 1-10. As a result, $t_{0.9}$ (= time required for temperature reaches 90% of its steady-state value) was reached in about 18.5 s. Furthermore, varying P_{ill} from 0.5 to 50 mW does not affect $t_{0.9}$ (Fig. S1-4j). Therefore, even if I analyze the same inclusion with different P_{ill} , the difference does not affect the time required for the system to reach its steady state. However, according to simulation of Català et al. (2017), the temperature of microbeads in water reaches 90% of its steady

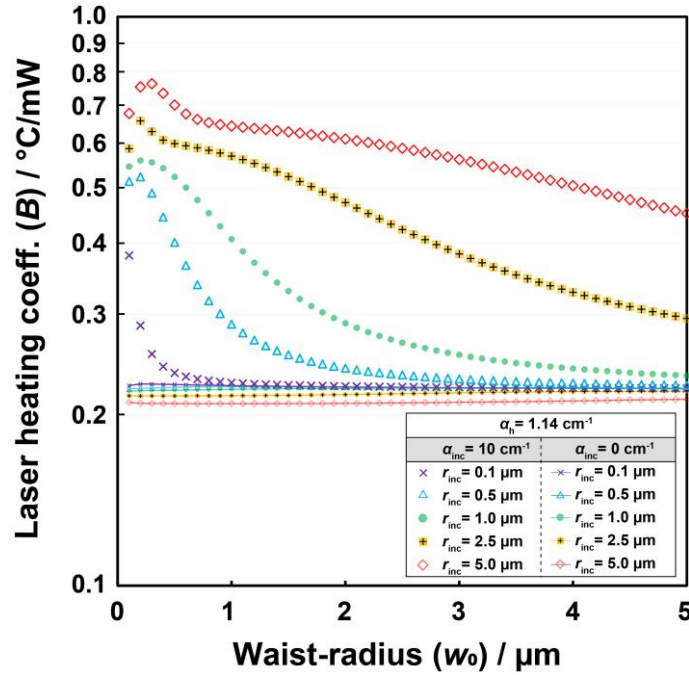


Figure1-9 Simulated laser heating coefficient as a function of waist-radius (w_0), inclusion radius (r_{inc}), and absorption coefficient of the inclusion (α_{inc}). When α_{inc} is 0 cm^{-1} , the laser heating coefficient is constant independent of the w_0 , but the laser heating coefficient becomes smaller with increasing r_{inc} . However, when α_{inc} is 10 cm^{-1} , the laser heating coefficient increases with decreasing w_0 . When $\alpha_{\text{inc}} = 10 \text{ cm}^{-1}$, the r_{inc} is larger with a larger laser heating coefficient. The following parameters are used for simulations: $T_{\text{sample}} = 25 \text{ } ^\circ\text{C}$, $\lambda = 532 \text{ nm}$, $P_{\text{ill}} = 5 \text{ mW}$, $w_0 = 0.1\text{--}5.0 \text{ } \mu\text{m}$, $\alpha_{\text{inc}} = 0$ and 1000 m^{-1} , $z_{\text{inc}} = 10 \text{ } \mu\text{m}$, $r_{\text{inc}} = 0.1\text{--}5.0 \text{ } \mu\text{m}$, $K_{\text{inc}} = 0.08 \text{ W/mK}$, $k_{\text{inc}} = 0.02 \text{ mm}^2/\text{s}$, $H_h = 200 \text{ } \mu\text{m}$, $R_h = 1 \text{ mm}$, $K_h = 5.5 \text{ W/mK}$, $k_h = 2.05 \text{ mm}^2/\text{s}$, $\alpha_h = 114 \text{ m}^{-1}$, $n_h = 1.65$, $h_{\text{a/s}} = 5 \text{ W/m}^2\text{K}$, and $h_{\text{g/s}} = 10 \text{ W/m}^2\text{K}$.

state value only after 1 ms, which is four orders of magnitude lower than my results. To clarify the causes of such differences in $t_{0.9}$, I investigated the effects of experimental parameters on $t_{0.9}$ (Fig. S1-4). Additionally, I simulated $t_{0.9}$ as functions of these parameters under four boundary conditions: $h_{g/s} = 0, 10, 1000 \text{ W/m}^2\text{K}$, and Dirichlet boundary condition (Fig. S1-5). As a result, the only parameters that can change $t_{0.9}$ as many as 4 orders of magnitude was the boundary condition. Therefore, because Català et al. (2017) set the boundary condition to the Dirichlet condition, the extremely small $t_{0.9}$ in their simulations will be attributable to the assumption of high heat flux at the boundary.

6.1.4 Laser irradiation time required for homogenization at a certain laser power

Figure 1-6a shows the laser irradiation time required for 0.4 °C rise in an inclusion in spinel

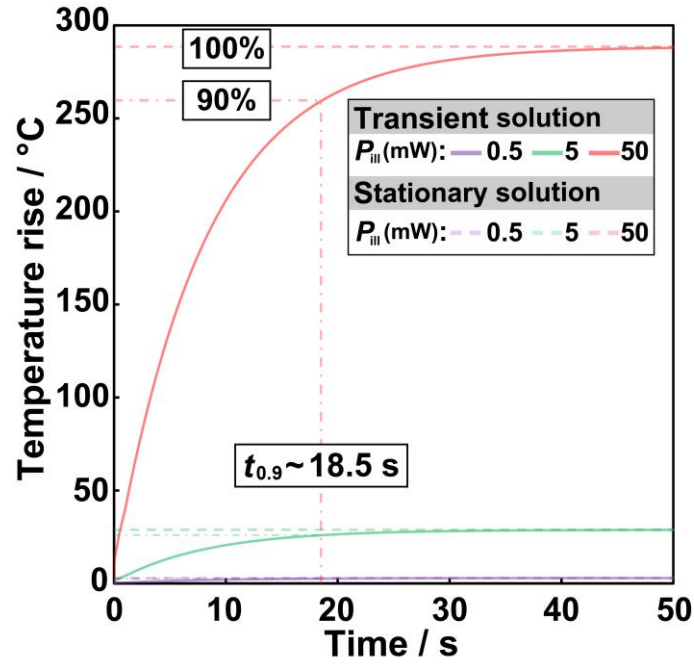


Figure1-10 Temporal evolution of the temperature rise of inclusions when irradiated with a 0.5, 5, or 50 mW laser. Optical and geometrical parameters of the host mineral and inclusion used for calculation are spinel and spinel03 fi139, respectively, as listed in Tables 1 and 3. With time, it approaches the temperature rise of the steady-state solution shown by the dotted horizontal line. Horizontal dashed–dotted lines show the temperature rise of 90% of its steady-state value. $t_{0.9}$ represents the time at which the temperature reaches 90% of its steady-state value. Parameters used for simulations are the following: $T_{\text{sample}} = 25 \text{ }^{\circ}\text{C}$, $\lambda = 532 \text{ nm}$, $P_{\text{III}} = 0.5\text{--}50 \text{ mW}$, $w_0 = 1.46 \text{ }\mu\text{m}$, $\alpha_{\text{inc}} = 0 \text{ m}^{-1}$, $z_{\text{inc}} = 2.6 \text{ }\mu\text{m}$, $r_{\text{inc}} = 2.0 \text{ }\mu\text{m}$, $K_{\text{inc}} = 0.08 \text{ W/mK}$, $k_{\text{inc}} = 0.02 \text{ mm}^2/\text{s}$, $H_{\text{h}} = 42 \text{ }\mu\text{m}$, $R_{\text{h}} = 0.534 \text{ mm}$, $K_{\text{h}} = 5.5 \text{ W/mK}$, $k_{\text{h}} = 1.79 \text{ mm}^2/\text{s}$, $\alpha_{\text{h}} = 2030 \text{ m}^{-1}$, $n_{\text{h}} = 1.72$, $h_{\text{a/s}} = 5 \text{ W/m}^2\text{K}$, and $h_{\text{g/s}} = 10 \text{ W/m}^2\text{K}$.

(spinel03 fi139). The simulation conditions are listed in the caption of Fig. 1-6. Results show that the time required for a 0.4 °C rise increases as P_{ill} decreases (solid lines in Fig. 1-6a). The solid lines approach asymptotically to P_{ill} required for the 0.4 °C temperature rise obtained by solving the stationary solution (vertical dashed-dotted lines). In addition, the time necessary for 0.4 °C rise became shorter as hg/s increases.

6.2. Experiments

6.2.1 Laser heating coefficient as functions of experimental, geometrical, and optical variables

The total of 36 laser heating coefficients obtained from both homogenization observation (17 data) and Raman spectroscopy (19 data) are presented in Fig. 1-11 as functions of host mineral and inclusion parameters. Note that, the effect of the uncertainty in the density estimation by microthermometry on the laser heating coefficient is very small and can be ignored (Fig. S1-6). Although I measured B using two independent methods, B_{Raman} tended to be larger than B_{Th} (Table 5).

Our experimentally obtained results show linear correlation between α_h and B (Fig. 10a). Using both experimental methods, the mean B were (quartz <<) olivine < opx $\approx$ cpx << spinel (Fig. 1-11a and Table 5). Additionally, I found negative correlations between B and each of H_h , R_h , and K_h (Figs. 1-11b to 1-11d). However, these correlations are not necessarily causal because they might be apparent relations caused by parameters that are highly influential to B (see section 7.2 for details). In my experiments, I measured B_{Raman} and B_{Th} of fluid inclusions in olivine with a radius of 4.5–22.2 μm and 2.9–22.2 μm , respectively, but no remarkable r_{inc} dependence of B was observed (Fig. 1-11e). From my simulations, B at $r_{inc} = 2.9 \mu m$ was only 1.1 times larger than B at $r_{inc} = 22.2 \mu m$. Therefore, at least for $r_{inc} < 22 \mu m$, I conclude from both the experimental and simulation results that r_{inc} has little impact on B . My experimentally obtained results show no systematic relation between z_{inc} and B (Fig. 1-11f). For example, B_{Raman} (or B_{Th}) of the shallowest fluid inclusions for each host mineral species is identical to those of the deepest one, within the error (Fig. 1-11f).

6.2.2 Laser irradiation time required for homogenization at a certain laser power

In earlier studies, the boundary condition in the model was assumed to be the Dirichlet condition (e.g., Català et al., 2017). To test whether this assumption holds under the experimental conditions of the present study, I measured the time necessary for homogenization at a certain P_{ill} . As a result, it took more than 0.1 s to homogenize when P_{ill} was greater than the minimum laser power

required for homogenization ($(P_0 + P_1)/2$) (Fig. 1-6b). Especially for inclusions in olivine, it took tens of seconds to homogenize at $P_{\text{III}} > (P_0 + P_1)/2$. The steady state might not have been reached in 30 s. Based on my simulations, it takes only $10^{-4} - 10^{-1}$ s to reach 90% of its steady state temperature when

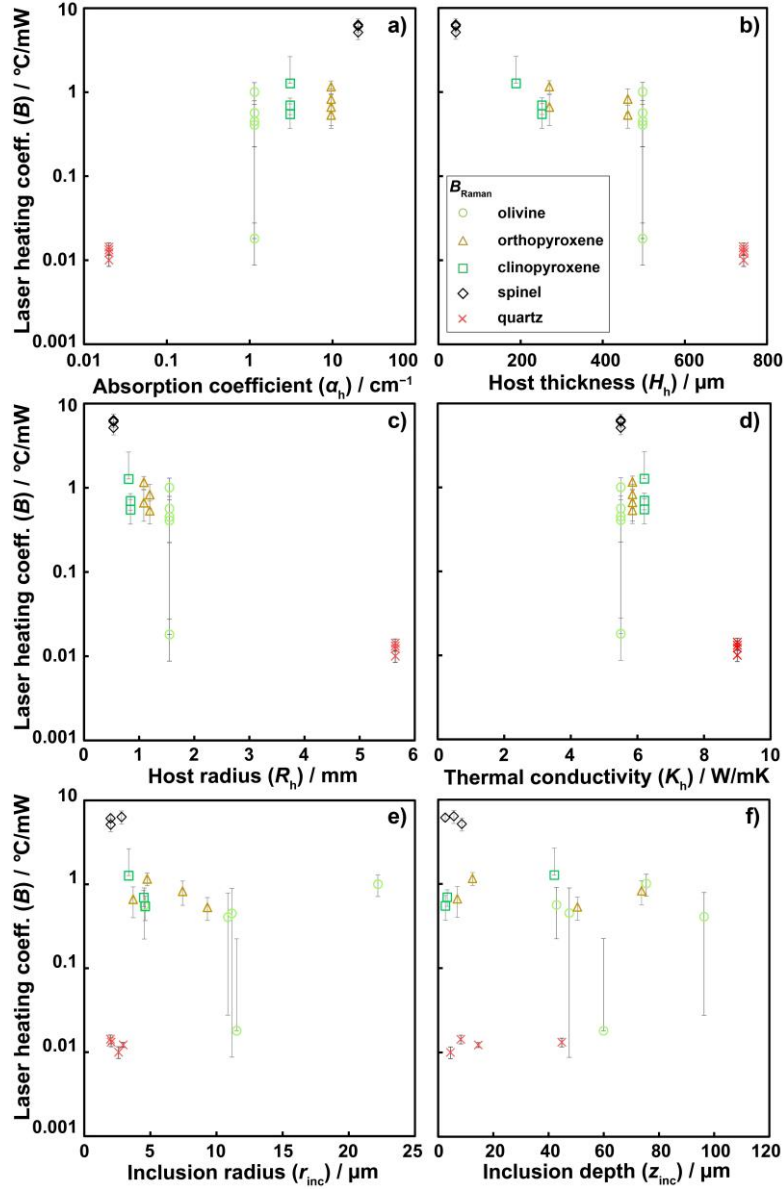


Figure1-11 Relations between material parameters and the laser heating coefficient of fluid inclusions measured by hot band thermometer: a) absorption coefficient of the host mineral, b) host mineral thickness, c) circle equivalent radius of the host mineral, d) thermal conductivity of the host mineral, e) radius of the fluid inclusion, and f) the distance of the fluid inclusion from the sample surface. Each graph shows a total of 19 data obtained using a hot band thermometer (B_{Raman}). Sample geometry, absorption coefficient, thermal conductivity, and laser heating coefficient are presented in Tables 1, 3, and 4.

the boundary condition is the Dirichlet condition (Fig. S1-4). Consequently, unlike earlier studies, the boundary condition is at least not a Dirichlet condition in my experimental conditions because it took a much longer time to reach a steady state.

7. Discussion

7.1. Comparison of laser heating coefficient measured from two independent experiments

In the present study, I measured B using two independent methods: the B_{Raman} tended to yield larger values than B_{Th} (Table 5). Figure 1-12 shows 15 $B_{\text{Raman}}/B_{\text{Th}}$ that were measured using both methods. All the ratios are greater than 1, except for data from olivine01 fi06. The mean values of $B_{\text{Raman}}/B_{\text{Th}}$ for each mineral species are 6.3 for olivine ($n = 5$), 1.5 for orthopyroxene ($n = 4$), 1.5 for clinopyroxene ($n = 3$), and 1.7 for spinel ($n = 3$). Therefore, this bias is apparently particularly pronounced in the case of fluid inclusion in olivine. In the following, I discuss the possible causes of uncertainty of B for each method.

Two possibilities exist for the B_{Raman} to be systematically high: 1) systematic overestimation of temperature because of the calibration error of Eq. 1-5, and 2) the silver block of Linkam stage

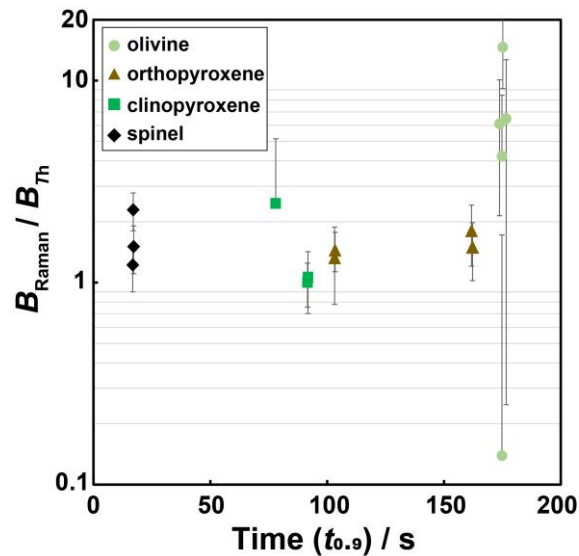


Figure1-12 A total of 15 $B_{\text{Raman}}/B_{\text{Th}}$ for which the laser heating coefficient was measured using two methods. All but one data were $B_{\text{Raman}}/B_{\text{Th}} > 1$. Error bars are calculated using B_{Raman} , B_{Th} , $\sigma_{B_{\text{Raman}}}$, and $\sigma_{B_{\text{Th}}}$ based on standard error-propagation procedures. $t_{0.9}$ is the time required to reach 90% of the temperature increase when irradiating an inclusion with the minimum laser power required to increase the temperature by ΔT from T_{initial} to T_{h} . Also, $t_{0.9}$ was calculated using finite element method with the geometry and physical property of the respective inclusions and host minerals, ΔT , and T_{h} (Tables 1, 3, and 5).

absorbs the laser light coming through the sample and generates extra heat. Regarding the former case, I confirmed that Eq. 1-5 is consistent with data obtained from a natural fluid inclusion using a Linkam stage (Fig. 1-3 and Table S1-3). It is unlikely that B_{Raman} will be overestimated because of the calibration curve itself. For the latter case, I observed a slight temperature rise of the Linkam stage during Raman spectroscopic analysis with high P_{ill} (Table S1-2). For example, during the analysis of olivine02 fi01, the temperature of the stage increased by 0.2 °C as P_{ill} increased from 4.2 to 14.2 mW and decreased by 0.3 °C as P_{ill} decreased from 14.2 to 4.2 mW. To evaluate the effects of heat generation from the silver block, the Raman spectra of quartz01 fi56 were measured by varying P_{ill} from 4.2 to 14.2 mW. Because P_{ill} of <15 mW induced almost no heating in inclusions in quartz, it should be originated from the silver block if the laser-induced heating is observed. The measurements were taken at Hokkaido University under the same conditions as those described in section 5.1.2. As a result, the temperature calculated from $[I_{H.B.}^+ + I_{H.B.}]/[I_{F.D.}^+ + I_{F.D.}]$ was constant irrespective of P_{ill} (Fig. S1-5 and Table S1-6). Heat generation derived from the silver block did not occur. In conclusion, overestimation of B_{Raman} is not expected.

I defined B_{Th} as $\Delta T/(P_0 + P_1)/2$. Therefore, if $P_0 + P_1$ was overestimated, for example the temperature in the sample did not reach a steady state, then B_{Th} could be underestimated. The main difference between the two methods is the laser irradiation time. They were, respectively, 30–600 and 30 s for B_{Raman} and B_{Th} measurements. Therefore, the system might not have reached steady state during B_{Th} measurements with a short irradiation time. In this case, P_0 is overestimated. If P_0 and P_1 are overestimated in this way, then B_{Th} is underestimated. If this is the primary cause of high $B_{\text{Raman}}/B_{\text{Th}}$, then $B_{\text{Raman}}/B_{\text{Th}}$ is greatest in the inclusions where $t_{0.9}$ is the greatest (i.e., the inclusions that take the longest time to reach steady state). To verify the effect of time necessary for homogenization on $B_{\text{Raman}}/B_{\text{Th}}$, I presented $B_{\text{Raman}}/B_{\text{Th}}$ as a function of $t_{0.9}$ (Fig. 1-12). The value of $t_{0.9}$ was calculated using finite element method with the geometry and physical property of the respective inclusions and host minerals, ΔT , and T_h (Tables 1, 3, and 5). For the simulations, $h_{g/s}$ was set as 10 W/m²K and $h_{a/s}$ as 5 W/m²K. Although the entire inclusion must be present in the host mineral for simulation (i.e., $z_{\text{inc}} > r_{\text{inc}}$), the r_{inc} of cpx03 fi14 and 15 are larger than z_{inc} . Therefore, because z_{inc} and r_{inc} have no effect on $t_{0.9}$ (Figs. S1-3g and S1-3h), the calculation was performed assuming that $r_{\text{inc}} = 2 \mu\text{m}$ so that $z_{\text{inc}} > r_{\text{inc}}$. According to my simulations, $t_{0.9}$ is the maximum for inclusions in olivine (Fig. 1-12). Additionally, my experiments clarified that inclusions in olivine take longer to behave asymptotically than those in other host minerals (Fig. 1-6b). Therefore, the $B_{\text{Raman}}/B_{\text{Th}}$ values of inclusions in the olivine are the highest might be that the inclusions in the olivine did not reach a steady state during B_{Th} measurements.

Consequently, deviation from the steady state might contribute to the high $B_{\text{Raman}}/B_{\text{Th}}$. The accurate estimation of B based on homogenization observations requires that the laser irradiation time be similar to the actual measurement time by Raman spectroscopy, especially when expected that $t_{0.9}$ is long (e.g., large H_h or small k_h samples).

The method of estimating B based on homogenization observation requires no calibration. It can therefore readily evaluate the temperature rise of inclusions because of laser heating compared to that based on Raman spectra. However, as discussed above, irradiation is necessary until the sample temperature reaches the steady state for estimation of B by homogenization observation. Furthermore, because of the small ΔT ($0.3 < \Delta T < 0.8$ °C in the present study), the measured B can vary greatly even for a small sample temperature fluctuation of about ± 0.1 °C. Nevertheless, it is difficult to perform homogenization observations with temperature fluctuations of 0.1 °C for the required duration (5–10 min in the present study) because of room temperature fluctuation and heat generation caused by absorption of the silver block. Therefore, attention must be devoted to the sample temperature and irradiation time when quantifying B by homogenization observations.

From the discussion presented above, almost all $B_{\text{Raman}}/B_{\text{Th}}$ are higher, probably because of the underestimation of B_{Th} . In addition, in section 7.3, I estimate B of olivine01fi13 using the temperature dependence of distance of the Fermi diad splits and obtain $B = 1.1 \pm 0.5$ °C/mW. This value is markedly greater than that of B_{Th} ($= 0.09 \pm 0.02$ °C/mW) for the same inclusion, but consistent with that of B_{Raman} ($= 0.6 \pm 0.3$ °C/mW) (Table 5). Therefore, although B was measured using two independent methods in this study, B measured using a hot band thermometer is regarded as more reliable. In the following discussion, I only use B_{Raman} .

7.2. Influential variables on the laser heating of inclusions

Mao et al. (2005) proposed a laser heating model that describes a temperature profile in the focal plane at the middle of the chamber and parallel to the coverslips. Based on the model, Haro-González et al. (2013) presented the following relation at radial distance w_0 ($= 0.6\lambda/NA$) from the optical axis of focus as

$$B = \frac{\alpha_h}{2\pi K_h} \times \ln \left[\frac{H_h \times NA}{0.6\lambda} \right], \quad (1-7)$$

where K_h denotes the thermal conductivity, H_h represents the sample thickness, NA stands for the numerical aperture of an objective, and λ shows the laser wavelength.

Although earlier studies have argued that B is proportional to α_h/K_h (e.g., Català et al., 2017), I found that such conditions are limited to those in which the boundary condition is a Dirichlet

condition. Also, the effect of K_h on B decreases as the heat transport at the interface decreases (Fig. S1-2d). The host minerals used for this study have K_h of 5.5–9.0 W/mK. Therefore, the expected difference in B is only about twice as large at most. In addition, because the boundary condition is not a Dirichlet condition in my experiments (see section 6.2.2), the expected effect of K_h on B is much less than twice as large. Therefore, K_h is not the dominant factor in determining B , at least for the host minerals used for this study. However, if a large difference exists in K_h between materials (e.g., diamond and barite), then such K_h differences cause differences in B .

As one might infer from Eq. 1-7, the logarithmic relation between H_h and B is also confirmed by my simulation (Fig. 1-8b). To verify the effect of H_h on B from experimental data, I should compare the B of fluid inclusions in the same host mineral species with different thicknesses (Fig. 1-8a). Therefore, I use two orthopyroxene grains (opx06 and opx09) having almost identical R_h , but different H_h (461 and 270 μm , respectively) for comparison. As a result, no significant difference of measured B was found between them (Fig. 1-11b). This lack of difference is reasonable because my simulations show B as almost independent of H_h when $H_h > 200 \mu\text{m}$. That result constitutes evidence that the effect of H_h on B is low compared with those of α_h within the parameter range that might occur in the inclusion study. Nevertheless, because B decreases rapidly as H_h decreases when $H_h < 100 \mu\text{m}$, the thinner sample better suppresses laser heating and thermal damage (Figs. 1-8b and S1-2b).

From the discussion presented above, the effects of H_h and K_h on B are small. From my simulations, the λ and w_0 effects on B are negligible, at least when $\alpha_{\text{inc}} < \alpha_h$ (Figs. 1-8j and 1-8k). Therefore, as expected from Eq. 1-7 and earlier studies, the dominant factor which determines B will be α_h (Català et al., 2017). Indeed, my simulation and experimentally obtained results showed a linear relation between them (Figs. 1-8a, 1-11a, and S1-2a). The spinel is about 10^3 times larger α_h than that of quartz: the measured B_{Raman} of spinel is approx. 6 $^\circ\text{C}/\text{mW}$, which is 600 times larger than that of quartz (approx. 0.01 $^\circ\text{C}/\text{mW}$). In addition, B of orthopyroxene, clinopyroxene, and olivine, which have an intermediate α_h , fall between approx. 0.1 and 1 $^\circ\text{C}/\text{mW}$, which lies between those of spinel and quartz. This order is equal to the order of α_h except for the order of clinopyroxene and orthopyroxene. Therefore, although it remains possible that parameters other than α_h affect B to some extent, my experiments and simulations support that the experimental parameter with the most influence on the B would be α_h , within the parameter range that could occur in the inclusion study, as suggested by results of earlier studies (Haro-González et al., 2013; Català et al., 2017).

According to Català et al. (2017), the boundary distance from the optical axis has little effect on B at least boundary distance $> 80 \mu\text{m}$ (i.e., $R_h > 80 \mu\text{m}$). However, unlike their results, my

simulation results showed negative correlation between R_h and B (Figs. 1-8c and S1-2c). This discrepancy is expected to result from the difference in boundary conditions because Català et al. (2017) assumed a Dirichlet boundary condition, whereas I assumed a convective heat flux. In fact, when the glass–sample boundary condition is changed to the Dirichlet boundary condition in my simulation, R_h at which the relation between R_h and B reaches a plateau decreases drastically from approx. $R_h = 4$ mm to 0.2 mm (red circles in Fig. S1-2c). Therefore, the discrepancy of the simulation result is explainable by the difference of boundary conditions. To evaluate the effect of R_h on B from the experimental data, I need host minerals with different R_h . However, I have not prepared such samples in this study. Therefore, the effect of R_h on B cannot be discussed further from my experimental data. Nonetheless, earlier reports describe that even quartz, which has very small α_h , is heated to a considerable degree by a laser when R_h is small (Chio et al., 2003). Therefore, it would be effective NOT to make the host mineral too small during sample preparation to reduce the damage and spectral changes caused by the excitation laser.

Regarding the effects of r_{inc} on B , Peterman et al. (2003) concluded that only a small effect derives from the size of the trapped beads. By contrast, Català et al. (2017) concluded that B logarithmically decreases concomitantly with increasing bead size. It is related directly to the radial temperature profile. However, their data cannot be compared directly to those of the present study because both their experimental and simulation results have been based on the temperature of the buffer (either water or glycerol) rather than in the beads. Both my experimental and simulation results, which evaluated B of the inclusion itself, reveal that r_{inc} has little impact on B , when the inclusion radius is smaller than 22 μm . By contrast, my simulations indicate that the extremely large inclusion ($r_{inc} > \sim 30$ μm) shows B decrease concomitantly with increasing size (r_{inc}) because the temperature rise from the focused laser is restricted near the focal point (inset in Figs. 1-7 and 1-8g). Such a restriction of the temperature rise region has also been reported by Català et al. (2017). When I assume the case with $\alpha_{inc} > \alpha_h$, possible case for solid inclusions, the larger inclusions are more likely to be heated. The effect of laser heating must be considered when comparing results obtained from inclusions with highly different size (Fig. 1-9).

The experiments reported by Català et al. (2017) demonstrated that heating was decreased significantly when the laser was focused on a particle in water and placed 10 μm from the bottom of glass–water boundary; whereas B remained almost constant irrespective of depth in the case where the laser focus was distant from the bottom by >10 μm . They argued that the temperature rise from the focused laser around the focal point was restricted, with volume as small as 10 μm . Therefore, when

the focus is close to the glass with a lower α/K , the heat produced by the laser is dissipated efficiently to the glass. In contrast, my simulation results show the B dependence on z_{inc} only when the glass–sample boundary condition was in a Dirichlet condition (Fig. S1-2h). Even in such a condition, B is almost constant near the $z = 0$ plane. Furthermore, the experimentally obtained results showed no z_{inc} dependence of B . Raman spectroscopy is usually applied to shallow inclusions rather than the bottom of the sample because the increase in inclusion depth generally makes it difficult to obtain the Raman scattered light of the inclusions efficiently (e.g., Everall, 2010). Therefore, z_{inc} dependence of B is negligible in a normal analysis environment. For that reason, no bias is found in measurements of inclusions with various depths. However, it is noteworthy that the proximity of inclusion to the thin-section surface might modify the residual pressure of inclusions (Mazzucchelli et al., 2018; Zhong et al., 2020).

Català et al. (2017) and Peterman et al. (2003) asserted that heating is governed mainly by laser absorption in the surrounding buffer, but not in the particles. In earlier studies, absorption coefficients of beads at their excitation wavelength were 0.06 cm^{-1} (polystyrene) and $5 \times 10^{-5} \text{ cm}^{-1}$ (silica), which were sufficiently lower than those of the surrounding buffer: water (0.14 cm^{-1}) and glycerol (0.21 cm^{-1}). Their results are consistent with my simulation results, which suggest that α_{inc} did not affect B when α_{inc} was lower than α_{h} . Here I consider two typical fluid species, CO_2 and H_2O , as examples. In the case of CO_2 , α_{inc} at 532 nm is expected to be much smaller than that of quartz, which has the smallest α_{h} used for this study. Therefore, it is reasonable to assume $\alpha_{\text{inc}} = 0$ for the evaluation of laser heating in inclusions from Fig. 1-8i. Similarly, α_{inc} of pure water at 532 nm is approx. $2 \times 10^{-4} \text{ cm}^{-1}$. Its temperature and salinity dependence are negligible; the assumption of $\alpha_{\text{inc}} = 0$ is also valid for brine fluid inclusions (Pegau et al., 1997; Röttgers et al., 2014). Conversely, the impact of α_{inc} cannot be negligible when $\alpha_{\text{inc}} > \alpha_{\text{h}}$ (Fig. 1-8i). For that case, B is controlled strongly by r_{inc} , α_{inc} , and w_0 (Figs. 1-8i and 1-9). Therefore, for $\alpha_{\text{inc}} > \alpha_{\text{h}}$, bias attributable to laser heating can occur when measuring inclusions of different r_{inc} and α_{inc} or with different objective lenses.

In summary, α_{h} , R_{h} , and $h_{\text{g/s}}$ have significant effects on B , but r_{inc} and z_{inc} do not affect B . Therefore, to reduce the temperature rise during the analysis of inclusions, it is effective to make the host mineral larger and thinner and to increase the heat flow rate at the boundary. In addition, α_{h} depends on the wavelength. Therefore, if the optimal excitation laser setting and sample geometry are selected, then the inclusion temperature during the analysis will be suppressed; the obtained data will approach the true value. To help researchers to reach such optimal analytical conditions, α_{h} of representative rock-forming minerals and their wavelength dependence are presented in Table S1-7.

7.3. Correction methods of laser heating effects on Raman spectra

As the inclusion temperature during Raman spectroscopy increases concomitantly with increasing P_{ill} , the effect of laser heating on the Raman spectrum can be minimized by lowering P_{ill} to the greatest extent possible. However, the lowest P_{ill} does not mean that the laser heating effect on the Raman spectrum is completely absent. Therefore, depending on the situation, it is necessary to make some corrections to the measured data. In the following, I discuss how corrections should be made to the Raman spectral features when inclusions are suspected to be heated by a laser.

To illustrate the correction procedure, as an example, I measured Raman spectra of CO₂-rich fluid inclusions at various P_{ill} . The density of the fluid inclusions (ρ) was estimated from their peak positions. To ascertain the density of CO₂-rich fluid inclusion, several groups have improved Raman CO₂ densimeters and have demonstrated the density dependence of distance of Fermi diad splits ($\Delta = \nu_{\text{FD}}^+ - \nu_{\text{FD}}^-$) (Fig. S1-1) (Rosso and Bodnar, 1995; Yamamoto et al., 2002; Kawakami et al., 2003; Yamamoto and Kagi, 2006; Song et al., 2009; Fall et al., 2011; Wang et al., 2011; Lamadrid et al., 2017; Yuan et al., 2017; Wang et al., 2019; Hagiwara et al., 2020; Le et al., 2020; Sublett et al., 2020b). Therefore, ρ can be found from the measured Δ . However, because the relation between Δ and ρ depends on temperature, if the inclusions are heated to a considerable degree by the laser, then the obtained Δ must be corrected to ascertain a more reliable density specifically (e.g., Wang et al., 2019).

To derive a correction method, the relation between P_{ill} and Δ was investigated using the fluid inclusion in quartz (quartz01 fi56) and that in olivine (En2A oli02 fi13). The analysis was conducted using a grating of 1,800 grooves/mm; in all other respects, the analytical procedures are the same as those described in section 5.2. Analyses were conducted along both P_{ill} increasing (circle symbol) and decreasing (triangle symbol) cycles with four P_{ill} of 4.2, 7.7, 10.9, and 14.3 mW (Fig. 1-11). The measured Δ (Δ^{raw}) are first calibrated using measured and known distances between the Ne lines according to the explanation presented by Lamadrid et al. (2017) ($\Delta^{\text{Ne calib}}$ in Table 5). Subsequently, discrepancies in the calibration curves between laboratories were corrected by adding the correction term δ_{Δ} to $\Delta^{\text{Ne calib}}$. Finally, corrected Δ are defined as $\Delta^{\text{Ne \& Qtz calib}} = \Delta^{\text{Ne calib}} + \delta_{\Delta}$. δ_{Δ} was calculated using Eq. 10 of Hagiwara et al. (2020), Eq. 8 of Sublett et al. (2020), and the 8 $\Delta^{\text{Ne calib}}$ obtained from fluid inclusions in quartz. Detailed calculation processes of δ_{Δ} are shown in Table S1-7. The values of ρ_{Raman} calculated using substituting T_{sample} and $\Delta^{\text{Ne \& Qtz calib}}$ into Eq. 8 of Sublett et al. (2020) and P_{ill} at that time are presented in Table 5. The spectra were obtained five times at each P_{ill} .

The mean values of $\Delta^{\text{Ne}} \& \text{Qtz calib}$ were presented in Fig. 1-11b. Their standard deviations (1σ) were shown as error bars.

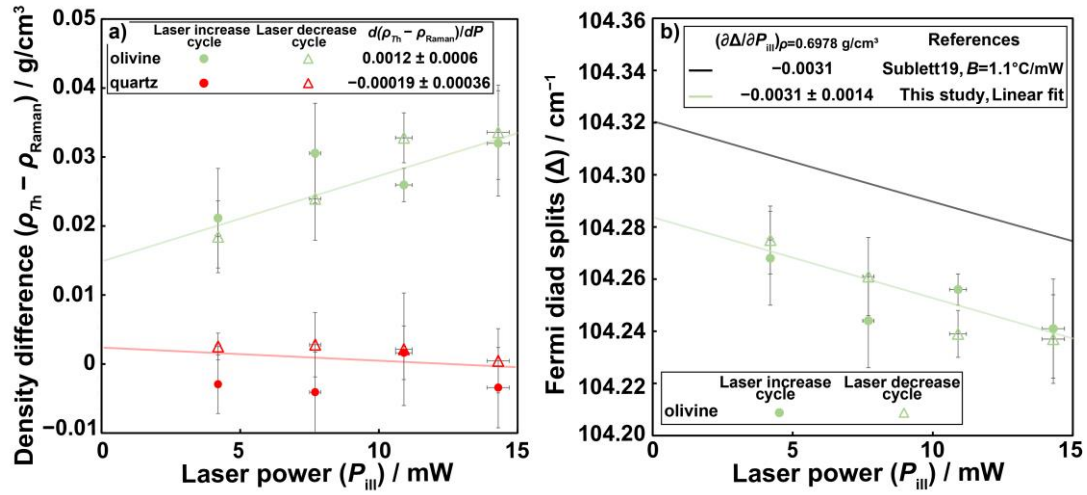


Figure1-13 a) Laser power dependence of the difference between the density of CO_2 calculated from the homogenization temperature (ρ_{th}) and the density calculated from the Fermi diad splits (ρ_{Raman}). ρ_{Raman} was calculated by substituting $\Delta^{\text{Ne}} \& \text{Qtz calib}$ and the temperature monitored in Linkam stage into Eq. 8 of Sublett et al. (2020). The stage temperature and ρ_{Raman} are presented in Table 6. I measured fluid inclusions in olivine (olivine02 fi13) and quartz (quartz01 fi56), with data plotted respectively as green and red symbols. The measurements were made with the laser power increasing cycle (circle) and decreasing cycle (triangle). In the case of inclusions in olivine, ρ_{Raman} is underestimated with increasing laser power. However, in the case of inclusions in quartz, ρ_{Raman} was kept constant with increasing laser power. b) Relation between Δ of fluid inclusions in olivine (olivine02 fi13) and laser power. The green solid line shows the linear fit (York method) to eight data points. The line slope is $-0.0031 \pm 0.0014 \text{ cm}^{-1}/\text{mW}$. The black line represents calculated relations between laser power and Fermi diad split using Eq. 8 of Sublett et al. (2020). The sample temperature was assumed to be 27.2°C with laser power of 0 mW. The calculated slopes of the relations between Δ and laser power at laser heating coefficients of 1.1°C/mW were $-0.0031 \text{ cm}^{-1}/\text{mW}$.

Table1-5 Measured fluid density, distance of Fermi diad splits, sample temperature, and laser power.

Sample	ρ_{Th} g/cm ³	P_{ill} mW	$\sigma_{\rho_{ill}}$ mW	T_{sample} °C	Δ^{raw} cm ⁻¹	$\Delta^{Ne \text{ calib}}$ cm ⁻¹	$\Delta^{Ne \text{ \& Qtz calib } a}$ cm ⁻¹	σ_{Δ} cm ⁻¹	ρ_{Raman}^b g/cm ³	$\sigma_{\rho_{Raman}}^c$ g/cm ³	$\rho_{Th} - \rho_{Raman}$ g/cm ³
olivine02 fi13	0.6978	4.2	0.1	27.2	104.168	104.181	104.268	0.018	0.6767	0.0072	0.0211
	0.6978	7.7	0.2	27.4	104.144	104.157	104.244	0.018	0.6672	0.0072	0.0306
	0.6978	10.9	0.3	27.2	104.157	104.169	104.256	0.006	0.6718	0.0024	0.0260
	0.6978	14.3	0.4	27.2	104.144	104.154	104.241	0.019	0.6658	0.0076	0.0320
	0.6978	14.3	0.4	27.2	104.137	104.150	104.237	0.017	0.6642	0.0068	0.0336
	0.6978	10.9	0.3	27.2	104.139	104.152	104.239	0.009	0.6650	0.0036	0.0328
	0.6978	7.7	0.2	27.2	104.162	104.174	104.261	0.015	0.6739	0.0060	0.0239
	0.6978	4.2	0.1	27.1	104.174	104.188	104.275	0.013	0.6794	0.0052	0.0184
quartz01 fi56	0.7858	4.2	0.1	26.6	104.447	104.467	104.554	0.011	0.7887	0.0043	-0.0029
	0.7858	7.7	0.2	26.9	104.454	104.469	104.556	0.015	0.7899	0.0058	-0.0041
	0.7858	10.9	0.3	27.3	104.436	104.453	104.540	0.010	0.7842	0.0039	0.0016
	0.7858	14.3	0.4	27.3	104.451	104.466	104.553	0.015	0.7892	0.0058	-0.0034
	0.7858	14.3	0.4	27.3	104.442	104.456	104.543	0.012	0.7853	0.0047	0.0005
	0.7858	10.9	0.3	27.2	104.439	104.452	104.539	0.021	0.7837	0.0082	0.0021
	0.7858	7.7	0.2	27.3	104.438	104.450	104.537	0.012	0.7830	0.0047	0.0028
	0.7858	4.2	0.1	27.2	104.437	104.451	104.538	0.005	0.7833	0.0019	0.0025

^a $\Delta^{Ne \text{ \& Qtz calib}}$ is defined as " $\Delta^{Ne \text{ calib}} + \delta_{\Delta}$ " cm⁻¹. δ_{Δ} can be found by optimizing Eq. 10 of Hagiwara et al. (2020) to the minimum and is determined as 0.087 cm⁻¹.

^b ρ_{Raman} is density calculated by substituting T_{sample} and $\Delta^{Ne \text{ \& Qtz calib}}$ into Eq. 8 of Sublett et al. (2020).

^c $\sigma_{\rho_{Raman}}$ is density error calculated by substituting T_{sample} and $\Delta^{Ne \text{ \& Qtz calib}} + \sigma_{\Delta}$ into Eq. 8 of Sublett et al. (2020)

The relations between P_{ill} and $\rho_{\text{Th}} - \rho_{\text{Raman}}$ are presented in Fig. 1-13a. The solid lines in Fig. 1-13a show a linear fit (York method) to eight data points. In the case of the inclusion in quartz, the slope was $-0.00019 \pm 0.00036 \text{ g/cm}^3/\text{mW}$, showing no significant positive or negative correlation with P_{ill} , at least in the studied P_{ill} range. As determined in this study, the B of fluid inclusion in quartz is about $0.01 \text{ }^\circ\text{C/mW}$. Therefore, the expected laser-induced temperature rise is at most $0.2 \text{ }^\circ\text{C}$. The Δ drop caused by laser heating is only 0.0006 cm^{-1} , which is well below the measurement precision of Δ . If no correlation exists between P_{ill} and the spectral features, then no correction is needed because the laser heating effect is negligible, at least within the studied P_{ill} range.

To ascertain whether spectral features of inclusions in a given mineral are unaffected by P_{ill} , it is desirable to select the inclusions that are most likely to be heated by the laser from all the inclusions to be analyzed. In other words, the fluid inclusions in the host mineral having the thickest and smallest diameter are optimal for evaluation. Some minerals have α_{h} varying with composition. The measurement of inclusions in such minerals must consider B differing in different compositional zones even in a single grain. Indeed, infrared studies of inclusions have revealed that even synthetic fluid inclusions in a single mineral grain, which are expected to have similar fluid composition and density, show different phase-transition temperatures depending on the compositions of the surrounding host phase (Casanova et al., 2018). Therefore, it is important to repeat this work (i.e., obtain the spectra of each inclusion while varying P_{ill}), even in a single crystal, if the host phase has significant compositional variation.

In the case of inclusion in olivine, the relation between $\rho_{\text{Th}} - \rho_{\text{Raman}}$ and P_{ill} shows a significant positive correlation; the slope was $0.0012 \pm 0.0006 \text{ g/cm}^3/\text{mW}$ (Fig. 1-13a). Earlier reports have described that even for fluids with constant density, ρ_{Raman} is underestimated as the temperature increases (Wang et al., 2011; Yuan et al., 2017; Wang et al., 2019; Sublett et al., 2020b), which is consistent with my experimentally obtained results (Fig. 1-13a). Therefore, to obtain a more accurate ρ_{Raman} , the data must be measured using lower P_{ill} or corrected to account for the laser heating effect.

If the target spectral properties (here Δ) and temperature are almost linearly correlated at constant ρ , then the intercept of the linear fit between Δ and P_{ill} can be regarded as Δ at 0 mW . To verify the linearity of the relation between Δ and temperature at constant ρ , we calculated the relation between them at $\rho = 0.698 \text{ g/cm}^3$ using Eq. 8 of Sublett et al. (2020). For the calculation, we assumed $B = 1.1 \text{ }^\circ\text{C/mW}$ so that the obtained slope of the line in the calculations corresponds with that obtained from measured relation between Δ and P_{ill} . As a result, although their equation is not a linear function, it shows an almost linear relation at least within P - T of my interest (black line in Fig. 1-13a). Therefore,

the intercept at the linear fit of the measured Δ ($\Delta = 104.283 \pm 0.016 \text{ cm}^{-1}$) is regarded as being the true value corrected for the laser heating effect because Δ and P_{III} is linearly correlated (Fig. 1-13a). Assuming that the error of the correction term δ_{Δ} determined in Table S1-7 is also 0.016 cm^{-1} , the final error of the obtained intercept is $\sqrt{0.016^2 + 0.016^2} = 0.023 \text{ cm}^{-1}$. In addition, because the standard error of Eq. 8 of Sublett et al. (2020) is reported as $\pm 0.006 \text{ g/cm}^3$, the error of Δ at 0.698 g/cm^3 is expected to be $\pm 0.015 \text{ cm}^{-1}$, which is the difference of Δ obtained by Eq. 8 of Sublett et al. (2020) applied for the conditions of $\rho = 0.698 \text{ g/cm}^3$ and $\rho = 0.704$ (or 0.692) g/cm^3 at the temperature of $27.2 \text{ }^{\circ}\text{C}$. Therefore, deviation of measured intercept ($\Delta = 104.283 \text{ cm}^{-1}$) from calculated one ($\Delta = 104.321 \text{ cm}^{-1}$) is almost equal to the sum of the errors of the measured and calculated Δ . By this series of analyses, the laser heating effect on Δ of a single fluid inclusion can be corrected. However, if the relation between the Raman spectral properties and temperature is not linear in the P - V - T - X range of interest, then the intercept should be obtained by fitting with a function that best describes the relation.

However, it is very time-consuming to perform a series of operations (i.e., to obtain the spectra of each inclusion while varying P_{III}) to estimate the intercept values for dozens of inclusions. Fortunately, however, if the temperature dependence of the calibration curve is known, then there is no need to repeat this series of operations if only B can be determined. This is true because, once B is known, the temperature of the inclusions in the analysis is calculable. We can correct the laser heating effect using a calibration curve with known temperature dependence. In the following, we explain how to estimate B from the relation between the Raman spectral features and P_{III} of an inclusion when the temperature dependence of the calibration curve is known.

For a Raman CO_2 densimeter, the slope of the relation between Δ and P_{III} ($\partial\Delta/\partial P_{\text{III}}$) depends on ρ and B . Consequently, from the relation between Δ , ρ , and T obtained in an earlier study, B satisfying the measured $(\partial\Delta/\partial P_{\text{III}})_{\rho}$ is obtainable. According to Eq. 8 of Sublett et al. (2020), B satisfying $(\partial\Delta/\partial P_{\text{III}})_{\rho} = -0.0031 \pm 0.0014$ at $\rho = 0.698 \text{ g/cm}^3$ is $B = 1.1 \pm 0.5 \text{ }^{\circ}\text{C/mW}$ (Fig. 1-13a). This result is consistent with the actual B of oli02 fi13, $B_{\text{Raman}} = 0.6 \pm 0.3 \text{ }^{\circ}\text{C/mW}$ (Table 4). Therefore, if the temperature dependence of the calibration curve is known, but B is unknown, then one can find B using the procedure described above. The precision of the measurement of B depends on the degree of temperature dependence of the calibration curve, but it is possible to determine B more accurately by performing the above series of analyses over a wider P_{III} range. However, if the relation between temperature and target spectral feature at desired P - V - T - X conditions is unknown, then B cannot be estimated by the procedure described above. Therefore, under such conditions, the raw data should be corrected by estimating the value of the intercept from the relation between the Raman spectral

features and P_{ill} .

To evaluate the effect of laser heating on the geological application of inclusion analysis, as an example, we consider an example of pressure estimation from a CO₂ fluid inclusion in a mantle xenolith. Oglialoro et al. (2017) showed the existence of a magma storage region located in the lower oceanic crust at a depth of 0.26–0.34 GPa beneath the El Hierro Volcano, Canary Islands, based on the density of CO₂-rich inclusions in mantle xenoliths. For example, when measuring Δ of a CO₂ fluid inclusion of 0.7 g/cm³ in spinel assuming $P_{\text{ill}} = 10$ mW and $B = 6.0$ °C/mW, the inclusion temperature during the analysis reaches 85 °C; the Δ would drop by 0.16 cm⁻¹ lower than the true value according to Eq. 8 of Sublett et al. (2020). Results show that the density obtained from the measured Δ is 0.636 g/cm³, which is 9% lower than the true value. If we calculate the CO₂ trapping depth based on this density and assuming 1000°C, then the result would be 0.28 GPa, which is 0.06 GPa lower than the true depth (0.34 GPa). Pressures are calculated following the method described by Pitzer and Sterner (1994). Because this deviation is much larger than the uncertainty of depth derived from the error in the temperature estimation (± 30 °C corresponding to ± 0.01 GPa), laser heating can be a major source of error. However, for inclusions with $B = 1.0$ °C/mW, such as those hosted in olivine and pyroxene, the underestimate of depth provenance is only 0.01 GPa, which is in similar range to the error derived from the temperature estimation. Therefore, the effect of laser heating is not so great. Therefore, although correcting the effects that laser heating will give data closer to the true values, such corrections are not necessarily required for the geological application when inclusions have small B .

Results of this study show that the use of the lowest P_{ill} can reduce the deviation of the measured Raman spectral feature from the true value. Therefore, the Raman data obtained under such conditions will be approximately equal to the true value. Corrections for the effects of laser heating are not always necessary because those effects depend on the quality of the data which the researcher desires. However, at least when comparing data obtained from different mineral species, the presence or absence of laser heating effect should be described. In addition, if the laser heating effect on the measured values is not negligible, we recommend reporting of how the ideal measurement conditions were reached and what corrections were made to the raw data to interpret them.

8. Conclusions

Two independent experiments and heat transport simulations were combined to determine the laser heating coefficient (°C/mW) of the inclusions hosted in olivine, orthopyroxene, clinopyroxene, spinel, and quartz. We identify the influential parameters on the laser heating of the

inclusions during Raman spectroscopic analysis. One of the two experimental methods estimates B from the slope of the linear fitting of the inclusion temperature and P_{ill} obtained with a hot band thermometer. In the other method, B was estimated by determining the minimum laser power required to homogenize the fluid when the laser is irradiated to the fluid inclusion at a condition where the homogenization temperature is slightly higher than the room temperature. Although these two methods were used to obtain B , B obtained using a hot band thermometer (B_{Raman}) is probably more reliable than that obtained by homogenization observation (B_{Th}) because B_{Th} is likely to be underestimated.

Using both methods, the average B of inclusions in each host mineral was in the order of (quartz $\ll$) olivine $<$ opx $\approx$ cpx $\ll$ spinel. Because this order is equal to the order of α_{h} , except that clinopyroxene and orthopyroxene are in reverse order, the most influential experimental parameter on B would be α_{h} , as suggested by earlier studies and my simulations. Aside from the α_{h} , the host mineral thickness and size and the heat transport at the boundaries can be the main factors that control B . Therefore, it is possible to reduce B to some extent by adjusting the shape of the host mineral during the sample preparation process. However, the radius and depth of inclusions have little effect on B if $\alpha_{\text{h}} > \alpha_{\text{inc}}$. Therefore, if researchers find that the physicochemical properties of inclusions measured by Raman spectroscopic analysis depend on the inclusion size or the distance from the sample surface, then laser heating can be excluded from the cause of that dependence.

For small host minerals and translucent minerals such as Cr-spinel, the temperature of the inclusions can rise tens or hundreds of degrees, even with the laser power typically used for inclusion analysis. For such situations in which the effects of laser heating are unavoidable, we propose some recommendations for the correction of laser heating effects on measured Raman spectra features. With such treatment, even if the Raman spectral features are altered by laser heating, results obtained from Raman spectroscopy become accurate.

Acknowledgements

Part of Chapter 1 was published as a paper titled “Experimental variable effects on laser heating of inclusions during Raman spectroscopic analysis” in *Chemical Geology* in January 2021. This achievement was greatly facilitated by the comments and support of co-authors Kenta Yoshida, Akira Yoneda, Junji Torimoto, and Junji Yamamoto.

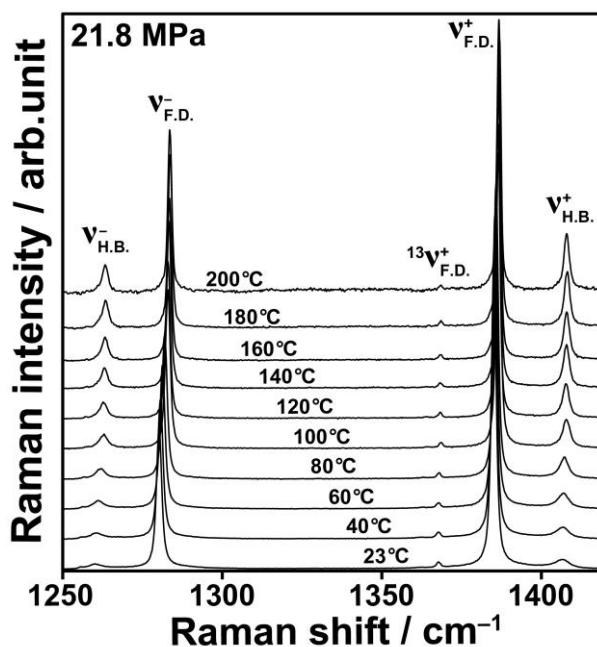
I thank Takashi Yoshino for his help in using joint-use facilities of the Institute for Planetary Materials, Okayama University. I thank R. J. Bakker and an anonymous reviewer for constructive reviews that greatly improved this part of manuscript.

Appendix: Supporting information

Supplementary data to Chapter1 (TableS1-1 to S1-7) can be found online at <https://doi.org/10.1016/j.chemgeo.2020.119928>.

S-1. Experimental calibration for the relation between density, temperature, and hot band to Fermi diad intensity ratio

A CO₂ molecule has four vibration modes: a symmetric stretching mode (ν_1), an antisymmetric stretching mode (ν_3), and two bending modes (ν_{2a} and ν_{2b}). Two strong bands at 1388.2 cm⁻¹ ($\nu_{F.D.}^+$) and 1285.4 cm⁻¹ ($\nu_{F.D.}^-$) are designated as the ν_1 - $2\nu_2$ Fermi diad (Gordon and McCubbin, 1966) (Fig. S1-1). The $2\nu_2$ and ν_1 modes have almost equal energies and identical symmetry species. Therefore, they perturb each other in the excited state through Fermi resonance (Fermi, 1931). Two peaks with much lower intensity next to the Fermi diad (1264.8 and 1409.0 cm⁻¹; $\nu_{H.B.}^-$ and $\nu_{H.B.}^+$) are designated as hot bands. For estimating CO₂ fluid temperature during Raman analysis, hot band thermometer have been developed by using high pressure optical cell (HPOC) (Rosso and Bodnar, 1995; Arakawa et al., 2008; Hagiwara et al., 2018).



FigureS1-1 Raman spectra of CO₂ fluids containing the two main bands of the Fermi diad of ¹²CO₂ ($\nu_{F.D.}^-$ and $\nu_{F.D.}^+$) and the hot bands ($\nu_{H.B.}^-$ and $\nu_{H.B.}^+$). The peak at 1369.4 cm⁻¹ is attributed to the ¹³C¹⁶O₂ isotopic species ($^{13}\nu_{F.D.}^+$). Temperature effects on Raman spectra of CO₂ at constant pressure, 21.8 MPa. Intensity of both $\nu_{H.B.}^-$ and $\nu_{H.B.}^+$ increase monotonically with temperature.

Since the experimental calibrations of earlier studies do not cover P – T conditions of my interest, to expand applicable P – T range of this method to higher pressure and temperature, we measured Raman spectra of CO₂ from 23 to 200 °C in approximately 20 °C increments under 10 temperature conditions. Specific temperature, pressure, and density conditions are plotted in Fig. 1-3 and listed in Table S1-1. Fluid densities are calculated according to equation of state of Span and Wagner (1996). A detailed description of the experimental apparatuses used for high-pressure Raman spectroscopic investigation is presented in Hagiwara et al. (2020). We pressurized the CO₂ fluid gradually while maintaining the temperature constant. Furthermore, we measured the Raman spectra twice under each P – T condition. To remove air from the high-pressure system, the high-pressure line was flushed with CO₂ (99.99% purity; Sun Chemical Corp.) for about 30 s before pressurizing the fluid. The temperature was measured using a K-type thermocouple placed in direct contact with the fluid. The fluid temperature during analysis was kept to uncertainty below ± 0.2 °C through PID control of the cartridge heater. The room temperature was 22.1–23.6 °C throughout the analysis. We measured pressures using a PG-2TH digital pressure transducer with a manometer (WGA-650A; Kyowa Electronic Instruments Co., Ltd.). The overall accuracy of the pressure transducer was $\pm 0.2\%$. The accuracy compensation temperature of the pressure gauge is –10 to 70 °C. We concluded that the area near the pressure gauge is near room temperature and that it is sufficiently lower than 70 °C because the pressure gauge and HPOC are connected by sufficiently long stainless steel pressure-transmitting tubing (0.01 inch inner diameter, 1/16 inch outer diameter, and 1 m length) to thermal equilibrium with room temperature. Therefore, we ignored the temperature-dependence of the pressure gauge. The pressure changes during analyses was less than ± 0.1 MPa.

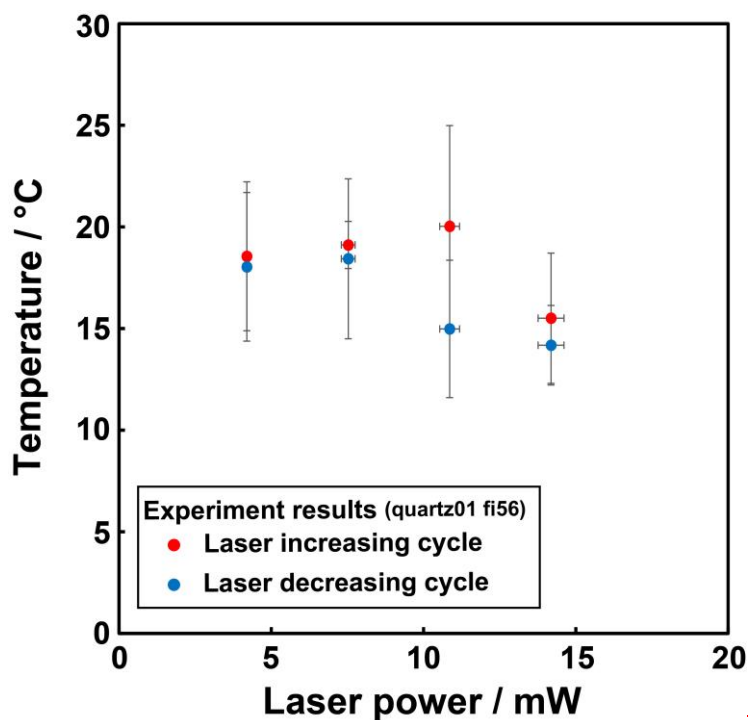
Raman spectra of the CO₂ fluid were obtained using a micro-Raman spectrum analysis system set up at the Hokkaido University Museum, with 1,800 grooves/mm grating. Raman spectra were acquired using diode-pumped solid-state laser (532 nm, Gem 532; Laser Quantum) excitation, a spectrometer with 75 cm focal length (Acton SP-2750; Princeton Instruments, Inc.), and a CCD camera (1650 $\times$ 200 pixels, 16- μ m width, iVac; Andor Technology). A Nikon microscope (ECLIPSE E600-POL) with a $\times 10$ (T Plan SLWD; Nikon Corp.; N.A. = 0.2) objective was used to focus on the samples.

The intensity of Raman spectra was calibrated using a tungsten bulb. Relative intensity correction factor can be used to correct the measured spectra for the energy-dependent sensitivity of the system by multiplying the correction function by the raw spectrum. The intensity correction was

performed using a spectrum data processing software (GRAMS/AI) and the files containing the relative intensity correction factor. In this study, using the software, baseline correction was performed with liner function between 1,200 and 1,450 cm^{-1} , and then each CO_2 band was fitted to a Gaussian and Lorentzian mixing curve. Spectra were collected in a single window ranging from 1007.53 to 1485.58 cm^{-1} . The duration of every Raman analysis is 200 s. The laser power was approx. 15 mW at the sapphire window surface.

S-2. Correction for measured hot band to Fermi diad intensity ratio obtained from natural fluid inclusions

To confirm whether the relation between ρ , T , and $[I_{H.B.}^+ + I_{H.B.}] / [I_{F.D.}^+ + I_{F.D.}]$ of natural fluid inclusions is in consistent with Eq. 1-5, the CO_2 -rich fluid inclusions in quartz with a known density (0.786 g/cm^3) are heated externally using a Linkam stage and the relation between them was



FigureS1-2 Measured fluid temperature as a function of laser power for the fluid inclusion in quartz (quartz01 fi56). Red and blue circles represent the data measured along laser increasing and decreasing cycles, respectively. Error bars for temperature and laser power are standard deviation ($n = 5$) and 3%, respectively (Table S1-2). There is no significant positive relation between fluid temperature and laser power. Therefore, I excluded the possibility of the contribution of heat generation from the silver block of Linkam stage on measured laser heating coefficient during Raman analysis.

determined and compared with Eq. 1-5. These experiments were conducted using Raman systems setup at Hokkaido University Museum. The analytical conditions are the same as those described in section 5.2. Hot band to Fermi diad intensity ratios were obtained at 26, 40, 60, 80, and 100 °C with both temperature increasing and decreasing cycles. Each measured hot band to Fermi diad intensity ratio was average of 5 measurements. Measurements were performed at 7.7 mW, which is sufficiently low power to avoid laser heating for quartz (Fig. S1-2 and Table S1-2).

If the laser heating effect is negligible, sensitivity calibrated $[I_{H.B.}^+ + I_{H.B.}]/[I_{F.D.}^+ + I_{F.D.}]$ of a certain CO₂ fluid inclusion with known ρ_{Th} obtained at known T ($([I_{H.B.}^+ + I_{H.B.}]/[I_{F.D.}^+ + I_{F.D.}])_i^{sens. calib, ave}$) should be equal to those obtained by substituting ρ_{Th} and T into Eq. 1-5 ($([I_{H.B.}^+ + I_{H.B.}]/[I_{F.D.}^+ + I_{F.D.}])_i^{calc}$). However, $([I_{H.B.}^+ + I_{H.B.}]/[I_{F.D.}^+ + I_{F.D.}])_i^{sens. calib, ave}$ were always higher than $([I_{H.B.}^+ + I_{H.B.}]/[I_{F.D.}^+ + I_{F.D.}])_i^{calc}$ (Table S1-4). The average difference between measured and calculated intensity ratio was 0.0075 and its standard deviation was 0.0015 ($n = 9$). Therefore, there is significant difference between them. The cause of this mismatch is unknown, but all the difference between the measured and calculated values were almost constant (Table S1-4). Therefore, to correct the mismatch between measured and calculated intensity ratio, measured ratios are translated using a certain value $\delta_{HB/FD}$ that represents the deviation of intensity ratio at a given T and ρ . Using 9 hot band to Fermi diad intensity ratios, correction term $\delta_{HB/FD}$ can be found by optimizing the following residual sum of squares (RSS) to the minimum.

$$RSS = \sum_i^n \left(\left(\frac{I_{HB}^+ + I_{HB}}{I_{FD}^+ + I_{FD}} \right)_i^{sens. calib, ave} - \left\{ \left(\frac{I_{HB}^+ + I_{HB}}{I_{FD}^+ + I_{FD}} \right)_i^{calc} - \delta_{HB/FD} \right\} \right)^2. \quad (S1-1)$$

As a result, I derived $\delta_{HB/FD} = -0.0075$. Data used for calculation are presented in Table S1-4. Corrected hot band to Fermi diad intensity ratios are plotted as square (increasing cycle) and triangle (decreasing cycle) symbols on Fig. 1-3. It is confirmed that the relation between ρ , T , and $[I_{H.B.}^+ + I_{H.B.}]/[I_{F.D.}^+ + I_{F.D.}]$ of the natural fluid inclusion is almost the same as that obtained in the HPOC experiment by adding the correction term $\delta_{HB/FD}$ to $([I_{H.B.}^+ + I_{H.B.}]/[I_{F.D.}^+ + I_{F.D.}])_i^{sens. calib, ave}$ (Fig. 1-3). Similarly, to correct the data obtained at Japan Agency for Marine-Earth Science and Technology, I calculated $\delta_{HB/FD}$ using 2 data measured at approx. 21 °C and derived $\delta_{HB/FD} = -0.0101$ (Table S1-5).

S-3. Waist-radius estimation

The theoretical diffraction-limited waist-radius and Rayleigh range are calculated as $w_0 = \lambda/(\pi NA)$ and $z_0 = (\pi w_0^2)/\lambda$, respectively. However, actual waist-radius can be broadened primarily due

to a discrepancy between the ideal divergence angle of a Gaussian beam and reality and the intrinsic asymmetry of the incident beam. Therefore, before performing heat transport simulation, I evaluate the actual spot-size of the excitation beam.

For waist-radius estimation, the bitmap image of the spot reflected from the surface of a silicon wafer is extracted in ASCII format in 24-bit or 32-bit red, green, and blue intensity matrices, and converted them to 8-bit greyscale images using imageJ software. I determined the pixel resolution of image ($\mu\text{m}/\text{pixel}$) by using microscale for each objective. Measurement of actual waist-radius can be performed by fitting greyscale image to following 2D Gaussian profile.

$$z = I \times \exp \left\{ -\frac{1}{2} \left\{ \frac{(x \cos \theta + y \sin \theta - x_c \cos \theta - y_c \sin \theta)^2}{\omega_1} \right\} - \frac{1}{2} \left\{ \frac{(-x \sin \theta + y \cos \theta + x_c \sin \theta - y_c \cos \theta)^2}{\omega_2} \right\} \right\}, \quad (\text{S1-2})$$

where z is the greyscale value, I is the estimated maximum greyscale value, x_c is the x center, y_c is the y center, ω_1 is the x width, ω_2 is the y width, and θ is the rotation angle of 2D gaussian profile. In this study, the waist-radius was defined by $1/e^2$ width. The cross-sectional area of the 2D Gaussian function at $1/e^2 \sim 0.135$ times the maximum value of the intensity (that is, the $z = I/e^2$ plane) is obtained by substituting $z = I/e^2$ into the Eq. S1-2 and represented by:

$$\left\{ \left(\frac{x \cos \theta + y \sin \theta - x_c \cos \theta - y_c \sin \theta}{\omega_1} \right)^2 + \left(\frac{-x \sin \theta + y \cos \theta + x_c \sin \theta - y_c \cos \theta}{\omega_2} \right)^2 \right\} = 4. \quad (\text{S1-3})$$

Algebraically, Eq. S1-3 can be rearranged to yield generalized ellipse: $Ax^2 + 2Hxy + By^2 + 2Gx + 2Fy + C = 0$. Area of generalized ellipse is given by:

$$\text{Area} = \frac{\pi \times (AF^2 + BG^2 + CH^2 - ABC - 2FGH)}{(AB - H^2)^{1.5}}. \quad (\text{S1-4})$$

By combination of Eqs. S1-2 to S1-4, a cross-sectional area where the laser intensity is $1/e^2$ is obtained. In this study, the equivalent circle radius of the obtained cross section was defined as the actual waist-radius. The calculated actual waist-radius for each objective is $1.46 \mu\text{m}$ for LU Plan $\times 50$ (used at Hokkaido University) and $1.0 \mu\text{m}$ for TU Plan $\times 50$ (used at Japan Agency for Marine-earth Science and Technology).

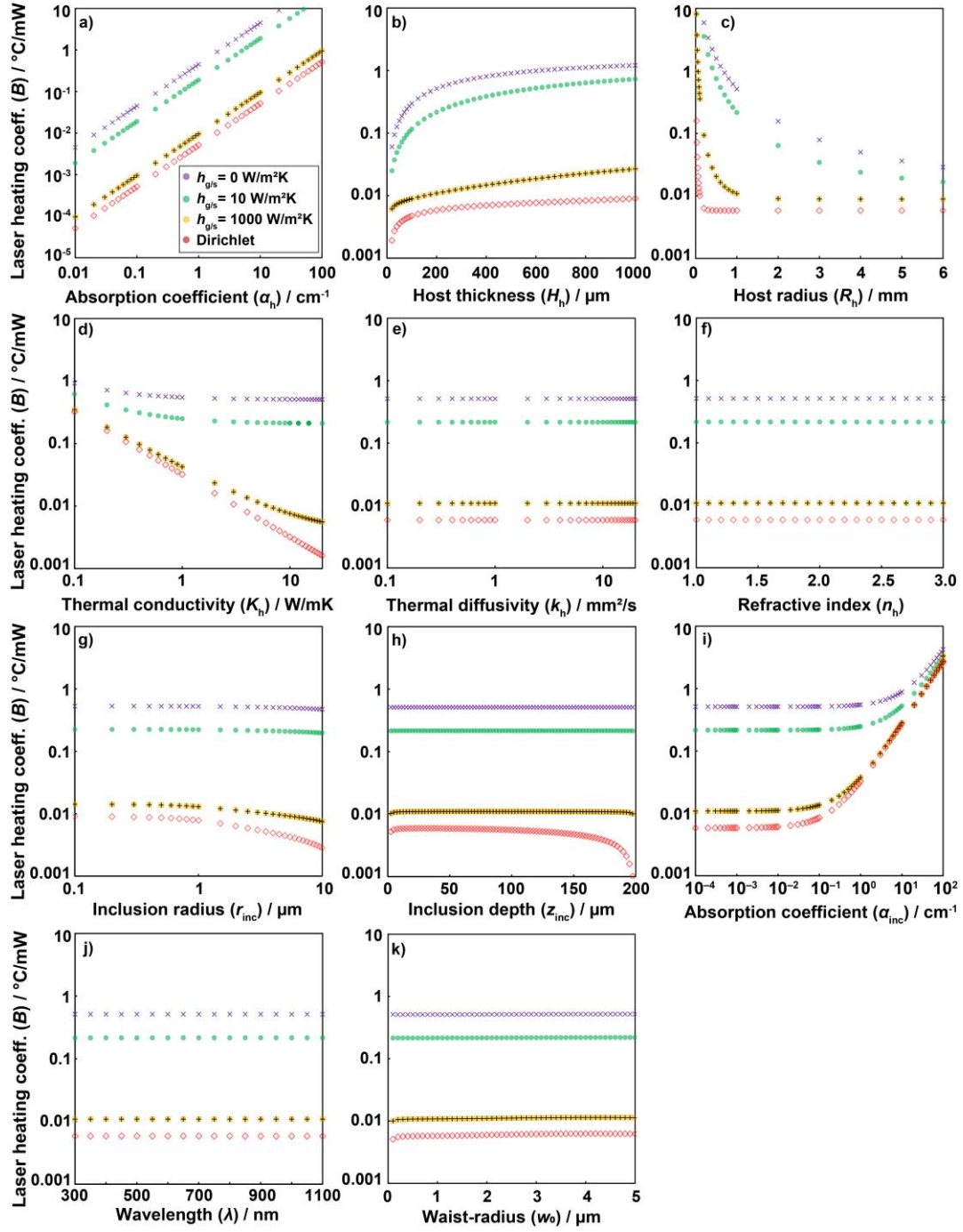
S-4. Time required for temperature reaches 90% of its steady state value as functions of experimental, geometrical, and optical variables

In the section 6.1.2, I assessed the effect of experimental, optical, and geometrical

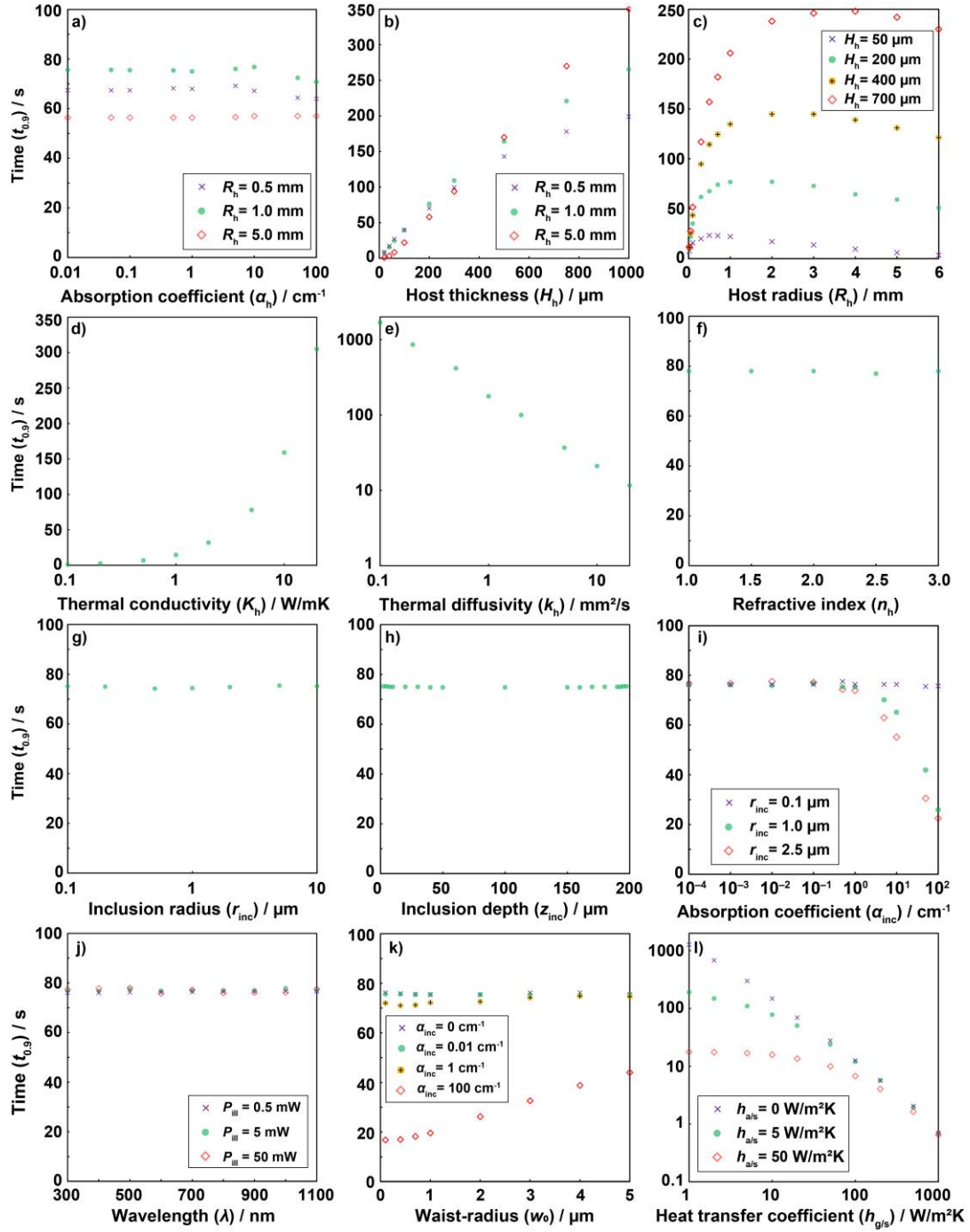
parameters on B by assuming stationary temperature distribution (Figs. 1-8 and S1-3). However, since such parameters can influence on the processes of the system reaches its steady state, it is important to access the effect of these parameters. Fig. S1-4 shows the time required for temperature reaches 90% of its steady-state value ($t_{0.9}$) as functions of those parameters.

K_h and k_h had a major effect on $t_{0.9}$ among the thermal transport and optical parameters specific to the host mineral (α_h , K_h , k_h , and n_h): K_h has positive correlation with $t_{0.9}$ and $t_{0.9}$ follows an exponential decay with k_h (Fig. S1-4d and S1-4e). On the other hand, n_h and α_h have no effect on $t_{0.9}$ (Figs. S1-4a and S1-4f). At least in the thickness of 20 to 1000 μm , $t_{0.9}$ increases monotonically with H_h , but its slope depends somewhat on R_h (Fig. S1-4b). On the other hand, the relations between R_h and $t_{0.9}$ is not monotonous, and $t_{0.9}$ increases rapidly with R_h until it reaches the maximum value, but after that, $t_{0.9}$ gradually decreases with R_h (Fig. S1-4c). Regarding inclusion parameters, both z_{inc} and r_{inc} have no effect on $t_{0.9}$ (Figs. S1-4g and S1-4h). Similarly, α_{inc} does not affect $t_{0.9}$ for α_{inc} lower than 10^{-1} – 10^0 cm^{-1} . However, $t_{0.9}$ decreases with α_{inc} for α_{inc} higher than 10^{-1} – 10^0 cm^{-1} (Fig. S1-4i). Fig. S1-4j evaluates the effect of λ on $t_{0.9}$ at constant α_h . As a result, λ has no effect on $t_{0.9}$. In addition, P_{ill} does not affect $t_{0.9}$ (Fig. S1-4j). At $\alpha_{\text{inc}} = 100$ or 1 cm^{-1} , a positive correlation between $t_{0.9}$ and α_{inc} was observed, but at $\alpha_{\text{inc}} = 0$ or 0.01 cm^{-1} , $t_{0.9}$ was constant regardless of w_0 (Fig. S1-4k). On the other hand, $t_{0.9}$ strongly depends on both $h_{\text{a/s}}$ and $h_{\text{g/s}}$ (Fig. S1-4l). Higher heat transfer coefficients are associated with lower $t_{0.9}$. I also simulated $t_{0.9}$ as functions of these parameters under four boundary conditions: $h_{\text{g/s}} = 0, 10, 1000 \text{ W/m}^2\text{K}$, and Dirichlet boundary condition ($T = 25 \text{ }^\circ\text{C}$ at the boundary) (Fig. S1-5). For all simulation conditions, $t_{0.9}$ was found to be highly dependent on the boundary condition: $t_{0.9}$ decrease with increasing $h_{\text{g/s}}$. Furthermore, for all conditions, $t_{0.9}$ was minimized when the glass–sample boundary was Dirichlet condition.

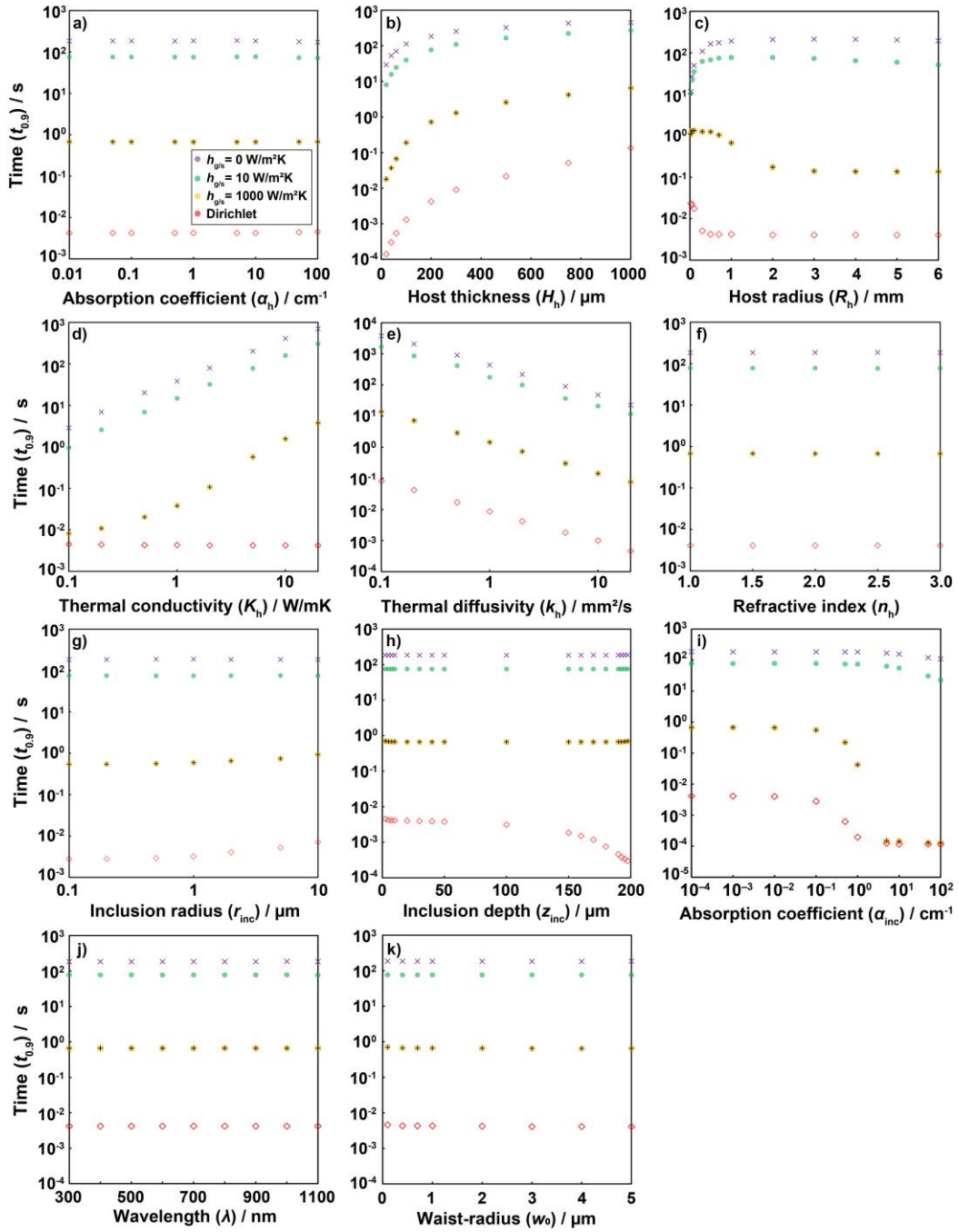
In summary, H_h , R_h , K_h , k_h , $h_{\text{a/s}}$, and $h_{\text{g/s}}$ can be the primary parameters which can change $t_{0.9}$ more than one order of magnitude within the range of my simulation conditions. On the other hand, α_h , n_h , r_{inc} , z_{inc} , and λ do not affect $t_{0.9}$. In addition, α_{inc} and w_0 have little impact on $t_{0.9}$. Therefore, from my simulations, the extremely small $t_{0.9}$ reported by Català et al. (2017) will be due to assumption of high heat flux at the boundary (see more detail in section 6.1.3).



FigureS1-3 Simulated laser heating coefficient as functions of a-f) host mineral, g-i) inclusion, and j-k) experimental parameters. Purple, green, yellow, and red symbols represent $h_{g/s} = 0, 10, 1000$ W/m²K, and Dirichlet boundary condition ($T = 25$ °C), respectively. Parameters used for simulations are basically as follows otherwise used as variables: $T_{\text{sample}} = 25$ °C, $\lambda = 532$ nm, $P_{\text{ill}} = 5$ mW, $w_0 = 1.46$ μm, $\alpha_{\text{inc}} = 0$ m⁻¹, $z_{\text{inc}} = 10$ μm, $r_{\text{inc}} = 2.5$ μm, $K_{\text{inc}} = 0.08$ W/mK, $k_{\text{inc}} = 0.02$ mm²/s, $H_h = 200$ μm, $R_h = 1$ mm, $K_h = 5.5$ W/mK, $k_h = 2.05$ mm²/s, $\alpha_h = 114$ m⁻¹, $n_h = 1.65$, $h_{a/s} = 5$ W/m²K, and $h_{g/s} = 10$ W/m²K.



FigureS1-4 Simulated time required for temperature reaches 90% of its steady-state value as functions of a-f) host mineral, g-i) inclusion, and j-l) experimental parameters. Parameters used for simulations are basically as follows otherwise used as variables in each figure: $T_{\text{sample}} = 25 \text{ }^\circ\text{C}$, $\lambda = 532 \text{ nm}$, $P_{\text{ill}} = 5 \text{ mW}$, $w_0 = 1.46 \mu\text{m}$, $\alpha_{\text{inc}} = 0 \text{ m}^{-1}$, $z_{\text{inc}} = 10 \mu\text{m}$, $r_{\text{inc}} = 2.5 \mu\text{m}$, $K_{\text{inc}} = 0.08 \text{ W/mK}$, $k_{\text{inc}} = 0.02 \text{ mm}^2/\text{s}$, $H_h = 200 \mu\text{m}$, $R_h = 1 \text{ mm}$, $K_h = 5.5 \text{ W/mK}$, $k_h = 2.05 \text{ mm}^2/\text{s}$, $\alpha_h = 114 \text{ m}^{-1}$, $n_h = 1.65$, $h_{a/s} = 5 \text{ W/m}^2\text{K}$, and $h_{g/s} = 10 \text{ W/m}^2\text{K}$.

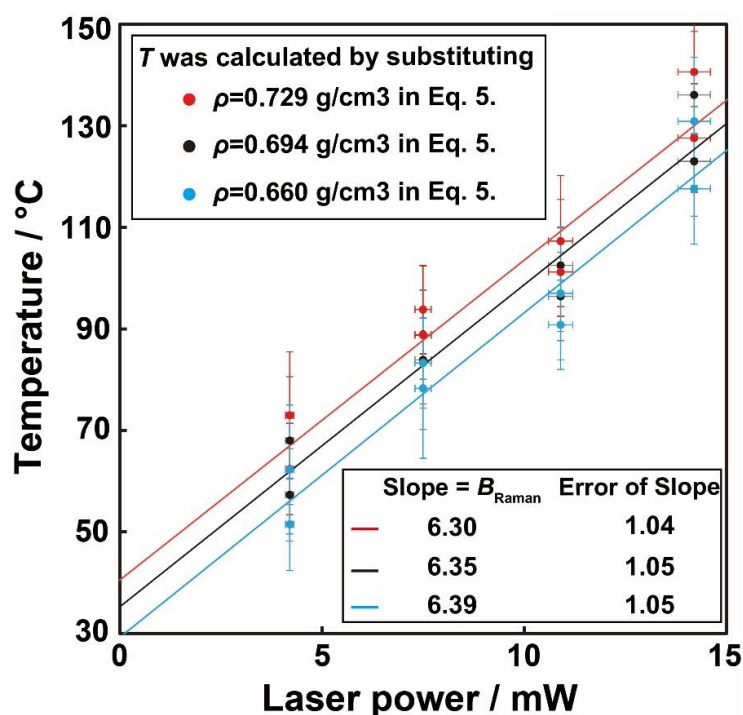


FigureS1-5 Simulated time required for temperature reaches 90% of its steady-state value as functions of a-f) host mineral, g-i) inclusion, and j-k) experimental parameters. Purple, green, yellow, and red symbols represent $h_{g/s}=0, 10, 1000 \text{ W/m}^2\text{K}$, and Dirichlet boundary condition ($T=25 \text{ }^\circ\text{C}$), respectively. Parameters used for simulations are basically as follows otherwise used as variables in each figure: $T_{\text{sample}} = 25 \text{ }^\circ\text{C}$, $\lambda = 532 \text{ nm}$, $P_{\text{ill}} = 5 \text{ mW}$, $w_0 = 1.46 \text{ } \mu\text{m}$, $\alpha_{\text{inc}} = 0 \text{ m}^{-1}$, $z_{\text{inc}} = 10 \text{ } \mu\text{m}$, $r_{\text{inc}} = 2.5 \text{ } \mu\text{m}$, $K_{\text{inc}} = 0.08 \text{ W/mK}$, $k_{\text{inc}} = 0.02 \text{ mm}^2/\text{s}$, $H_h = 200 \text{ } \mu\text{m}$, $R_h = 1 \text{ mm}$, $K_h = 5.5 \text{ W/mK}$, $k_h = 2.05 \text{ mm}^2/\text{s}$, $\alpha_h = 114 \text{ m}^{-1}$, $n_h = 1.65$, $h_{a/s} = 5 \text{ W/m}^2\text{K}$, and $h_{g/s} = 10 \text{ W/m}^2\text{K}$.

S-5. Potential errors in laser heating coefficients caused by uncertainties in density estimation by microthermometry

Fluid inclusion density is determined from homogenization temperature and using the equations of state of Span and Wagner (1996). However, the inclusions used in this study have compositions of approximately binary H₂O-CO₂, whereas the EOS of Span and Wagner (1996) are given for pure CO₂ only. According to Wang et al (2019), the presence of water can lead to uncertainties in density estimation by microthermometry.

To investigate the effect of density perturbations on B , I calculated B variation when the density varies by $\pm 5\%$. Since fluid density can be generally determined with an accuracy of ± 0.001 g/cm³ (corresponding to $\pm 0.14\%$ at 0.7 g/cm³) by microthermometry, $\pm 5\%$ error considered here is much larger than would be expected. A spinel03 fi163 was used as an example of the calculation because I obtained the highest temperature from this sample by hot band thermometer. The density of



FigureS1-6 Relations between laser power and temperature of a fluid inclusion in spinel (En2A spinel03 fi163). The density of this fluid inclusion is 0.694 g/cm³. The temperature is calculated by substituting the hot-band to Fermi diad intensity ratio and the three densities (0.694, 0.729, and 0.660 g/cm³) into Eq. 1-5, indicated by the black, red, and blue symbols, respectively. Even if there is a 5% uncertainty in the density substituted into Eq. 1-5, the resulting slope (i.e. B_{Raman}) is almost constant.

spinel03 fi163 is found to be 0.694 g/cm^3 by microthermometry, and the B_{Raman} is $6.35 \pm 1.05 \text{ (}^\circ\text{C/mW)}$. A change in density of $\pm 5\%$ results in a density of 0.729 and 0.660 g/cm^3 , respectively. Substituting the hot band to Fermi diad intensity ratio and density into Eq. 1-5, and plotting the relation between temperature and laser power, I get Fig. S1-6.

As can be seen from Fig. S1-6, even if there is a large error of 5% in the density estimate, the resulting slope (i.e., B_{Raman}) is almost identical to the value of $6.35 \text{ }^\circ\text{C/mW}$ (6.30 - 6.39). Thus, the effect of density fluctuation on B is negligible because variability of B derived from the density uncertainty ($\pm 0.05 \text{ }^\circ\text{C/mW}$) is much smaller than the error of slope derived from the analytical error of each point ($\sim \pm 1.05 \text{ }^\circ\text{C/mW}$). This is because $d[I_{H.B.}^+ + I_{H.B.}]/[I_{F.D.}^+ + I_{F.D.}]/dT$ is almost density-independent in Eq. 1-5. Therefore, even if there is a considerably large uncertainty in the density estimation, the method is very robust because density has little effect on the obtained B_{Raman} .

Chapter2: 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

1. Introduction

Fluid inclusions with compositions approximated as CO₂-rich systems are common in many geologic environments, including hydrothermal ore deposits (Roedder, 1984; Klein and Fuzikawa, 2010; Bodnar et al., 2014), medium-grade to high-grade metamorphic rocks (Newton et al., 1980; Roedder, 1984; Lamb et al., 1987; Touret, 2001; Lamadrid et al., 2014b), and mantle xenoliths (Roedder, 1984; Andersen and Neumann, 2001; Frezzotti et al., 2012a). In many geological settings, the density of those fluid inclusions has been studied to track volcanic plumbing systems (Hansteen et al., 1998; Zanon and Frezzotti, 2013; Levresse et al., 2016; Oglialoro et al., 2017), to ascertain the depth provenance of mantle xenoliths (Yamamoto et al., 2002; Yamamoto et al., 2007; Bali et al., 2008; Yamamoto et al., 2012; Yamamoto et al., 2014), and to identify the pre-eruptive volatile contents of magmas (Moore et al., 2015; Robidoux et al., 2018; Hanyu et al., 2020; Mironov et al., 2020; Venugopal et al., 2020; Allison et al., 2021). Although microthermometry is the principal method for estimating the density of CO₂-rich inclusions, this method is effective only when inclusion is sufficiently large to measure the CO₂ homogenization temperature accurately because change in the fluid phase is determined using an optical microscope. This size limitation is generally approximately 5 μm (Rosso and Bodnar, 1995). Furthermore, if the host mineral has a large absorption coefficient of visible light, then measuring the homogenization temperature might be difficult, even for inclusions larger than 5 μm . Additionally, because the accuracy decreases at low and extremely high densities, microthermometry is applicable only when the density of CO₂ inclusions is 0.65–1.18 g/cm³ (Kobayashi et al., 2012).

Raman spectroscopy is used as an alternative or complementary technique to estimate CO₂ fluid density when estimating fluid density by microthermometry is difficult. The method is applicable to a wide density range of 0.0–1.24 g/cm³ and to small inclusions down to sub-micrometer size and to inclusions in colored minerals, where the homogenization temperature is difficult to measure, as long as Raman scattering photons with a sufficient number for quantitative analysis reach the detector (Kobayashi et al., 2012). The fluid density is estimated using the density-dependence of the wavenumber difference of the two large peaks ($\nu_{\text{F.D.}}^+$ and $\nu_{\text{F.D.}}^-$) of the CO₂ Raman spectrum (Fig. 1). Raman-based CO₂ densimetry uses the relation between CO₂ fluid density (ρ) and Fermi

diad splitting ($\Delta = \nu_{\text{F.D.}}^+ - \nu_{\text{F.D.}}^-$). Although Raman CO₂ densimeter is useful, some caution is necessary for application of this method to density measurements of natural fluid inclusions: 1) Effect of intermolecular interactions between CO₂ and trace molecules other than CO₂ on the spectral properties of CO₂ (Seitz et al., 1996; Chen et al., 2004; Wang et al., 2011; Yuan et al., 2017; Lamadrid et al., 2018; Le et al., 2019; Wang et al., 2019; Hagiwara et al., 2020; Le et al., 2020; Sublett et al., 2020a), 2) discrepancy in the Δ - ρ relations derived in earlier studies (Lamadrid et al., 2017; Hagiwara et al., 2020), and 3) apparent density reduction because of the local temperature rise caused by excitation lasers (Hagiwara et al., 2021). Regarding the first problem, this method has been improved vigorously to quantify the fluid pressure in inclusions with various P - V - T - x properties. Its applicability is now expanding to include the CO₂ $\pm$ N₂ $\pm$ CH₄ (Seitz et al., 1996; Hacura, 1997; Wang et al., 2011; Lamadrid et al., 2018; Le et al., 2020; Sublett et al., 2020b) and CO₂-H₂O $\pm$ NaCl systems (Chen et al., 2004; Wang et al., 2011; Yuan et al., 2017; Wang et al., 2019; Hagiwara et al., 2020). The second difficulty can be resolved by adding to the measured Δ a correction term δ , which can be found by optimizing the residual sum of squares between the density estimated by any Δ - ρ relation from the Δ values of several standard fluid inclusions and the known density to the minimum (Hagiwara et al., 2020). Alternatively, in the region where the Δ - ρ relation can be approximated linearly, it is also effective to derive an original Δ - ρ relation applicable to the Raman system to be used, using two standard fluid inclusions with known density (Lamadrid et al., 2017). For the third one, because $(\partial\Delta/\partial T)_\rho$ is always negative, at least in the density range investigated by earlier studies (Wang et al., 2019; Sublett et al., 2020b), the density estimated from the measured Δ might be underestimated if the excitation laser causes unintended heating. Nevertheless, few examples exist to verify the conditions and the extent to which it affects the measurement accuracy (Hagiwara et al., 2021).

To assess the uncertainty that laser heating imposes on density estimation, one must ascertain the amount of change in Δ when the temperature of a fluid inclusion with a certain density ρ is increased unintentionally by $T^\circ\text{C}$ because of laser heating, i.e., $|(\partial\Delta/\partial T)_\rho|$. The value of $|(\partial\Delta/\partial T)_\rho|$ can be obtained directly from the Δ - ρ - T relation. Several attempts have been undertaken to characterize high P - T CO₂ Raman spectra (Bondarenko, 1986; Kawakami et al., 2003; Chen et al., 2004; Wang et al., 2011; Wang et al., 2019; Sublett et al., 2020b). The temperature dependence of Δ at a given density ($|(\partial\Delta/\partial T)_\rho|$) below 0.7 g/cm³ was found to be smaller for lower densities (Wang et al., 2019; Sublett et al., 2020b). However, regarding the density dependence of $|(\partial\Delta/\partial T)_\rho|$ at > 0.7 g/cm³, several studies have yielded somewhat different conclusions (Wang et al., 2011; Wang et al.,

2019; Sublett et al., 2020b). According to the Δ - ρ - T relation for pure CO₂ derived by Wang et al. (2019) using a high-pressure optical cell (HPOC), $|(\partial\Delta/\partial T)_\rho|$ becomes smaller at higher densities, greater than 0.7 g/cm³. However, when using the relation derived by Sublett et al. (2020b), $|(\partial\Delta/\partial T)_\rho|$ becomes larger at higher densities above 0.7 g/cm³, which is inconsistent with results reported by Wang et al. (2019). Therefore, some disagreement exists with results of earlier studies of density dependence of $|(\partial\Delta/\partial T)_\rho|$ conducted at densities higher than 0.7 g/cm³.

The density dependence of $|(\partial\Delta/\partial T)_\rho|$ is consistent at low densities but inconsistent at high densities in earlier studies perhaps because few data have been reported for earlier studies undertaken in conditions above ambient temperature and at densities higher than 1.0 g/cm³ (Fig. 2). For this study, I extended the pressure range of investigation markedly beyond that of earlier studies. I examined the Δ - ρ - T relation at 23–200°C and 7.2–248.7 MPa using a HPOC filled with pure CO₂ having density of 0.694–1.203 g/cm³. Based on the results, I acquired calibration curves to estimate density at various temperatures. Then I compared the curves with those obtained from published data. Results show that, for densities higher than 0.7 g/cm³, $|(\partial\Delta/\partial T)_\rho|$ was expected to become smaller with increasing density. Combined with results of earlier studies, $|(\partial\Delta/\partial T)_\rho|$ appears to reach a maximum value at around 0.6–0.7 g/cm³. The underestimation of density by laser heating is severest in this density region. Finally, to elucidate how the fluid density and physical properties of the host minerals affect the amount of fluid density underestimation by laser heating in the analysis of fluid inclusions, the value of Δ of CO₂-rich fluid inclusions with various densities in Cr-spinel and orthopyroxene was measured at various laser powers. The goal of this study is investigation of the Δ - ρ - T relation in the high-density region, which has not been investigated to date. The results can clarify the density dependence of $|(\partial\Delta/\partial T)_\rho|$ and suggest an analytical method to estimate the CO₂ density of natural fluid inclusions accurately from the measured Δ , even in the presence of laser heating.

2. CO₂ Raman spectra

Next, I briefly explain the CO₂ Raman peak configuration. A CO₂ molecule has four vibration modes: a symmetric stretching mode (ν_1), an antisymmetric stretching mode (ν_3), and two bending modes (ν_{2a} and ν_{2b}). Additionally, it is predicted to exhibit one Raman active (ν_1) and three IR active (ν_3 plus a degenerate ν_2 vibration) bands. By contrast, CO₂ has a characteristic Raman spectrum that includes multiple peaks in the adjacent region of 1250–1450 cm⁻¹ (Fig. 1). The wavenumber of the first overtone of the doubly degenerate bending vibration (ν_2) was approximately

equal to that of the predicted symmetric stretch (ν_1) vibration. Because two levels are sufficiently close together in energy and are of the same symmetry, they will be mutually repellent: one going up in energy and the other going down. This vibrational resonance, which shifts the wavenumbers away from their expected wavenumbers, is called Fermi resonance (Fermi, 1931). This Fermi resonance causes the excited admixed states to split into two strong CO₂ lines designated as the Fermi diad, with nominal wavenumbers of 1388.2 cm⁻¹ ($\nu_{F.D.}^+$; Fig. 1) and 1285.4 cm⁻¹ ($\nu_{F.D.}^-$; Fig. 1).

Several groups have improved CO₂ densimeters and have demonstrated the density dependence of the distance of the Fermi diad ($\Delta = \nu_{F.D.}^+ - \nu_{F.D.}^-$) (Wang and Wright, 1973; Wright and Wang, 1973; Bertrán, 1983; Garrabos et al., 1989a; Rosso and Bodnar, 1995; Yamamoto et al., 2002; Kawakami et al., 2003; Yamamoto and Kagi, 2006; Song et al., 2009; Fall et al., 2011; Wang et al., 2011; Lamadrid et al., 2017; Yuan et al., 2017; Le et al., 2019; Wang et al., 2019; Hagiwara et al., 2020; Le et al., 2020; Sublett et al., 2020b). Earlier studies have demonstrated that both Fermi diad bands increase monotonically with increasing temperature (Fig. 2-1a) (Wang et al., 2011; Yuan et al., 2017; Sublett et al., 2020b). Particularly, the lower Fermi diad band increases at a slightly higher

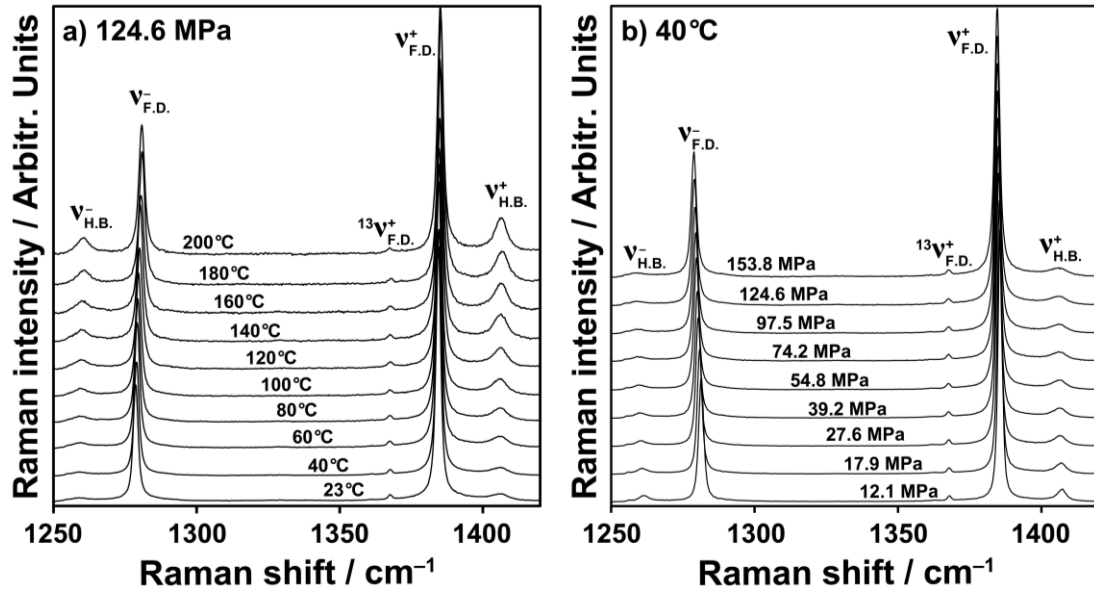


Figure 2-1 Raman spectra of CO₂ fluids containing the two main bands of the Fermi diad of ¹²CO₂ ($\nu_{F.D.}^-$ and $\nu_{F.D.}^+$) and the hot bands ($\nu_{H.B.}^-$ and $\nu_{H.B.}^+$). The peak at 1369.4 cm⁻¹ is attributed to the ¹³C¹⁶O₂ isotopic species ($^{13}\nu_{F.D.}^+$). (a) Temperature effects on the Raman vibrational wavenumbers of CO₂ at 124.6 MPa. Wavenumbers of both $\nu_{F.D.}^-$ and $\nu_{F.D.}^+$ increase monotonically with increasing temperature. (b) Effects of pressure on the Raman vibrational wavenumbers of CO₂ at 40°C. Wavenumbers of both $\nu_{F.D.}^-$ and $\nu_{F.D.}^+$ decrease monotonically with increasing pressure.

$\partial v/\partial T$ rate than the upper band. However, both Fermi diad bands decrease monotonically with increasing density (Fig. 2-1b) (Wright and Wang, 1973; Garrabos et al., 1980; Garrabos et al., 1989b; Wang et al., 2011). The lower Fermi diad band decreases at a slightly higher $|\partial v/\partial \rho|$ rate than the upper band (Wright and Wang, 1973; Garrabos et al., 1980; Garrabos et al., 1989b).

3. Experimental

3.1 High-pressure and high-temperature optical cell

I used a high-temperature and high-pressure cell (PC-400 ms; Syn Corp.) to investigate the temperature-dependence of Δ - ρ relations. The high-pressure cell can create a fluid with respective maximum pressure and temperature of 400 MPa and 200°C, but because the pressure resistance of the high-pressure generator is 200 MPa, the uppermost pressure is limited by the pressure resistance of the high-pressure generator. To measure the fluid at higher pressure than the resistance of the high-pressure generator, high-pressure fluid was generated using two pressurization methods. One is isothermal compression, by which pressure is applied with a hydraulic jack while maintaining the cell temperature constant. Using this method, measurements were performed from 23°C to 200°C in approximately 20°C increments under 10 temperature conditions. Under the experimental conditions, the CO₂ was single-phase. In addition, spectra were acquired up to 153.8 MPa under each temperature condition. I pressurized the CO₂ fluid gradually while maintaining the temperature constant. Furthermore, I measured the Raman spectra twice under each P - T condition. The P - T conditions measured using this method are shown by filled red squares on P - T projection of the CO₂ phase diagram calculated according to the explanation by Pitzer and Sterner (1994) EOS (Fig. 2-2). Regarding the other method, the pressure was increased at first to 153.8 MPa while maintaining the high-pressure cell at a low temperature (approx. -10°C) using a cryogen. Subsequently, I closed valve-1 between the cell and the high-pressure generator. I raised the cell temperature to the target. Using the latter method, I were able to generate fluid with pressures of 153.5–248.7 MPa, which is higher than the pressure resistance of the high-pressure generator. Using this method, after reaching the target temperature, the Raman spectrum was measured while gradually reducing the pressure by loosening valve-1 (Fig. 2-3). The measurements are repeated more than three times at each P - T condition. The measurements are taken at temperatures from 60°C to 200°C in 20°C increments under eight temperature conditions. The P - T conditions measured using the latter method are shown by the open blue squares in Fig. 2-2 together with P - T conditions measured in earlier studies using HPOC and fused silica capillary capsules (FSCC)

(Bondarenko, 1986; Fall et al., 2011; Wang et al., 2011; Le et al., 2019; Wang et al., 2019; Le et al., 2020; Sublett et al., 2020b). Detailed P – T measurement conditions are presented in Tables S2-1 and S2. Hereinafter, I designate the former and latter experiments respectively as “isothermal pressurization experiments” and “near isochoric heating experiments.”

Fig. 2-3 is a schematic drawing of the HPOC and its attached components. To remove air from the high-pressure system, the high-pressure line was flushed with CO₂ (99.99% purity; Sun Chemical Corp.) for about 30 s before pressurizing the fluid. The temperature was measured using a K-type thermocouple placed in direct contact with the fluid. The fluid temperature during analysis

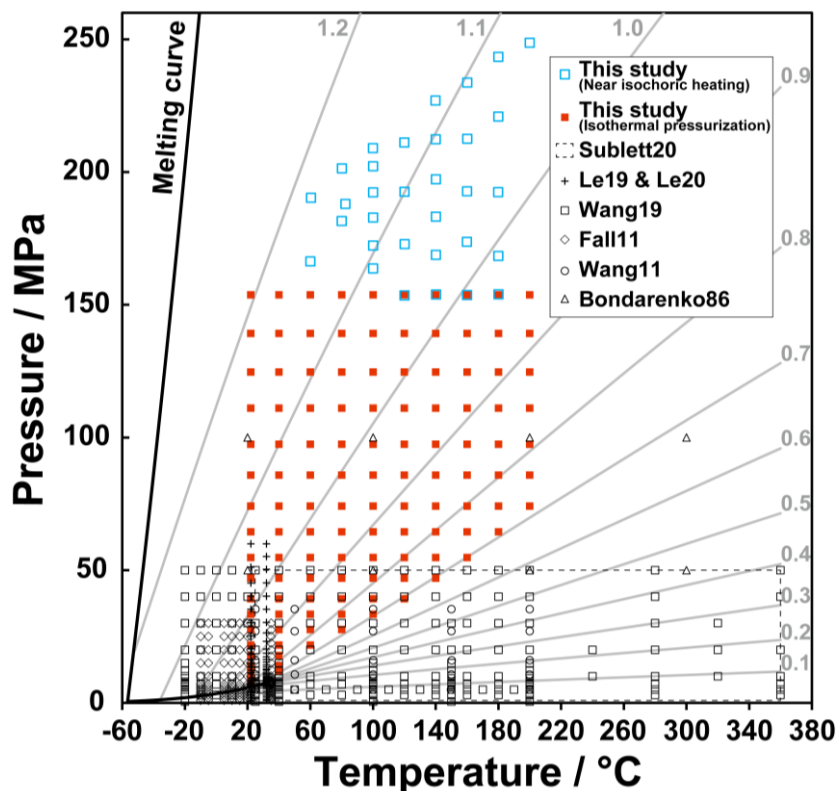


Figure2-2 P – T projection of the CO₂ phase diagram showing locations of all data measured for this study. Filled red squares show P – T conditions at which measurements are made using isothermal pressurization experiments. Open blue squares denote P – T conditions at which measurements are made using near isochoric heating experiments. The black symbols give P – T conditions under which measurements were made in earlier studies using a high-pressure optical cell and fused silica capillary capsule (Bondarenko, 1986; Fall et al., 2011; Wang et al., 2011; Le et al., 2019; Le et al., 2020; Sublett et al., 2020b). Black solid lines are phase coexistence curves. Grey ones are isochore calculated using Pitzer and Sterner (1994) EOS. Contours are labeled according to fluid density (g/cm³). The data shown are those presented in Tables S2-1 and S2-2.

was kept to uncertainty below $\pm 0.2^\circ\text{C}$ through PID control of the cartridge heater. The room temperature was $22.1\text{--}23.6^\circ\text{C}$ throughout the analysis. I measured pressures using a PG-2TH digital pressure transducer with a manometer (WGA-650A; Kyowa Electronic Instruments Co., Ltd.). The overall accuracy of the pressure transducer was $\pm 0.2\%$. The accuracy compensation temperature of the pressure gauge was -10 to 70°C . I inferred that the area near the pressure gauge was approximately room temperature and that it was sufficiently lower than 70°C because the pressure gauge and high-pressure cell were connected by sufficiently long stainless steel pressure-transmitting tubing (0.01 inch (0.03 cm) inner diameter, 1/16 inch (0.16 cm) outer diameter, 1 m length) to thermal equilibrium with room temperature. Therefore, I ignored the temperature dependence of the pressure gauge. The pressure changes during analyses of isothermal pressurization experiments and near isochoric heating experiments were, respectively, less than ± 0.1 MPa and ± 1.1 MPa. In the case of the near isochoric heating experiments, the pressure change during the analysis was large because of the large pressure difference between the high-pressure cell and generator.

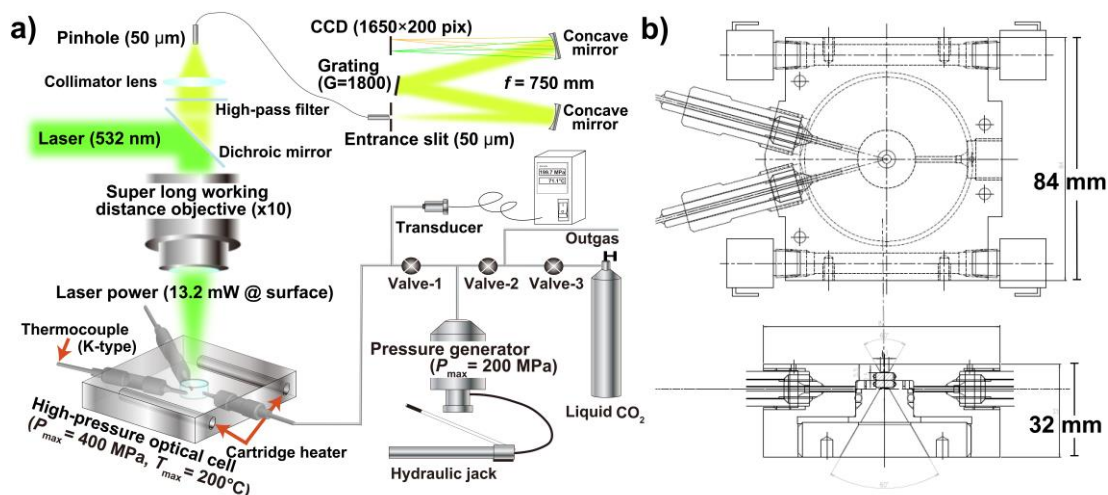


Figure 2-3 (a) Schematic diagram of experimental apparatus used for high- P - T Raman spectroscopic investigation. CO₂ is loaded into the HPOC from the right side through stainless steel tubing with outer diameter of 1/16 inch. During the near isochoric heating experiments, the fluid pressure in the cell was adjusted by gradually loosening valve-1. The excitation laser (532 nm) was focused on the CO₂ fluid through a 10 $\times$ objective lens. The laser power was 13.2 mW at the surface of optical window. (b) Cross-sections of the HPOC. It is equipped with a 2.5-mm-thick sapphire optical window that is transparent to visible light.

3.2 Measurement of Raman spectra of CO₂ in a HPOC at constant laser power

Raman spectra of the CO₂ fluid were obtained using a micro-Raman spectrum analysis system set up at the Hokkaido University Museum. Raman spectra were acquired during excitation by a diode-pumped solid-state laser (532 nm, Gem 532; Laser Quantum), and were acquired using a spectrometer with 75 cm focal length (Acton SP-2750; Princeton Instruments, Inc.) and a CCD camera (1650 × 200 pixels, 16 μm width, iVac; Andor Technology). A 50-μm core diameter multimode fiber served as the pinhole for confocality and as the entrance slit to the spectrometer. The laser power (P_{III}) was 13.2 mW at the sapphire window surface. The excitation laser was focused through a super long working distance 10× objective (T Plan SLWD; Nikon Corp.; N.A. = 0.2). The wavenumber dispersion for each pixel of the present Raman system when using a grating of 1800 lines/mm was 0.28 cm⁻¹/pixel at 1400 cm⁻¹. The accuracy in identification of peak position was enhanced further by application of a curve-fitting technique (Fukura et al., 2006). Earlier studies demonstrated that least-squares fitting improves precision by approx. 30 times compared to the value based on the detector pixel resolution (Izraeli et al., 1999; Fukura et al., 2006). Each CO₂ band was fitted to a Gaussian and Lorentzian mixing curve. Spectra were collected in a single window ranging from 1007.53 to 1485.58 cm⁻¹, which covers the main peaks of the Fermi diad of CO₂ and two well-established reference peaks of neon occurring at 1221.73 and 1449.19 cm⁻¹. Data were collected using two accumulations of 50 s or 100 s.

This study did not specifically examine the absolute value of the peak position, but instead emphasized investigation of the difference in the peak position of Fermi diad, which is not susceptible to the nonlinearity of the optical system. Nevertheless, to reduce mechanical errors in the optical system induced by changes in the measurement environment, the measured values were corrected using the atomic emission spectrum of the Ne lamp fixed to the optical system. Although Lamadrid et al. (2017) calibrated Δ using the two Ne lines appearing at 1031 and 1458 cm⁻¹ surrounding the Fermi diad, the Δ was calibrated using the following equation because the wavelengths of the excitation lasers used for this study differ from the wavelengths used for theirs.

$$\Delta_{\text{Ne calib}} = \Delta^{\text{raw}} \times \left(\frac{227.46}{\Delta_{\text{mes}}^{\text{Ne}}} \right) \quad (2-1)$$

In that equation, $\Delta_{\text{Ne calib}}$ denotes the corrected splitting of the Fermi diad, $\Delta_{\text{mes}}^{\text{Ne}}$ represents the measured separation between 1449.19 and 1221.73 cm⁻¹ Ne emission lines. Δ^{raw} stands for the measured splitting of Δ in the CO₂ Raman spectrum. Tables S2-1 and S2-2 show the wavenumber difference of corrected Δ ($\Delta_{\text{Ne calib}}$) together with the P – T conditions of the fluid.

3.3 Measurement of CO₂ Raman spectra as a function of laser power

3.3.1 HPOC experiments

To assess the temperature-dependence of Δ - ρ relations accurately, the local heating caused by the focused laser must also be considered because it might affect the Raman spectrum in a similar fashion to that by which the cartridge heater heats the HPOC and the fluids. A traditional means of finding a fluid temperature via Raman analysis is to measure the signal strengths of a particular Raman band at the Stokes and anti-Stokes positions and to calculate the temperature using a Boltzmann distribution of the ground and first excited state populations (Tuschel, 2016).

However, in the case of CO₂, the temperature measurement can be performed more accurately using two peaks with much lower intensity next to the Fermi diad (1264.8 and 1409.0 cm⁻¹; $\nu_{\text{H.B.}}^-$ and $\nu_{\text{H.B.}}^+$), designated as hot bands (Dickinson et al., 1929). Hot bands putatively arise from transitions that originate from excited vibrational states that are higher in energy than the ground vibrational state and which are attributable to the thermal energy of the molecules. The hot bands are also attributable to Fermi resonance between $\nu_1 + \nu_2$ and $3\nu_2$ (Herzberg, 1945). Earlier studies have assessed CO₂ hot band availability for use as a thermometer (Brown and Steeper, 1991; Rosso and Bodnar, 1995; Arakawa et al., 2008; Hagiwara et al., 2018; Hagiwara et al., 2021). These thermometers use the hot band to Fermi diad intensity ratio ($[I_{\text{H.B.}}^+ + I_{\text{H.B.}}^-] / [I_{\text{F.D.}}^+ + I_{\text{F.D.}}^-]$). Peak heights of $\nu_{\text{F.D.}}^+$, $\nu_{\text{F.D.}}^-$, $\nu_{\text{H.B.}}^+$, and $\nu_{\text{H.B.}}^-$ are represented respectively as $I_{\text{F.D.}}^+$, $I_{\text{F.D.}}^-$, $I_{\text{H.B.}}^+$, and $I_{\text{H.B.}}^-$. The latter thermometer is superior to the former thermometer because the anti-Stokes to Stokes intensity ratio is about an order of magnitude smaller than the hot band to Fermi diad intensity ratio in the studied P - T conditions. Moreover, obtaining both anti-Stokes and Stokes bands simultaneously requires measurement of a much wider wavenumber range, extending from -1280 cm⁻¹ (anti-Stokes peak of $\nu_{\text{F.D.}}^-$) to 1280 cm⁻¹ (Stokes peak of $\nu_{\text{F.D.}}^+$), compared to the wavenumber range required for hot band thermometers, extending from 1260 cm⁻¹ ($\nu_{\text{H.B.}}^-$) to 1410 cm⁻¹ ($\nu_{\text{H.B.}}^+$), resulting in lower wavenumber resolution. In the studied P - T region, temperature enhancement of about >4°C can be detected using a hot-band thermometer (Hagiwara et al., 2018). Therefore, to investigate the influence of the local laser heating, I monitored the change of Δ and hot band to Fermi diad intensity ratio while changing P_{III} at two pressure conditions: 7.2 and 153.8 MPa.

I measured Δ and the hot band to Fermi diad intensity ratio using the same 10× objective (T Plan SLWD, N.A. = 0.2; Nikon Corp.) and excitation laser (532 nm) as those used for the HPOC experiments. Measurements were made while changing P_{III} at the sample surface from 1.7 to 16.7 mW. The P_{III} during the experiments were measured using a laser power meter (PD300-ROHS; Ophir

Optronics Ltd.). The uncertainty of the measured P_{ill} was $\pm 3\%$. The fluid pressures were 7.2 MPa and 153.8 MPa at 23°C, respectively corresponding to 0.783 g/cm³ and 1.204 g/cm³. The spectrum was measured five times at each P_{ill} . Table 1 presents the results.

3.3.2 Natural fluid inclusions

I selected a total of seven CO₂-rich fluid inclusions hosted in mineral separates of orthopyroxene and Cr-spinel, which are derived from a mantle xenolith designated as “En2A” from Ennokentiev, Sikhote-Alin, Far Eastern Russia. Petrological descriptions were presented by Yamamoto et al. (2012). The fluid inclusion compositions were investigated using Raman

Table2-1 Variation of hot bands to the Fermi diad intensity ratio and Δ of CO₂ in HPOC at 153.8 and 7.2 MPa at different laser powers

ρ^a g/cm ³	T °C	P MPa	P_{ill} mW	$\Delta_{\text{Ne calib}}^b$ cm ⁻¹	Error ^c cm ⁻¹	HBR ^d	Error ^c
1.204	23.0	153.8	1.7	105.833	0.009	0.0226	0.0022
1.204	23.0	153.8	9.3	105.829	0.010	0.0210	0.0016
1.204	22.9	153.8	11.3	105.819	0.013	0.0217	0.0009
1.204	23.0	153.8	13.3	105.828	0.006	0.0202	0.0006
1.204	23.0	153.8	16.7	105.828	0.006	0.0205	0.0015
0.783	22.7	7.2	1.7	104.376	0.022	0.0368	0.0015
0.784	22.6	7.2	9.3	104.370	0.010	0.0373	0.0006
0.783	22.7	7.2	11.3	104.370	0.008	0.0369	0.0007
0.783	22.7	7.2	13.3	104.359	0.006	0.0363	0.0005
0.783	22.7	7.2	16.7	104.373	0.005	0.0362	0.0007

^a Densities calculated according to Span and Wagner (1996) EOS.

^b Calculated from Eq. 2-1.

^c Error is standard deviation ($n = 5$).

^d HBR: Hot bands to the Fermi diad intensity ratio.

spectroscopic analysis. Volatile species other than CO₂ are not detected from the seven inclusions. Although no H₂O liquid phase was visible under microscopic observation, trace amounts of H₂O might be wetting the wall of inclusions (Berkesi et al., 2009; Lamadrid et al., 2014b). For the fluid inclusions in orthopyroxene, the partial homogenization temperatures of the carbonate phase to liquid were measured using a heating-cooling stage (THMS600; Linkam Scientific Instruments

Ltd.) at Hokkaido University. Homogenization temperature was not reported for Cr-spinel because of its high absorption coefficient, which made observation of the phase transition difficult, but the density estimated from the measured Δ value is presented in Table 2. The instrument was calibrated using the melting points of H₂O (0.0 °C) in synthetic pure H₂O fluid inclusions. Homogenization was recorded at the heating rate of 0.1 °C/min. Fluid densities are calculated as described by Span and Wagner (1996).

Table2-2 Relation between Δ_{calib} and P_{ill} obtained from natural fluid inclusions with various densities, and the density corrected for the effect of laser heating ($\rho_{\Delta_{\text{intercept}}}$) as estimated from the relation.

Sample name	$\rho_{T_h}^a$ g/cm ³	$\rho_{\Delta_{\text{intercept}}}^b$ g/cm ³	$\rho_{\Delta_{\text{calib}}}^c$ g/cm ³	P_{ill} mW	$\sigma_{P_{\text{ill}}}$ mW	Δ_{calib} cm ⁻¹	σ_{Δ}^e cm ⁻¹	$\Delta_{\text{intercept}}$ cm ⁻¹	Error ^f cm ⁻¹	$(\partial\Delta/\partial P_{\text{ill}})_{\rho}$ cm ⁻¹ /mW	Error ^f cm ⁻¹ /mW
spinel03 fi031	n.d.	1.201	1.198	4.7	0.14	105.827	0.024	105.848	0.035	-0.0038	0.0033
			1.197	7.9	0.24	105.819	0.029				
			1.195	11.9	0.36	105.807	0.018				
			1.191	14.4	0.43	105.785	0.028				
spinel04 fi026	n.d.	0.919	0.897	4.7	0.14	104.730	0.023	104.793	0.033	-0.0127	0.0032
			0.885	7.9	0.24	104.696	0.027				
			0.871	11.9	0.36	104.657	0.047				
			0.853	14.4	0.43	104.606	0.022				
spinel03 fi146	n.d.	0.737	0.714	4.7	0.14	104.232	0.020	104.290	0.024	-0.0143	0.0020
			0.690	7.9	0.24	104.173	0.014				
			0.665	11.9	0.36	104.111	0.010				
			0.655	14.4	0.43	104.088	0.008				
spinel03 fi154	n.d.	0.377 ^d	0.363	4.7	0.14	103.360 ^d	0.056	103.393 ^d	0.036	-0.0075	0.0033
			0.350	7.9	0.24	103.330 ^d	0.013				
			0.341	11.9	0.36	103.309 ^d	0.011				
			0.325	14.4	0.43	103.273 ^d	0.021				
opx07 fi008	1.167	1.170	1.169	4.7	0.14	105.672	0.011	105.675	0.013	-0.0015	0.0011
			1.166	7.9	0.24	105.659	0.009				
			1.165	11.9	0.36	105.655	0.012				
			1.165	14.4	0.43	105.655	0.006				
opx06 fi010	0.914	0.898	0.896	4.7	0.14	104.728	0.020	104.730	0.018	-0.0016	0.0013
			0.893	7.9	0.24	104.719	0.010				
			0.888	11.9	0.36	104.706	0.010				
			0.889	14.4	0.43	104.708	0.003				
opx06 fi005	0.704	0.707	0.699	4.7	0.14	104.195	0.012	104.215	0.013	-0.0047	0.0012
			0.692	7.9	0.24	104.178	0.006				
			0.682	11.9	0.36	104.154	0.011				
			0.681	14.4	0.43	104.150	0.007				

^a Densities calculated using Span and Wagner^[63] EOS from measured partial homogenization temperatures of the carbonate phase to liquid; +25.4°C for opx06 fi005, +2.2°C for opx06 fi010, and -53.4°C for opx07 fi008. n.d.: not determined.

^b $\rho_{\Delta_{\text{intercept}}}$ was obtained by substituting $\Delta_{\text{intercept}}$ and 20°C into Eq. 2-2.

^c $\rho_{\Delta_{\text{calib}}}$ was obtained by substituting Δ_{calib} and 20°C into Eq. 2-2.

^d Density for this sample is obtained by substituting $\Delta_{\text{intercept}}$ into Equation of Kawakami et al.^[42] because the experimental calibration of Eq. 2-2 of this study did not cover density lower than approx. 0.7 g/cm³.

^e Error is standard deviation ($n = 5$).

^f Error is standard error.

The individual inclusions were measured in the order of 4.7, 11.6, 7.9, and 14.4 mW using almost identical Raman apparatus to that described section 3.2. The only difference from the configuration explained above is the objective lens: a 50× objective lens (LU Plan, N.A. = 0.8; Nikon Corp.) was used. The sample was placed on a glass slide. During the measurement, room temperature was maintained at 20.5±1.0°C. Considering that the temperature increases of inclusions per unit laser power in Cr-spinel and orthopyroxene were, respectively, approx. 6°C/mW and approx. 1°C/mW (Hagiwara et al., 2021), this variation in room temperature is sufficiently smaller than the expected temperature increases of inclusions during analysis. Given the same temperature increase of inclusions per unit of laser power, the CO₂-rich phase of all inclusions is homogenized into a single supercritical fluid, liquid, or gas phase during the analysis. Measurements were taken five times at each P_{ill} . Table 2 presents the average Δ value of five measurements and their standard deviation (1σ) at each P_{ill} . The duration of every Raman analysis is three accumulations of 100 s for inclusion in Cr-spinel and two accumulations of 100 s for those in orthopyroxene. This is because, in the case of Cr-spinel, both incident laser and Raman scattering light are more absorbed by the host mineral because of its high absorption coefficient, resulting in a low number of CO₂ Raman scattering photons detected per unit time.

The measured Δ (Δ^{raw}) values are first calibrated using measured and known distances between the Ne lines according to the explanation presented by Lamadrid et al. (2017) ($\Delta_{\text{Ne calib}}$ in Table S2-3). Subsequently, discrepancies in the calibration curves between laboratories were corrected by adding the correction term $\delta_{\text{Eq. 2-2}}$ to $\Delta_{\text{Ne calib}}$. Finally, corrected Δ (Δ_{calib}) are defined as $\Delta_{\text{calib}} = \Delta_{\text{Ne calib}} + \delta_{\text{Eq. 2-2}}$. According to Hagiwara et al. (2020), $\delta_{\text{Eq. 2-2}}$ was calculated using Eq. 2-2, Eq.10 of Hagiwara et al. (2020), and the 2 $\Delta_{\text{Ne calib}}$ obtained from the standard fluid inclusions with known density (0.786 and 1.167 g/cm³). Using the correction procedures described above, the differences between known density of standard fluid inclusions and density calculated by substituting Δ_{calib} into Eq. 2-2 were found to be less than 0.2%. The values of $\delta_{\text{Eq. 2-2}}$ are shown in Table S2-3.

4. Results

4.1 Temperature-dependence of Δ - ρ relations

I investigated the P – T dependence of Δ at temperatures of 23–200°C and pressures of 7.2–248.7 MPa using HPOC. In this study, the density corresponding to the P – T conditions of every analysis was calculated using the method described by Span and Wagner (1996) EOS for CO₂. In all, total of 151 Δ values obtained from 23 to 200°C are portrayed in Fig. 2-4a. In agreement with results reported from earlier studies, all Δ values shift systematically to higher values with increasing density at constant temperature (Rosso and Bodnar, 1995; Yamamoto et al., 2002; Kawakami et al., 2003; Yamamoto and Kagi, 2006; Song et al., 2009; Fall et al., 2011; Wang et al., 2011; Lamadrid et al., 2017; Yuan et al., 2017; Wang et al., 2019; Le et al., 2020; Sublett et al., 2020b). In addition, the $(\partial\rho/\partial\Delta)_T$ rates obtained from my data decrease gradually with increasing density, especially at high density. This tendency was also observed from earlier studies conducted at high density (Fig. 2-4b) (Kawakami et al., 2003; Yamamoto and Kagi, 2006; Fall et al., 2011; Hagiwara et al., 2020). The $(\partial\Delta/\partial T)_\rho$ rate was found to be negative in all density regions studied, from 0.7 to 1.2 g/cm³, which is consistent with results obtained from earlier studies for 0.0 to 1.0

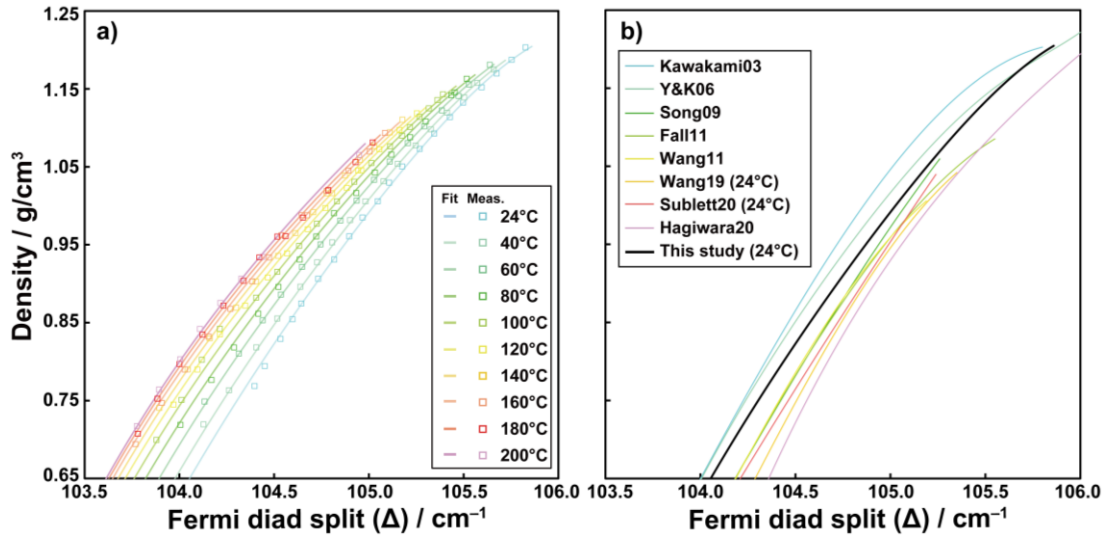


Figure2-4 (a) Relation of CO₂ density and Fermi diad (Δ) as a function of temperature. Raman spectra of CO₂ are measured at temperatures of 23–200°C and pressures of 7.2–248.7 MPa using HPOC. For this study, the density corresponding to the temperature and pressure condition of every analysis was calculated according to Span and Wagner (1996) EOS for CO₂. The data shown are those from Tables S2-1 and S2-2. (b) Comparison of published Δ – ρ relations. All densimeters shown are within the density region in which calibration measurements were made and effective at near room temperature (Kawakami et al., 2003; Yamamoto and Kagi, 2006; Song et al., 2009; Fall et al., 2011; Wang et al., 2011; Wang et al., 2019; Hagiwara et al., 2020; Sublett et al., 2020b).

g/cm³ (Bondarenko, 1986; Wang et al., 2011; Wang et al., 2019; Le et al., 2020; Sublett et al., 2020b).

The main findings obtained from HPOC experiments are that the temperature derivative of Δ at constant density ($(\partial\Delta/\partial T)_\rho$) depends strongly on the density and that the $(\partial\Delta/\partial T)_\rho$ rates are always negative, even at high density (Fig. 2-4a). Although the temperature dependence of the Δ - ρ relations exists throughout the entire density range that was analyzed (0.7–1.2 g/cm³), $|(\partial\Delta/\partial T)_\rho|$ rates are maximum at approx. 0.7 g/cm³; they decrease as density increases from 0.7 g/cm³ (Fig. 2-5c).

4.2 Regression analysis and error analysis

The respective P - T changes during analysis of the isothermal pressurization experiments were less than ± 0.1 MPa and $\pm 0.1^\circ\text{C}$. The P - T condition shown in Table S2-2 is an average value obtained during analysis of the near isochoric heating experiments. The P - T variation during the analysis was less than ± 1.1 MPa and $\pm 0.5^\circ\text{C}$ (Table S2-2). Density change caused by P - T fluctuation during Raman analysis was lower than ± 0.0028 g/cm³ (Tables S2-1 and S2-2). Measurements of 153.8 MPa at 120, 140, 160, and 180°C were taken in both the isothermal pressurization experiments (increasing pressure cycle) and near isochoric heating experiments (decreasing pressure cycle) to evaluate the effects of differences in the pressurization method. The differences of Δ of the four pairs were -0.018 , -0.029 , $+0.029$, and $+0.024$ cm⁻¹, respectively, at 120, 140, 160, and 180°C. No systematic error resulted from the difference in the pressure generation method.

To estimate the fluid density from the sample temperature and measured Δ , we conducted regression analysis. The density of CO₂ fluid inclusions at elevated temperatures can be found using the following polynomial equation.

$$\rho = a + bT^2 + cT^3 + d\Delta + e\Delta^2 + f\Delta^3 + g\Delta T + h\Delta^2 T + i\Delta T^2 + j\exp(\Delta) \quad (2-2)$$

Therein, a through j represent fitting parameters ($a = -61821.3575$, $b = -3.3585 \times 10^{-4}$, $c = 1.56567 \times 10^{-8}$, $d = 1781.1957586$, $e = -17.112171653$, $f = 0.0548181541$, $g = 0.00119219$, $h = -0.0000112203$, $i = 3.12805 \times 10^{-6}$, and $j = -1.02847 \times 10^{-46}$). In that equation, ρ (g/cm³), T (°C), and Δ (cm⁻¹), respectively represent the fluid density, temperature, and Fermi diad splits of CO₂. It is noteworthy that “ T ” is not included in the explanatory variables in Eq. 2-2 because we selected them so that the p -values of all explanatory variables are less than 0.05. Instead, $\exp(\Delta)$ was added as an explanatory variable, which is particularly useful in reflecting the characteristic that $(\partial\rho/\partial\Delta)_T$ becomes smaller at higher densities. Because the p -values of all explanatory variables are less than 0.008,

they are influential factors for the objective variable. Eq. 2-2 has a coefficient of determination (R^2) of 0.999. Eq. 2-2 is valid in the experimentally calibrated regime of $23^\circ\text{C} \leq T \leq 200^\circ\text{C}$ and $0.7 \text{ g/cm}^3 \leq \rho \leq 1.2 \text{ g/cm}^3$ (Fig. 2-2). The half of the difference between the upper and lower bounds of the prediction interval at 1σ of the Equation (2) was lower than $\pm 0.0057 \text{ g/cm}^3$. Finally, the uncertainty in the density estimation based on Equation (2), which takes into account both the uncertainty in the model and the density variation during the analysis, is $\pm \sqrt{0.0028^2 + 0.0057^2} \approx 0.006 \text{ g/cm}^3$.

4.3 Laser heating effects during HPOC experiments

Absorption of excitation laser light by the optical window of the HPOC or CO_2 fluid itself might cause unintentional local temperature enhancement. In that case, Δ can be expected to decrease concomitantly with increasing P_{ill} because Δ decreases concomitantly with increasing temperature at constant density (Fig. 2-4). However, all Δ values are within the range of error (Fig. 2-6a and 2-6b). No systematic decrease was observed to occur along with the increase of P_{ill} (Fig. 2-6a and 2-6b). Similarly, hot bands to the Fermi diad intensity ratio can increase with P_{ill} because it increases concomitantly with increasing temperature at constant density (Brown and Steeper, 1991; Rosso and Bodnar, 1995; Arakawa et al., 2008; Hagiwara et al., 2018; Hagiwara et al., 2021). Although a temperature change of about $> 4^\circ\text{C}$ can be detected from the hot bands to the Fermi diad

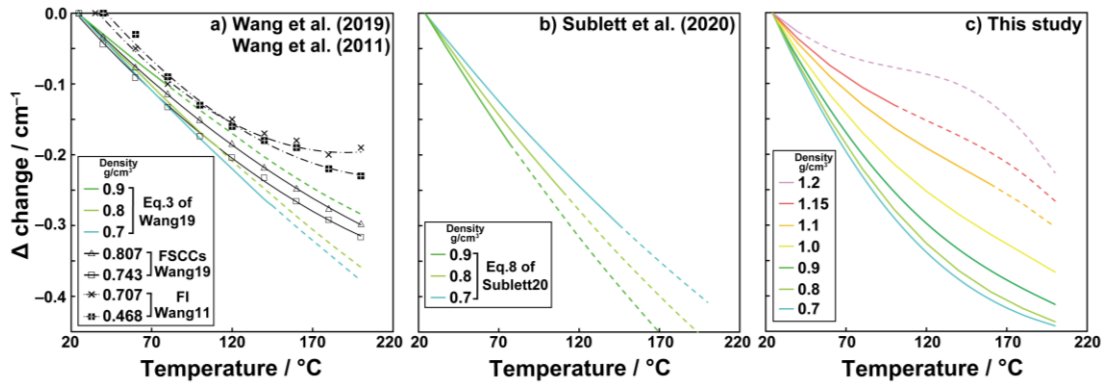


Figure 2-5 Δ change relative to initial Δ obtained at approx. 24°C as a function of temperature. Colored solid lines show the temperature dependence of Δ at constant density calculated using (a) Eq. 3 of Wang et al. (2019), (b) Eq. 8 of Sublett et al. (2020b), and (c) Eq. 2-2 of this study. The dotted 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. (a, b) Colored solid lines are isochores at 0.7, 0.8, and 0.9 g/cm^3 . (a) Black solid lines with open symbols are data obtained from the FSCCs with densities of 0.807 and 0.743 g/cm^3 by Wang et al. (2019). Dashed-dotted lines show data obtained from the fluid inclusions with densities of 0.707 and 0.468 g/cm^3 by Wang et al. (2011). (c) Colored solid lines are isochores at 0.7, 0.8, 0.9, 1.0, 1.1, 1.15, and 1.2 g/cm^3 .

intensity ratio, the intensity ratio does not change systematically with P_{ill} (Fig. 2-6c and 2-6d) (Hagiwara et al., 2018). Therefore, results demonstrate that the influence of laser heating is lower than 4°C, at least under the present analytical conditions. Nevertheless, to avoid possible heating effects, measurements are taken at the sample surface with P_{ill} of 13.2 mW. Therefore, the maximum laser heating during the HPOC experiment, if any, is about 3°C (approx. $4 \times \frac{13.2}{16.7}^{\circ}\text{C}$). This temperature enhancement is sufficiently lower than the experimental temperature range of 23–200°C. Therefore, I can ignore laser heating effects in the HPOC experiments.

4.4 Laser heating effects during natural fluid inclusion analysis

Because Δ decreases monotonically with laser power (Table 2), the intercept of the linear fitting between Δ_{calib} and P_{ill} ($\Delta_{\text{intercept}}$) can be regarded as Δ without laser heating. For estimating the best fit straight line to data, I applied bivariate least-squares fitting method (York method) using OriginPro9.0 software (OriginLab Corporation, Northampton, US). Fig. 2-7 presents the relation between “ $\Delta_{\text{intercept}} - \Delta_{\text{calib}}$ ” and laser power. For all fluid inclusions, Δ tends to decrease with laser power. The slope of the relation between Δ and laser power ($\partial\Delta/\partial P_{\text{ill}}\rho$) is, invariably, significant and

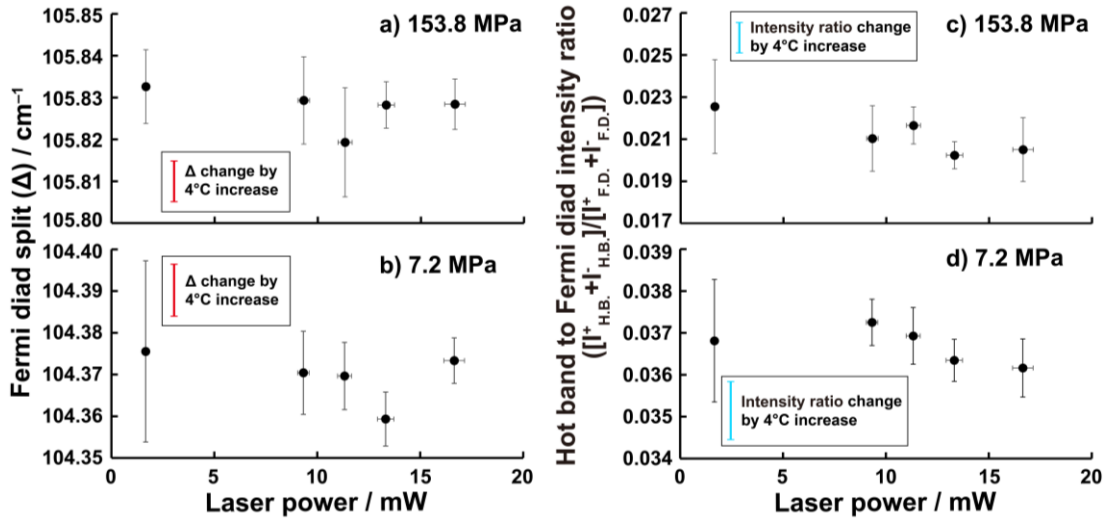


Figure 2-6 Fermi diad split (Δ) (a, b) and hot band to the Fermi diad intensity ratio (c, d) of CO_2 with pressures of 153.8 MPa (a, c) and 7.2 MPa (b, d) as a function of the laser power at the sapphire window surface. Red bars represent the expected Δ change attributable to the temperature change of 4°C under measured P – T conditions calculated using Eq. 2. The blue bar represents the expected $[I_{\text{H.B.}}^+ + I_{\text{H.B.}}^-] / [I_{\text{F.D.}}^+ + I_{\text{F.D.}}^-]$ change attributable to temperature change of 4°C under measured P – T conditions calculated using Eq. 5 of Hagiwara et al. (2021). Measurements were made five times at each laser power. Error bars represent 1σ . Data shown are from Table 1.

negative (Table 2). Details underlying the reason for this negative slope are explained in Section 5.2, but it is not attributable to the monotonic drift of the Raman system because the measurements were performed in the order of 4.7, 11.9, 7.9, and 14.4 mW without monotonically increasing (or decreasing) P_{ill} .

Fig. 2-7a presents data for fluid inclusions with densities of 1.201, 0.919, 0.737, and 0.377 g/cm³ in Cr-spinel. For inclusions with density higher than 0.7 g/cm³, densities are calculated by substituting $\Delta_{\text{intercept}}$ into Eq. 2-2. For inclusions with density lower than 0.7 g/cm³, Δ_{calib} was defined as $\Delta_{\text{Ne calib}} + \delta_{\text{Kawakami03}}$, where $\delta_{\text{Kawakami03}}$ was calculated from the Δ - ρ relation of Kawakami et al. (2003), Eq. 10 of Hagiwara et al. (2020), and Δ_{calib} for two standard fluid inclusions (Table S2-3). Then, the density was calculated by substituting $\Delta_{\text{intercept}}$ into the Δ - ρ relation presented by Kawakami et al. (2003). For the three inclusions with densities greater than 0.7 g/cm³, $|(\partial\Delta/\partial P_{\text{ill}})_{\rho}|$ is shown to become smaller for higher densities (Fig. 2-7a). A similar trend was obtained for fluid inclusions with densities of 1.167, 0.914, and 0.704 g/cm³ in orthopyroxene. However, the $|(\partial\Delta/\partial P_{\text{ill}})_{\rho}|$ of fluid inclusions with density of 0.377 g/cm³ in Cr-spinel is -0.0075 ± 0.0033 cm⁻¹/mW, which is clearly lower than that of 0.737 g/cm³ (-0.0143 ± 0.0020 cm⁻¹/mW). This is consistent with results of earlier studies, which show that below approx. 0.7 g/cm³, $|(\partial\Delta/\partial T)_{\rho}|$ becomes a smaller value at lower densities (Wang et al., 2019; Sublett et al., 2020b).

5. Discussion

5.1 Effects of density on $\partial\Delta/\partial T$: Comparison with results of earlier studies

Many earlier studies have clarified details of the temperature dependence of the relation between Δ and density (Bondarenko, 1986; Kawakami et al., 2003; Chen et al., 2004; Fall et al., 2011; Wang et al., 2011; Yuan et al., 2017; Wang et al., 2019; Le et al., 2020; Sublett et al., 2020b). 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. After reviewing earlier studies, I eventually chose to compare the results reported by Sublett et al. (2020b), Wang et al. (2019), and Wang et al. (2011) with those of the present study. Details of the process of selecting the earlier studies to be used for comparison with this study are presented in Supporting Information.

Earlier studies have examined the density dependence of $|(\partial\Delta/\partial T)_\rho|$. Reports have described that $|(\partial\Delta/\partial T)_\rho|$ becomes smaller at lower densities (Fig. S2-1) (Wang et al., 2019; Sublett et al., 2020b). By contrast, regarding density dependence of $|(\partial\Delta/\partial T)_\rho|$ at $> 0.7 \text{ g/cm}^3$, several studies have yielded somewhat different conclusions (Wang et al., 2011; Wang et al., 2019; Sublett et al., 2020b). According to the Δ - T - ρ relation for pure CO_2 derived by Wang et al. (2019) using HPOC, $|(\partial\Delta/\partial T)_\rho|$ becomes smaller at densities higher than 0.7 g/cm^3 (Fig. 2-5a). This is supported by the fact that their data obtained using FSCC shows that $|(\partial\Delta/\partial T)_\rho|$ is larger at 0.743 g/cm^3 than at 0.807 g/cm^3 . However, using the relation derived by Sublett et al. (2020b), $|(\partial\Delta/\partial T)_\rho|$ becomes larger at densities higher than 0.7 g/cm^3 , which is inconsistent with the results reported by Wang et al. (2019) (Fig. 2-5b). Furthermore, Wang et al. (2011) investigated the temperature dependence of Δ at 35–200°C and 40–200°C, respectively using natural and synthetic fluid inclusions in quartz with densities of 0.7074 and 0.4676 g/cm^3 . Results respectively portray that Δ decreased concomitantly with increasing temperature up to 200°C by 0.19 cm^{-1} and 0.24 cm^{-1} (Figure 2-5a). Comparing the results obtained from the two fluid inclusions by Wang et al. (2011), there appears to be little density

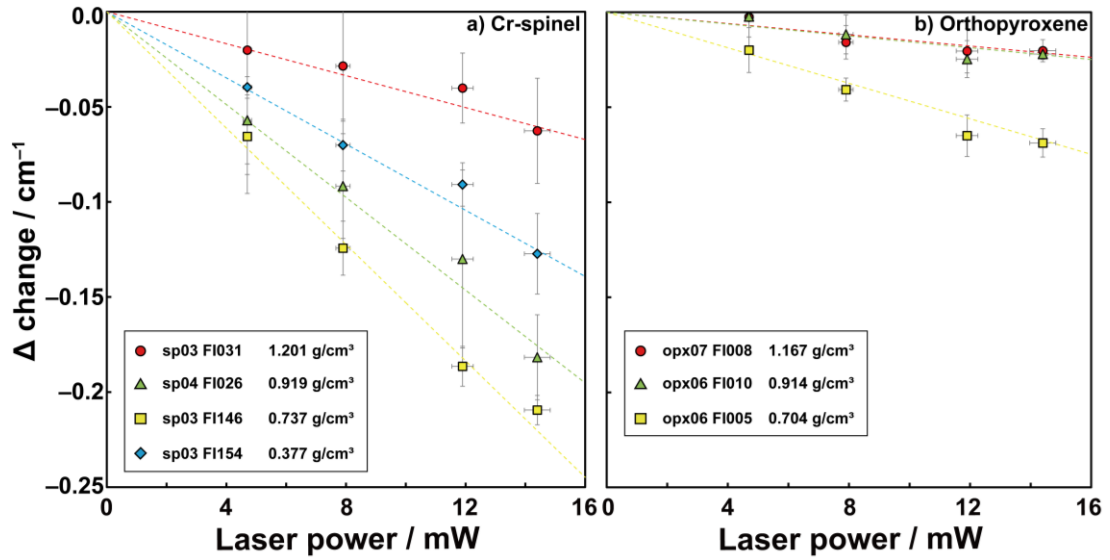


Figure2-7 Δ change of CO_2 -rich fluid inclusions hosted in Cr-spinel and orthopyroxene versus laser power. The vertical axis shows deviation of the measured Δ (Δ_{calib}) from the Δ value at 0 mW ($\Delta_{\text{intercept}}$) estimated from the intercept of the linear fit of the measured Δ and laser power. Error bars for Δ show the standard deviation ($n = 5$). Those for laser power are 3%. Dashed lines show linear fit (York method) to four data points. (a) Red, green, yellow, and blue symbols respectively represent fluid inclusions with densities of 1.201, 0.919, 0.737, and 0.377 g/cm³ in Cr-spinel. (b) Red, green and yellow symbols respectively represent fluid inclusions with densities of 1.167, 0.914, and 0.704 g/cm³ in orthopyroxene.

dependence of $|(\partial\Delta/\partial T)_\rho|$. Therefore, disagreement exists between earlier studies of the density dependence of $|(\partial\Delta/\partial T)_\rho|$ at densities higher than 0.7 g/cm³.

My results demonstrate that $|(\partial\Delta/\partial T)_\rho|$ decreases concomitantly with increasing density for densities higher than 0.7 g/cm³ (Fig. 2-5c), which is consistent with results reported by Wang et al. (2019). My results support the results reported by Wang et al. (2019) more than those of Sublett et al. (2020b), probably because Wang et al. (2019) obtained more data at high densities than Sublett et al. (2020b) did. Therefore, this study, which specifically examined high-density data, yielded results that are rather consistent with those reported by Wang et al. (2019) for densities higher than 0.7 g/cm³. The fluid inclusions of Wang et al. (2011) at 0.7074 and 0.4676 g/cm³ had similar $|(\partial\Delta/\partial T)_\rho|$, perhaps because the density was 0.7074–0.4676 g/cm³ at which the sign of $d|(\partial\Delta/\partial T)_\rho|/d\rho$ is reversed. Consequently, the two fluid inclusions used by Wang et al. (2011) might have coincidentally had densities for which $|(\partial\Delta/\partial T)_\rho|$ is comparable mutually. Strictly speaking, however, the effect of the amount of H₂O in the CO₂-rich inclusions should also be considered, as described by Wang et al. (2019), but because the amount of H₂O is unknown, I do not discuss it further.

In summary, the combination of my Δ – T – ρ relation in the high-density region and that in the low-density region investigated in results of earlier studies suggests that density at which the sign of $\partial|(\partial\Delta/\partial T)_\rho|/\partial\rho$ is reversed exists around 0.6–0.7 g/cm³. Therefore, when the density of CO₂ fluid inclusions is measured using a Raman CO₂ densimeter, fluid inclusions with densities of approximately 0.6–0.7 g/cm³ are the most susceptible to Δ change because of laser heating.

5.2 Apparent density reduction caused by laser heating

5.2.1 Causes of variation in $(\partial\Delta/\partial P_{\text{III}})_\rho$

The values of Δ obtained from the fluid inclusions clearly decrease concomitantly with increasing P_{III} . The decrease shows density dependence (Fig. 2-7). These features can be explained well by the Δ – T – ρ relation (i.e., $(\partial\Delta/\partial T)_\rho$ is always negative and $|(\partial\Delta/\partial T)_\rho|$ reaches its maximum at 0.6–0.7 g/cm³) and the monotonic temperature increase of the inclusion with increasing P_{III} , but other factors that can engender variations in $(\partial\Delta/\partial P_{\text{III}})_\rho$ must also be examined carefully. Another mechanism that causes a reduction in Δ with increasing P_{III} is the expansion of the inclusions during analysis. In this mechanism, a monotonic increase in the temperature of the inclusion with increasing P_{III} causes the inclusion to expand and the fluid density to decrease. Naturally, as the density decreases, Δ decreases. Consequently, Δ is expected to decrease concomitantly with increasing P_{III} . Fortunately, however, I can use the density dependence of $|(\partial\Delta/\partial P_{\text{III}})_\rho|$ to distinguish which of the above two

mechanisms is dominant. If the volume expansion of inclusions is the main reason for the decrease in Δ , then the decrease in Δ should be larger for denser fluids. This is true because, for example, the increase in internal pressure by heating from room temperature to +50°C is +80 MPa for 1.2 g/cm³, +33 MPa for 0.9 g/cm³, +17 MPa for 0.7 g/cm³, and +5 MPa for 0.3 g/cm³. Therefore, for an equal amount of heating, the internal pressure increased for denser fluids (see steepness of isochore in Fig. 2-2). The inclusions tend to expand (Hagiwara et al., 2019). Therefore, if the expansion of inclusions is the main reason for the decrease in Δ , then denser fluids can be expected to have larger $|(\partial\Delta/\partial P_{\text{ill}})_\rho|$. However, the actual trend obtained is opposite to the trend expected by the volume expansion of inclusions. Therefore, I infer that volume expansion is not the main reason for the decrease in Δ in the fluid inclusions.

Next, the difference in the temperature increase of individual inclusions during analysis can also be a factor causing variation in $|(\partial\Delta/\partial P_{\text{ill}})_\rho|$. In other words, the inclusions with density of 0.737 g/cm³ of Cr-spinel and 0.704 g/cm³ of orthopyroxene have the highest $|(\partial\Delta/\partial P_{\text{ill}})_\rho|$ in their respective host minerals, probably because those inclusions were the hottest during analysis. Because Hagiwara et al. (2021) have demonstrated that the size and depth from the sample surface of the selected inclusions have little effect on laser heating, they will be excluded as factors in the difference in the magnitude of $|(\partial\Delta/\partial P_{\text{ill}})_\rho|$. In fact, no systematic correlation exists between the size and depth of inclusions and $|(\partial\Delta/\partial P_{\text{ill}})_\rho|$ (Tables 2 and S2-3). Furthermore, according to earlier studies, the temperature increase per unit of laser power in the same host mineral is almost identical for different inclusions (Hagiwara et al., 2021). Therefore, the difference in heating rates can be excluded as a reason for the difference in $|(\partial\Delta/\partial P_{\text{ill}})_\rho|$ between inclusions.

If one assumes that the temperature increase per unit laser power is nearly constant for inclusions in the same host mineral, then $|(\partial\Delta/\partial T)_\rho| = |(\partial\Delta/\partial P_{\text{ill}})_\rho|/(dT/dP_{\text{ill}}) \propto |(\partial\Delta/\partial P_{\text{ill}})_\rho|$. Therefore, similarly to the density dependence of $|(\partial\Delta/\partial T)_\rho|$ predicted by the HPOC experiment, $|(\partial\Delta/\partial P_{\text{ill}})_\rho|$ also can be expected to have a maximum value of around 0.6–0.7 g/cm³, and $|(\partial\Delta/\partial P_{\text{ill}})_\rho|$ can be expected to decrease as the density increases at >0.7 g/cm³. In fact, inclusions with densities closest to 0.6–0.7 g/cm³ have the largest $|(\partial\Delta/\partial P_{\text{ill}})_\rho|$ in each host mineral. In addition, for inclusions in both orthopyroxene and Cr-spinel, for densities higher than 0.7 g/cm³, the higher the density, the smaller the $|(\partial\Delta/\partial P_{\text{ill}})_\rho|$, which is consistent with the trend expected from HPOC experiments. Therefore, one can infer that the combination of laser heating and the temperature dependence of the Δ – ρ relations is responsible for the observed features of $|(\partial\Delta/\partial P_{\text{ill}})_\rho|$, such as $(\partial\Delta/\partial P_{\text{ill}})_\rho$ always being negative and $|(\partial\Delta/\partial P_{\text{ill}})_\rho|$ being largest for inclusions with densities closest to 0.6–0.7 g/cm³.

5.2.2 Accurate density estimation in the presence of laser heating

As expected from the results of HPOC experiments, the greatest decrease in Δ for fluid inclusions in the 0–14.4 mW range was observed for the fluid inclusions in Cr-spinel with density closest to 0.6–0.7 g/cm³. For this inclusion (spinel03 fi146), the density estimated by substituting the Δ_{calib} measured at 14.4 mW without considering the effects of laser heating into Eq. 2-2 is 0.655 g/cm³, whereas the density obtained by substituting the $\Delta_{\text{intercept}}$ corrected for the effect of laser heating into Eq. 2-2 is 0.737 g/cm³. In this case, the density is underestimated by 0.082 g/cm³ (approx. 12%). In addition, for the fluid inclusion of 0.373 g/cm³ (spinel03 fi154), where $|(\partial\Delta/\partial P_{\text{ill}})_\rho|$ is smaller than that of the inclusion of 0.737 g/cm³, the decrease in density itself is 0.052 g/cm³, which is smaller than that of the inclusion of 0.737 g/cm³. However, in percent notation, the density underestimation is 15%, which is severer than that of 0.737 g/cm³. Therefore, even though $|(\partial\Delta/\partial P_{\text{ill}})_\rho|$ is small at densities lower than 0.6–0.7 g/cm³, the relative underestimation of density because of laser heating might be rather more severe than for inclusions at 0.6–0.7 g/cm³. Therefore, for inclusions in host minerals such as Cr-spinel, which have a large absorption coefficient and which are affected strongly by laser heating, the density might be underestimated by about >10%, even at typical laser power of 15 mW. For such inclusions, some correction is necessary to estimate the density accurately. Underestimation of the density of fluid inclusions in orthopyroxene (0.704 g/cm³, opx06 fi005), which has almost identical density to that of spinel03 fi146, is 3.4% according to the calculation presented above, which is one-fourth that of Cr-spinel. The reason for this difference in density underestimation might be that the temperature increase of the inclusions in Cr-spinel is greater than that in orthopyroxene because the absorption coefficient of Cr-spinel (approx. 20 cm⁻¹) (Taran et al., 2014) is larger than that of orthopyroxene (approx. 9 cm⁻¹) (Taran and Langer, 2001). For an inclusion with density of 1.201 g/cm³ in Cr-spinel, the underestimation is only 0.9% (= 0.010 g/cm³) under the conditions described above. Therefore, for densities of approx. 1.1–1.2 g/cm³, where $|(\partial\Delta/\partial T)_\rho|$ is small, the underestimation of density because of laser heating is small, even in host minerals that are extremely sensitive to laser heating, such as Cr-spinel. Therefore, at such very high densities, the effect of laser heating can be neglected in many cases.

The following is an explanation of how to estimate the density accurately even in the presence of laser heating, based on data of opx06 fi005, which had the largest $|(\partial\Delta/\partial P_{\text{ill}})_\rho|$ among inclusions with known density. The densities obtained by substituting Δ_{calib} into Eq. 2-2 without correcting for the effect of laser heating ($\rho_{\Delta_{\text{calib}}}$) are 0.699 ± 0.005 g/cm³ at 4.7 mW, 0.692 ± 0.003

g/cm³ at 7.9 mW, 0.682 ± 0.005 g/cm³ at 11.9 mW, and 0.681 ± 0.003 g/cm³ at 14.4 mW, respectively, which become lower than the known density of 0.704 g/cm³ as the laser power increases (Table 2). In the case of inclusions in orthopyroxene, at laser powers below 4.7 mW, the deviation between ρ_{T_h} and $\rho_{\Delta_{\text{calib}}}$ is less than 0.005 g/cm³ (= 0.7%). The effect of laser heating on density estimation is almost equivalent to the density uncertainty in the calibration curve itself. Thereby, the effect of laser heating can be ignored. However, at 14.4 mW, the deviation between ρ_{T_h} and $\rho_{\Delta_{\text{calib}}}$ is 0.023 g/cm³ (= 3.4%), which is clearly an underestimation of the true value. In this way, when the effect of heating cannot be neglected, substituting $\Delta_{\text{intercept}}$, corrected for the effect of laser heating, into the Δ - ρ relation yields a value of 0.707 ± 0.005 g/cm³, which is consistent with the true value (0.704 g/cm³) within the error (Table 2).

In light of the points raised above, one must ascertain whether correlation exists between the Δ value and laser power in the laser power region bracketing the laser power to be used for the measurement when measuring a sample for which the effect of laser heating on Δ is unknown. If a significant positive value of $|(\partial\Delta/\partial P_{\text{ill}})_\rho|$ is obtained, as observed in the natural fluid inclusions of this study, then that value indicates that Δ is reduced by the laser heating and indicates that the density is somewhat underestimated if not corrected for that effect. However, if $|(\partial\Delta/\partial P_{\text{ill}})_\rho|$ is not significantly positive, as observed for HPOC in this study and for colorless quartz in earlier studies (Hagiwara et al., 2021), then one can infer that the effect of laser heating is negligible, at least in that laser power region. If the effect of laser heating is found to be present, then the correction method described in the paragraph above is useful to estimate the density more accurately, whether or not a correction is applied depends on the quality of the data desired by the researchers. However, at least when comparing and interpreting Δ obtained from different mineral species, the presence or absence of laser heating effects should be noted. If laser heating effects on the measurements are not negligible, then I recommend some report of how the ideal measurement conditions were reached and what corrections were made to the raw data to interpret them.

6. Conclusions

Raman spectra of CO₂ were measured at 23–200°C and 7.2–248.7 MPa using a high-pressure optical cell. Δ - ρ relations have temperature-dependence throughout all the density range analyzed (0.7–1.2 g/cm³), at least higher than 23°C. Fermi diad splits (Δ) of all observed Raman bands increased systematically with increasing density at constant temperature. They decreased concomitantly with increasing temperature at constant density. In addition, the $|(\partial\Delta/\partial T)_\rho|$ is maximum

at approx. 0.7 g/cm³; it decreases as the density increases from approx. 0.7 g/cm³. In combination with the results of the earlier study, I conclude that $|(\partial\Delta/\partial T)_\rho|$ increases gradually from 0.0 g/cm³ to 0.6–0.7 g/cm³; it then decreases as the density increases to 1.2 g/cm³. Therefore, if the inclusion temperature is increased by a certain temperature T by laser heating, the largest decrease in Δ will be observed for inclusions with density of 0.6–0.7 g/cm³. In contrast, fluid inclusions with very high densities of 1.1–1.2 g/cm³ are less affected by laser heating because of the small $|(\partial\Delta/\partial T)_\rho|$.

To confirm that the density dependence of $|(\partial\Delta/\partial T)_\rho|$ predicted by HPOC experiments is also valid for natural fluid inclusions, I measured Δ for fluid inclusions with densities ranging from approx. 0.3–1.2 g/cm³ in Cr-spinel and orthopyroxene at varying laser powers. As expected from HPOC experiments, I found that, above 0.7 g/cm³, $|(\partial\Delta/\partial P_{\text{ill}})_\rho|$ decreased concomitantly with increasing density. Below 0.7 g/cm³, it decreased concomitantly with decreasing density. Furthermore, even though $|(\partial\Delta/\partial P_{\text{ill}})_\rho|$ become smaller at lower densities below 0.6–0.7 g/cm³, the relative underestimation of density (in % notation) because of laser heating might be rather more severe than for inclusions at 0.6–0.7 g/cm³. The key finding is that for host minerals with large absorption coefficients at the excitation laser wavelength, laser heating can underestimate the CO₂ density by more than 10%, even at typical laser powers used for inclusion analysis. Therefore, if one needs to estimate the density of inclusions with high accuracy, then one approach is to select laser power at which the effect of laser heating on Δ can be ignored. If the decrease in Δ because of laser heating is not negligible, even at the lowest probable laser power, then a more accurate fluid density is obtainable by estimating the intercept Δ ($\Delta_{\text{intercept}}$, i.e. Δ at 0 mW) from the correlation between Δ and laser power, and substituting it into the Δ - ρ relation.

Acknowledgements

Part of Chapter 2 was accepted as a paper titled “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” in *Journal of Raman Spectroscopy*. This achievement was greatly facilitated by the comments and support of co-authors Tetsuma Kawano, Kohei Takahata, Junji Torimoto, and Junji Yamamoto.

I would like to thank Marie-Camille Caumon for constructive reviews that greatly improved this part of manuscript. I am grateful to Robert J. Bodnar and Eszter Sendula for their comments related to the original draft of this manuscript.

Appendix: Supporting Information

S-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, I 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 (1986) 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. (1980) 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 (Fig. 2b of Bondarenko (1986)). However, Bondarenko (1986) 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 my Eq. 2-2, I infer that the measurement precision of Δ of Bondarenko (1986) was worse than that of the present Raman system. Chen et al. (2004) 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 (1986). However, Chen et al. (2004) 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 Fig. 3 of Chen et al. (2004). Kawakami et al. (2003) 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 Fig. 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. I therefore excluded data reported by Bondarenko (1986), Chen et al. (2004), and Kawakami et al. (2003) from the discussion.

The second criterion is pressure measurement accuracy. Yuan et al. (2017) used HDAC to investigate characteristics of the Raman spectrum of CO₂–H₂O±CH₄±NaCl fluid at 22–400°C and

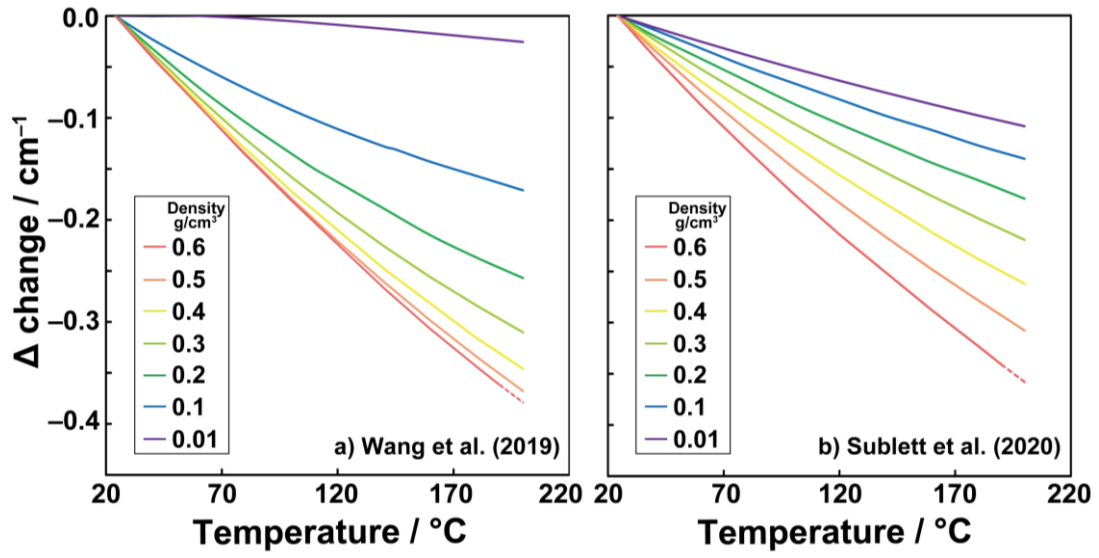
5–1200 MPa. They reported the relation among ΔD , temperature, and pressure, where ΔD represents the wavenumber shifts of measured Δ relative to the reference values measured at 23°C and 6 MPa. However, the densimeter reported by Yuan et al. (2017) differs considerably from the densimeter described in other published reports (Kawakami et al., 2003; Yamamoto and Kagi, 2006; Song et al., 2009; Fall et al., 2011; Wang et al., 2011; Lamadrid et al., 2017). The main cause for these discrepancies between the report by Yuan et al. (2017) and earlier reports appears to be a large pressure uncertainty (± 40 MPa) because Yuan et al. (2017) 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 my 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. I therefore excluded results reported by Yuan et al. (2017) from the discussion.

The third criterion is the fluid temperature during measurement. Fall et al. (2011) 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 my experimental temperatures are higher than 23°C , data measured at 35°C are the only data which can be compared with my own. However, it is difficult to discuss the temperature-dependence of Δ from such a small temperature variation. In fact, I 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 (Fig. 4b of Fall et al. (2011)). Therefore, because a sufficient temperature difference is necessary to discuss the temperature-dependence of Δ , I excluded results reported by Fall et al. (2011) from the discussion.

As illustrated by the reasons presented above, data of earlier studies that might be compared with my results are limited to those reported by Sublett et al. (2020b), Wang et al. (2019), and Wang et al. (2011), but they engender mutually contradictory results related to the density-dependence of $|\partial\Delta/\partial T)_\rho|$.

S-2. Effect of density on $\partial\Delta/\partial T$ at density lower than 0.6 g/cm^3

Fig. S2-1 shows the density dependence of $|(\partial\Delta/\partial T)_\rho|$ below 0.6 g/cm^3 calculated by Eq. 8 in Sublett et al. (2020b) and Eq. 3 in Wang et al. (2019). In both results, the value of $|(\partial\Delta/\partial T)_\rho|$ increases as the density increases from 0.01 to 0.6 g/cm^3 . In combination with the results of previous studies, it is suggested that there exists a density around $0.6\text{--}0.7 \text{ g/cm}^3$ where the sign of $d|(\partial\Delta/\partial T)_\rho|/d\rho$ is reversed.



FigureS2-1 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) Eq. 3 of Wang et al. (2019) and b) Eq. 8 of Sublett et al. (2020b). 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/cm^3 .

Chapter3: Why CO₂ fluid inclusions in mantle xenoliths have different densities depending on mineral species and inclusion size: Evaluation of laser heating effect on measured density

1. Introduction

Fluid densities of fluid inclusions in mantle xenoliths have been used to elucidate the P – T history of host xenoliths because the prevailing pressure at the source region of the xenoliths controls fluid density in inclusions at the time of fluid entrapment. Thus, fluid density can be used as a geobarometer to infer the depth where the transporting magma dislodged the peridotite fragments of the wall rocks surrounding the magma conduit. However, some factors may modify original fluid density within the inclusions during exhumation processes and complicate the use of the fluid inclusions as geobarometers. Among these factors are:

1. decrepitation (explosion) driven by the differential stress caused by the difference between fluid pressure and external pressure;
2. plastic deformation (stretching) driven by differential stress caused by the difference between fluid pressure and external pressure;
3. fluid diffusion driven by the chemical potential gradient of the fluid between the fluid and the grain boundary;
4. elastic volume changes of inclusions due to differences in thermoelastic properties of fluid and host minerals;
5. density change of fluid due to chemical reaction between fluid and host mineral;
6. precipitation of melt components that were dissolved in CO₂ under high P – T conditions.

In fact, perhaps as a result of a combination of these mechanisms, systematic changes in the density of fluid inclusions, depending on the mineral species and the size of the inclusion, have been reported.

First, regarding the size dependence of the density of inclusions, to the best of my knowledge, all studies have reported that the smaller the inclusion, the higher the density, regardless of the mineral species, and this is interpreted to be because the larger the inclusion, the more plastic deformation is likely to occur because there are more dislocations around the inclusion. Next, Yamamoto et al. (2012) studied the density dependence of the four main mineral species in the spinel lherzolite and reported that the fluid density is in the order of Cr-spinel > orthopyroxene = clinopyroxene > olivine. Many other studies have also compared the densities of inclusions in orthopyroxene, clinopyroxene, and olivine, and reported that inclusions in pyroxene are denser than those in olivine. On the other hand,

there are some reports that there is no significant difference in the density of inclusions in olivine and orthopyroxene, and that inclusions in olivine are denser than those in orthopyroxene. In the case of phenocrysts, olivine has been reported to have a higher density than pyroxene, probably due to the fact that olivine is crystallized early in the crystal fractionation process and traps fluid at a greater depth. Therefore, the depth provenance estimated from the density of inclusions depends on both the inclusion size and host mineral species to be measured.

However, such dependence may be artificially introduced by the properties of the measurement technique itself. For example, when CO₂ density is estimated using microthermometry, heating of inclusions by transmitted light may homogenize the gas phase into the liquid phase at a lower temperature than the true temperature, resulting in an overestimation of density. On the other hand, in the case of density estimation by Raman CO₂ densimeter, the density may be underestimated due to laser heating.

In this study, to prove that the size-dependence and mineral species-dependence of the density of fluid inclusions are not caused by the properties of the measurement technique itself, we investigated the size-dependence of the density of fluid inclusions with diameters ranging from less than 1 μm to several tens of μm in olivine, orthopyroxene, orthopyroxene, clinopyroxene, and Cr spinel. To measure the density of fluids above 1.179 g/cm³ and submicron fluid inclusions, the density was measured using a Raman CO₂ densitometer rather than microthermometry in this study.

The objectives of this study are three-fold. First, to measure the densities of fluid inclusions in the four main minerals in spinel lherzolite using the Raman CO₂ densimeter and to report the mineral species dependence. Second, to report the dependence of fluid density on fluid inclusion diameter for each mineral. The third is to prove that the mineral species and size dependence of the density of fluid inclusions in a mantle xenolith obtained using a Raman CO₂ densitometer is not an artificial result of laser heating.

2. Samples

Fluid inclusions in olivine, orthopyroxene, clinopyroxene, and Cr-spinel are derived from a mantle xenolith named as “En2A” from Ennokentiev, Sikhote-Alin, Far Eastern Russia. Petrological descriptions were presented by Yamamoto et al. (2012). I selected a total of 563 fluid inclusions from doubly polished chips: 149 from olivine, 175 from orthopyroxene, 106 from clinopyroxene, and 133 from Cr-spinel (Figs. 3-1 to 3-4). To confirm whether there was a difference in fluid density among mineral grains of the same mineral species, fluid inclusions were selected from several grains (i.e., 3 mineral grains from olivine, 3 from orthopyroxene, 4 from clinopyroxene, and 3 from Cr-spinel). As

a result, fluid inclusions were selected from 3 fluid inclusion assemblages from olivine, 9 from orthopyroxene, 7 from clinopyroxene, and 5 from Cr-spinel.

3. Methods

3.1 Raman setup

Raman spectra of the CO₂ fluid were obtained using a micro-Raman spectrum analysis system set up at the Hokkaido University Museum. Raman spectra were acquired during excitation by a diode-pumped solid-state laser (532 nm, Gem 532; Laser Quantum), and were acquired using a spectrometer with 75 cm focal length (Acton SP-2750; Princeton Instruments, Inc.) and a CCD camera (1650 × 200 pixels, 16 μm width, iVac; Andor Technology). A 50-μm core diameter multimode fiber served as the pinhole for confocality and as the entrance slit to the spectrometer. The laser power (P_{ill}) was 8.0 mW at the sample surface. The excitation laser was focused through a 50× objective (LUPlan; Nikon Corp.; N.A. = 0.8). The wavenumber dispersion for each pixel of the present Raman system when using a grating of 1800 lines/mm was 0.28 cm⁻¹/pixel at 1400 cm⁻¹. The accuracy in identification of peak position was enhanced further by application of a curve-fitting technique (Fukura et al., 2006). Earlier studies demonstrated that least-squares fitting improves precision by approx. 30 times compared to the value based on the detector pixel resolution (Izraeli et al., 1999; Fukura et al., 2006). Each CO₂ band was fitted to a Gaussian and Lorentzian mixing curve. Spectra were collected in a single window ranging from 1007.53 to 1485.58 cm⁻¹, which covers the main peaks of the Fermi diad of CO₂ and two well-established reference peaks of neon occurring at 1221.73 and 1449.19 cm⁻¹. Data were collected using two accumulations of 300 s or 600 s.

This study did not specifically examine the absolute value of the peak position, but instead emphasized investigation of the difference in the peak position of Fermi diad, which is not susceptible to the nonlinearity of the optical system. Nevertheless, to reduce mechanical errors in the optical system induced by changes in the measurement environment, the measured values were corrected using the atomic emission spectrum of the Ne lamp fixed to the optical system. Although Lamadrid et al. (2017) calibrated Δ using the two Ne lines appearing at 1031 and 1458 cm⁻¹ surrounding the Fermi diad, the Δ was calibrated using the following equation because the wavelengths of the excitation lasers used for this study differ from the wavelengths used for theirs.

$$\Delta_{\text{Ne calib}} = \Delta^{\text{raw}} \times \left(\frac{227.46}{\Delta_{\text{mes}}^{\text{Ne}}} \right) \quad (2-1)$$

In that equation, $\Delta_{\text{Ne calib}}$ denotes the corrected splitting of the Fermi diad, $\Delta_{\text{mes}}^{\text{Ne}}$ represents the measured separation between 1449.19 and 1221.73 cm^{-1} Ne emission lines. Δ^{raw} stands for the measured splitting of Δ in the CO_2 Raman spectrum. To correct the discrepancy in the Δ - ρ relations derived in earlier studies, I applied the correction method proposed by Hagiwara et al. (2020). In this

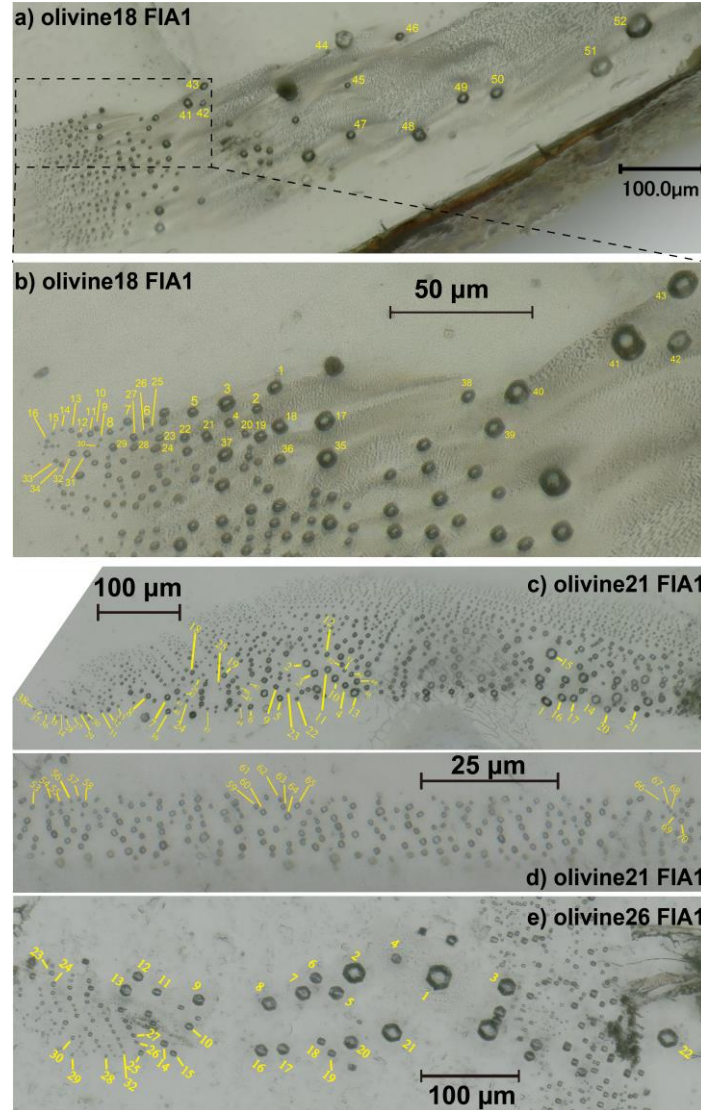


Figure3-1 Photomicrographs of studied fluid inclusions hosted in olivine. (a) olivine18 FIA1. (b) enlarged view of (a). (c) olivine21 FIA1. (d) back side of olivine21 FIA1 (e) olivine26 FIA1. A total of 149 fluid inclusions are selected from 3 grains. The numbers assigned to the fluid inclusions in each photo are used to identify the inclusion in each grain and correspond to the numbers shown in Appendix. The blue numbers indicate fluid inclusions with low density, which are considered to be decrepitated. To increase the depth of field in their photomicrographs, multi-focus (“stacking”) techniques were applied.

method, a correction term δ is added to $\Delta_{real}^{corrected}$ to estimate the density accurately using the $\Delta-\rho$ relation of Hagiwara et al. (2020). To calculate the correction term δ , the two standard fluid inclusions with densities of 0.914 and 1.167 g/cm³ were used. See Hagiwara et al. (2020) for detailed methods. The measured fluid densities are listed in Table S1.

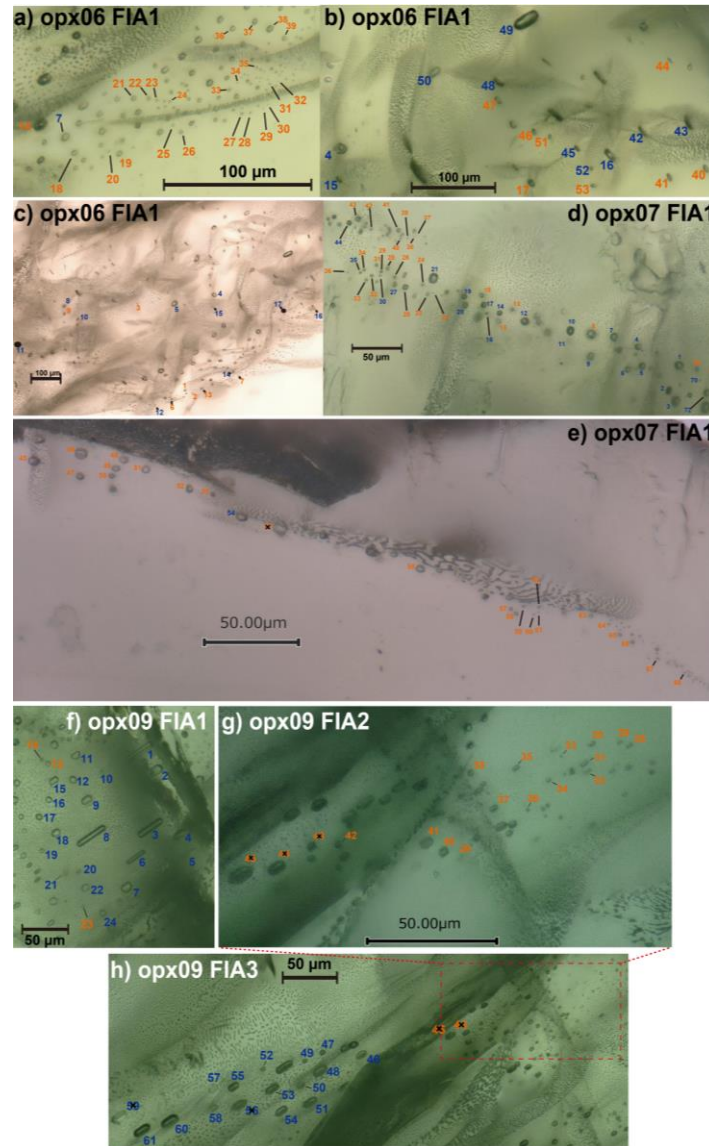


Figure3-2 Photomicrographs of studied fluid inclusions hosted in orthopyroxene. (a, b, and c) opx06 FIA1. (d) opx07 FIA1. (e) opx07 FIA2. (f) opx09 FIA1. (g) opx09 FIA2. (h) opx09 FIA3. A total of 175 fluid inclusions are selected from 3 grains. The numbers assigned to the fluid inclusions in each photo are used to identify the inclusion in each grain and correspond to the numbers shown in Appendix. The blue numbers indicate fluid inclusions with low density, which are considered to be decrepitated. To increase the depth of field in their photomicrographs, multi-focus (“stacking”) techniques were applied.

3.2 Extraction of shape parameters of inclusions

The respective sizes and depths of the fluid inclusions were measured using a 2000× objective (VH-ZST; Keyence Co.) with a digital microscope (VHX-5000; Keyence Co.). The

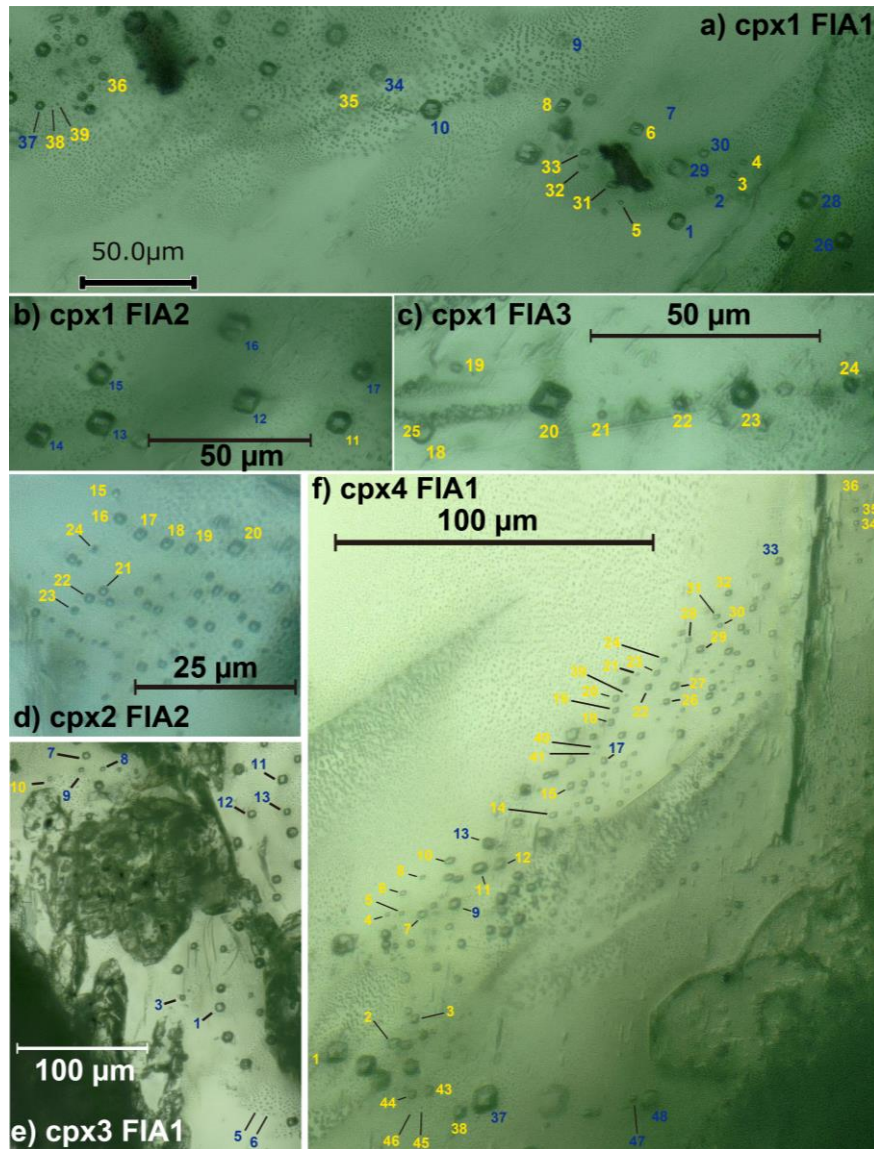


Figure3-3 Photomicrographs of studied fluid inclusions hosted in clinopyroxene. (a) cpx1 FIA1. (b) cpx1 FIA2. (c) cpx1 FIA3. (d) cpx2 FIA2. (e) cpx3 FIA1. (f) opx4 FIA1. A total of 106 fluid inclusions are selected from 4 grains. The numbers assigned to the fluid inclusions in each photo are used to identify the inclusion in each grain and correspond to the numbers shown in Appendix. The blue numbers indicate fluid inclusions with low density, which are considered to be decrepitated. To increase the depth of field in their photomicrographs, multi-focus (“stacking”) techniques were applied.

projected area of fluid inclusions was measured automatically by identifying the outline of a fluid inclusion using the brightness contrast. The inclusion radius (r_{inc}) was defined by the equivalent circle radius of the obtained projected area. I calculated the depth of the inclusion from the distance between the mechanical position for focus at the top of the host mineral and at a position where I obtained a sharp image of a fluid inclusion. The actual depth (z_{inc}) is calculated approximately by the simple expression of $z_{inc} = \text{refractive index of host mineral } (n_h) \times \text{measured depth}$. The values of n_h of olivine, orthopyroxene, clinopyroxene, spinel, and quartz are, respectively, 1.65, 1.66, 1.65, 1.72, and 1.55 (Lucey, 1998; Palik, 1998; Ghosh, 1999). The measured fluid densities inclusion diameter, depth, and shape parameters are listed in Table S1.

4. Results

The diameter of the inclusions calculated from the equivalent diameter of the projected area are in the range of 0.78–28.3 μm for olivine, 0.88–22.9 μm for orthopyroxene, 0.71–11.0 μm for clinopyroxene, and 1.13–8.23 μm for Cr-spinel, respectively (Table S3-1). The fluid densities are in the range of 0.046–1.081 g/cm^3 for olivine, 0.038–1.173 g/cm^3 for orthopyroxene, 0.375–1.172 g/cm^3

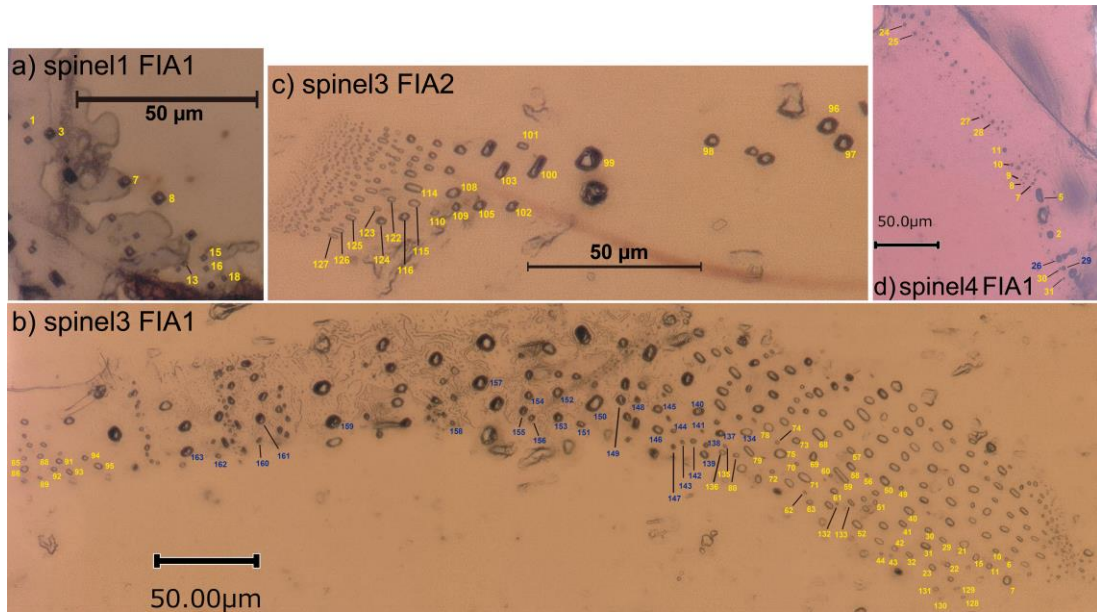


Figure3-4 Photomicrographs of studied fluid inclusions hosted in Cr-spinel. (a) spinel1 FIA1. (b) spinel3 FIA1. (c) spinel3 FIA2. (d) spinel4 FIA1. A total of 133 fluid inclusions are selected from 3 grains. The numbers assigned to the fluid inclusions in each photo are used to identify the inclusion in each grain and correspond to the numbers shown in Table S1. The blue numbers indicate fluid inclusions with low density, which are considered to be decrepitated. To increase the depth of field in their photomicrographs, multi-focus (“stacking”) techniques were applied.

for clinopyroxene, and 0.112–1.206 g/cm³ for Cr-spinel, respectively (Table S3-1).

Fig. S3-5 and S3-6 shows the relationship between the fluid density and the diameter of all the fluid inclusions measured. In the case of inclusions in orthopyroxene, clinopyroxene, and spinel, the gap separating high-density fluid inclusions from low-density fluid inclusions exists around 1.05 g/cm³. Meanwhile, in the case of inclusions in olivine, the gap is around 0.6–0.8 g/cm³.

Since the density of dense fluid inclusions is used to estimate the depth of origin of the mantle xenoliths, the dense cluster region is enlarged in Fig. S3-7. Fig. S3-7 shows that the fluid inclusions in the high-density region have different densities depending on the mineral species, with absolute values of Cr-spinel > orthopyroxene = clinopyroxene > olivine. In the case of inclusions in

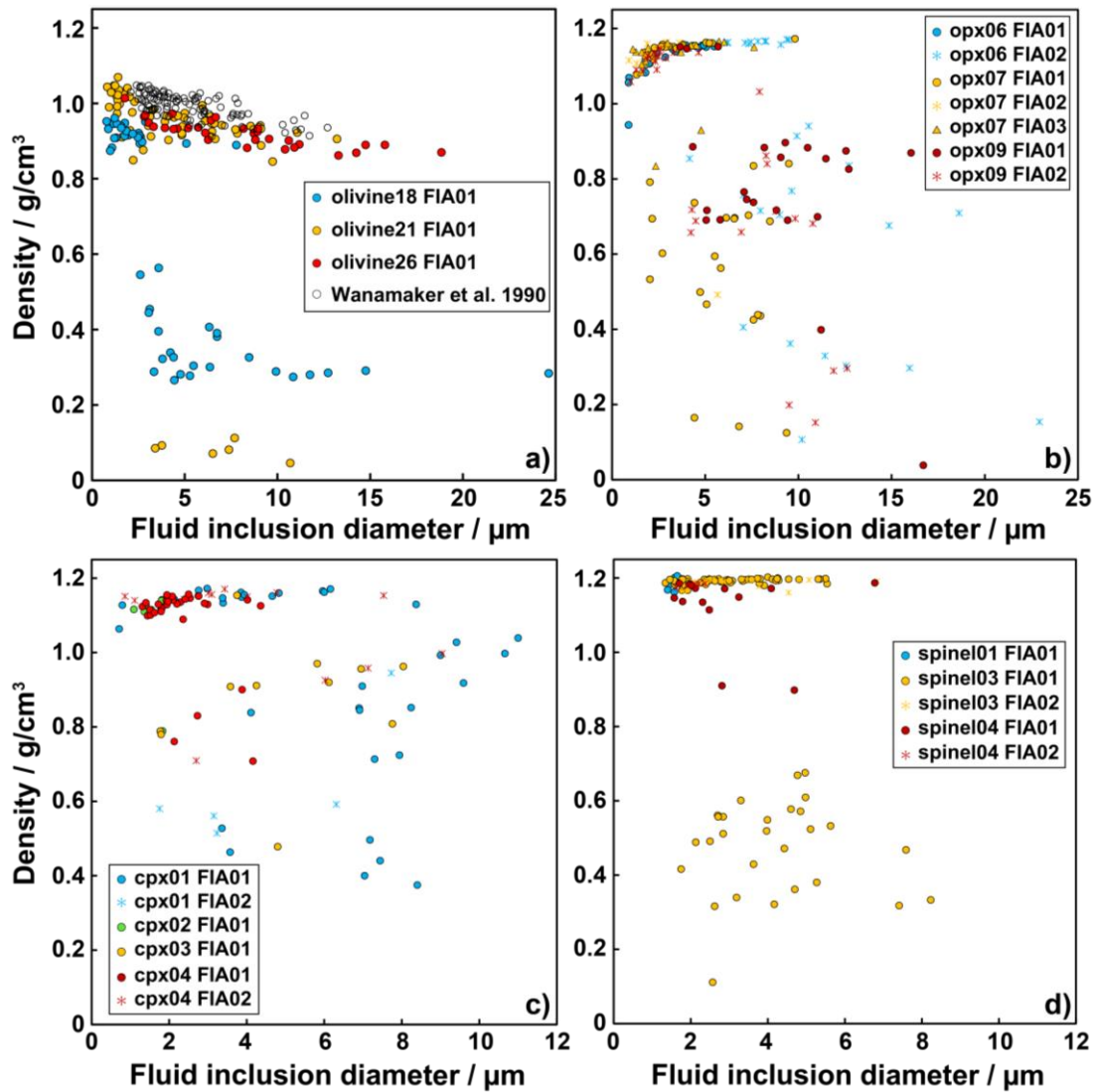


Figure3-5 Relation between fluid inclusion density and radius for inclusions in a) olivine, b) orthopyroxene, c) clinopyroxene, and d) Cr-spinel. Plotted data are shown in Table S3-1.

Cr-spinel, orthopyroxene, and clinopyroxene, the smaller the inclusion, the lower the density tends to be, and especially the density decreases sharply after a radius of 1.5 μm . However, inclusions in olivine tend to be denser for smaller inclusions.

5. Discussion

5.1 Mineral species dependence of fluid density

Many studies have reported the mineral species dependence of inclusion density. The previous studies can be classified according to the mineral species analyzed: four mineral species including olivine, orthopyroxene, clinopyroxene, and Cr-spinel (Yamamoto et al., 2007; Yamamoto and Kagi, 2008; Yamamoto et al., 2011; Yamamoto et al., 2012), four mineral species including olivine, orthopyroxene, clinopyroxene, and garnet (Frezzotti et al., 1992), three mineral species including olivine, orthopyroxene, and clinopyroxene (De Vivo et al., 1988; De Vivo et al., 1990; Yamamoto et al., 2002; Sapienza et al., 2005), two mineral species including olivine and orthopyroxene (Neumann

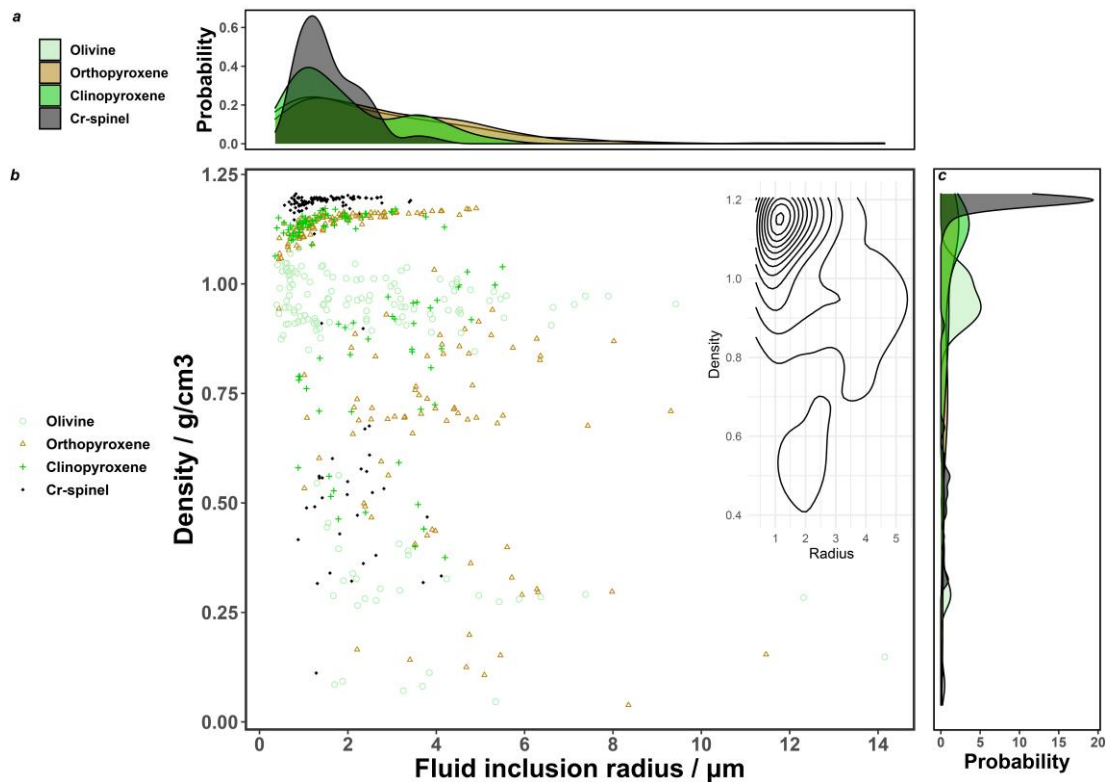


Figure3-6 Relation between fluid inclusion density and radius. a) Probability density distribution of the inclusion radius. b) The symbol in light green indicates data from olivine, brown shows orthopyroxene, emerald green represents clinopyroxene, and black denotes Cr-spinel. c) Probability density distribution of the inclusion density.

et al., 1995). Hansteen et al. (1998) used trapped rocks from several localities and compared up to three species.

Although the number of cases in which the fluid density in Cr-spinel has been measured is very limited, all of them report a density clearly higher than that of orthopyroxene, clinopyroxene, and olivine, which is consistent with the results of the present study. In addition, many studies have shown that orthopyroxene and clinopyroxene have almost the same density, whereas fluid density in pyroxene is clearly denser than that of olivine, which is also consistent with the present study. However, the cause of these mineral species dependencies is not well understood. At least, it has been reported in previous studies that dislocations are abundant around inclusions in olivine, and the relationship between density and size also suggests the existence of plastic deformation, suggesting that the reason for the low density of fluid inclusions in olivine is the expansion of the inclusion volume due to plastic deformation. However, the cause of the difference in density between Cr-spinel and pyroxene is still unknown.

In the following, I will discuss whether laser heating during analysis contributes to the differences in fluid density between mineral species. According to Chapter 2, $(\partial\Delta/\partial T)_p$ is always

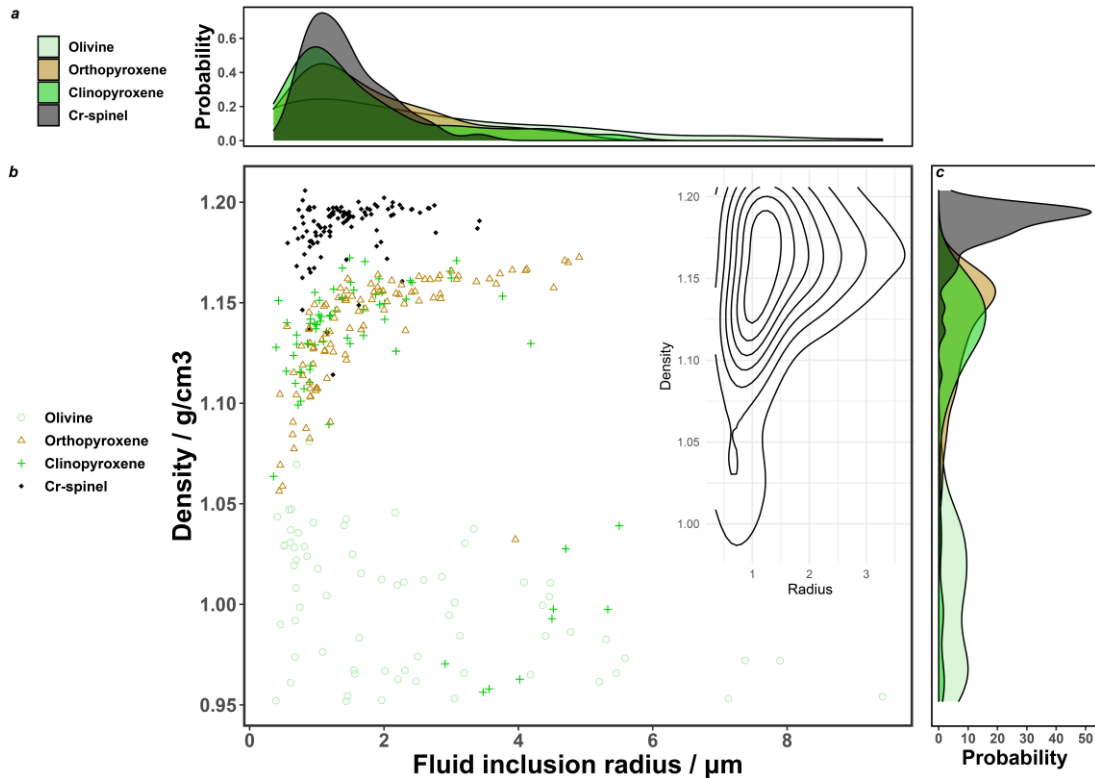


Figure3-7 Enlarged view of the high-density region (approx. 0.95–1.20 g/cm³) in Figure3-6.

negative. Therefore, if Δ is affected by laser heating, the density of inclusions in Cr-spinel, which has the largest temperature increase per unit laser power, should be the most underestimated, since there is not much difference between the densities of inclusions in pyroxene and Cr-spinel. Combining the fact that the laser power during the analysis was 8 mW and the laser heating coefficient of Cr-spinel is 6 °C/mW, the temperature of inclusions in Cr-spinel should have increased by $8 \times 6 = 48$ °C during the analysis. Therefore, when the room temperature is 23°C, the temperature during the analysis is $23 + 48 = 71$ °C. Here, I consider the case where the Δ value of CO₂ fluid inclusions in Cr-spinel is 105.8321 cm⁻¹. According to Equation 2-2, if the density is obtained by substituting this Δ value into the calibration curve at 23°C, it will be 1.200 g/cm³. However, in reality, the temperature should have risen to 71°C due to laser heating, and thus the density should be estimated using the calibration curve at 71°C. In that case, the density obtained would be 1.207 g/cm³. However, considering that the density estimation error of the Raman CO₂ densitometer is ± 0.005 g/cm³, the underestimation of density by laser heating has little effect on the results. This means that laser heating has little effect on very dense fluid inclusions, such as fluid inclusions in mantle xenoliths, because $|(\partial\Delta/\partial T)_\rho|$ becomes smaller at higher densities.

Similarly, let's use the laser heating coefficient of pyroxene to calculate the underestimation of density (1°C/mW), considering the case where the Δ value of CO₂ fluid inclusions in pyroxene is 105.6667 cm⁻¹. According to Equation 2-2, the density obtained by substituting this Δ value into the calibration curve at 23°C is 1.170 g/cm³. However, in reality, the temperature should have risen to 31°C due to laser heating, and thus the density should be estimated using the calibration curve at 31°C. In this case, the density obtained is 1.173 g/cm³. Therefore, the density is underestimated by 0.003 g/cm³, however, considering the density estimation error of the Raman CO₂ density system of ± 0.005 g/cm³, the underestimation of the density by laser heating has little effect on the results. Therefore, it is clear that laser heating has little effect on the measurement results, at least when the density of high-density CO₂ fluid is obtained using the Raman CO₂ densitometer under the low laser power condition of about 8 mW, as in this study. Therefore, the mineral species dependence of the densities obtained in this study, i.e., the higher densities of fluid inclusions in the order of Cr-spinel, orthopyroxene, clinopyroxene, and olivine, is not due to systematic errors caused by the analytical method.

Therefore, it is clear that laser heating has little effect on the measurement results, at least when the density of high-density CO₂ fluid is obtained using the Raman CO₂ density system under the low laser power condition of about 8 mW, as in this study. Therefore, the mineral species dependence of the densities obtained in this study, i.e., the higher densities of fluid inclusions in the order of Cr-

spinel, orthopyroxene, clinopyroxene, and olivine, is not due to systematic errors caused by the analytical method.

The factors that cause mineral species dependence are elastic and plastic deformation of minerals, diffusion of fluids, host-fluid reactions, and phase separation. In this study, we evaluated the effect of elastic deformation on the mineral species dependence of density, because elastic deformation is not time-dependent and its properties are easier to evaluate than those of other factors, since many data on its properties are available.

To show the change in density due to elastic deformation, the relative density compared to the density at the time of trapping is shown in the Figure 3-8. Here, we calculate the elastic deformation that occurs when fluid inclusions in mantle-trapped rocks reach the surface at 1000°C and 1.127 GPa. The calculations are based on the equation of state of MgAl_2O_4 constrained in the Appendix of this study, the EoS of orthopyroxene and clinopyroxene of Faccincani et al. (2021), and the EoS of olivine of Angel et al. (2018). The leftmost point is the relative density when the density at the time of trapping was 1.177 g/cm³, so the value is 1.0. The leftmost point is the relative density at the density of 1.177 g/cm³. Effect of elastic deformation on the density of fluid inclusions in mantle-trapped rocks at 1000°C and 1.127 GPa when they reach the surface. at the time of trapping, so the value is 1.0, and the middle point is the relative density when only elastic deformation occurs before the rock reaches the surface conditions, i.e. 0 GPa and 25°C. From this figure, we can see that if only elastic deformation had occurred, the fluid density in all minerals would have increased by about 2%. The dependence of the fluid density on the mineral type shows that olivine has the highest density and spinel has the lowest density, which is completely opposite to the actual measurement results, supporting the existence of a mechanism other than elastic deformation to change the density. The rightmost point shows the relative density calculated assuming that the inclusions in the spinel are only affected by elastic deformation. Since this assumption is not known to be correct, what is meaningful is what percentage of density reduction is required compared to the density of spinel, which means that a mechanism is required to reduce the density of pyroxene by 5% and olivine by 10% compared to spinel. In this study, we found that elastic deformation could not explain the dependence of the measured density on mineral type, and that a 5% and 10% density reduction was required for each mineral type compared to spinel. In addition to elastic deformation, these other factors need to be considered in the future, but these discussions will be more difficult than elastic deformation because of the effects of time, which is highly uncertain, and parameters whose values are not constrained.

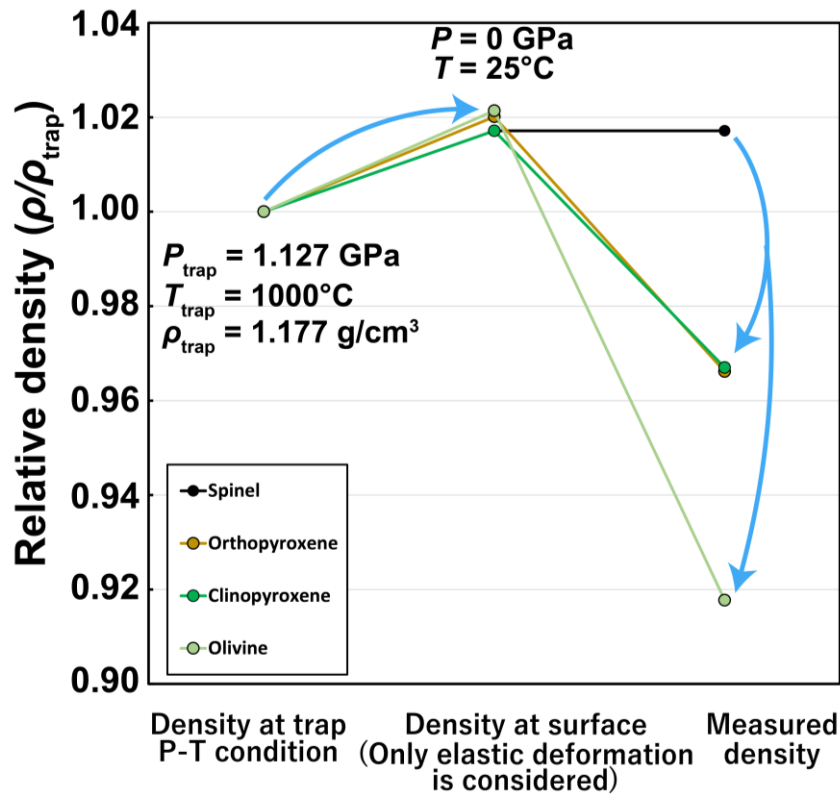


Figure3- 8 Effect of elastic deformation on the density of fluid inclusions in mantle xenoliths at 1000°C and 1.127 GPa when they reach the surface.

5.2 Inclusion size dependence of fluid density

5.2.1 Positive correlation between fluid density and inclusion size observed in fluid inclusions in olivine

To the best of my knowledge, previous studies investigating fluid inclusions in mantle xenolith and olivine phenocryst have shown that the fluid inclusion density in olivine, orthopyroxene, and clinopyroxene become denser the smaller they are (Roedder, 1984; Andersen et al., 1987; De Vivo et al., 1988; Wanamaker and Evans, 1989; Hansteen et al., 1991; Frezzotti et al., 1992; Andersen et al., 1995; Sapienza et al., 2005; Hidas et al., 2010; Berkesi et al., 2019). However, in the present study, only olivine showed the same size dependence of density as in previous studies. The negative correlation between the diameter of inclusions and fluid density has also been confirmed in high-pressure experiments using synthetic fluid inclusions (Vityk and Bodnar, 1998). They found that when synthetic NaCl–H₂O inclusions in quartz were re-equilibrated at 625°C for 7 and 30 days under

conditions of fluid inclusion pressure > confining pressure (internal overpressure of 2.1 kbar), the homogenization temperature was lower for smaller inclusions. They explain that this size dependence of density occurs because large inclusions already have a significant number of dislocations around them and therefore begin to deform as soon as differential pressure is applied, whereas small inclusions do not deform until dislocations occur in the host. A high density of dislocations was found around fluid inclusions in olivine in mantle xenolith of the same locality as the material used in this study, suggesting that deformation due to plastic deformation occurred (Yamamoto et al., 2008; Yamamoto et al., 2011). Therefore, the negative correlation between fluid density and inclusion diameter observed in olivine in this study is considered to be caused by plastic deformation.

5.2.2 Negative correlation between fluid density and inclusion size observed in fluid inclusions in orthopyroxene, clinopyroxene, and Cr-spinel

For inclusions in orthopyroxene, clinopyroxene, and Cr-spinel, a negative correlation between fluid density and inclusion diameter was observed, contrary to that in olivine. To my knowledge, this trend has never been reported before. One of the reasons why such a trend was observed in this study may be that Raman CO₂ densimeter was used as a density measurement method, which enabled us to measure the density of small inclusions with diameters of ~3 µm or less, which is difficult to measure by microthermometry, which has been adopted in most previous studies. In fact, a remarkable size-dependence was confirmed for samples with a diameter of 1.5 µm or less, and it would have been difficult to observe such size-dependence by microthermometry even for the samples used in this study.

Thus, it must be carefully judged whether the data considered to be new findings reflect physicochemical processes experienced by fluid inclusions or artificially produced results due to systematic errors caused by analytical methods or biases in sample selection. In particular, the Raman CO₂ densimeter, which has been improved and developed throughout Chapters 1 and 2, is still in its developing stage, and there may be unknown systematic errors related to size dependence. Considering the temperature dependence of the Raman CO₂ densimeter revealed in Chapter 2, if smaller inclusions are more easily heated by the excitation laser, the density will apparently decrease for smaller inclusions. Therefore, the positive correlation between density and inclusion diameter may be caused by laser heating.

In this study, the excitation laser power was set to 8 mW for the analysis. According to Hagiwara et al. (2021), the smaller the inclusion, the larger the temperature rise per unit laser power, however, when comparing the laser heating coefficients of inclusions with a radius of 0.1 µm and those

with a radius of 10 μm , the difference is only about 10%. Combining the laser heating coefficient of orthopyroxene and clinopyroxene of about $1^\circ\text{C}/\text{mW}$ with the laser power of 8mW during analysis, the temperature increase during analysis was about 8.0°C and 8.8°C for inclusions with radii of 0.1 μm and 10 μm , respectively, with a difference of only 0.8°C for a 10% difference in laser heating coefficient. According to Equation 2-2, the change in Δ caused by a temperature difference of 0.8°C at a density around $1.17 \text{ g}/\text{cm}^3$ is 0.002 cm^{-1} , which is much smaller than the typical measurement accuracy of Δ of $1\sigma = 0.02 \text{ cm}^{-1}$. Therefore, it is unlikely that laser heating would cause the size dependence as observed in this study.

6. Conclusions

In this study, I measured the density of fluid inclusions in mantle xenoliths in Far Eastern Russia using a Raman CO_2 densimeter and reported the mineral species and inclusion diameter dependence of fluid density. The mineral species dependence of the fluid density was in agreement with previous studies. However, the size dependence of fluid density was observed to be lower for inclusions in orthopyroxene, clinopyroxene, and Cr-spinel with smaller inclusion diameters, which has not been reported previously. Although the effect of laser heating was considered as a factor causing these mineral species and size dependencies, it was found that laser heating had little effect on the measured densities, at least under the analytical conditions of this study. Therefore, the mineral species and size dependences obtained in this study are not artificially introduced by systematic errors caused by the analytical method, but reflect naturally occurring physicochemical processes.

Appendix: Supporting Information

S-1. List of the measured inclusion diameter, depth, shape parameter, and density.

The size, depth, shape parameters, and fluid density of a total of 563 inclusions measured using digital microscopy and Raman spectroscopy are shown below.

Table S3-1 List of the measured inclusion diameter, depth, shape parameter, and density.

	Area	Perimeter	Max. diameter	Min. diameter	Diameter	Roundness	Aspect ratio	Depth	Density
	μm^2	μm	μm	μm	μm	—	—	μm	g/cm^3
En2A olivine 18 fi 01	17.9	15.7	5.2	4.2	4.8	0.91	1.23	10.7	0.282
En2A olivine 18 fi 02	8.8	11.2	3.7	2.9	3.3	0.88	1.28	22.4	0.288
En2A olivine 18 fi 03	23.5	18.1	6.1	4.7	5.5	0.9	1.28	8.3	0.304
En2A olivine 18 fi 04	7.6	10.0	3.2	2.9	3.1	0.97	1.12	26.6	0.454
En2A olivine 18 fi 05	10.1	11.7	3.8	3.2	3.6	0.94	1.19	6.6	0.563
En2A olivine 18 fi 06	2.5	5.7	1.8	1.6	1.8	0.94	1.12	3.8	0.948
En2A olivine 18 fi 07	5.4	8.5	2.8	2.4	2.6	0.94	1.15	2.5	0.911
En2A olivine 18 fi 08	3.0	6.2	2.1	1.7	2.0	0.98	1.22	8.1	0.915
En2A olivine 18 fi 09	0.6	2.9	0.9	0.8	0.9	0.92	1.22	13.2	0.932
En2A olivine 18 fi 10	2.4	5.7	1.8	1.6	1.8	0.92	1.12	4.5	0.914
En2A olivine 18 fi 11	2.7	6.2	2.0	1.7	1.9	0.87	1.21	9.2	0.926
En2A olivine 18 fi 12	1.3	4.2	1.4	1.2	1.3	0.93	1.14	8.6	0.909
En2A olivine 18 fi 13	1.9	5.1	1.7	1.4	1.6	0.91	1.17	2.5	0.940
En2A olivine 18 fi 14	0.9	3.6	1.2	0.9	1.1	0.89	1.34	2.0	0.882
En2A olivine 18 fi 15	1.1	3.8	1.2	1.1	1.2	0.92	1.14	3.3	0.946
En2A olivine 18 fi 16	1.4	4.4	1.5	1.3	1.3	0.9	1.15	9.6	0.946
En2A olivine 18 fi 17	35.7	22.3	7.3	6.1	6.7	0.9	1.21	42.9	0.381
En2A olivine 18 fi 18	21.9	17.7	5.7	4.9	5.3	0.88	1.17	43.7	0.277
En2A olivine 18 fi 19	14.0	13.7	4.6	3.6	4.2	0.94	1.27	44.2	0.339
En2A olivine 18 fi 20	5.3	8.3	2.8	2.3	2.6	0.96	1.23	37.5	0.545
En2A olivine 18 fi 21	11.3	12.4	4.2	3.3	3.8	0.92	1.25	30.0	0.322
En2A olivine 18 fi 22	7.3	9.8	3.2	2.7	3.1	0.96	1.21	27.1	0.445
En2A olivine 18 fi 23	5.0	8.3	2.9	2.1	2.5	0.91	1.36	21.5	0.921
En2A olivine 18 fi 24	6.5	9.6	3.5	2.1	2.9	0.89	1.67	30.7	0.952
En2A olivine 18 fi 25	1.1	5.0	1.5	1.1	1.2	0.58	1.32	12.2	0.908
En2A olivine 18 fi 26	0.8	3.3	1.1	0.9	1.0	0.86	1.24	12.0	0.874
En2A olivine 18 fi 27	5.2	8.5	2.8	2.3	2.6	0.89	1.23	16.2	0.894
En2A olivine 18 fi 28	5.1	8.4	2.9	2.1	2.6	0.91	1.34	25.1	0.914
En2A olivine 18 fi 29	5.8	8.8	2.9	2.4	2.7	0.94	1.18	21.6	0.898
En2A olivine 18 fi 30	0.5	2.6	0.9	0.7	0.8	0.88	1.35	17.7	0.952
En2A olivine 18 fi 31	4.8	8.1	2.6	2.3	2.5	0.92	1.16	25.9	0.910
En2A olivine 18 fi 32	3.8	7.2	2.4	2.0	2.2	0.92	1.20	25.2	0.920
En2A olivine 18 fi 33	1.9	4.8	1.6	1.4	1.6	1.06	1.13	24.6	0.935
En2A olivine 18 fi 34	1.2	4.3	1.4	1.1	1.2	0.78	1.27	29.5	0.961
En2A olivine 18 fi 35	31.6	27.3	6.9	6.0	6.4	0.53	1.15	71.6	0.300
En2A olivine 18 fi 36	10.0	12.3	4.1	3.2	3.6	0.83	1.29	66.8	0.395

En2A olivine 18 fi 37	15.1	19.3	5.1	3.8	4.4	0.51	1.35	48.8	0.327
En2A olivine 18 fi 38	15.5	19.2	5.1	4.0	4.4	0.53	1.29	49.2	0.266
En2A olivine 18 fi 39	35.5	22.6	7.4	6.2	6.7	0.87	1.20	79.4	0.391
En2A olivine 18 fi 40	56.3	28.7	9.4	7.8	8.5	0.86	1.21	60.1	0.326
En2A olivine 18 fi 41	108.4	39.2	12.9	10.7	11.8	0.89	1.21	38.1	0.280
En2A olivine 18 fi 42	47.5	26.2	8.7	6.9	7.8	0.87	1.27	58.1	0.889
En2A olivine 18 fi 43	77.2	38.5	11.3	8.9	9.9	0.66	1.27	29.0	0.289
En2A olivine 18 fi 44	20.3	16.9	6.0	4.3	5.1	0.9	1.39	20.6	0.894
En2A olivine 18 fi 45	31.3	20.8	7.1	5.6	6.3	0.91	1.26	120.5	0.407
En2A olivine 18 fi 46	92.5	36.3	12.1	10.0	10.9	0.88	1.20	36.8	0.274
En2A olivine 18 fi 49	127.2	43.8	13.9	11.7	12.7	0.83	1.19	230.5	0.285
En2A olivine 18 fi 50	171.1	51.9	16.8	13.0	14.8	0.8	1.29	244.2	0.291
En2A olivine 18 fi 51	476.3	83.8	28.0	21.9	24.6	0.85	1.28	277.5	0.284
En2A olivine 18 fi 52	629.1	96.6	31.7	25.2	28.3	0.85	1.26	232.3	0.148
En2A olivine 21 fi 02	64.7	30.2	9.8	8.4	9.1	0.89	1.16	89.1	0.941
En2A olivine 21 fi 03	63.7	29.8	9.9	8.4	9.0	0.9	1.17	71.0	0.937
En2A olivine 21 fi 04	48.2	25.8	8.3	7.4	7.8	0.91	1.12	47.9	0.920
En2A olivine 21 fi 05	46.5	25.5	8.1	7.2	7.7	0.9	1.12	26.4	0.112
En2A olivine 21 fi 06	34.6	22.4	7.8	5.6	6.6	0.87	1.37	14.9	0.906
En2A olivine 21 fi 07	42.8	24.2	7.7	7.1	7.4	0.92	1.08	36.3	0.081
En2A olivine 21 fi 08	33.3	21.6	7.1	5.9	6.5	0.9	1.19	39.6	0.071
En2A olivine 21 fi 09	32.9	21.4	7.1	6.0	6.5	0.9	1.19	47.9	0.925
En2A olivine 21 fi 10	65.0	30.1	9.8	8.6	9.1	0.9	1.15	64.4	0.933
En2A olivine 21 fi 11	57.4	28.1	9.0	8.2	8.6	0.92	1.10	82.5	0.940
En2A olivine 21 fi 12	27.7	19.6	6.7	5.1	5.9	0.9	1.31	110.6	0.995
En2A olivine 21 fi 13	89.8	36.6	12.1	10.1	10.7	0.84	1.20	26.4	0.046
En2A olivine 21 fi 14	96.3	37.2	11.7	10.6	11.1	0.87	1.10	46.2	0.922
En2A olivine 21 fi 15	137.0	44.0	13.9	12.5	13.2	0.89	1.11	141.9	0.906
En2A olivine 21 fi 16	74.5	32.8	11.3	8.1	9.7	0.87	1.38	29.7	0.846
En2A olivine 21 fi 17	65.3	30.2	9.6	8.8	9.1	0.9	1.09	49.5	0.889
En2A olivine 21 fi 18	19.6	16.3	5.3	4.6	5.0	0.93	1.14	77.6	0.974
En2A olivine 21 fi 19	32.1	21.0	6.9	5.9	6.4	0.91	1.17	69.3	0.966
En2A olivine 21 fi 21	38.4	23.0	7.4	6.7	7.0	0.91	1.11	26.4	0.942
En2A olivine 21 fi 22	18.5	16.3	5.5	4.2	4.9	0.87	1.33	7.6	0.939
En2A olivine 21 fi 23	18.4	16.1	5.3	4.2	4.8	0.89	1.27	29.2	0.916
En2A olivine 21 fi 24	11.1	12.4	4.3	3.2	3.8	0.91	1.34	26.4	0.093
En2A olivine 21 fi 25	3.9	7.2	2.4	1.9	2.2	0.94	1.26	45.4	0.850
En2A olivine 21 fi 26	3.3	6.5	2.1	1.8	2.1	0.98	1.21	58.4	0.928
En2A olivine 21 fi 27	2.1	5.2	1.8	1.4	1.6	0.96	1.30	4.6	0.910
En2A olivine 21 fi 28	6.7	9.4	3.2	2.5	2.9	1	1.25	3.0	0.954

En2A olivine 21 fi 29	12.2	13.2	4.2	3.5	3.9	0.88	1.20	10.2	0.952
En2A olivine 21 fi 30	12.8	13.7	4.5	3.8	4.0	0.86	1.19	8.1	0.967
En2A olivine 21 fi 31	8.3	11.0	3.8	2.8	3.3	0.87	1.37	8.3	0.983
En2A olivine 21 fi 32	19.3	16.6	5.5	4.3	5.0	0.88	1.27	11.1	0.962
En2A olivine 21 fi 33	7.6	10.6	3.4	2.7	3.1	0.85	1.24	16.8	0.967
En2A olivine 21 fi 34	1.4	4.2	1.5	1.1	1.4	1.01	1.32	9.6	0.974
En2A olivine 21 fi 35	3.7	7.2	2.3	2.0	2.2	0.9	1.16	7.4	0.976
En2A olivine 21 fi 36	1.7	6.5	1.7	1.4	1.5	0.51	1.17	6.9	0.999
En2A olivine 21 fi 37	1.4	4.8	1.5	1.2	1.3	0.76	1.21	9.2	1.019
En2A olivine 21 fi 38	4.1	9.3	2.5	2.2	2.3	0.59	1.18	6.8	1.004
En2A olivine 21 fi 39	32.4	27.7	7.0	6.2	6.4	0.53	1.12	10.6	0.947
En2A olivine 21 fi 40	7.3	12.8	3.4	2.7	3.0	0.56	1.26	13.5	0.941
En2A olivine 21 fi 41	9.1	11.7	4.2	2.6	3.4	0.83	1.61	26.6	0.085
En2A olivine 21 fi 42	6.0	9.2	3.1	2.3	2.8	0.88	1.34	32.0	0.876
En2A olivine 21 fi 43	7.9	10.6	3.5	2.9	3.2	0.88	1.23	10.9	0.912
En2A olivine 21 fi 44	13.3	13.9	4.7	3.5	4.1	0.87	1.34	7.8	0.903
En2A olivine 21 fi 45	15.4	14.5	5.0	3.9	4.4	0.92	1.31	29.2	0.963
En2A olivine 21 fi 46	18.4	16.5	5.2	4.4	4.8	0.85	1.18	38.8	0.920
En2A olivine 21 fi 47	7.7	10.7	3.5	2.7	3.1	0.85	1.32	40.1	0.965
En2A olivine 21 fi 48	34.1	22.2	7.1	6.2	6.6	0.87	1.14	31.7	0.947
En2A olivine 21 fi 49	46.9	26.3	8.2	7.6	7.7	0.86	1.08	46.2	0.931
En2A olivine 21 fi 50	31.2	21.2	6.8	5.8	6.3	0.87	1.18	60.1	0.913
En2A olivine 21 fi 51	16.8	15.7	5.4	4.0	4.6	0.85	1.36	68.5	0.967
En2A olivine 21 fi 52	29.1	21.2	6.8	5.6	6.1	0.81	1.21	78.7	0.953
En2A olivine 21 fi 53	1.2	4.0	1.3	1.1	1.2	0.93	1.23	5.8	1.037
En2A olivine 21 fi 54	1.4	4.5	1.5	1.2	1.3	0.87	1.25	4.3	1.028
En2A olivine 21 fi 55	1.2	4.1	1.4	1.0	1.2	0.86	1.36	4.3	1.031
En2A olivine 21 fi 56	0.8	3.5	1.2	1.0	1.0	0.85	1.20	4.0	1.029
En2A olivine 21 fi 57	1.1	4.1	1.3	1.1	1.2	0.79	1.21	5.1	1.047
En2A olivine 21 fi 58	2.1	5.8	1.8	1.5	1.6	0.78	1.16	7.6	1.029
En2A olivine 21 fi 59	1.5	4.9	1.6	1.3	1.4	0.79	1.18	10.7	1.008
En2A olivine 21 fi 60	2.3	5.8	1.9	1.6	1.7	0.86	1.15	11.9	1.024
En2A olivine 21 fi 61	1.7	5.1	1.8	1.3	1.5	0.81	1.38	5.4	1.036
En2A olivine 21 fi 62	1.5	5.0	1.5	1.3	1.4	0.73	1.18	7.4	0.992
En2A olivine 21 fi 63	1.5	4.9	1.6	1.2	1.4	0.78	1.33	10.9	1.022
En2A olivine 21 fi 64	3.2	7.4	2.2	1.9	2.0	0.75	1.16	14.9	1.018
En2A olivine 21 fi 65	2.8	6.6	2.1	1.7	1.9	0.82	1.26	10.2	1.041
En2A olivine 21 fi 66	0.5	2.8	0.9	0.8	0.8	0.84	1.17	5.3	1.044
En2A olivine 21 fi 67	0.7	3.1	1.2	0.8	0.9	0.9	1.51	6.3	0.990
En2A olivine 21 fi 68	0.8	3.6	1.2	0.9	1.0	0.82	1.32	7.1	1.029

En2A olivine 21 fi 69	1.2	4.3	1.5	1.0	1.2	0.82	1.46	10.9	1.047
En2A olivine 21 fi 70	1.5	4.8	1.5	1.3	1.4	0.84	1.17	12.9	1.070
En2A olivine 26 fi 01	278.7	65.2	20.0	17.8	18.8	0.82	1.12	98.2	0.954
En2A olivine 26 fi 02	195.9	53.6	17.0	15.0	15.8	0.86	1.13	98.7	0.972
En2A olivine 26 fi 03	138.7	45.3	14.4	12.9	13.3	0.85	1.12	86.0	0.947
En2A olivine 26 fi 04	55.0	28.0	9.1	7.8	8.4	0.88	1.16	122.8	0.965
En2A olivine 26 fi 05	88.5	36.1	11.7	10.2	10.6	0.85	1.15	73.6	0.982
En2A olivine 26 fi 06	59.7	29.2	9.6	7.9	8.7	0.88	1.21	93.1	1.000
En2A olivine 26 fi 07	98.2	37.5	12.2	10.6	11.2	0.88	1.15	69.8	0.973
En2A olivine 26 fi 08	93.5	37.1	12.1	10.1	10.9	0.85	1.19	59.4	0.966
En2A olivine 26 fi 09	62.5	29.8	9.6	8.5	8.9	0.88	1.13	79.7	1.004
En2A olivine 26 fi 10	32.3	21.3	6.9	5.9	6.4	0.89	1.16	44.1	1.030
En2A olivine 26 fi 11	35.0	22.3	7.4	5.9	6.7	0.89	1.24	94.9	1.037
En2A olivine 26 fi 12	52.4	26.9	8.8	7.5	8.2	0.91	1.18	116.2	1.011
En2A olivine 26 fi 13	63.0	30.3	9.7	8.4	9.0	0.86	1.15	94.9	1.011
En2A olivine 26 fi 14	25.7	19.1	6.2	5.1	5.7	0.89	1.22	15.7	1.014
En2A olivine 26 fi 15	21.1	17.0	5.7	4.5	5.2	0.92	1.25	4.6	1.012
En2A olivine 26 fi 16	71.6	32.2	10.5	8.7	9.6	0.87	1.21	9.9	0.986
En2A olivine 26 fi 17	61.0	29.7	9.5	8.2	8.8	0.87	1.16	14.2	0.984
En2A olivine 26 fi 18	30.8	20.8	6.8	5.6	6.3	0.89	1.22	22.3	0.984
En2A olivine 26 fi 19	29.2	20.2	6.7	5.4	6.1	0.9	1.24	9.9	1.001
En2A olivine 26 fi 20	85.1	35.0	11.3	9.9	10.4	0.87	1.15	24.3	0.961
En2A olivine 26 fi 21	159.5	48.0	15.6	13.4	14.3	0.87	1.16	39.3	0.953
En2A olivine 26 fi 22	170.9	49.6	16.0	13.8	14.8	0.87	1.16	51.0	0.972
En2A olivine 26 fi 23	14.8	14.4	4.8	3.8	4.3	0.9	1.24	129.9	1.046
En2A olivine 26 fi 24	16.6	15.5	5.2	4.0	4.6	0.86	1.30	115.7	1.011
En2A olivine 26 fi 25	15.1	14.5	4.6	4.1	4.4	0.91	1.13	10.2	1.010
En2A olivine 26 fi 26	7.3	10.1	3.5	2.6	3.1	0.91	1.34	22.9	1.025
En2A olivine 26 fi 27	12.1	12.9	4.3	3.4	3.9	0.92	1.26	32.8	1.012
En2A olivine 26 fi 28	6.2	9.1	3.0	2.6	2.8	0.93	1.15	6.8	1.039
En2A olivine 26 fi 29	6.5	9.4	3.1	2.6	2.9	0.92	1.23	9.9	1.043
En2A olivine 26 fi 30	8.6	10.9	3.5	3.0	3.3	0.91	1.15	33.3	1.015
En2A olivine 26 fi 32	2.5	5.6	1.8	1.5	1.8	0.99	1.18	12.2	1.081
En2A opx 06 fi 01	70.6	34.7	11.1	8.6	9.5	0.74	1.29	52.3	1.170
En2A opx 06 fi 02	43.6	25.2	8.3	6.8	7.5	0.87	1.22	26.2	1.164
En2A opx 06 fi 03	40.0	24.6	7.7	6.6	7.1	0.83	1.16	50.1	1.162
En2A opx 06 fi 04	173.4	51.1	17.1	13.4	14.9	0.84	1.28	73.7	0.676
En2A opx 06 fi 05	272.4	65.3	22.2	15.8	18.6	0.8	1.40	50.5	0.709
En2A opx 06 fi 06	30.3	20.8	6.9	5.5	6.2	0.88	1.26	31.7	1.163
En2A opx 06 fi 07	35.8	22.3	7.4	6.2	6.8	0.9	1.19	47.5	1.160

En2A opx 06 fi 08	87.2	36.3	11.9	9.1	10.5	0.83	1.30	63.9	0.941
En2A opx 06 fi 09	69.1	32.5	11.9	7.5	9.4	0.82	1.59	41.8	1.171
En2A opx 06 fi 10	77.3	36.4	13.3	7.1	9.9	0.73	1.87	22.2	0.914
En2A opx 06 fi 11	123.8	43.4	14.9	10.8	12.6	0.83	1.37	17.3	0.303
En2A opx 06 fi 12	39.1	23.6	7.7	6.3	7.1	0.88	1.22	23.1	0.758
En2A opx 06 fi 13	64.3	32.2	11.3	7.0	9.1	0.78	1.61	32.4	1.157
En2A opx 06 fi 14	63.5	32.2	10.9	7.7	9.0	0.77	1.42	62.3	0.705
En2A opx 06 fi 15	49.7	28.8	10.3	5.8	8.0	0.76	1.78	44.7	0.716
En2A opx 06 fi 16	127.1	48.7	18.5	8.1	12.7	0.67	2.29	39.2	0.835
En2A opx 06 fi 17	72.9	33.9	11.7	7.9	9.6	0.8	1.47	22.1	0.768
En2A opx 06 fi 18	20.0	16.6	5.6	4.5	5.0	0.91	1.26	28.1	1.151
En2A opx 06 fi 19	18.3	16.2	5.4	4.2	4.8	0.87	1.29	10.8	1.155
En2A opx 06 fi 20	3.2	6.5	2.1	1.8	2.0	0.95	1.20	13.8	1.107
En2A opx 06 fi 21	15.0	14.4	4.8	4.1	4.4	0.91	1.18	56.8	1.155
En2A opx 06 fi 22	9.0	11.1	3.5	3.2	3.4	0.92	1.09	52.1	1.138
En2A opx 06 fi 23	4.0	7.2	2.4	2.0	2.2	0.96	1.17	49.1	1.126
En2A opx 06 fi 24	3.0	6.2	2.0	1.8	2.0	1	1.12	42.7	1.106
En2A opx 06 fi 25	2.6	5.8	1.9	1.6	1.8	0.95	1.15	17.1	1.103
En2A opx 06 fi 26	8.3	10.5	3.4	3.0	3.2	0.93	1.13	9.0	1.146
En2A opx 06 fi 27	4.5	7.8	2.5	2.1	2.4	0.92	1.19	9.8	1.136
En2A opx 06 fi 28	2.6	5.8	1.9	1.6	1.8	0.97	1.16	8.8	1.103
En2A opx 06 fi 29	0.7	2.9	1.0	0.8	0.9	0.96	1.14	3.0	1.069
En2A opx 06 fi 30	0.6	2.8	0.9	0.8	0.9	0.96	1.22	8.6	0.944
En2A opx 06 fi 31	2.5	5.6	1.8	1.6	1.8	1.01	1.13	28.4	1.110
En2A opx 06 fi 32	0.6	2.9	0.9	0.8	0.9	0.92	1.11	25.7	1.056
En2A opx 06 fi 33	6.4	9.2	3.1	2.6	2.9	0.94	1.19	36.0	1.124
En2A opx 06 fi 34	2.5	5.7	1.8	1.7	1.8	0.96	1.11	39.2	1.083
En2A opx 06 fi 35	3.1	6.4	2.1	1.8	2.0	0.95	1.13	47.8	1.107
En2A opx 06 fi 36	16.6	15.1	5.0	4.1	4.6	0.92	1.20	88.8	1.149
En2A opx 06 fi 37	19.0	16.2	5.3	4.5	4.9	0.92	1.20	88.8	1.156
En2A opx 06 fi 38	23.5	18.3	6.2	4.7	5.5	0.88	1.31	88.3	1.152
En2A opx 06 fi 39	12.4	13.0	4.2	3.7	4.0	0.93	1.14	76.5	1.156
En2A opx 06 fi 40	53.4	29.3	11.2	6.1	8.3	0.78	1.85	19.6	1.167
En2A opx 06 fi 41	48.0	28.4	10.9	5.4	7.8	0.75	2.02	16.1	1.166
En2A opx 06 fi 42	102.5	51.6	22.0	5.9	11.4	0.48	3.71	63.6	0.330
En2A opx 06 fi 43	200.1	61.0	23.7	11.6	16.0	0.68	2.05	60.4	0.297
En2A opx 06 fi 44	25.3	20.6	8.0	3.7	5.7	0.75	2.19	131.0	1.154
En2A opx 06 fi 45	38.9	24.9	9.2	4.9	7.0	0.79	1.86	50.5	0.406
En2A opx 06 fi 46	42.3	26.4	9.5	5.7	7.3	0.76	1.68	75.5	1.159
En2A opx 06 fi 47	53.0	30.1	11.1	5.7	8.2	0.74	1.96	116.4	1.166

En2A opx 06 fi 48	71.7	39.0	14.9	5.9	9.6	0.59	2.51	125.7	0.362
En2A opx 06 fi 49	412.9	86.8	33.3	15.0	22.9	0.69	2.22	166.3	0.154
En2A opx 06 fi 50	87.2	44.7	15.6	7.2	10.2	0.53	2.15	0.0	0.107
En2A opx 06 fi 51	24.7	19.2	7.0	4.6	5.6	0.84	1.50	0.0	1.162
En2A opx 06 fi 52	13.6	14.4	5.2	3.1	4.2	0.83	1.67	0.0	0.854
En2A opx 06 fi 53	29.8	21.0	7.7	4.7	6.2	0.85	1.63	0.0	1.162
En2A opx 07 fi 01	56.4	28.7	8.7	8.3	8.5	0.86	1.05	13.4	0.687
En2A opx 07 fi 02	36.5	23.5	8.2	5.5	6.8	0.83	1.48	21.7	0.142
En2A opx 07 fi 03	68.9	31.8	10.5	8.3	9.4	0.86	1.27	41.3	0.125
En2A opx 07 fi 04	34.0	21.7	6.8	6.4	6.6	0.91	1.06	12.3	0.697
En2A opx 07 fi 05	33.7	22.4	7.1	6.1	6.6	0.84	1.17	16.3	0.694
En2A opx 07 fi 06	29.5	20.4	6.8	5.4	6.1	0.89	1.26	34.4	0.697
En2A opx 07 fi 07	45.2	25.7	8.2	7.0	7.6	0.86	1.17	7.0	0.835
En2A opx 07 fi 08	75.6	32.7	10.3	9.4	9.8	0.89	1.10	10.6	1.173
En2A opx 07 fi 09	49.7	26.7	8.7	7.2	8.0	0.88	1.21	42.8	0.436
En2A opx 07 fi 10	45.2	25.8	8.6	6.5	7.6	0.85	1.33	23.2	0.425
En2A opx 07 fi 11	20.2	16.7	5.3	4.8	5.1	0.91	1.10	47.5	0.467
En2A opx 07 fi 12	48.0	25.7	8.4	7.4	7.8	0.91	1.13	31.0	0.439
En2A opx 07 fi 13	8.6	10.8	3.5	3.0	3.3	0.93	1.15	10.8	1.151
En2A opx 07 fi 14	17.6	15.6	5.1	4.4	4.7	0.9	1.16	31.7	0.499
En2A opx 07 fi 15	19.9	17.0	5.6	4.7	5.0	0.87	1.19	46.3	1.163
En2A opx 07 fi 16	5.7	8.8	2.9	2.4	2.7	0.92	1.18	35.0	0.602
En2A opx 07 fi 17	26.7	19.2	6.2	5.3	5.8	0.91	1.18	17.1	0.563
En2A opx 07 fi 18	15.5	14.6	4.8	4.1	4.5	0.91	1.18	4.3	1.154
En2A opx 07 fi 19	15.3	14.4	4.8	4.0	4.4	0.93	1.21	18.4	0.165
En2A opx 07 fi 20	23.9	18.2	5.9	5.0	5.5	0.9	1.19	32.4	0.594
En2A opx 07 fi 21	70.6	31.8	10.7	8.3	9.5	0.88	1.29	7.5	0.841
En2A opx 07 fi 22	1.4	4.1	1.4	1.0	1.3	1.05	1.41	28.6	1.077
En2A opx 07 fi 23	9.3	11.3	4.0	2.9	3.4	0.91	1.36	37.5	1.147
En2A opx 07 fi 24	7.3	9.9	3.2	2.9	3.1	0.93	1.12	29.7	1.153
En2A opx 07 fi 25	22.6	18.0	5.9	5.0	5.4	0.88	1.17	40.3	1.162
En2A opx 07 fi 26	6.5	9.5	3.0	2.5	2.9	0.92	1.18	30.7	1.156
En2A opx 07 fi 27	15.4	14.6	4.9	3.9	4.4	0.91	1.28	48.5	0.737
En2A opx 07 fi 28	11.4	12.6	4.2	3.4	3.8	0.9	1.22	15.4	1.158
En2A opx 07 fi 29	5.7	8.9	2.9	2.5	2.7	0.9	1.17	24.1	1.157
En2A opx 07 fi 30	3.3	6.5	2.3	1.8	2.0	0.96	1.27	33.7	0.792
En2A opx 07 fi 31	6.4	9.2	3.1	2.5	2.9	0.95	1.20	11.6	1.152
En2A opx 07 fi 32	6.5	9.3	3.1	2.5	2.9	0.94	1.22	39.2	1.151
En2A opx 07 fi 33	5.5	8.6	2.8	2.3	2.6	0.93	1.22	48.3	1.152
En2A opx 07 fi 34	4.1	7.5	2.5	2.0	2.3	0.9	1.23	29.7	1.149

En2A opx 07 fi 35	3.2	6.5	2.1	1.9	2.0	0.96	1.14	40.2	0.533
En2A opx 07 fi 36	2.4	5.6	1.8	1.5	1.8	0.99	1.18	56.6	1.137
En2A opx 07 fi 37	0.6	2.6	0.9	0.7	0.9	1.17	1.35	10.6	1.104
En2A opx 07 fi 38	1.4	4.0	1.4	1.1	1.3	1.05	1.24	18.8	1.115
En2A opx 07 fi 39	2.5	5.9	2.0	1.5	1.8	0.91	1.27	27.1	1.107
En2A opx 07 fi 40	2.8	6.0	2.0	1.7	1.9	0.97	1.20	36.0	1.127
En2A opx 07 fi 41	10.2	11.9	3.9	3.1	3.6	0.91	1.23	8.6	1.159
En2A opx 07 fi 42	6.7	9.5	3.0	2.8	2.9	0.93	1.07	27.2	1.162
En2A opx 07 fi 43	25.2	18.7	6.2	5.2	5.7	0.91	1.19	5.5	1.163
En2A opx 07 fi 44	18.0	15.7	5.0	4.6	4.8	0.92	1.08	25.4	0.492
En2A opx 07 fi 45	25.9	19.0	6.3	5.4	5.7	0.9	1.16	8.1	0.930
En2A opx 07 fi 46	28.4	20.6	6.7	5.2	6.0	0.84	1.28	21.7	1.166
En2A opx 07 fi 47	11.5	12.8	4.2	3.4	3.8	0.88	1.22	6.6	1.164
En2A opx 07 fi 48	16.1	15.4	5.1	4.1	4.5	0.85	1.26	28.1	1.159
En2A opx 07 fi 49	10.8	12.6	4.5	3.0	3.7	0.86	1.52	17.6	1.155
En2A opx 07 fi 50	7.0	9.9	3.5	2.6	3.0	0.89	1.36	10.0	1.137
En2A opx 07 fi 51	14.0	13.9	4.6	3.9	4.2	0.91	1.19	21.6	1.161
En2A opx 07 fi 52	11.8	13.3	4.5	3.5	3.9	0.84	1.30	15.9	1.155
En2A opx 07 fi 54	21.7	17.6	6.2	4.4	5.3	0.87	1.40	2.8	0.834
En2A opx 07 fi 56	13.1	13.8	4.9	3.4	4.1	0.86	1.44	6.3	1.150
En2A opx 07 fi 57	2.9	6.2	2.1	1.8	1.9	0.96	1.16	5.3	1.149
En2A opx 07 fi 58	3.9	7.4	2.4	2.0	2.2	0.89	1.23	0.7	1.148
En2A opx 07 fi 59	1.9	5.0	1.6	1.4	1.5	0.92	1.14	16.1	1.128
En2A opx 07 fi 60	1.3	3.8	1.3	1.0	1.3	1.09	1.34	15.3	1.084
En2A opx 07 fi 61	1.0	3.3	1.2	0.9	1.1	1.09	1.35	18.9	1.138
En2A opx 07 fi 62	2.5	5.6	1.8	1.5	1.8	0.99	1.19	27.2	1.145
En2A opx 07 fi 63	3.9	7.1	2.5	1.9	2.2	0.97	1.32	11.8	1.126
En2A opx 07 fi 64	2.0	5.0	1.6	1.4	1.6	1	1.14	13.4	1.119
En2A opx 07 fi 65	2.5	5.7	1.9	1.6	1.8	0.97	1.24	8.5	1.137
En2A opx 07 fi 66	2.6	5.8	2.0	1.5	1.8	0.94	1.30	7.1	1.130
En2A opx 07 fi 67	2.0	5.1	1.7	1.4	1.6	0.94	1.26	4.6	1.114
En2A opx 07 fi 68	1.5	4.5	1.6	1.2	1.4	0.94	1.29	3.3	1.104
En2A opx 07 fi 69	21.4	17.6	5.8	4.8	5.2	0.87	1.20	8.5	1.162
En2A opx 07 fi 70	3.6	7.0	2.3	2.0	2.2	0.94	1.14	21.7	0.694
En2A opx 07 fi 71	3.6	7.1	2.4	2.0	2.2	0.91	1.18	9.1	1.131
En2A opx 07 fi 72	42.1	24.2	7.6	7.1	7.3	0.91	1.07	6.5	0.704
En2A opx 09 fi 01	202.1	79.1	33.7	7.0	16.0	0.41	4.84	7.1	0.869
En2A opx 09 fi 02	123.6	44.2	15.8	9.3	12.6	0.8	1.70	13.6	0.875
En2A opx 09 fi 03	219.0	74.4	31.0	7.8	16.7	0.5	3.99	30.0	0.038
En2A opx 09 fi 04	98.7	41.3	15.7	7.6	11.2	0.73	2.07	26.1	0.399

En2A opx 09 fi 05	126.7	69.6	30.2	4.6	12.7	0.33	6.54	30.5	0.826
En2A opx 09 fi 06	95.3	54.3	22.9	4.7	11.0	0.41	4.90	36.4	0.699
En2A opx 09 fi 07	103.3	39.6	12.9	9.9	11.5	0.83	1.31	43.2	0.854
En2A opx 09 fi 09	86.5	37.3	12.7	8.2	10.5	0.78	1.55	24.9	0.883
En2A opx 09 fi 10	14.7	14.5	4.6	4.2	4.3	0.88	1.10	15.9	0.886
En2A opx 09 fi 11	67.8	32.8	11.2	7.8	9.3	0.79	1.44	11.6	0.897
En2A opx 09 fi 12	52.5	27.8	8.9	7.8	8.2	0.85	1.14	19.9	0.883
En2A opx 09 fi 13	25.4	19.3	6.2	5.4	5.7	0.86	1.16	20.4	1.152
En2A opx 09 fi 14	12.6	13.6	4.3	3.9	4.0	0.86	1.10	22.4	1.146
En2A opx 09 fi 15	64.4	31.9	11.2	6.8	9.1	0.8	1.64	23.1	0.857
En2A opx 09 fi 16	40.9	24.4	7.5	6.9	7.2	0.87	1.09	30.7	0.746
En2A opx 09 fi 17	45.2	25.5	8.5	7.3	7.6	0.87	1.17	35.4	0.738
En2A opx 09 fi 18	69.7	32.7	10.5	8.3	9.4	0.82	1.26	37.5	0.690
En2A opx 09 fi 19	20.4	17.2	5.4	4.9	5.1	0.86	1.10	45.2	0.716
En2A opx 09 fi 20	20.0	17.8	6.4	3.8	5.1	0.8	1.71	47.8	0.691
En2A opx 09 fi 21	26.4	19.6	6.4	5.3	5.8	0.86	1.20	47.6	0.691
En2A opx 09 fi 22	61.0	30.3	9.7	8.2	8.8	0.84	1.19	48.8	0.717
En2A opx 09 fi 23	10.4	12.4	3.9	3.4	3.6	0.86	1.14	54.4	1.152
En2A opx 09 fi 24	39.4	23.9	7.7	6.8	7.1	0.87	1.13	53.1	0.765
En2A opx 09 fi 28	2.9	7.6	2.8	1.3	1.9	0.63	2.17	15.1	1.128
En2A opx 09 fi 29	2.2	6.0	2.2	1.3	1.7	0.76	1.72	10.5	1.087
En2A opx 09 fi 30	4.9	9.2	3.3	1.7	2.5	0.71	1.91	9.8	1.126
En2A opx 09 fi 31	4.6	9.4	3.5	1.5	2.4	0.65	2.41	17.8	1.129
En2A opx 09 fi 32	4.1	8.6	3.3	1.5	2.3	0.68	2.27	18.8	1.135
En2A opx 09 fi 33	0.8	3.4	1.1	0.9	1.0	0.84	1.28	5.0	1.059
En2A opx 09 fi 34	2.8	6.6	2.2	1.6	1.9	0.82	1.38	18.6	1.119
En2A opx 09 fi 35	5.0	8.9	3.3	1.9	2.5	0.8	1.69	6.0	1.142
En2A opx 09 fi 36	1.3	4.4	1.4	1.2	1.3	0.87	1.11	29.2	1.091
En2A opx 09 fi 37	6.5	9.9	3.5	2.2	2.9	0.83	1.57	23.2	1.122
En2A opx 09 fi 38	4.5	7.9	2.5	2.1	2.4	0.93	1.18	0.0	1.091
En2A opx 09 fi 39	4.2	7.7	2.7	1.9	2.3	0.87	1.38	53.6	1.112
En2A opx 09 fi 40	8.7	10.8	3.8	2.9	3.3	0.94	1.28	45.3	1.137
En2A opx 09 fi 41	16.9	15.4	5.2	4.0	4.6	0.9	1.31	41.0	1.136
En2A opx 09 fi 42	5.3	8.6	2.8	2.3	2.6	0.91	1.19	30.2	1.146
En2A opx 09 fi 46	49.1	28.6	10.6	5.7	7.9	0.76	1.86	33.5	1.032
En2A opx 09 fi 47	15.8	14.8	5.2	3.9	4.5	0.9	1.33	8.6	0.688
En2A opx 09 fi 48	91.2	38.8	14.1	7.9	10.8	0.76	1.79	37.7	0.682
En2A opx 09 fi 49	14.1	14.2	4.9	3.4	4.2	0.87	1.42	15.8	0.657
En2A opx 09 fi 50	37.7	23.8	8.3	5.7	6.9	0.83	1.45	46.5	0.659
En2A opx 09 fi 51	93.5	39.8	14.9	7.6	10.9	0.74	1.96	73.0	0.152

En2A opx 09 fi 52	14.4	14.5	5.1	3.4	4.3	0.87	1.51	5.6	0.718
En2A opx 09 fi 53	75.8	36.6	13.9	6.6	9.8	0.71	2.09	39.8	0.695
En2A opx 09 fi 54	70.9	33.7	12.8	6.7	9.5	0.78	1.91	72.0	0.199
En2A opx 09 fi 55	60.7	31.0	10.7	6.5	8.8	0.79	1.65	13.8	0.714
En2A opx 09 fi 57	54.3	29.3	10.7	6.6	8.3	0.8	1.62	8.5	0.840
En2A opx 09 fi 58	53.6	29.6	11.2	5.9	8.3	0.77	1.90	36.4	0.862
En2A opx 09 fi 60	124.8	46.1	17.3	8.4	12.6	0.74	2.05	31.9	0.296
En2A opx 09 fi 61	110.9	44.6	17.2	7.4	11.9	0.7	2.32	27.1	0.290
En2A cpx 01 fi 01	37.4	23.8	7.9	6.1	6.9	0.83	1.28	2.0	0.851
En2A cpx 01 fi 02	8.9	11.0	3.5	3.2	3.4	0.92	1.08	15.5	0.528
En2A cpx 01 fi 03	7.0	9.9	3.3	2.7	3.0	0.89	1.20	25.9	1.172
En2A cpx 01 fi 04	6.0	9.0	3.1	2.3	2.8	0.92	1.33	33.8	1.167
En2A cpx 01 fi 05	2.5	6.0	2.2	1.4	1.8	0.89	1.56	8.6	1.117
En2A cpx 01 fi 06	29.8	20.4	7.1	5.6	6.2	0.9	1.25	36.6	1.171
En2A cpx 01 fi 07	89.3	36.3	12.4	9.7	10.7	0.85	1.28	58.7	0.997
En2A cpx 01 fi 08	27.9	20.8	7.3	4.7	6.0	0.82	1.56	17.5	1.166
En2A cpx 01 fi 09	38.3	23.9	8.0	5.9	7.0	0.84	1.37	44.1	0.910
En2A cpx 01 fi 10	49.5	26.4	8.6	7.2	7.9	0.89	1.19	13.2	0.724
En2A cpx 01 fi 11	55.1	28.5	9.5	7.6	8.4	0.85	1.24	8.6	1.130
En2A cpx 01 fi 12	69.6	31.7	11.0	8.6	9.4	0.87	1.28	20.6	1.028
En2A cpx 01 fi 13	72.2	32.6	11.2	8.9	9.6	0.85	1.26	8.1	0.918
En2A cpx 01 fi 14	63.6	30.4	10.1	8.2	9.0	0.87	1.24	6.4	0.993
En2A cpx 01 fi 15	55.4	28.7	9.2	7.6	8.4	0.84	1.21	26.1	0.375
En2A cpx 01 fi 16	95.1	37.2	12.2	10.2	11.0	0.86	1.19	36.6	1.039
En2A cpx 01 fi 17	38.9	24.3	7.8	6.4	7.0	0.83	1.22	24.4	0.400
En2A cpx 01 fi 18	19.0	16.2	5.3	4.3	4.9	0.92	1.23	14.5	0.874
En2A cpx 01 fi 19	4.4	7.6	2.6	2.1	2.4	0.96	1.26	19.6	1.143
En2A cpx 01 fi 20	47.0	27.1	9.2	6.7	7.7	0.81	1.38	9.6	0.945
En2A cpx 01 fi 21	2.4	5.5	1.7	1.6	1.8	0.99	1.05	20.3	0.580
En2A cpx 01 fi 22	7.8	10.4	3.4	2.9	3.2	0.9	1.20	11.7	0.561
En2A cpx 01 fi 23	31.3	21.2	6.8	6.0	6.3	0.88	1.12	5.9	0.592
En2A cpx 01 fi 24	8.2	10.5	3.5	3.0	3.2	0.93	1.15	11.7	0.515
En2A cpx 01 fi 25	18.3	16.4	5.4	4.4	4.8	0.85	1.22	2.5	1.160
En2A cpx 01 fi 26	40.5	24.1	7.8	6.9	7.2	0.88	1.12	11.6	0.496
En2A cpx 01 fi 27	11.6	13.2	4.2	3.6	3.9	0.83	1.18	1.5	1.162
En2A cpx 01 fi 28	43.5	25.1	8.1	7.1	7.4	0.87	1.15	23.6	0.441
En2A cpx 01 fi 29	53.4	27.8	9.2	7.3	8.2	0.87	1.26	27.7	0.852
En2A cpx 01 fi 30	13.3	13.8	4.7	3.6	4.1	0.87	1.29	34.0	0.839
En2A cpx 01 fi 31	17.1	16.0	6.1	3.8	4.7	0.84	1.62	9.1	1.152
En2A cpx 01 fi 32	9.1	12.4	4.6	2.4	3.4	0.74	1.93	12.0	1.134

En2A cpx 01 fi 33	9.0	11.6	4.2	2.6	3.4	0.85	1.63	18.3	1.147
En2A cpx 01 fi 34	41.9	24.4	7.9	6.9	7.3	0.88	1.14	31.7	0.714
En2A cpx 01 fi 35	28.3	20.6	7.3	5.5	6.0	0.84	1.32	21.8	1.162
En2A cpx 01 fi 36	11.8	13.0	4.4	3.4	3.9	0.87	1.29	19.1	1.149
En2A cpx 01 fi 37	10.0	11.6	3.9	3.3	3.6	0.93	1.17	10.2	0.463
En2A cpx 01 fi 38	0.4	2.5	0.8	0.6	0.7	0.83	1.31	3.6	1.064
En2A cpx 01 fi 39	0.5	2.7	0.9	0.7	0.8	0.84	1.36	3.3	1.128
En2A cpx 01 fi 40	12.2	14.2	4.8	3.4	3.9	0.76	1.42	11.4	1.155
En2A cpx 01 fi 41	37.6	23.2	7.9	6.4	6.9	0.88	1.24	23.3	0.845
En2A cpx 01 fi 42	3.6	7.5	2.5	1.9	2.1	0.8	1.32	1.5	1.143
En2A cpx 02 fi 16	2.6	5.9	2.0	1.5	1.8	0.94	1.33	11.9	0.789
En2A cpx 02 fi 17	2.6	5.9	2.0	1.6	1.8	0.92	1.26	14.2	1.142
En2A cpx 02 fi 18	2.4	5.7	2.0	1.4	1.8	0.92	1.42	15.2	1.129
En2A cpx 02 fi 19	2.5	5.6	2.0	1.6	1.8	1.01	1.26	18.8	1.140
En2A cpx 02 fi 20	5.9	9.0	3.2	2.4	2.8	0.92	1.34	21.0	1.153
En2A cpx 02 fi 21	1.5	4.7	1.6	1.3	1.4	0.86	1.20	18.2	1.129
En2A cpx 02 fi 22	1.9	5.0	1.7	1.4	1.5	0.93	1.19	17.2	1.115
En2A cpx 02 fi 23	1.5	4.3	1.5	1.1	1.4	0.98	1.38	17.5	1.110
En2A cpx 02 fi 24	0.9	3.6	1.3	0.8	1.1	0.9	1.50	12.0	1.116
En2A cpx 03 fi 01	47.3	25.9	8.2	7.4	7.8	0.89	1.11	3.3	0.809
En2A cpx 03 fi 03	18.1	16.0	5.1	4.6	4.8	0.88	1.10	0.8	0.478
En2A cpx 03 fi 05	2.5	5.7	1.8	1.5	1.8	0.97	1.18	2.6	0.789
En2A cpx 03 fi 06	2.5	5.6	1.9	1.5	1.8	1.01	1.23	0.2	0.780
En2A cpx 03 fi 07	29.4	20.5	6.4	5.6	6.1	0.88	1.16	20.0	0.920
En2A cpx 03 fi 08	10.1	12.0	4.1	3.1	3.6	0.88	1.34	20.8	0.909
En2A cpx 03 fi 09	14.2	14.3	4.9	3.5	4.3	0.87	1.41	17.5	0.911
En2A cpx 03 fi 10	11.1	12.4	4.4	3.2	3.8	0.9	1.37	8.1	1.154
En2A cpx 03 fi 11	50.8	27.5	9.2	7.0	8.0	0.84	1.31	59.2	0.963
En2A cpx 03 fi 12	37.9	23.2	7.6	6.2	7.0	0.89	1.22	45.4	0.956
En2A cpx 03 fi 13	26.6	19.4	6.6	5.3	5.8	0.89	1.25	55.6	0.970
En2A cpx 04 fi 01	44.5	25.6	9.0	6.8	7.5	0.85	1.32	7.3	1.153
En2A cpx 04 fi 02	12.6	13.5	4.8	3.3	4.0	0.87	1.46	27.6	1.150
En2A cpx 04 fi 03	7.5	10.5	3.7	2.4	3.1	0.86	1.51	2.3	1.156
En2A cpx 04 fi 04	1.4	4.2	1.5	1.1	1.3	0.98	1.37	15.0	1.124
En2A cpx 04 fi 05	1.6	4.7	1.7	1.1	1.4	0.94	1.47	19.8	1.099
En2A cpx 04 fi 06	2.6	5.8	2.1	1.5	1.8	0.95	1.40	8.6	1.119
En2A cpx 04 fi 07	7.0	9.8	3.4	2.6	3.0	0.92	1.27	22.9	1.130
En2A cpx 04 fi 08	1.8	5.0	1.8	1.3	1.5	0.92	1.46	6.8	1.101
En2A cpx 04 fi 09	11.9	12.8	4.5	3.4	3.9	0.91	1.30	33.3	0.900
En2A cpx 04 fi 10	6.7	9.8	3.5	2.4	2.9	0.88	1.44	6.6	1.132

En2A cpx 04 fi 11	14.9	14.5	5.3	3.6	4.4	0.9	1.45	19.1	1.126
En2A cpx 04 fi 12	12.7	13.5	4.8	3.3	4.0	0.87	1.45	29.5	1.142
En2A cpx 04 fi 13	13.6	13.6	4.4	3.8	4.2	0.92	1.16	11.2	0.708
En2A cpx 04 fi 14	4.4	7.7	2.7	2.0	2.4	0.91	1.33	24.8	1.089
En2A cpx 04 fi 15	5.1	8.2	2.8	2.2	2.5	0.95	1.29	14.7	1.146
En2A cpx 04 fi 17	3.6	6.9	2.3	1.8	2.1	0.94	1.30	26.6	0.761
En2A cpx 04 fi 18	4.1	7.6	2.6	2.0	2.3	0.91	1.32	12.7	1.136
En2A cpx 04 fi 19	3.8	7.6	2.8	1.9	2.2	0.83	1.49	9.9	1.131
En2A cpx 04 fi 20	4.6	7.7	2.7	2.1	2.4	0.97	1.28	5.1	1.144
En2A cpx 04 fi 21	1.8	4.8	1.7	1.2	1.5	0.96	1.41	1.8	1.116
En2A cpx 04 fi 22	3.3	6.6	2.4	1.8	2.1	0.95	1.34	9.6	1.144
En2A cpx 04 fi 23	2.9	6.2	2.1	1.6	1.9	0.96	1.33	8.1	1.140
En2A cpx 04 fi 24	3.1	6.4	2.2	1.6	2.0	0.96	1.34	5.0	1.139
En2A cpx 04 fi 25	2.1	5.2	1.8	1.3	1.6	0.97	1.39	1.7	1.107
En2A cpx 04 fi 26	3.5	6.7	2.3	1.9	2.1	0.96	1.23	23.8	1.141
En2A cpx 04 fi 27	6.0	9.1	3.3	2.3	2.8	0.91	1.41	20.8	1.152
En2A cpx 04 fi 28	3.0	6.4	2.1	1.7	1.9	0.9	1.28	6.1	1.129
En2A cpx 04 fi 29	4.9	8.3	3.0	2.1	2.5	0.9	1.44	13.7	1.157
En2A cpx 04 fi 30	2.3	5.6	1.9	1.4	1.7	0.95	1.39	11.6	1.130
En2A cpx 04 fi 31	3.4	6.7	2.5	1.7	2.1	0.94	1.49	9.2	1.151
En2A cpx 04 fi 32	3.0	6.5	2.3	1.5	1.9	0.88	1.47	2.6	1.155
En2A cpx 04 fi 33	5.9	8.8	3.1	2.3	2.7	0.96	1.38	3.0	0.830
En2A cpx 04 fi 34	2.5	5.8	2.1	1.4	1.8	0.93	1.45	12.7	1.110
En2A cpx 04 fi 35	3.0	6.2	2.1	1.7	2.0	0.99	1.28	6.3	1.137
En2A cpx 04 fi 36	1.6	4.4	1.5	1.2	1.4	1.01	1.27	4.6	1.134
En2A cpx 04 fi 37	64.2	30.9	10.7	8.4	9.0	0.84	1.27	28.4	0.998
En2A cpx 04 fi 38	17.9	16.1	5.5	4.3	4.8	0.87	1.27	7.8	1.161
En2A cpx 04 fi 39	1.0	3.4	1.2	1.0	1.1	1.05	1.16	6.8	1.140
En2A cpx 04 fi 42	39.9	24.1	8.1	6.4	7.1	0.86	1.27	52.3	0.958
En2A cpx 04 fi 43	9.2	11.8	3.9	2.9	3.4	0.83	1.36	46.5	1.171
En2A cpx 04 fi 44	7.1	9.8	3.3	2.8	3.0	0.94	1.21	35.3	1.160
En2A cpx 04 fi 45	0.6	3.3	1.1	0.7	0.9	0.69	1.51	6.4	1.151
En2A cpx 04 fi 47	5.7	9.0	2.9	2.4	2.7	0.89	1.21	1.0	0.709
En2A cpx 04 fi 48	28.5	20.3	6.8	5.3	6.0	0.87	1.28	12.9	0.926
En2A sp 01 fi 001	2.0	5.1	1.7	1.3	1.6	0.96	1.26	10.1	1.201
En2A sp 01 fi 003	5.4	8.6	2.9	2.3	2.6	0.92	1.28	6.0	1.197
En2A sp 01 fi 007	6.9	9.7	3.2	2.6	3.0	0.92	1.26	5.5	1.192
En2A sp 01 fi 008	8.2	10.6	3.5	3.0	3.2	0.92	1.18	5.8	1.200
En2A sp 01 fi 013	1.6	4.7	1.5	1.3	1.4	0.93	1.17	6.5	1.182
En2A sp 01 fi 015	2.1	5.3	1.7	1.5	1.7	0.97	1.16	2.2	1.206

En2A sp 01 fi 016	1.5	4.5	1.5	1.2	1.4	0.97	1.24	5.7	1.168
En2A sp 01 fi 018	1.9	5.0	1.7	1.3	1.6	0.97	1.26	2.1	1.162
En2A sp 03 fi 006	2.5	5.7	1.9	1.6	1.8	0.97	1.16	14.8	1.181
En2A sp 03 fi 007	15.7	14.5	4.6	4.2	4.5	0.93	1.08	10.1	1.199
En2A sp 03 fi 010	4.3	8.1	3.0	1.7	2.4	0.84	1.76	11.9	1.197
En2A sp 03 fi 011	5.8	8.7	3.0	2.4	2.7	0.96	1.22	9.6	1.195
En2A sp 03 fi 014	12.0	13.5	4.9	3.0	3.9	0.83	1.62	14.3	1.180
En2A sp 03 fi 015	9.2	11.3	3.7	3.0	3.4	0.9	1.21	10.5	1.195
En2A sp 03 fi 016	2.5	5.8	2.0	1.5	1.8	0.91	1.35	7.9	1.167
En2A sp 03 fi 021	11.2	12.4	4.0	3.4	3.8	0.92	1.18	11.5	1.186
En2A sp 03 fi 022	4.8	8.1	2.9	2.1	2.5	0.92	1.40	5.7	1.197
En2A sp 03 fi 023	7.5	10.3	3.6	2.4	3.1	0.88	1.49	5.3	1.193
En2A sp 03 fi 028	12.6	13.5	4.9	3.0	4.0	0.86	1.62	15.0	1.202
En2A sp 03 fi 029	6.6	10.2	3.8	2.1	2.9	0.81	1.82	9.1	1.194
En2A sp 03 fi 030	6.9	9.8	3.5	2.5	3.0	0.9	1.42	11.2	1.195
En2A sp 03 fi 031	13.3	14.5	5.3	2.9	4.1	0.8	1.86	5.3	1.197
En2A sp 03 fi 032	6.6	9.9	3.8	2.1	2.9	0.85	1.78	4.5	1.194
En2A sp 03 fi 038	11.3	13.0	4.7	2.8	3.8	0.84	1.67	11.7	1.198
En2A sp 03 fi 040	14.3	14.6	5.3	3.1	4.3	0.84	1.72	9.1	1.200
En2A sp 03 fi 041	8.8	11.6	4.3	2.4	3.4	0.82	1.79	7.2	1.192
En2A sp 03 fi 042	6.6	9.5	3.3	2.5	2.9	0.92	1.34	-0.2	1.191
En2A sp 03 fi 043	2.0	5.0	1.6	1.4	1.6	1	1.13	-1.4	1.183
En2A sp 03 fi 044	2.0	5.1	1.7	1.3	1.6	0.97	1.32	-0.3	1.189
En2A sp 03 fi 049	2.9	6.1	2.0	1.7	1.9	0.99	1.15	11.0	1.197
En2A sp 03 fi 050	16.2	15.5	5.5	3.5	4.5	0.85	1.60	10.7	1.197
En2A sp 03 fi 051	4.5	7.9	2.6	2.1	2.4	0.92	1.24	7.7	1.193
En2A sp 03 fi 052	14.4	14.8	5.5	3.1	4.3	0.83	1.76	2.1	1.194
En2A sp 03 fi 059	24.1	23.6	10.0	2.9	5.5	0.55	3.49	10.1	1.185
En2A sp 03 fi 060	2.0	4.9	1.7	1.3	1.6	1.01	1.32	8.9	1.193
En2A sp 03 fi 061	8.6	11.1	3.9	2.7	3.3	0.88	1.43	6.5	1.197
En2A sp 03 fi 062	2.5	5.7	2.0	1.4	1.8	0.97	1.45	2.8	1.198
En2A sp 03 fi 063	5.9	9.2	3.2	2.2	2.7	0.88	1.46	2.1	1.198
En2A sp 03 fi 068	23.8	19.3	7.2	3.8	5.5	0.8	1.93	18.9	1.198
En2A sp 03 fi 069	13.9	13.8	4.6	3.8	4.2	0.92	1.20	11.9	1.193
En2A sp 03 fi 070	2.5	5.8	2.1	1.4	1.8	0.95	1.46	8.1	1.178
En2A sp 03 fi 071	22.5	18.8	7.1	3.9	5.4	0.8	1.81	8.6	1.197
En2A sp 03 fi 072	2.9	6.2	2.1	1.6	1.9	0.94	1.29	4.8	1.191
En2A sp 03 fi 073	9.6	11.8	3.9	3.0	3.5	0.87	1.33	14.6	1.197
En2A sp 03 fi 074	2.7	5.9	2.0	1.6	1.8	0.97	1.26	14.6	1.181
En2A sp 03 fi 075	22.2	17.9	6.2	4.5	5.3	0.87	1.39	9.6	1.197

En2A sp 03 fi 078	18.1	15.9	5.3	4.4	4.8	0.9	1.21	16.3	1.196
En2A sp 03 fi 079	14.1	15.8	6.2	2.6	4.2	0.71	2.36	8.6	1.198
En2A sp 03 fi 080	4.9	8.4	3.0	1.9	2.5	0.87	1.60	4.6	1.194
En2A sp 03 fi 085	3.9	7.2	2.5	2.0	2.2	0.95	1.25	11.5	1.187
En2A sp 03 fi 086	10.9	12.6	4.3	3.2	3.7	0.87	1.33	9.3	1.199
En2A sp 03 fi 088	5.3	8.6	3.1	2.1	2.6	0.9	1.48	14.4	1.196
En2A sp 03 fi 089	2.5	6.0	2.2	1.3	1.8	0.89	1.67	5.3	1.196
En2A sp 03 fi 091	6.1	9.3	3.2	2.4	2.8	0.89	1.34	11.2	1.190
En2A sp 03 fi 092	4.9	8.4	3.0	2.0	2.5	0.87	1.50	6.2	1.195
En2A sp 03 fi 093	6.1	9.3	3.3	2.1	2.8	0.89	1.56	5.7	1.193
En2A sp 03 fi 094	5.4	8.7	2.9	2.3	2.6	0.91	1.27	8.9	1.192
En2A sp 03 fi 095	10.1	12.2	4.3	2.8	3.6	0.85	1.54	5.3	1.196
En2A sp 03 fi 096	20.2	16.9	5.9	4.4	5.1	0.89	1.36	19.3	1.195
En2A sp 03 fi 097	18.4	16.1	5.3	4.4	4.8	0.89	1.20	9.3	1.197
En2A sp 03 fi 099	36.7	23.3	7.9	5.9	6.8	0.85	1.35	21.7	1.191
En2A sp 03 fi 100	16.2	18.0	7.1	2.6	4.5	0.63	2.76	22.9	1.161
En2A sp 03 fi 102	6.1	9.4	3.5	2.2	2.8	0.87	1.54	9.5	1.194
En2A sp 03 fi 103	11.2	13.7	5.2	2.5	3.8	0.75	2.10	22.0	1.178
En2A sp 03 fi 105	6.5	9.6	3.6	2.3	2.9	0.88	1.60	8.6	1.191
En2A sp 03 fi 108	10.3	12.4	4.5	2.8	3.6	0.84	1.60	14.8	1.194
En2A sp 03 fi 109	3.5	6.9	2.2	1.8	2.1	0.93	1.21	8.6	1.187
En2A sp 03 fi 110	2.3	5.8	2.2	1.2	1.7	0.87	1.79	7.1	1.196
En2A sp 03 fi 114	9.4	13.0	5.1	2.2	3.5	0.7	2.35	17.4	1.194
En2A sp 03 fi 115	6.2	9.9	3.7	2.1	2.8	0.8	1.71	13.6	1.195
En2A sp 03 fi 116	5.2	8.6	3.1	2.1	2.6	0.89	1.50	8.9	1.197
En2A sp 03 fi 122	3.3	6.6	2.3	1.7	2.0	0.94	1.37	16.5	1.189
En2A sp 03 fi 123	2.6	6.0	2.2	1.4	1.8	0.89	1.62	14.3	1.165
En2A sp 03 fi 124	4.7	8.0	2.8	2.1	2.4	0.91	1.35	7.6	1.194
En2A sp 03 fi 125	4.4	8.2	3.1	1.8	2.4	0.82	1.71	8.4	1.193
En2A sp 03 fi 126	4.5	9.2	3.7	1.6	2.4	0.67	2.37	4.8	1.185
En2A sp 03 fi 127	3.0	7.3	2.9	1.3	2.0	0.71	2.31	1.2	1.185
En2A sp 03 fi 128	2.9	6.7	2.5	1.5	1.9	0.82	1.72	4.6	1.167
En2A sp 03 fi 129	4.5	9.0	3.5	1.5	2.4	0.69	2.38	4.0	1.183
En2A sp 03 fi 130	1.4	4.4	1.6	1.1	1.3	0.91	1.46	2.2	1.187
En2A sp 03 fi 131	4.5	7.9	2.7	2.1	2.4	0.9	1.28	1.5	1.188
En2A sp 03 fi 132	1.7	4.9	1.7	1.1	1.5	0.89	1.46	7.4	1.196
En2A sp 03 fi 133	7.2	10.7	4.1	2.1	3.0	0.79	1.96	7.9	1.188
En2A sp 03 fi 134	19.4	17.1	6.4	3.8	5.0	0.83	1.70	10.1	0.676
En2A sp 03 fi 135	3.0	6.3	2.2	1.5	2.0	0.95	1.51	7.6	1.185
En2A sp 03 fi 136	7.1	10.1	3.5	2.4	3.0	0.86	1.49	4.3	1.193

En2A sp 03 fi 137	12.5	13.3	4.7	3.3	4.0	0.89	1.41	8.6	0.549
En2A sp 03 fi 138	6.4	9.5	2.9	2.7	2.8	0.88	1.07	5.2	0.512
En2A sp 03 fi 139	12.4	13.3	4.5	3.4	4.0	0.88	1.35	2.6	0.519
En2A sp 03 fi 140	19.5	17.0	5.9	3.9	5.0	0.85	1.49	11.2	0.609
En2A sp 03 fi 141	2.4	5.5	1.9	1.4	1.8	1.01	1.38	6.0	0.416
En2A sp 03 fi 142	6.3	9.2	3.1	2.5	2.8	0.95	1.21	3.6	0.557
En2A sp 03 fi 143	3.6	6.9	2.4	1.7	2.1	0.95	1.38	0.9	0.489
En2A sp 03 fi 144	4.9	7.9	2.8	2.1	2.5	0.98	1.31	5.0	0.491
En2A sp 03 fi 145	16.6	15.3	5.3	3.9	4.6	0.89	1.36	3.8	0.578
En2A sp 03 fi 146	17.9	16.2	5.7	3.9	4.8	0.86	1.49	5.7	0.669
En2A sp 03 fi 147	5.2	8.3	2.8	2.3	2.6	0.96	1.24	4.3	0.112
En2A sp 03 fi 148	8.6	10.7	3.6	3.0	3.3	0.94	1.19	12.7	0.601
En2A sp 03 fi 149	18.5	16.0	5.2	4.4	4.9	0.91	1.18	14.1	0.572
En2A sp 03 fi 150	53.2	28.4	9.8	6.5	8.2	0.83	1.52	12.2	0.333
En2A sp 03 fi 151	10.3	12.2	4.3	2.8	3.6	0.88	1.53	9.5	0.429
En2A sp 03 fi 152	21.8	17.4	5.8	4.8	5.3	0.91	1.22	17.9	0.380
En2A sp 03 fi 153	17.4	15.5	4.9	4.5	4.7	0.91	1.07	11.9	0.362
En2A sp 03 fi 154	13.7	13.6	4.3	3.9	4.2	0.93	1.11	14.8	0.321
En2A sp 03 fi 155	15.4	14.7	4.9	3.9	4.4	0.89	1.27	9.1	0.472
En2A sp 03 fi 156	8.0	10.3	3.5	2.8	3.2	0.94	1.23	7.6	0.340
En2A sp 03 fi 157	43.1	24.7	8.4	6.6	7.4	0.89	1.27	17.5	0.318
En2A sp 03 fi 158	5.4	8.7	2.8	2.4	2.6	0.9	1.15	3.8	0.316
En2A sp 03 fi 159	45.3	25.3	8.6	7.0	7.6	0.89	1.23	10.7	0.468
En2A sp 03 fi 160	5.7	9.0	3.3	2.0	2.7	0.89	1.65	4.0	0.561
En2A sp 03 fi 161	20.5	16.7	5.5	4.6	5.1	0.92	1.19	11.9	0.524
En2A sp 03 fi 162	5.8	8.7	3.1	2.3	2.7	0.95	1.33	1.7	0.557
En2A sp 03 fi 163	24.9	18.8	6.8	4.8	5.6	0.89	1.44	5.7	0.533
En2A sp 04 fi 002	13.1	13.6	4.5	3.5	4.1	0.89	1.28	9.8	1.172
En2A sp 04 fi 005	36.2	26.2	10.0	4.3	6.8	0.66	2.31	11.2	1.187
En2A sp 04 fi 007	3.1	6.9	2.3	1.5	2.0	0.83	1.52	8.1	1.183
En2A sp 04 fi 008	2.5	6.0	2.0	1.6	1.8	0.89	1.23	1.0	1.137
En2A sp 04 fi 009	1.0	3.8	1.3	1.1	1.1	0.86	1.26	1.1	1.180
En2A sp 04 fi 010	3.5	7.2	2.6	1.7	2.1	0.87	1.52	2.2	1.173
En2A sp 04 fi 011	8.3	10.6	3.5	2.9	3.3	0.92	1.23	1.0	1.149
En2A sp 04 fi 024	4.2	7.4	2.5	2.0	2.3	0.95	1.25	4.0	1.135
En2A sp 04 fi 025	4.9	8.7	2.8	2.3	2.5	0.81	1.19	4.8	1.114
En2A sp 04 fi 026	17.3	15.6	5.2	4.0	4.7	0.89	1.32	7.9	0.898
En2A sp 04 fi 027	3.2	6.9	2.3	1.8	2.0	0.84	1.33	4.0	1.180
En2A sp 04 fi 028	6.5	10.1	3.4	2.5	2.9	0.81	1.34	8.4	1.171
En2A sp 04 fi 029	6.2	9.2	3.1	2.3	2.8	0.91	1.32	6.5	0.910

En2A sp 04 fi 030	1.9	5.2	1.7	1.4	1.6	0.91	1.22	6.5	1.146
En2A sp 04 fi 031	2.3	5.8	1.9	1.5	1.7	0.85	1.28	5.8	1.186
En2A sp 04 fi 032	4.4	7.8	2.5	2.2	2.4	0.91	1.15	0.0	1.186
En2A sp 04 fi 033	3.8	7.6	2.7	1.7	2.2	0.83	1.58	0.0	1.185
En2A sp 04 fi 034	3.5	7.6	2.7	1.7	2.1	0.76	1.58	0.0	1.183
En2A sp 04 fi 035	2.8	6.4	2.3	1.6	1.9	0.87	1.43	0.0	1.179
En2A sp 04 fi 036	2.1	5.5	1.8	1.6	1.6	0.86	1.17	0.0	1.174

S-2. Constraining equation of state of MgAl_2O_4 .

S-2.1 Chemical composition effect on thermoelastic properties

Since the purpose of this study is to determine the equation of state (EoS) of the MgAl_2O_4 end member component, I focus only on the data sets obtained from samples close to the end member composition. However, the selected datasets include some natural samples, which contain a small amount of end member components other than MgAl_2O_4 . For example, among the samples included in the dataset selected for this study, the sample with the largest total contribution of end member components other than MgAl_2O_4 is $\text{Mg}(\text{Fe}^{3+}_{0.078}\text{Al}_{0.922})_2\text{O}_4$ from Martignago et al (2006), which still does not exceed 8 mol%. Here I review the chemical composition dependence of the thermoelastic properties of spinels to determine whether it is appropriate to use their data to constrain the EoS of the MgAl_2O_4 .

S-2.1.1 Bulk modulus (K_0)

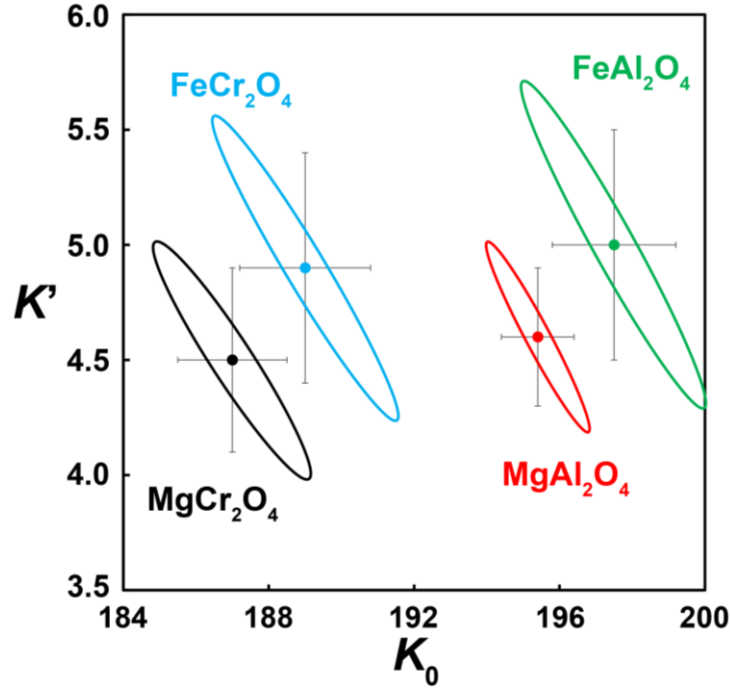
S-2.1.1.1 Mg# effect on K_0

In previous studies, the volume-pressure relationship was investigated by in situ volumetric measurements under high pressure using a diamond anvil cell, and the volumetric modulus of the main end member components of spinel was estimated as follows (Nestola et al., 2007; 2014; 2015): MgAl_2O_4 (ordered) (195.4(10) GPa), MgCr_2O_4 (187.0(15)) GPa, FeAl_2O_4 (197.5(17) GPa), FeCr_2O_4 (189.0(18) GPa) (Figure S3-1). From Figure S3-1, the K_T of FeAl_2O_4 is slightly larger than that of MgAl_2O_4 (ordered), but is the same within the uncertainties. Furthermore, the K_T obtained from disordered MgAl_2O_4 by Nestola et al. (2007) is 196.6(1.1), which is completely indistinguishable from that of FeAl_2O_4 , thus the effect of Mg# on K_T can be neglected at present.

Bruschini et al. (2018) used Brillouin spectroscopy to investigate the Mg# dependence of K_S at ambient condition in MgAl_2O_4 - FeAl_2O_4 solid solution using six samples with compositions of Mg# = 52.1, 63.3, 80.2, 92.5, 97.9, and 100. They reported that K_S is constant irrespective of composition when Fe^{2+} content is low ($\text{Fe}^{2+} \leq 0.202$), but K_S tends to decrease slightly when $\text{Fe}/(\text{Fe} + \text{Mg})$ is above 0.388. However, the effect of Mg# on K_S is very limited, as the samples with the highest and lowest Mg# in their measurements agree within uncertainty.

By combining $K_0=193.9(17)$ GPa reported by Nestola et al. (2015) and $\gamma=1.21$ and $\alpha=15.6 \times 10^{-6} \text{ (K}^{-1}\text{)}$, Bruschini et al. (2018) estimated the K_S of FeAl_2O_4 to be 194.8(17) GPa, which is significantly different from the K_S of $\text{MgAl}_2\text{O}_4=198(2)$, and therefore he argued that the smaller the Mg#, the smaller the K_S . However, the pressure values reported by Nestola et al. (2015) need to be corrected by the new quartz pressure scale of Scheidl et al. (2016), and the correction gives a K_T of 197.5(17) GPa for FeAl_2O_4 . Recalculating the K_S value for FeAl_2O_4 using this value gives $K_S=198.6(17)$, which agrees within uncertainty with the K_S for MgAl_2O_4 .

These results show that Mg# does not affect the bulk modulus of MgAl₂O₄ and FeAl₂O₄, since both K_T and K_S of MgAl₂O₄ and FeAl₂O₄ agree within the uncertainty.



FigureS3- 1 K_{T0} and K' and their confidence ellipses (1σ) obtained by fitting the EoS of third order Birch-Murnaghan EoS to the PV relations of MgAl₂O₄, FeAl₂O₄, MgCr₂O₄, and FeCr₂O₄ (Nestola et al., 2015, 2014, 2007). Before the fitting, original pressure values were rescaled by using the renewed quartz pressure scale of Scheidl et al.(2016).

S-2.1.1.2 Cr# effect on K_0

Correcting the pressure values of PV data reported in Nestola et al. (2014) with the new quartz pressure scale of Scheidl et al. (2016), the K_T for MgAl₂O₄ and MgCr₂O₄ are 195.4(10) GPa and 187.0(15) GPa, respectively. Therefore, there is a detectable difference in K_T between the end member components of the MgAl₂O₄-MgCr₂O₄ solid solution. This means that for every 0.1 change in Cr#, K_T changes by approximately 0.8 GPa, assuming that K_T behaves in an ideal mixed manner as a function of Cr#. Since a small difference in K_T of 0.8 GPa is difficult to distinguish from typical PV data, there is no possibility of a significant change in K_T from the MgAl₂O₄ end member component to spinels with Cr# up to about 0.1. Therefore, I conclude that spinels with $0 < \text{Cr\#} < 0.1$ can be used to constrain the EoS of MgAl₂O₄.

To the best of our knowledge, there are no measurements of K_S for MgCr₂O₄ or MgAl₂O₄-MgCr₂O₄ solid solutions, and thus the effect of Cr# on K_S cannot be discussed at present.

S-2.1.1.3 Non-stoichiometry effect on K_0

Nestola et al. (2009) reported a K_T of 171(2) GPa for a non-stoichiometric spinel with a chemical composition of ${}^T(\text{Mg}_{0.4}\text{Al}_{0.6}){}^M(\text{Al}_{1.8}\square_{0.2})\text{O}_4$. This is clearly lower than the K_T of 195.0(10) GPa for stoichiometric MgAl_2O_4 . Therefore, non-stoichiometric spinel should not be used to constrain the EoS.

S-2.1.2 Pressure derivative of K_0 (K')

S-2.1.2.1 Mg# and Cr# effect on K'

It is clear from Fig. S3-1 that for the main end member components of spinel, the K' values all agree within the uncertainty, and moreover that the values are at least greater than 4.0. Therefore, K' does not depend significantly on Mg# or Cr#. Also, when fitting spinel PV data with Birch-Murnaghan EoS, at least more than 3rd order BM EoS should be used.

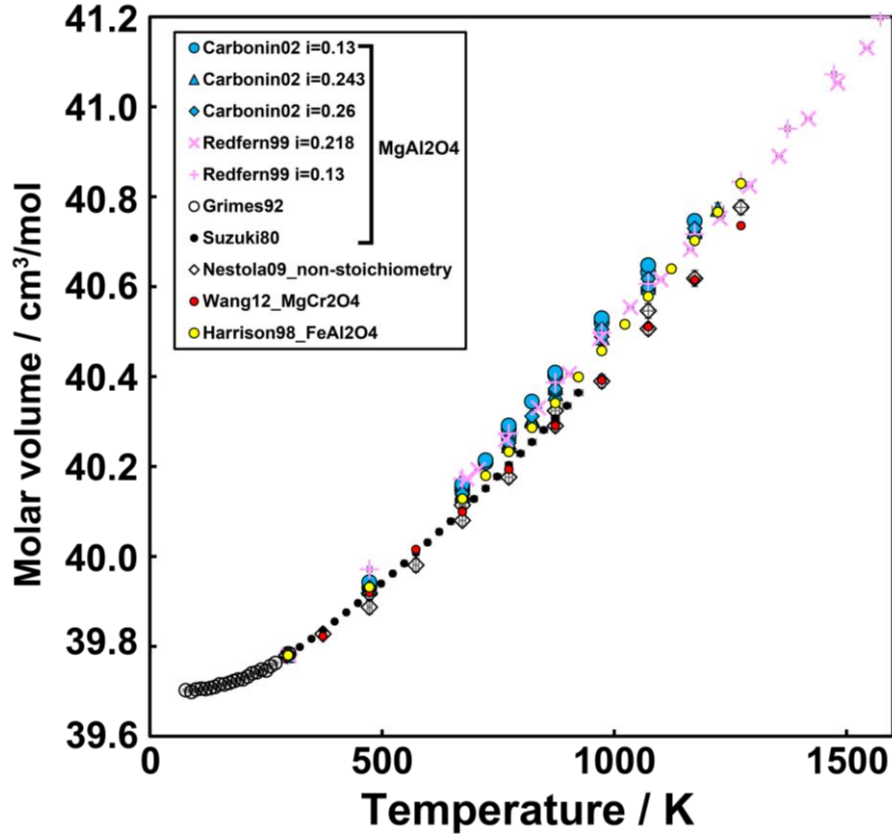
S-2.1.2.2 Non-stoichiometry effect on K'

Nestola et al. (2009) reported a K' value of 7.3(6) for a non-stoichiometric spinel with a chemical composition of ${}^T(\text{Mg}_{0.4}\text{Al}_{0.6}){}^M(\text{Al}_{1.8}\square_{0.2})\text{O}_4$. This value is clearly higher than the K' of 4.6(3) for the stoichiometric MgAl_2O_4 . Therefore, the non-stoichiometric spinel should not be used to constrain the EoS.

S-2.1.3 Thermal expansion coefficient (α)

S-2.1.3.1 Mg# effect on α

Singh et al. (1975) investigated the thermal expansion of synthetic spinel (MgAl_2O_4) and natural spinel ($\text{Mg}_{0.93}\text{Fe}_{0.07}\text{Al}_2\text{O}_4$) under the same conditions and found that the average thermal expansion of synthetic spinel was higher than that of natural spinel. This indicates that a decrease in Mg# results in a decrease in the average thermal expansion coefficient in the temperature range of interest. Similar conclusions are drawn from the work of Rigby et al. (1946) on spinel and hercynite. However, when the V/T relation of Harrison et al. (1998) is plotted together with MgAl_2O_4 , it is found to lie between that of Carbonin et al. (2002) and Suzuki and Kumazawa (1980), and no clear conclusion can be drawn at this point about the effect of Mg# on thermal expansion (Figure S3-2).



FigureS3- 2 The relationship between the volume and temperature of MgAl_2O_4 (Carbonin et al., 2002; Grimes and Al-Ajaj, 1992; Redfern et al., 1999; Suzuki and Kumazawa, 1980), non-stoichiometry MgAl_2O_4 (Nestola et al., 2009), FeAl_2O_4 (Harrison et al., 1998), MgCr_2O_4 (Wang et al., 2012). All data are normalized to $39.78 \text{ cm}^3/\text{mol}$ at room temperature and pressure.

S-2.1.3.2 Cr# effect on α

Wang et al. (2012) investigated the VT relationship of MgCr_2O_4 , and when plotted simultaneously with the VT data of MgAl_2O_4 , their results are plotted almost on the same curve as the MgAl_2O_4 VT data of Suzuki and Kumazawa (1980) (Figure S3-2). Since the VT data of Suzuki and Kumazawa (1980) is the data set with the lowest coefficient of thermal expansion among the VT data of MgAl_2O_4 , the coefficient of thermal expansion of MgCr_2O_4 is equal to or lower than that of MgAl_2O_4 . Therefore, for MgAl_2O_4 - MgCr_2O_4 solid solution, it is possible that the thermal expansion coefficient is smaller for larger Cr#, but it is also possible that it does not depend on Cr#.

S-2.1.3.3 Non-stoichiometry effect on α

Nestola et al. (2009) investigated the thermal expansion coefficient of non-stoichiometric MgAl_2O_4 . The results showed that the thermal expansion coefficient of non-stoichiometric

MgAl₂O₄ is smaller than that of all previously reported non-stoichiometric MgAl₂O₄ (Figure S3-2). Therefore, the data set used to constrain the EoS should not include non-stoichiometric MgAl₂O₄ data.

S-2.1.4 Unit cell parameter (*a*)

S-2.1.4.1 Mg# effect on *a*

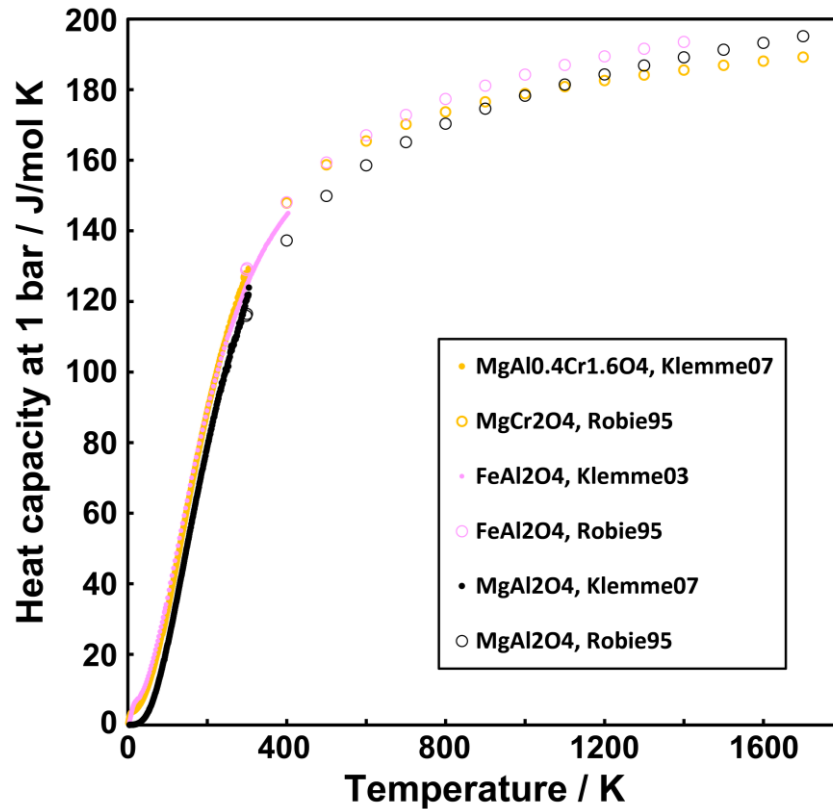
Bruschini et al. (2018) investigated the change of unit cell parameter of MgAl₂O₄-FeAl₂O₄ in the range of Mg#=100-52. The results showed that the unit cell parameter increases with decreasing Mg# when the degree of order-disorder is the same: $a = 0.000744 \cdot (100 - \text{Mg\#}) + 8.086$.

S-2.1.4.2 Cr# effect on *a*

Bosi and Andreozzi (2017) studied the change of unit cell parameter along MgAl₂O₄-MgCr₂O₄. They showed that the unit cell parameter of the spinel increases linearly with increasing Cr content due to the substitution of Cr³⁺ with Al³⁺, which has a larger atomic radius than Al³⁺, and the relation is $a = 0.00248 \cdot \text{Cr\#} + 8.087$ (Bosi and Andreozzi, 2017).

S-2.1.5 Heat capacity at constant pressure

Figure S3-3 shows the temperature dependence of the isobaric heat capacity of MgAl₂O₄, FeAl₂O₄, and MgCr₂O₄. Since the low temperature data of MgCr₂O₄ end member were not available, I plotted the heat capacity of MgCr_{1.4}Al_{0.4}O₄, which is closest to the MgCr₂O₄ end member component among the available data, instead of MgCr₂O₄. This figure shows that the heat capacity of MgAl₂O₄ is the lowest from 0 to 1200 K among the three end member components, while the heat capacity of MgCr₂O₄ becomes the lowest above 1200 K.



FigureS3- 3 Temperature dependence of isobaric heat capacity of MgAl_2O_4 , FeAl_2O_4 , MgCr_2O_4 and $\text{MgCr}_{1.4}\text{Al}_{0.4}\text{O}_4$.

S-2.1.6 Conclusions for effect of chemical composition on thermoelastic properties

- K is little affected by $\text{Mg}\#$, but slightly affected by $\text{Cr}\#$ and decreases with increasing $\text{Cr}\#$. However, for $\text{Cr}\# < 0.1$, the effect of Cr is negligible compared to the uncertainty of the K measurement. For non-stoichiometric samples, K is significantly smaller.
- K' is not affected by either $\text{Mg}\#$ or $\text{Cr}\#$. For non-stoichiometric samples, K' is significantly larger.
- The effect of $\text{Mg}\#$ on the thermal expansion coefficient is not known. From the available experimental data, it is possible that the thermal expansion coefficient decreases with increasing $\text{Cr}\#$, but it is also possible that it remains almost unchanged.
- As $\text{Mg}\#$ increases, α decreases. The effect of $\text{Cr}\#$ is more significant.
- From 0 to 1200 K, the heat capacity of MgAl_2O_4 is the smallest, but above 1200 K, the heat capacity of MgCr_2O_4 is the smallest.

S-2.2 Effect of inversion degree on thermoelastic properties

S-2.2.1 Bulk modulus (K_0) and its pressure derivative

S-2.2.1.1 Simulation

In a typical solid, K_0 is expected to increase with increasing inversion degree because the

repulsive forces between atoms become stronger as the density increases (because the density increases with increasing inversion degree). However, Shukla et al. (2011) used MD to investigate the effect of inversion degree (i) on the bulk modulus and found that K_0 decreases slightly with increasing i in the range of i from 0 to 0.25 (see Figure 6 of Shukla et al. (2011)). To clarify the reason for this discrepancy, they calculated the effect of inversion on the physical properties of MgAl_2O_4 by dividing it into two parts: 1) the change in volume due to inversion, and 2) the change in the arrangement of atoms due to inversion. As a result, it is explained that from $i = 0$ to 0.25, the above two effects almost cancel each other, and the overall result is that K decreases only slightly with the increase of inversion degree.

Nunez-Valdez et al. (2018) investigated the effect of inversion degree on K by DFT. The results are in agreement with Shukla et al. (2011), where K decreases slightly with increasing i in the region between $i=0$ and 0.25 at 0 GPa (see Figure 4b of Nunez-Valdez et al. (2018)).

The above two papers claim that K decreases with increasing i , because K at $i = 0.25$ is slightly smaller than K at $i = 0$. However, it is the K values for $i = 0.125$ and 0.25 that should be compared, given that in most cases i is in the region of 0.125-0.25 in real samples (*i.e.*, not K with $i = 0$). Comparing the K values for $i = 0.125$ and 0.25 in both studies, it can be seen that K is independent of inversion degree. Thus, the simulation results suggest that K is independent of inversion degree for samples with $i = 0.125$ -0.25, which are more likely to be encountered in natural samples.

S-2.2.1.2 Experiments

Nunez-Valdez et al. (2018) used Brillouin scattering to investigate the inversion degree dependence of K_s . Among the samples they studied, the samples with the lowest inversion degree ($i = 0.136$) and the highest ($i = 0.286$) have K_s of 200(1) and 197.7(19) GPa, respectively, which are consistent with the uncertainty. Therefore, the effect of inversion degree on K is negligible.

Nestola et al. (2007) used XRD to investigate the relation between pressure and volume for ordered spinel ($i=0.15$) and disordered spinel ($i=0.27$). As they used quartz as a measure of pressure, the pressure values they reported were corrected using the EoS of Scheidl et al. (2016) before fitting with BM3. The resulting values of K_{T0} from the two samples are 195.4(10) and 197(2) GPa, respectively. These results indicate that the K_{T0} values agree within the uncertainty and that the effect of inversion degree on K is negligible.

From the results of Nestola et al. (2007), the K' of ordered spinel ($i=0.15$) and disordered spinel ($i=0.27$) are estimated to be 4.6(3) and 4.5(3), respectively, agreeing within the uncertainty. Therefore, the inversion degree does not affect K' .

S-2.2.2 Thermal expansion coefficient (α)

S-2.2.2.1 Simulation

Shukla et al. (2011) used MD to investigate the effect of inversion degree on the thermal expansion coefficient. The results show that in the range of $i=0.125$ to 0.25 , which is likely to be encountered in natural and synthetic samples, inversion degree has no effect on α (see Figure 7 of Shukla et al. (2011)).

S-2.2.2.2 Experiments

To investigate the effect of inversion degree on α , Carbonin et al. (2002) studied the relationship between temperature and volume using three samples with inversion degrees of $i = 0.13$, 0.243 and 0.26 at room temperature before analysis. As a result, it is reported that the thermal expansion coefficients are 27.5 , 26.8 and $27.2 \times 10^{-6} \text{ (K}^{-1}\text{)}$ from 298 to 1273 K , respectively, during the heating run. Therefore, no systematic effect of inversion degree on α has been observed. In addition, the temperature dependence of the unit cell parameter (da/dT) is consistent within uncertainty for both heating and cooling cycles for the same sample. Thus, the thermal expansion coefficient has little effect on the inversion degree.

S-2.2.3 Unit cell parameter (a)

Andreozzi et al. (2000) and Ma et al. (2021) examined the relationship between i and a at room temperature in the regions $i = 0.18\text{-}0.29$ and $i = 0.16\text{-}0.26$, respectively, to investigate the effect of inversion degree on the unit cell parameter. The results show that a decreases linearly with increasing i in both studies; Andreozzi et al. (2000) and Ma et al. (2021) report da/di of -0.0495 and $-0.0244 \text{ \AA}$, respectively. The reason for this difference is not clear, but may be due to the fact that Ma et al. (2021) used natural samples, the small number of data, and the large i uncertainty.

A decrease in the inversion degree from 0.25 to 0.18 implies an expansion of the unit cell parameter by 0.0049% (Andreozzi et al., 2000) and 0.0107% (Ma et al., 2021). This expansion corresponds to a pressure change of 0.044 GPa and 0.096 GPa , respectively, based on the VP data of Nestola et al (2007), so the change in inversion degree of the spinel inclusions or host minerals that a natural sample undergoes before reaching the surface may have a significant effect on the final inclusion pressure.

S-2.2.4 Conclusions for effect of inversion degree on thermoelastic properties

- In the case of MgAl_2O_4 with an inversion degree of $i = 0.125\text{-}0.25$, which is universal in natural and experimental samples, the difference in inversion degree does not affect K , K' , and α .
- The larger the inversion degree is, the smaller the unit cell parameter becomes.

S-2.3 Data handling

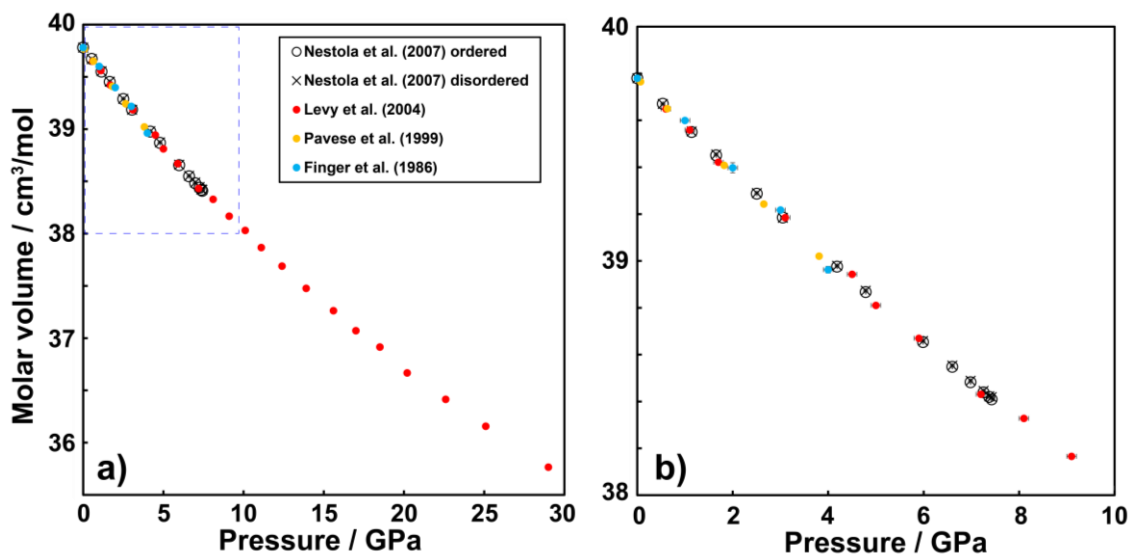
Here, I describe the treatment of VP , VT , PVT , KT , KP , KPT and C_pT data. Since the aim of this study is to determine the EoS of the MgAl_2O_4 end member component, I focus only on the data sets obtained using samples close to the end member component. The characteristics of the samples used in each paper and the details of the experimental methods are briefly summarized in Supplemental Table S3-2.

In addition to MgAl_2O_4 , other components such as MgCr_2O_4 , $\text{MgFe}^{3+}_2\text{O}_4$ and FeAl_2O_4 may be included in the selected datasets. In this study, the data were selected so that the total contribution of the components other than MgAl_2O_4 was less than 10 mol% at most. As a result, the sample with the farthest composition from the end member component in the data set is $\text{Mg}(\text{Fe}^{3+}_{0.078}\text{Al}_{0.922})_2\text{O}_4$ from Martignago et al. (2006), and the contribution of the end component other than MgAl_2O_4 is only 8 mol%.

S-2.3.1 VP data

S-2.3.1.1 General remarks for VP data handling

I have selected five previous studies that investigate the pressure dependence of volume, which may be useful in constraining the compressional part of MgAl_2O_4 EoS. Most of these studies report the volume in $\text{\AA}^3$. To use Mie-Grüneisen-Debye EoS, the volumes were converted to molar volumes before fitting. In the conversion to molar volume, the molar volume corresponding to 298 K and 1 bar for each dataset was normalized to the standard state molar volume of $39.78 \text{ cm}^3/\text{mol}$ for spinel as reported by Holland and Powell (2011). The relation between the normalized molar volume and pressure is shown in Figure S3-4.



FigureS3- 4 a) PV data from a previous study with the molar volume normalized to $39.78 \text{ cm}^3/\text{mol}$ at ambient temperature and pressure (Finger et al., 1986; Levy et al., 2003; Nestola et al., 2007; Pavese et al., 1999). b) Enlarged view of the area enclosed by the dotted line in a).

S-2.3.1.2 Nestola et al. (2007)

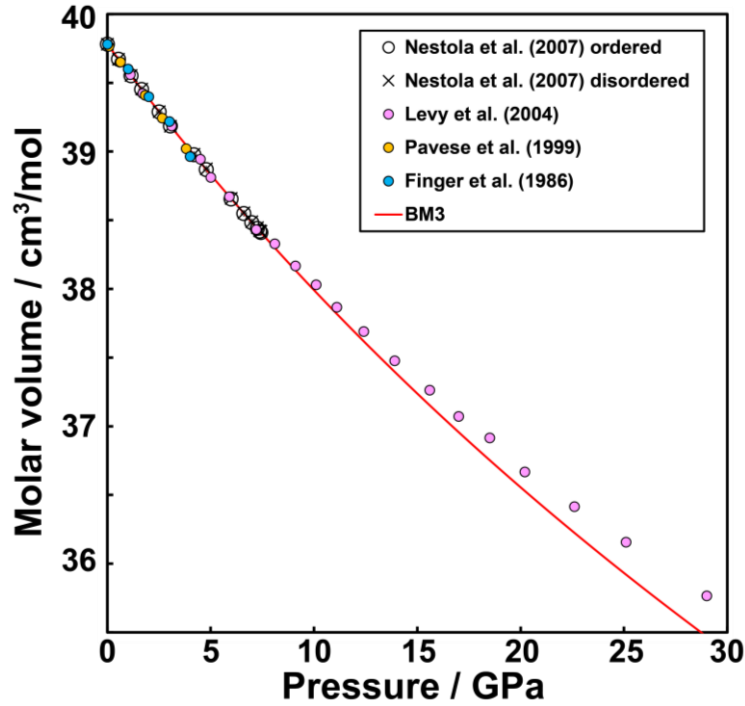
This study reports spinel PV data with two different inversion degrees (0.15 and 0.27), both of which were subjected to the data processing described below. Because the pressures in Nestola et al. (2007) were originally determined by using the quartz pressure scale of Angel et al. (1997), it was rescaled by using the revised quartz pressure scale of Scheidl et al. (2016). The temperature at the time of measurement was reported to be 298K, but the uncertainty was not reported. Therefore, in this study, the uncertainty was assumed to be $\pm 2\text{K}$.

S-2.3.1.3 Levy et al. (2003)

Levy et al. (2003) provide valuable data in the sense that they investigate the PV relationship from ambient pressure to extremely high pressures of 29 GPa, but because they use nitrogen as the pressure medium for their DAC experiment, the sample is likely to be non-hydrostatic condition at high pressure, as reported in Angel et al. (2007).

Figure S3-5 shows the results of fitting all the data of Nestola et al. (2007) and Levy et al. (2004) below 7.2 GPa using the third-order Birch-Mannahan equation of state, along with the VP data of four previous studies. It is obvious from the figure that the volume data above 7.2 GPa in Levy et al. (2004) are clearly shifted to the high-pressure side for the same volume compared to the fitting results. One of the reasons for this discrepancy is the use of ruby fluorescence as a pressure indicator in their study. This is because their experiment uses N_2 as a pressure medium, and it is highly likely that the pressure markers are placed under high deviatoric stress, in which

case it is inappropriate to use non-cubic pressure markers such as ruby as an index of mean stress (Chai and Michael Brown, 1996). Therefore, the Levy et al. (2003) data above 7.2 GPa were excluded from further fitting.



FigureS3- 5 PV data from published studies with the molar volume normalized to $39.78 \text{ cm}^3/\text{mol}$ at ambient temperature and pressure (Finger et al., 1986; Levy et al., 2003; Nestola et al., 2007; Pavese et al., 1999). Since Kruger et al. (1997) did not report the volume at ambient temperature and pressure, and the volume data could not be normalized, it is not plotted in this figure. A red line represents V/P relation obtained from a fit of the third-order Birch-Murnaghan EoS. In this fit, I used all the data of Nestola et al. (2007) and those of Levy et al. (2004) below 7.2 GPa.

S-2.3.1.4 Pavese et al. (1999)

The sample used by Pavese et al. (1999) is $\text{Mg}_{0.94}\text{Al}_{2.04}\text{O}_4$ and is therefore not stoichiometric; according to Nestola et al. (2009), non-stoichiometric spinels have a lower K_{T0} than stoichiometric spinel. In fact, a fit of a BM2 EoS using only the Pavese et al. (1999) data gives $K_{T0} = 190.1 (1.5) \text{ GPa}$, which is a significantly smaller bulk modulus compared to $K_{T0} = 195.4 (1.0) \text{ GPa}$ for the stoichiometric ordered spinel of Nestola et al. (2007). Therefore, the data reported by Pavese et al. (1999) was excluded from further fitting as it may show different elastic properties compared to the stoichiometric sample.

S-2.3.1.5 Kruger et al. (1997)

They reported the relation between volume and pressure of MgAl_2O_4 from 12.5 GPa to 66.9 GPa using Ar and 4:1 mixture of methanol:ethanol as pressure media. Angel et al. (2007) showed that the sample becomes subject to non-hydrostatic stress above 1.9 GPa and 9.8 GPa using Ar and a 4:1 mixture of methanol:ethanol as the pressure medium. Therefore, the data obtained by Kruger et al. (1997) are likely to have been obtained under non-hydrostatic conditions. Furthermore, they did not report the volume of the sample at ambient temperature and pressure, so that the data cannot be normalized for comparison with other studies. Therefore, the data reported by Kruger et al. (1997) were excluded from further fitting.

S-2.3.1.6 Finger et al. (1986)

The pressure data of Finger et al. (1986) are accompanied by a large uncertainty of ± 0.1 GPa. On the other hand, the pressure uncertainty reported by Nestola et al. (2007) ranges from ± 0.004 to ± 0.01 GPa, while the pressure uncertainty of Finger et al. (1986) is more than ten times larger than that of Nestola et al. (2007). In fact, when all the PV data reported by Finger et al. (1986) are used and fitted with third-order BM compressional EoS, the maximum value of the residue (ΔP_{max}) reaches 0.32 GPa, whereas in that of Nestola et al. (2007) is only 0.02 GPa. Therefore, the PV data of Finger et al. (1986) is not very useful for constraining the equation of state because of the large uncertainties. Therefore, the Finger et al. (1986) data were excluded from further fitting

S-2.3.1.7 Conclusions for data handling of PV data

In view of the above discussion, all the data of Nestola et al. (2007) and the data of Levy et al. (2004) below 7.2 GPa were used for fitting in this study. To avoid duplication and therefore over-weighting of the data at ambient conditions (which are scaled to our chosen reference volume), those data were removed from the PV data set used in this study.

S-2.3.2 VT data

S-2.3.2.1 General remarks for VT data handling

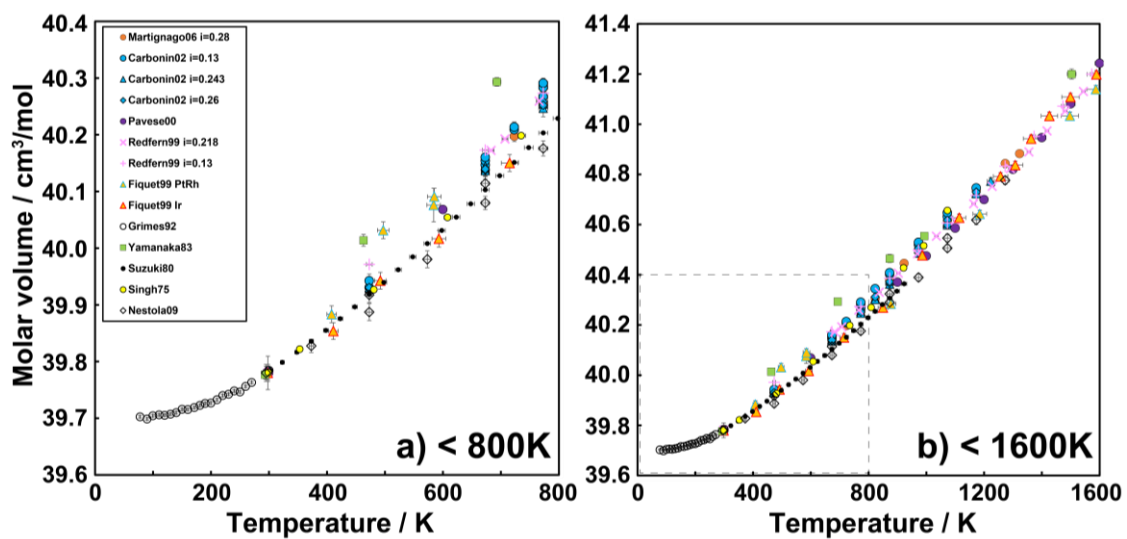
In the studies shown in Table S3-2, most of the volume data are reported in $\text{\AA}^3$. To use MGD-EoS, the volumes were converted to molar volumes before fitting. In the conversion to molar volume, the molar volume corresponding to 298 K and 1 bar for each dataset was normalized to the standard state molar volume of $39.78 \text{ cm}^3/\text{mol}$ for spinel as reported by Holland and Powell (2011). The relation between the normalized molar volume and pressure is shown in Figure S3-6.

In some studies, ‘room temperature’ data were obtained under non-standard conditions, and

not at 298 K. Thus, for example, normalizing the volume data obtained at 293 K to 39.78 cm³/mol (the volume assumed at standard conditions) overestimates the molar volume. To minimize the effect of such volume overestimation or underestimation, I corrected the normalized volume using the VT data of Grimes and Al-Ajaj (1992), who obtained volume data below 300 K with fine temperature intervals.

The following is an example of the correction procedure for a VT dataset, where room temperature data was obtained at 293 K. 1) The VT data of Grimes and Al-Ajaj (1992) is fitted using Kroll's thermal pressure EoS. 2) Normalize their data so that the volume at 298 K obtained by fitting is 39.78 cm³/mol. 3) Calculate the volume at 293 K when the volume at 298 K is 39.78 cm³/mol. The result is 39.771 cm³/mol. 4) Normalize their data so that the volume data obtained at 293 K is 39.771 cm³/mol.

In Figure S3-6a, only the data below 800 K are plotted because several studies have reported a rapid change in volume due to the order disorder transition above 800 K. However, the VT trend still shows a large difference between previous studies even below 800 K. Some studies reported the inversion degree at room temperature, but the difference in VT trend cannot be explained only by the inversion degree.



FigureS3- 6 VT data for MgAl₂O₄ below 800 K a) and below 1600K b) from a previous study with the molar volume normalized to 39.78 cm³/mol at ambient temperature and pressure (Carbonin et al., 2002; Fiquet et al., 1999; Grimes and Al-Ajaj, 1992; Martignago et al., 2003, 2006; Fabrizio Nestola et al., 2009; Pavese et al., 2000; Redfern et al., 1999; Singh et al., 1975; Suzuki and Kumazawa, 1980; Yamanaka and Takéuchi, 1983). Fiquet et al. (1999) utilized two different types of heating wires (PtRh and Ir wire) and performed the analysis under slightly different temperature conditions from each other.

Although Carbonin et al. (2002) and Redfern et al. (1999) reported data for both heating and cooling cycles, the same symbols are used in this figure regardless of the heating or cooling cycle.

S-2.3.2.2 Nestola et al. (2009)

Nestola et al. (2009) obtained VT data from 295 K to 1273 K using a sample with a non-stoichiometric chemical composition of $^T(\text{Mg}_{0.4}\text{Al}_{0.6})^M(\text{Al}_{1.8}\square_{0.2})\text{O}_4$. As can be seen from Fig. S3-6, Nestola et al. (2009) reported the smallest thermal expansion coefficient of MgAl_2O_4 reported so far. Therefore, it would not be appropriate to use this data to constrain the EoS of stoichiometric MgAl_2O_4 .

S-2.3.2.3 Martignago et al. (2006)

Since no temperature uncertainty has been reported, I took it to be 1% of the absolute temperature except at room temperature. The temperature uncertainty at room temperature was assumed to be 2K. This study uses three samples, but only the sample named 3dis can approximate the chemical composition of MgAl_2O_4 , so only the data for 3dis is plotted in Figure S3-1. The 3dis is a natural sample, which contains a small amount of Fe^{3+} and is expressed as $\text{Mg}(\text{Fe}^{3+}_{0.078}\text{Al}_{0.922})_2\text{O}_4$.

S-2.3.2.4 Martignago et al. (2003)

Since no temperature uncertainty has been reported, I took it to be 1% of the absolute temperature except at room temperature. The temperature uncertainty at room temperature was assumed to be 2 K. This study uses 4 samples with compositions of $(\text{Mg}_{1.003}\text{Mn}_{0.001}\text{Zn}_{0.002})(\text{Cr}_{0.066}\text{Al}_{1.928})\text{O}_4$, $(\text{Mg}_{0.999}\text{Mn}_{0.002}\text{Zn}_{0.007})(\text{Cr}_{0.123}\text{Al}_{1.868})\text{O}_4$, $(\text{Mg}_{0.995}\text{Mn}_{0.002}\text{Zn}_{0.0072})(\text{Cr}_{0.162}\text{Al}_{1.834})\text{O}_4$, and $(\text{Mg}_{0.997}\text{Mn}_{0.002}\text{Zn}_{0.0072})(\text{Fe}^{3+}_{0.079}\text{Al}_{1.920})\text{O}_4$.

S-2.3.2.5 Carbonin et al. (2002)

Carbonin et al. (2002) use natural samples with two different inversion degrees ($i=0.13$ and 0.243) named NATURAL and TRANS, and a synthetic sample with $i=0.243$ named SYN. In this study, all samples are analyzed in heating and cooling cycles. In the heating cycle, the temperature is not raised monotonically, but is raised and lowered repeatedly. However, below 800 K, such temperature increase and decrease did not affect the inversion degree and unit cell parameter, and the inversion degree and unit cell parameter measured at the same temperature agreed within the uncertainty range. Therefore, to avoid overweighting, only the first data point is plotted in Figure S3-1 for the overlapping temperature data. Since the temperature is monotonically decreasing in the cooling cycle, all data below 800 K are plotted in Figure S3-1.

S-2.3.2.6 Pavese et al. (2000)

Since no temperature uncertainty has been reported, I took it to be 1% of the absolute temperature except at room temperature. The temperature uncertainty at room temperature was assumed to be 2K. The inversion degree of the sample they studied was $i=0.18$ at room temperature and pressure.

S-2.3.2.7 Redfern et al. (1999)

They report an uncertainty of ± 5 K in temperature. Therefore, the uncertainty was assumed to be 5 K for all temperatures except room temperature. The uncertainty of the temperature at room temperature was assumed to be 2K. They reported data from two heating cycles and one cooling cycle, but the volume of the cooling cycle could not be normalized because there was no data at room temperature and pressure. Therefore, only the data for the heating cycle is plotted in Figure S3-1.

S-2.3.2.8 Fiquet et al. (1999)

They claim that their measured temperatures are accurate to within 50K. Therefore, taking into account that the maximum value of their temperature measurement is 2385K, I assumed that the temperature uncertainty is about 2% of the absolute temperature except at room temperature. The temperature uncertainty at room temperature was assumed to be 2K.

S-2.3.2.9 Grims and Al-Ajaj (1992)

Since they report a temperature sensor uncertainty of ± 0.5 K, I assumed that all data would have an uncertainty of 0.5K. However, they do not report the uncertainty in the unit cell parameter, so I fitted their V/T data using the Kroll thermal pressure EoS to estimate the volume uncertainty. I assumed that K' is 4.5. The maximum difference between the calculated volume and the reported volume was about $0.006 \text{ cm}^3/\text{mol}$. From the data scattering, I assumed the volume uncertainty is $0.002 \text{ cm}^3/\text{mol}$.

S-2.3.2.10 Yamanaka and Takeuchi (1983)

They report a temperature uncertainty of 20°C at 1800°C . Therefore, I assume that their temperature uncertainty is about 1% of the absolute temperature.

S-2.3.2.11 Suzuki and Kumazawa (1980)

Thermal expansion data of Suzuki and Kumazawa (1980) were obtained from Appendix Table 2 of Suzuki et al. (2000). Since no temperature uncertainty has been reported, I took it to

be 1%. Furthermore, they did not report any uncertainty in the length of the sample. To estimate the volume uncertainty, I used EoSfit7c to fit their V/T data below 800K with Kroll's thermal pressure EoS. From the data scattering, I assumed the volume uncertainty is 0.001 cm³/mol.

S-2.3.3 *PVT* data

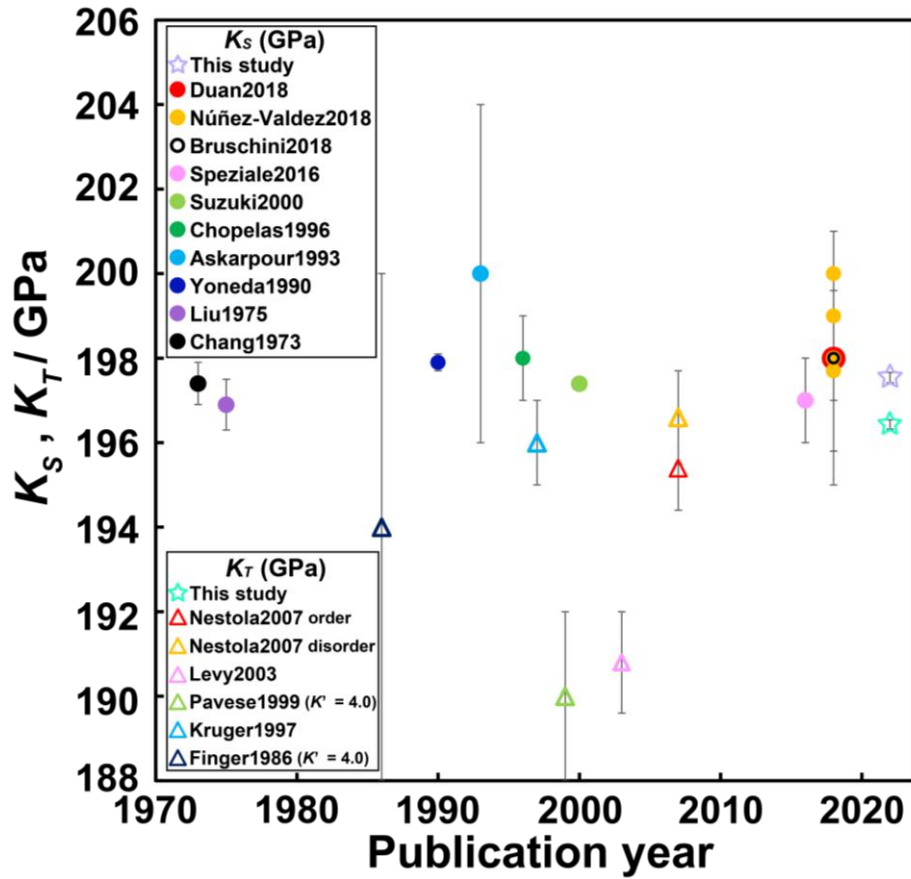
S-2.3.3.1 Meducin et al. (2004)

This is the only study to investigate the volume of MgAl₂O₄ as a function of both temperature and pressure. They used a sample with a very high inversion degree of 0.32 at ambient condition. The variation of the inversion degree during the analysis is also very large, ranging from 0.26 to 0.63. Therefore, the data of this study are not used for fitting, because it is assumed that not only temperature and pressure but also inversion degree has a large influence on the volume.

S-2.3.4 *Ks* data

S-2.3.4.1 General remarks for K_S data

Figure S3-7 summarizes the values of K_S at room temperature and ambient pressure reported so far and the year of publication. The data in Figure S3-3 are the K_{S0} values and their uncertainties reported in the respective papers without modification. In this section, I deal with papers that report only K_S at ambient temperature and pressure (Bruschini et al., 2018; Núñez-Valdez et al., 2018). Studies that investigate the temperature and pressure dependence of K_S are discussed in the following sections (Askarpour et al., 1993a; Chang and Barsch, 1973; Duan et al., 2018; Liu et al., 1975; Speziale et al., 2016; Suzuki et al., 2000; Yoneda, 1990).



FigureS3- 7 The relation between the reported ambient condition K_S (circle symbols) and K_T (triangle symbols) of MgAl_2O_4 and the publication year (Chang and Barsch 1973; Liu et al. 1975; Finger et al. 1986; Yoneda 1990; Askarpour et al. 1993; Chopelas 1996; Kruger et al. 1997; Pavese et al. 1999; Suzuki et al. 2000; Levy et al. 2003; Nestola et al. 2007; Speziale et al. 2016; Bruschini et al. 2018; Duan et al. 2018; Núñez-Valdez et al. 2018). Cynn et al. (1993) also reported the K_S at ambient condition, but it is not shown in this figure because they reported an unusually high value of $K_S = 210(6)$ GPa. An error bar for K_{S0} of Suzuki et al. (2000) is smaller than the symbol. The K_S and K_T calculated from the EoS constrained in this study are represented by star symbols.

S-2.3.4.2 Núñez-Valdez et al. (2018)

They have measured K_S of four spinel single crystals by combining X-ray diffraction and Brillouin scattering measurements at ambient conditions. The samples were three synthetic MgAl_2O_4 spinels with different degrees of inversion ($i = 0.198, 0.242, \text{ and } 0.286$) and one natural spinel of almost end member composition ($(\text{Mg}_{0.852}\text{Al}_{0.136}\text{Fe}_{0.008}\text{Zn}_{0.004})[\text{Mg}_{0.163}\text{Al}_{1.820}\text{Cr}_{0.013}\text{V}_{0.003}]\text{O}_4$) with inversion degree of 0.136. Since the inversion degree does not affect the value of K_S (see section 2.1), in this study all data were used for fitting to the constraint of EoS. The temperature uncertainty at room temperature was reported to be 1K.

S-2.3.4.3 Bruschini et al. (2018)

They reported K_s of six gem-quality synthetic crystals in the system $(\text{Mg}_{1-x}\text{Fe}^{2+}_x)\text{Al}_2\text{O}_4$ with $0 \leq x < 0.5$ by using single-crystal X-ray diffraction and Brillouin scattering. Since the dataset was selected so that the contribution of spinel end member components other than MgAl_2O_4 was less than 10 mol%, only the K_s data of MgAl_2O_4 was used for fitting from this study. The temperature uncertainty at room temperature was assumed to be 2K.

S-2.3.5 $K_s T$ data

S-2.3.5.1 Suzuki et al. (2000)

This study measured temperature dependence of K_s of synthetic stoichiometric MgAl_2O_4 spinel by using the resonant sphere technique from 293 K to 1167 K. However, the uncertainties in K_s reported by them are very small, ranging from 0.013 GPa to 0.050 GPa, compared to 0.2 GPa (Yoneda et al., 1990) to 3 GPa (Núñez-Valdez et al., 2018) reported in other studies. Therefore, to assess whether the reported uncertainties are valid, I calculated the difference in K_s for several pairs of data they obtained at approximately the same temperature. As a result, the difference in K_s between 1103 K and 1104 K is +0.269 GPa, between 992 K and 996 K is -0.121 GPa, between 930 K and 934 K is -0.411 GPa, between 874 K and 879 K is -0.154 GPa, between 755 K and 760 K is -0. The difference in K_s between 755K and 760K was -0.182 GPa, and the difference in K_s between 647K and 653K was -0.291 GPa. Considering that the differences are not systematic and that the largest difference is 0.411 GPa, the accuracy of the analysis is likely to be around 0.3 GPa rather than 0.05 GPa. Therefore, the uncertainty associated with the K_s data is assumed to be 0.3 GPa in this study. I also assume a temperature uncertainty of 1% relative to the absolute temperature, because no temperature uncertainty has been reported in this study.

S-2.3.5.2 Cynn et al. (1993)

This study measured temperature dependence of K_s of natural MgAl_2O_4 spinel by using the Rectangular Parallelepiped Ultrasonic Resonance from 298 K to 1003 K. The K_s measured by them at ambient condition was 210(6) GPa, which is clearly larger than the results of other studies (Figure S3-7). The uncertainty of the measurement is also very large, about 6 GPa. Therefore, their data is not useful for constraining the EoS and is excluded from the dataset used in the fitting.

S-2.3.5.3 Askarpour et al. (1993)

This study measured temperature dependence of K_s of synthetic stoichiometric MgAl_2O_4 spinel by using the Brillouin spectroscopy from 293 K to 1273 K. Although this study does not report the uncertainty in the K_s obtained, the variation in the K_s is clearly much higher than at

least the data of Suzuki et al. (2000). Therefore, their data are not effective in constraining the EoS and were excluded from the fitting.

S-2.3.5.4 Liu et al. (1975)

This study measured K_S value of synthetic stoichiometric MgAl_2O_4 spinel by the light-sound scattering technique in the Raman-Nath region. In this study, K_S at ambient temperature and pressure were reported, but K_S values at each temperature were not summarized in figures or tables, so the data could not be extracted.

S-2.3.6 $K_S P$ data

S-2.3.6.1 Speziale et al. (2016)

This study measured K_S of synthetic stoichiometric MgAl_2O_4 spinel by the Brillouin scattering up to 11.13 GPa. However, Speziale et al. (2016) is an AGU abstract, so details of the data are not available. A diagram showing the relation between pressure and K_S obtained by Speziale et al. (2016) is presented by Faccincani et al. (2021), but their diagram does not show the pressure uncertainty, nor does it show the information on the density data used to convert the measured sound velocity to elastic constants.

Through personal communication with Dr. Speziale, he provided us with data on pressure and sound velocity and their uncertainties. However, since they did not have the density data during the analysis, it was necessary to estimate the density of the sample at the temperature and pressure conditions analyzed from the EoS. However, since $K_S P$ data is used to estimate the EoS, this series of calculations requires iteration.

To estimate the initial value of the density, the EoS obtained by fitting the VP data (see section 3.1.7) with the third order Birch-Murnaghan EoS is used. Using this EoS, I calculated the density of the sample under each of the pressure conditions analyzed by Speziale et al. (2016) and combined it with the sound velocity data to calculate a first estimate of K_S . The obtained relationship between K_S and pressure was then used to constrain the BM3-MGD EoS. Next, I used the obtained BM3-MGD EoS to recalculate the density of the sample at each pressure condition analyzed by Speziale et al. (2016). After repeating the calculation twice, the obtained K_S values converged (Table S3-2); the uncertainty in K_S was calculated by propagating the uncertainty in sound velocity.

Table S3- 2 K_S values at each pressure obtained by iteration of density estimated from BM3-MGD EoS and sound velocity and pressure data obtained by Speziale et al. (2016).

Pressure	Initial value		1st iteration		2nd iteration		3rd iteration		
	Density	K_S	Density	K_S	Density	K_S	Density	K_S	esd K_S

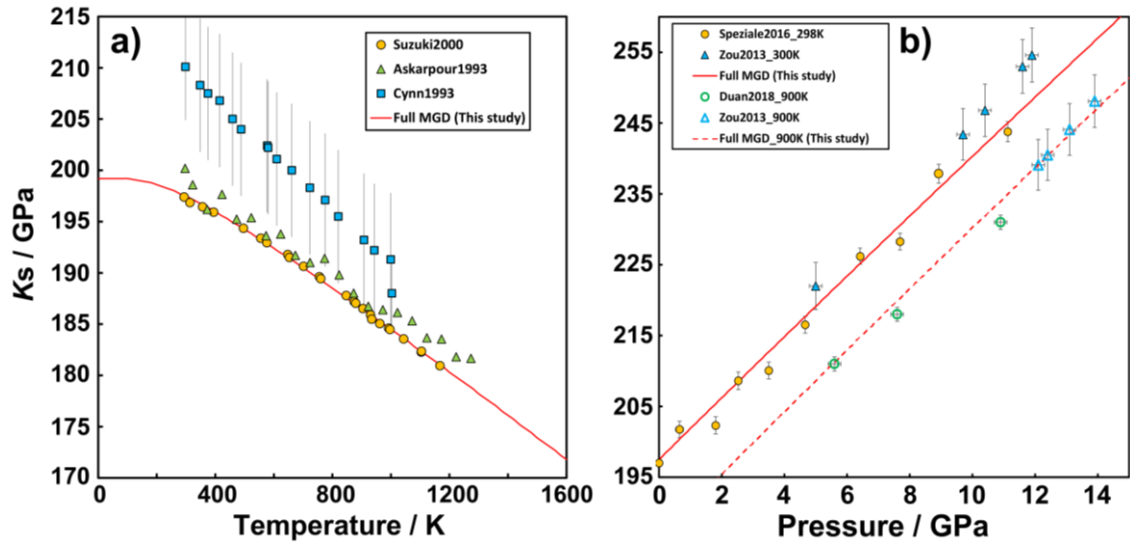
GPa	g/cm ³	GPa	g/cm ³	GPa	g/cm ³	GPa	g/cm ³	GPa	GPa
0.00	3.5760	197.01	3.5760	197.01	3.5760	197.01	3.5760	197.01	0.55
0.65	3.5878	201.75	3.5878	201.75	3.5878	201.75	3.5878	201.75	1.17
1.81	3.5996	201.82	3.6085	202.31	3.6085	202.31	3.6085	202.31	1.22
2.53	3.6115	208.08	3.6211	208.63	3.6211	208.63	3.6211	208.63	1.24
3.50	3.6234	209.23	3.6379	210.07	3.6379	210.07	3.6379	210.07	1.19
4.66	3.6354	215.21	3.6577	216.53	3.6577	216.53	3.6577	216.53	1.19
6.42	3.6474	223.77	3.6871	226.20	3.6870	226.20	3.6870	226.20	1.13
7.69	3.6594	225.30	3.7078	228.27	3.7077	228.27	3.7077	228.27	1.19
8.92	3.6715	234.30	3.7275	237.87	3.7274	237.86	3.7274	237.86	1.33
11.13	3.6836	238.72	3.7622	243.81	3.7620	243.80	3.7620	243.80	1.43

S-2.3.6.2 Yoneda (1990)

This study measured K_S value of synthetic stoichiometric MgAl_2O_4 spinel by the ultrasonic interferometry up to 7.78 GPa. However, in this study, K_S at ambient temperature and pressure were reported, but K_S values at each pressure were not summarized in figures or tables, so the data could not be extracted.

S-2.3.6.3 Chang and Birch (1973)

This study measured K_S value of synthetic stoichiometric MgAl_2O_4 spinel by the ultrasonic pulse superposition method up to 1.0 GPa. However, in this study, K_S at ambient temperature and pressure were reported, but K_S values at each pressure were not summarized in figures or tables, so the data could not be extracted.



FigureS3- 8 a) Relationship between K_S and temperature. The red line is the K_S - T relation obtained by fitting a full MGD EoS (Askarpour et al., 1993a; Cynn et al., 1993; Suzuki et al., 2000). b) Relationship between K_S and pressure. 298K data and 900K data are shown (Duan et al., 2018; Speziale et al., 2016; Zou et al., 2013). The K_S - P relationship obtained from the fit of the full MGD EoS is also depicted for 298K and 900K.

S-2.3.7 K_S PT data

S-2.3.7.1 Duan et al. (2018)

This study measured K_S value of synthetic stoichiometric MgAl_2O_4 spinel by single-crystal X-ray diffraction and Brillouin scattering up to 10.5 GPa and 1000 K. Duan et al. (2018) does not report any pressure uncertainties. Therefore, I assumed the pressure uncertainty as 0.2 GPa based on the data scatter in their graphs. In addition, they do not report temperature uncertainties. So, I assumed the temperature uncertainty as 1% at $T > 300\text{K}$ and 2K at 300K.

Their data at 1000 K were predominantly lower than the K_S calculated by the BM3-MGD EoS. Therefore, as expected from the DFT simulations of Núñez-Valdés et al. (2018), the 1000K data of Duan et al. (2018) were excluded in this study because the K_S may have been lowered due to the increased inversion degree in the 1000K measurements.

S-2.3.7.2 Zou et al. (2013)

This study measured K_S value of synthetic stoichiometric MgAl_2O_4 spinel by ultrasonic interferometry up to 14.2 GPa and 900 K. Zou et al. (2013) does not report pressure uncertainty. Therefore, I assumed the pressure uncertainty as 0.2 GPa based on the data scatter in their graphs. In addition, they do not report temperature uncertainty. So, I assumed the temperature uncertainty as 1% at $T > 300\text{K}$ and 2K at 300K. Furthermore, Zou et al. (2013) reports uncertainties are less

than 1.5% in the K_S . So, K_S uncertainties are assumed to be 1.5%.

Since their experiments used polycrystalline samples, if they had not annealed at high temperature prior to analysis, plastic deformation may have occurred during analysis under room temperature and high pressure conditions, making it undesirable to use these data to constrain the equation of state. In fact, their room temperature and high pressure K_S data are significantly higher than those of Speziale et al. (2016) at the same pressure, so the room temperature data of Zou et al. (2013) were excluded from further analysis.

S-2.3.8 $C_p T$ data

The following two datasets are available for the heat capacity properties of MgAl_2O_4 . Since the values at 298 K in Robie and Hemingway (1995) and Klemme and Ahrens (2007) were 115.94 and 120.3 (J/mol*K), respectively, I simply multiplied all the data in Robie and Hemingway (1995) by 1.0372 to obtain to smooth the data connection.

S-2.3.8.1 Robie and Hemingway (1995)

This study reports the heat capacity of MgAl_2O_4 at 1 bar from 298 K to 1800 K.

S-2.3.8.2 Klemme and Ahrens (2007)

This study reports the heat capacity of MgAl_2O_4 at 1 bar from 4.33 K to 305.2 K.

S-2.3.9 Full description for selected thermoelastic property data

The elastic properties of spinel have been studied extensively as a function of both pressure and temperature by means of different experimental techniques and computational studies. The thermoelastic properties of spinel have been investigated by computer simulations using various methods such as DFT (Mao et al., 2016; Núñez-Valdez et al., 2018; Ono et al., 2008), MD (Shukla et al., 2011), and HF (Catti et al., 1994). However, due to the limitations of the quasi-harmonic approximation, it is difficult to extend computer simulations to finite temperatures, so only experimental data were analyzed in this study.

Compression data obtained using various diffraction methods at room temperature are available up to 66.9 GPa. However, Kruger et al. (1997), who obtained data up to 66.9 GPa, did not report data at ambient temperature and pressure, and therefore the data cannot be normalized and used for further fitting. In addition, Levy et al. (2003) used N_2 as the pressure medium, and it would not be appropriate to use their VP data obtained at high pressure to constrain the EoS, because differential stresses may occur between the pressure marker ruby and the sample, especially at high pressures. However, at least for volume measurements below 7.5 GPa, their VP data are consistent within uncertainty with other studies, so their VP data will be used for further fitting only for data below 7.5 GPa. The PV data from

Pavese et al. (1999) and Finger et al. (1986) were excluded from the fitting because of their large uncertainties, but the excluded data are consistent (within large uncertainties) with the other data. The reason for excluding these data is that their inclusion in the fit would not make a significant difference to the refined parameters and would only increase the estimation uncertainty. I finally used the data of Nestola et al. (2007) and Levy et al. (2003) below 7.5 GPa for fitting, but excluded all data at ambient temperature and pressure to avoid overweighting of data (Table S3-3).

Data on the temperature variation of the volume (and cell parameters) at room pressure exist from 77 to 2288 K, but there is no consistency between the data, especially at higher temperatures (Figure S3-6). The reasons for these inconsistencies are not obvious from the published information. Of special importance for constraining both the appropriate thermal expansion model and its coefficients are the precise data collected below room temperature by X-ray powder diffraction (Grimes and Al-Ajaj, 1992). To constrain reliable thermal expansion data at high temperatures, I searched for a dataset that is consistent with other thermoelastic properties (VP , VT (low temperature), $K_S P$, $K_S T$ and $K_S PT$) using C_P -EoS. As a result, I decided to use the data set of Suzuki and Kumazawa (1980) for further fitting. The high confidence in their dataset is supported not only by the consistency with the C_P -EoS, but also by the fact that the values of θ_D obtained from the full MGD EoS fitting are close to those of previous studies.

To the best of our knowledge, only Meducin et al. (2004) have measured the volume of spinel at simultaneous high P and T . However, the sample they used has an unusually high inversion degree of 0.32 at ambient condition, and the change in inversion degree during analysis is very large (0.26-0.63), so it was excluded from the further fitting.

Total of five data measured by Brillouin spectroscopy by Núñez-Valdez et al. (2018) and Bruschini et al. (2018) for K_S at ambient temperature and pressure were used for fitting. The full elastic tensor of spinel as a function of temperature up to 1167 K was determined by Suzuki et al. (2000) using the resonant sphere technique, from which the variation of the adiabatic bulk moduli $K_S = -V(\partial P/\partial V)_S$ can be obtained. Other studies investigating the temperature dependence of K_S were excluded from further fitting because they did not agree with the K_T and K_S data at room temperature or had large uncertainties (Askarpour et al., 1993; Cynn et al., 1993). For the pressure dependence of K_S , the sound velocity data reported in Speziale et al. (2016) were provided by personal communication and converted to K_S for fitting according to the calibration procedure described in Section 3.6.1. Unfortunately, the results of the temperature or pressure dependence of the elastic tensor of spinel by Yoneda (1990), Liu et al. (1975), and Chang and Birch (1973) are reported only as derivatives of pressure or temperature and cannot be used for fitting.

Simultaneous high-temperature and high-pressure K_S measurements up to 13.9 GPa and 1000 K have been reported by Zou et al. (2013) and Duan et al. (2018). The data of Duan et al. (2018) at 1000 K were predominantly lower than the K_S calculated by the BM3-MGD EoS. Therefore, as expected

from the DFT simulations of Núñez-Valdés et al. (2018), the 1000K data of Duan et al. (2018) were excluded in this study because the K_S may have been lowered due to increased inversion degree in the 1000K measurements. Furthermore, the data of Zou et al. (2013) at room temperature and high pressure was excluded from the dataset because the K_S may be higher than the actual value due to the non-hydrostatic condition.

The dataset used to determine the elastic parameters of spinel therefore consists of 142 data (Table S3-3), made up of 66 direct measurements of elastic moduli, 21 direct measurements of dimensional changes with temperature by dilatometer, and 55 determinations of unit-cell parameters by diffraction.

Table S3- 3 Data used to determine elastic parameters for spinel.

Reference	Data type	Method	P range (GPa)	T range (K)	Ndata
Nestola et al. (2007)	PV	Single-crystal XRD	0.5357–7.424	Ambient	26/28
Levy et al. (2003)	PV	Powder XRD	0.6–7.2	Ambient	8/22
Grimes and Al-Ajaj (1992)	TV	Powder XRD	Ambient	77.5–300.1	21/21
Suzuki and Kumazawa (1980)	TV	Dilatometer	Ambient	303–798	21/34
Núñez-Valdez et al. (2018)	K_S	Brillouin spectroscopy	Ambient	Ambient	4/4
Bruschini et al. (2018)	K_S	Brillouin spectroscopy	Ambient	Ambient	1/6
Speziale et al. (2016)	$K_S P$	Brillouin spectroscopy	0–11.13	Ambient	10/10
Suzuki et al. (2000)	$K_S T$	Resonant sphere technique	Ambient	293–1167	25/25
Duan et al. (2018)	$K_S PT$	Brillouin spectroscopy	0–10.9	300–900	12/14
Zou et al. (2013)	$K_S PT$	Ultrasonic interferometry	5.7–13.9	300–900	14/19

‘Ndata’ is the number of data from each source used in the refinement of EoS parameters.

S-2.4 Fitting procedure

S-2.4.1 Workflow

1. The initial values of the compressional EoS parameters are obtained by fitting with third-order Birch-Murnaghan EoS using only the VP data.
2. From the sound velocity data of Speziale et al. (2016) and the density calculated with the EoS obtained in 1), I estimate the K_S at each pressure (= initial value in Table S3-2).
3. Using VP , VT (only for data below room temperature), K_S , $K_S T$, $K_S P$ and $K_S PT$, the fitting is performed with a q-compromise BM3-MGD EoS (Angel et al., 2020). The fitting parameters, K_0 and K' , are initially set to the values obtained in 1), and θ_D is not refined. The purpose here is to obtain the initial value of γ_0 .
4. Using VP , VT (only data below room temperature), K_S , $K_S T$, $K_S P$, $K_S PT$, and $C_P T$ data (i.e., all data except VT data above room temperature), I perform the fitting with C_P -EoS (Milani et al., 2017). The fitting parameters, K_0 , K' and γ_0 , are initially set to the values obtained in 3). q is

assumed to be 1.

5. Using the refined γ_0 values, I perform the fitting again with C_P -EoS. Here, q is also refined.
6. I plotted the VT relation from the EoS obtained in (5) and evaluated the consistency with the VT data of previous studies. The results are in agreement with those of Suzuki and Kumazawa (1980).
7. The VT data of Suzuki and Kumazawa (1980) is added to the dataset and the fitting is performed again with C_P -EoS. Refine all parameters except V_0 .
8. Using the same dataset as in (7), fitting with BM3-full MGD EoS with γ_0 set to 1.1 and q set to 1. Refine all parameters except V_0 .
9. Fitting is performed with BM3-q compromise MGD EoS and compared with the results of 8). Refine all parameters except V_0 .
10. Fitting is performed with BM3-HP2011 EoS and compared with the results of 8). Refine all parameters except V_0 .
11. The heating run data of Redfern et al. (1999) with an inversion of 0.13 and Carbonin et al. (2002) with an inversion of 0.13 are used as high temperature VT data instead of Suzuki and Kumazawa (1980)'s VT data and fitted with C_P -EoS. Refine all parameters except V_0 .
12. The same dataset as (11) is fitted with full MGD EoS. Refine all parameters except V_0 .

S-2.4.2 Compressional part EoS

I exclusively use the Birch-Murnaghan (BM EoS) for fitting of PV data. All experimental measurements of the PV compression curves of spinels show that K'_{T0} is significantly greater than 4, and therefore a 3rd-order BM EoS is required to fit the data (Table S3-3). This is also supported by direct measurements of the elastic modulus of spinel at room temperature and high pressure, which yielded $K'_{S0}=4.31(17)$, where K'_{S0} is significantly larger than 4 (Speziale et al., 2016) (see Figure S3-9b). There is no evidence in currently-available experimental data that would justify the use of 4th-order EoS.

Table S3- 4 Results of fitting the PV data of Nestola et al (2007) in BM EoS.

	MgAl ₂ O ₄ (Nestola et al., 2007)			MgAl ₂ O ₄ (Nestola et al., 2007)		
	Ordered			Disordered		
	BM2	BM3	BM4	BM2	BM3	BM4
V_0	39.7780(10)	39.7796(12)	39.7796(14)	39.7785(11)	39.7799(13)	39.7795(14)
K_0	197.5(3)	195.4(1.0)	195.4(2.0)	198.4(3)	197(2)	198(3)
K'	4	4.6(3)	4.6(1.5)	4	4.5(3)	3.6(1.6)
K''	-0.02	-0.025	-0.0(5)	-0.02	-0.02	0.2(5)
χ_w^2	0.6	0.23	0.25	1.05	0.83	0.87

$\Delta P_{\max}$	0.02	0.01	0.01	0.03	0.02	0.02
$P_{\text{obs}} - P_{\text{calc}}$	Systematic	Random	Random	Random	Random	Random

S-2.4.3 C_P -EoS fitting

Since VT data above room temperature has a large variability, a C_P -EoS was used to determine which VT data is consistent with other physical property data. The following data were used for C_P -EoS fitting.

- PV data: 26 data from Nestola et al. (2007) and 8 data below 7.2 GPa from Levy et al. (2004).
- VT data: 21 data from Grimes and Al-Ajaj (1992).
- K_S at ambient condition: 4 in Núñez-Valdés et al. (2018) and one in Bruschini et al. (2018).
- $K_S T$ data: 25 data from Suzuki et al. (2000).
- $K_S P$ data: 10 data from Speziale et al. (2016).
- $K_S P T$: 12 data from Duan et al. (2018) and 14 data from Zou et al. (2013).
- $C_P T$ data: Klemmen and Ahrens (2007) and Robie et al. (1995).

Note that I do not use the VT data above room temperature. Using the above datasets, fitting by C_P -EoS and plotting the VT relationship using the obtained EoS, only Suzuki and Kumazawa (1980) and Fiquet et al. (1999)'s VT data obtained by using a Ir heating wire were consistent with C_P -EoS (Figure S3-9). The $K_S T$, $K_S P$, PV , and $C_P T$ relations obtained by C_P -EoS were all consistent with the experimental results (Figure S3-10-12). The fitting by the C_P -EoS up to this point corresponds to (5) of the workflow, and the obtained EoS parameters are listed in Table S3-4.

In the above dataset, I used only low temperature VT data. I then added Suzuki and Kumazawa (1980)'s VT data from room temperature to 800 K and fitted with the C_P -EoS. This corresponds to (7) of the workflow. The resulting EoS parameters agree with all the EoS parameters obtained by workflow (5) within the uncertainty range (Table S3-4). The results of C_P -EoS fitting obtained by step (7) explain all the experimental data well (Figure S3-9-12), and furthermore, the χ_w^2 is reduced from 1.48 in step (5) to 1.28. Therefore, I concluded that, among the VT data of previous studies, the VT data of Suzuki and Kumazawa (1980) were the most consistent with the elasticity and heat capacity data.

The VT data of Suzuki and Kumazawa (1980) show a smaller thermal expansion coefficient than the other datasets. To show that data showing thermal expansion coefficients larger than those of Suzuki and Kumazawa (1980) are not consistent with C_P -EoS, I also performed C_P -EoS fitting using Redfern et al. (1999) and Carbonin et al. (2002) VT data instead of Suzuki and Kumazawa (1980) as VT data. This fitting corresponds to step (11) of the workflow and the EoS parameters are given in Table S3-4. As a result, the uncertainties of all EoS parameters became larger and the χ_w^2 increased significantly from 1.28 to 4.08. Therefore, it is confirmed that the data from the previous studies showing large thermal expansion are not consistent with the $C_P T$ data.

Table S3- 5 EoS parameters derived from the fitting of P – V – T – K – C_P data. Workflow No. corresponds to the number in chapter 4.1.

Workflow No.	(5)	(7)	(8)	(9)	(10)	(11)	(12)	Faccincani21
EoS type	C_P -EoS	C_P -EoS	Full MGD	qcomp MGD	HP2011	C_P -EoS	Full MGD	HP2011
V_0 (cm ³ /mol)	39.78	39.78	39.78	39.78	39.78	39.78	39.78	39.78
K_{0T} (GPa)	196.36(12)	196.34(12)	196.43(11)	194.90(11)	194.95(11)	196.4(3)	196.14(12)	194.8(2)
K'_{0T}	4.39(5)	4.39(5)	4.37(4)	4.90(4)	4.89(5)	4.37(8)	4.42(5)	4.64(7)
K'' (GPa ⁻¹)	-0.023	-0.023	-0.0224	-0.029	-0.029	-0.022	-0.023	-0.0254
α_V ($\times 10^{-5}$ K ⁻¹)	1.6563(10) ^e	1.6640(10) ^e	1.6765(10) ^e	1.6917(9) ^e	1.726(12)	1.7570(19) ^e	1.7916(11) ^e	1.86(2)
θ_{E0} (K)	-	-	-	-	671(10)	-	-	714(15)
θ_{D0} (K)	-	-	897(9)	918(16)	-	-	1040(10)	-
γ_0	1.092(8)	1.097(5)	1.135(10)	1.16(2)	1.15	1.160(10)	1.375(15)	1.17
q	2.17(8)	2.15(8)	1.94(8)	-	0	2.11(14)	1.57(8)	0
K_{0S} (GPa)	197.42(12) ^e	197.41(12) ^e	197.54(12) ^e	196.04(11) ^e	196.11(11) ^e	197.5(2) ^e	197.58(12) ^e	196.0(2) ^e
χ^2	1.48	1.28	1.23	3.33	3.29	4.08	1.33	0.93
$\Delta P_{\max}$ (GPa)	1.01	1.018	0.969	1.839	1.810	1.002	1.107	-
VT data used	<i>a</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>c</i>	<i>c</i>	<i>d</i>

^a Grimes and Al-Ajaj (1992)

^b Grimes and Al-Ajaj (1992) and Suzuki and Kumazawa (1980)

^c Grimes and Al-Ajaj (1992), heating run data of Redfern et al. (1999) with inversion degree of 0.13, and heating run data of Carbonin et al. (2002) with inversion degree of 0.13.

^d Grimes and Al-Ajaj (1992), Carbonin et al. (2002) with inversion degree of 0.13, and Martignago et al. (2003) with inversion degree of 0.114.

S-2.4.4 BM3-MGD EoS fitting

The following data were used for BM3-MGD EoS fitting in workflow step (8).

- PV data: 26 data from Nestola et al. (2007) and 8 data below 7.2 GPa from Levy et al. (2004).
- VT data: 21 data from Grimes and Al-Ajaj (1992) and 21 data from Suzuki and Kumazawa (1980)
- K_S at ambient condition: 4 in Núñez-Valdés et al. (2018) and one in Bruschini et al. (2018).
- $K_S T$ data: 25 data from Suzuki et al. (2000).
- $K_S P$ data: 10 data from Speziale et al. (2016).
- $K_S P T$: 12 data from Duan et al. (2018) and 14 data from Zou et al. (2013).

In Figure S3-9-12 the results of fitting the above datasets with the BM3-full MGD EoS are depicted by the red lines. The results show that the $K_S T$, $K_S P$, PV , and VT experimental data can be

explained by the BM3-full MGD EoS (Figures S3-9-11), but only the $C_P T$ experimental data cannot be explained (Figure S3-12). Here, the plotted line of $C_P T$ is based on the output of the `tvcal` command of `EoSfit7c`.

Since $C_P = (\alpha K_S V) / \gamma$, there are four possible reasons why the C_P obtained from BM-MGD EoS is lower than the experimental value: 1) α is smaller, 2) K_S is smaller, 3) V is smaller, and 4) γ is larger. For α , K_S , and V there will be no problem, since the relations obtained from the BM3-full MGD EoS are almost identical to the relations for $K_S T$, $K_S P$, $P V$, and $V T$ relationships obtained from the C_P -EoS. Therefore, the problem may not be with α , K_S , and V , but with γ . Hence, using the obtained C_P -EoS and Full MGD EoS, the relationship between γ and T was calculated and plotted in Figure S3-13. The results show that the γ obtained from the two EoS are significantly different, as expected from the EoS parameters in Table S3-4. According to equations (56) and (57) of Kroll et al. (2012), the definition of γ is different for MGD and the thermodynamic Gruneisen parameters. Therefore, if the γ_{MGD} obtained from the Full MGD EoS is converted to γ_{th} using equation (59) of Kroll et al. (2012), and then C_P is calculated, a $C_P T$ relationship harmonic with the experimental value may be obtained.

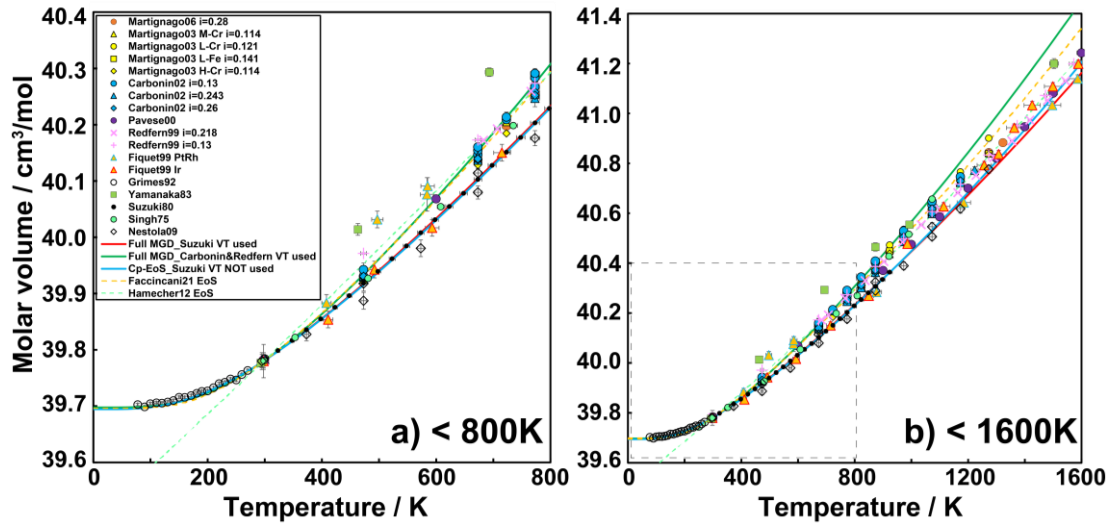
I also tried BM3-full MGD fitting using a dataset which gave a higher thermal expansion coefficient than the $V T$ data of Suzuki and Kumazawa (1980). For this purpose, Redfern et al. (1999) and Carbonin et al. (2002) $V T$ data were added instead of Suzuki and Kumazawa (1980). This fitting corresponds to (12) of the workflow and the EoS parameters are given in Table S3-4. As a result, the χ_w^2 increased from 1.23 to 1.33. The θ_D also increased from 897(9) K to 1040(10) K, which is a large deviation from the value of 866(18) K (Askarpour et al., 1993), 863 K (Suzuki and Kumazawa, 1980), and 883 K (Liu et al., 1975) reported in previous studies. Therefore, it can be inferred that the $V T$ data set of Suzuki and Kumazawa (1980) is more reliable not only in terms of the consistency with C_P -EoS but also in terms of the obtained value of θ_D .

S-2.4.5 BM3-q compromise MGD EoS fitting

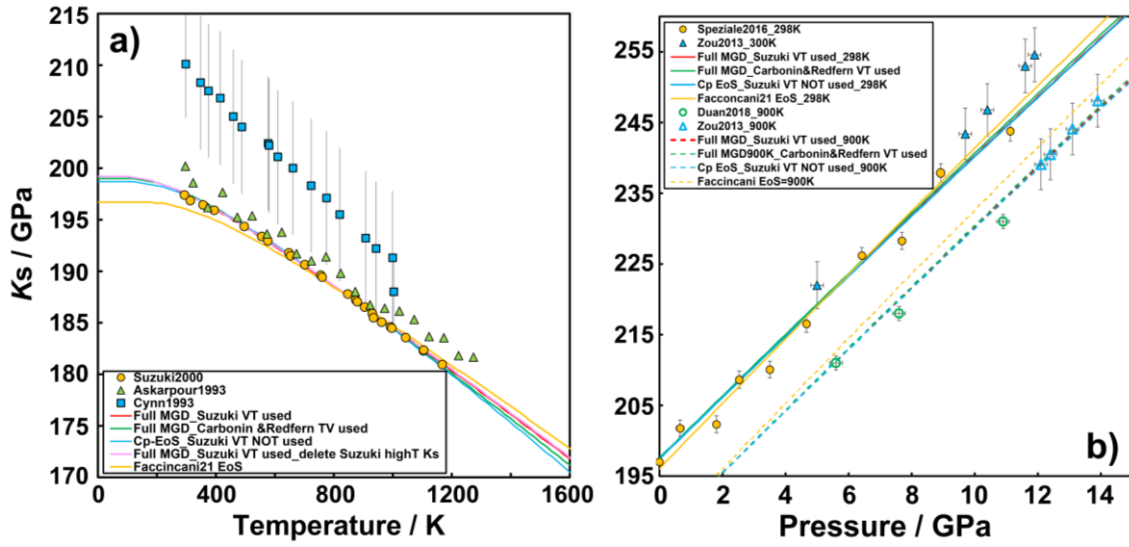
To compare the fitting results with the BM3 MGD EoS, I have also fitted the BM3-q compromise MGD EoS. This fitting corresponds to (9) of the workflow and the EoS parameters are given in Table S3-4. As a result, the fitting with BM3- q compromise MGD EoS is not appropriate because the χ_w^2 increased from 1.23 to 3.33. This confirms that the value of the parameter q for spinel is significantly greater than 1 as found in the refinements of both the C_P -EoS and the MGD EoS (Table S3-4).

S-2.4.6 BM3-HP2011 EoS fitting

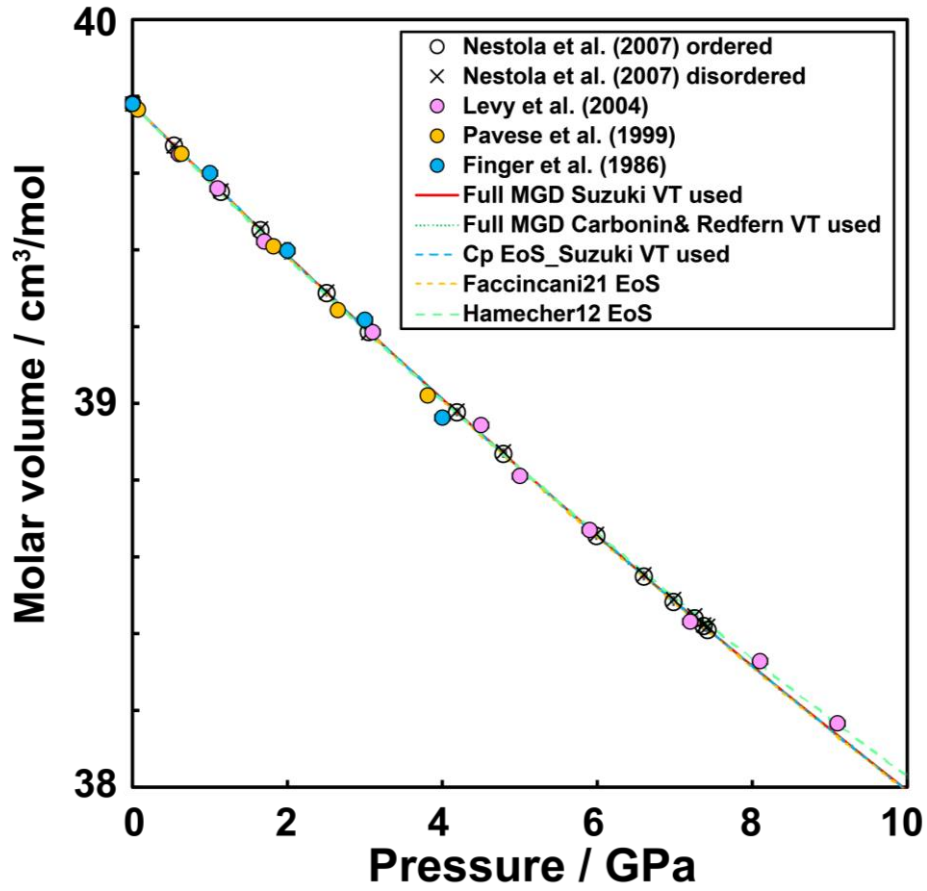
To compare the fitting results with the BM3 MGD EoS, I have also fitted the BM3-HP2011 EoS. This fitting corresponds to (10) of the workflow and the EoS parameters are given in Table S3-4. As a result, the fitting with BM3-HP2011 EoS is not appropriate because the χ_w^2 increased from 1.23 to 3.29.



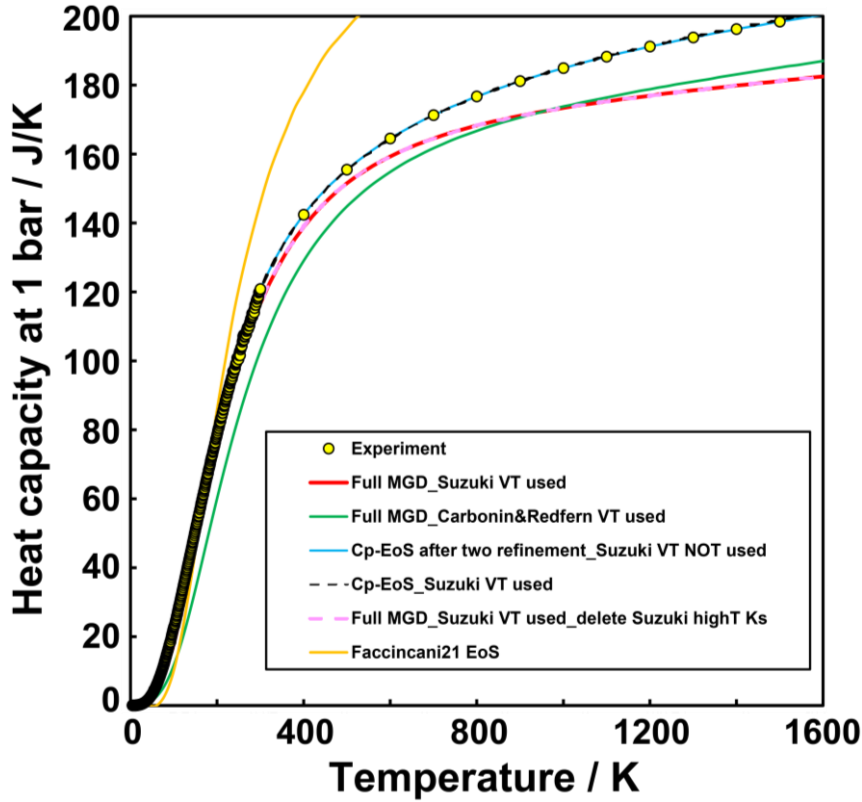
FigureS3- 9 VT data for MgAl_2O_4 below 800 K a) and below 1600K b) from a previous study with the molar volume normalized to $39.78 \text{ cm}^3/\text{mol}$ at ambient temperature and pressure (Carbonin et al., 2002; Fiquet et al., 1999; Grimes and Al-Ajaj, 1992; Martignago et al., 2006, 2003; Fabrizio Nestola et al., 2009; Pavese et al., 2000; Redfern et al., 1999; Singh et al., 1975; Suzuki and Kumazawa, 1980; Yamanaka and Takéuchi, 1983). The red, green, and blue solid lines are VT relations calculated from Full MGD EoS (VT data of Suzuki and Kumazawa (1980) were used), Full MGD EoS (VT data of Carbonin et al. (2002) and Redfern et al. (1999) were used), and C_P -EoS, respectively. The yellow and light green dashed lines are VT relations calculated from EoS presented by Faccincani et al. (2021) and Hamecher et al. (2012).



FigureS3- 10 a) Relationship between K_s and temperature (Askarpour et al., 1993a; Cynn et al., 1993; Suzuki et al., 2000). The red, green, and blue solid lines are K_sT relations calculated from full MGD EoS (VT data of Suzuki and Kumazawa (1980) were used), Full MGD EoS (VT data of Carbonin et al. (2002) and Redfern et al. (1999) were used), and C_p -EoS and Full MGD EoS, respectively. The yellow line is K_sT relations calculated from EoS presented by Faccincani et al. (2021). The pink line is the relationship obtained by full MGD fitting without the K_s data above 800 K from Suzuki et al. (2000) to eliminate the effect of the K_s decrease due to the order-disorder transition that may occur above 800 K. The presence or absence of K_s data above 800 K had no effect on the results. b) Relation between K_s and pressure at 298 K and 900 K (Duan et al., 2018; Speziale et al., 2016; Zou et al., 2013).



FigureS3- 11 PV data from a previous study with the molar volume normalized to $39.78 \text{ cm}^3/\text{mol}$ at ambient temperature and pressure (Finger et al., 1986; Levy et al., 2003; Nestola et al., 2007; Pavese et al., 1999). Since Kruger et al. (1997) did not report the volume at ambient temperature and pressure, and the volume data could not be normalized, it is not plotted in this figure. The blue and red lines are VT relations calculated from Cp -EoS and Full MGD EoS, respectively. The yellow and light green dashed lines are VT relations calculated from EoS presented by Faccincani et al. (2021) and Hamecher et al. (2012).



FigureS3- 12 Isobaric heat capacity C_P of spinel at room pressure. Data points are experimental data (Robie et al.,1995; Klemmen and Ahrens, 2007). Just 2 cycles of EoS refinement and recalculation of $C_V = (1 + \alpha\gamma T)^{-1}C_P$ leads to convergence of EoS parameters and agreement (solid blue line) with the experimental C_P values. However, when Suzuki and Kumazawa (1980) data were added as VT data and full MGD EoS fitting was performed, KsP , KsT , PV , and VT data could be explained, but only C_P data could not be explained (red line). Also, when fitting of full MGD EoS was done using Carbonin et al. (2002) and Redfern et al. (1999) VT data instead of Suzuki and Kumazawa (1980)'s VT data, similarly KsP , KsT , PV , and VT data could be explained, but only C_P data could not be explained (green line). The presence or absence of Ks data above 800 K had no effect on the results (pink line). The reason why the relationship between C_p and T does not agree with the experimental value is that the MGD EoS uses a very simplified pDOS (Kieffer, 1979). The yellow line is calculated from EoS presented by Faccincani et al. (2021). Here, the plotted lines of $C_P T$ are based on the output of the tvcal command of EoSfit7c.

S-2.4.7 Comparison with EoS of previous studies

S-2.4.7.1 Faccincani EoS

Faccincani et al. (2021) used only the disordered MgAl_2O_4 results of Nestola et al. (2007) as PV data and not the ordered MgAl_2O_4 data. However, in the present study, since the EoS parameters of ordered and disordered spinel reported by them are consistent with each other

within the error range, I use both data for constraining the EoS (Table S3-4). Furthermore, the Levy et al. (2004) data below 7.5 GPa are also used to constrain the EoS as they are consistent with the results of Nestola et al. (2007). Faccincani et al. (2021) do not report whether the pressure values reported by Nestola et al. (2007) have been corrected using the new quartz EoS (Scheidl et al., 2016). At least the value of 192(1) GPa for K_{T0} of MgAl_2O_4 reported in the text of Faccincani et al. (2021) is derived from pressure uncorrected PV data, therefore it is possible that the data set used for fitting is also uncorrected for pressure values.

They used data from Grimes and Al-Ajaj (1992), Carbonin et al. (2002) with an inversion degree of 0.13, and Martignago et al. (2003) with an inversion degree of 0.114 as VT data. It is not clear why Faccincani et al. (2021) selected these three VT data sets from among many others. The high-temperature VT data they used show higher thermal expansion coefficients than the Suzuki and Kumazawa (1980) VT data I selected. Therefore, their estimated volume expansion coefficient in the standard state is $1.86(2) (\times 10^{-5} \text{ K}^{-1})$, which is 11% higher in α_{V0} than that of 1.6765(10) obtained in this study.

For the $K_S P$ and $K_S T$ data they use the same dataset as ours for fitting. Although Speziale et al. (2016)'s $K_S P$ data have not yet been published, and it is not clear how Faccincani et al. (2021) have processed the data, when I extract the data plotted in their Supplementally figure by using webplotdigitalizer, I obtain almost identical values to those finally used in this study, with a maximum discrepancy of 0.2 GPa. The error they report for K_S is about 0.5 GPa for ambient pressure data and 1-2 GPa for other data, which is about the same as the value calculated in this study. Next, for the $K_S T$ data, since Suzuki et al. (2000) reported a very small error of about 0.05 GPa, Faccincani et al. (2021) assumed an error of 1% for their K_S , i.e. an error of about ± 2 GPa, in their fitting. On the other hand, I assume that the error is 0.3 GPa, because the maximum difference between the two data points taken by Suzuki et al. (2000) at almost the same temperature is 0.411 GPa. Also, they did not use the $K_S PT$ or $C_P T$ data for fitting.

The EoS parameters obtained by Faccincani et al. (2021) are slightly different from ours due to the differences in the datasets used and the EoS used for fitting as explained above. For example, their EoS gives $K_{0S} = 196.0(2)$ GPa for the adiabatic bulk modulus in the standard state, whereas I obtained a value of 197.54(12) GPa by full MGD fitting. Since the value of $K_{0S} = 196.0(2)$ GPa obtained by Faccincani et al. (2021) is lower than any of the values reported in previous studies (see Figure S3-7), it is likely that their EoS does not reflect the K_S data of previous studies (Figure S3-10a). On the other hand, our result, 197.54(12) GPa, is in agreement with many previous studies (see Figure S3-7). In addition, all of our fits using Cp-EoS and Full MGD EoS yielded $q > 1.5$, so the application of the thermal pressure EoS of Holland and Powell (2011), which assumes $q = 0$, to MgAl_2O_4 is inappropriate.

In summary, I suggest that our constrained EoS more accurately reflects the thermoelastic

properties of MgAl_2O_4 spinel than the EoS reported by Faccincani et al. (2021).

S-2.4.7.2 Hamecher EoS

They use the thermal pressure EoS and apply a very simple model, $\alpha K_T(T - T_0)$, as the expression for thermal pressure. This assumption is valid if αK_T is constant along the isochore, but in the case of MgAl_2O_4 this value is clearly not constant (Askapour et al., 1993). Therefore, the model they used for fitting is physically incorrect and their EoS should not be used.

S-2.4.8 Conclusions

I concluded that the most reliable V/T data are those reported by Suzuki and Kumazawa (1980) because those are consistent with V/T relation obtained from C_P EoS and the value of θ_D obtained with MGD EoS are close to those of previous studies. In this study, several types of EoS were used to fit the dataset, and among them, full MGD EoS was the best fit to the data in terms of having the smallest χ^2 and $\Delta P_{\max}$. Therefore, it is best to use the full MGD EoS as the EoS for MgAl_2O_4 .

As shown by Ma et al. (2021) and Andreozzi et al. (2000), the volume of MgAl_2O_4 depends weakly on the inversion degree. It has been reported that the change of inversion degree starts at 800-900 K. Therefore, in this study, I have fitted the V/T data obtained below 800 K, where the inversion degree is expected to change little during the analysis. Although the volume above 800 K is an extrapolation in our EoS, it is consistent with the results of Suzuki and Kumazawa (1980) at least up to 923 K (Figure S3-9). Therefore, our EoS will be valid below 923 K. Therefore, under the condition that the inversion of the sample is constant, our EoS is valid up to at least 923 K. Even if the inversion of the sample is constant, it is not clear whether the EoS is effective at higher temperatures. If a change in the inversion degree occurs, it is necessary to correct for the effect of the inversion degree on the volume. On the other hand, in the range $i = 0.125$ - 0.25 , i does not affect the K or the thermal expansion coefficient, so no correction is needed for those parameters.

A decrease in the inversion degree from 0.25 (equivalent to the inversion degree at equilibrium at 1173 K) to 0.18 (equilibrium inversion degree at around 800 K, where changes in inversion degree are less likely to occur) implies an expansion of the unit cell parameter by 0.0049% (Andreozzi et al., 2000) and 0.0107% (Ma et al., 2021). This expansion corresponds to a pressure change of 0.044 GPa and 0.096 GPa, respectively, based on the V/P data of Nestola et al (2007). For natural samples, the inversion degree in deep underground can be estimated from the model of Ma et al. (2021) if the equilibrium temperature is known, and the inversion degree at laboratory condition can be estimated by XRD and roughly by Raman spectroscopy. Combining the difference in inversion degree obtained in this way with the relationship between inversion degree and volume obtained by Andreozzi et al. (2000) and Ma et al. (2021), and the compressional EoS obtained here, I can estimate the change in the internal pressure of the inclusion due to the change in inversion degree. Even for samples where

changes in inversion degree have occurred, the above calculations will give an accurate estimate of the residual pressure of the inclusions.

General conclusions and perspectives

It has been about 40 years since Raman spectroscopy has been used for inclusion studies. In recent years, Raman spectroscopy has been actively applied to natural samples to quantify the chemical composition, density, strain, etc. of inclusions, and it has become increasingly important to ensure the accuracy and precision of the analytical method to enable inter-laboratory comparison of data. However, to the best of my knowledge, there has been no comprehensive study of the effect of laser heating during Raman spectroscopy on the measurement results in the long history of the technique. Therefore, the temperature increase per unit of laser power for inclusions in quartz, olivine, orthopyroxene, clinopyroxene, and Cr-spinel reported in this study may be used by inclusion researchers to guide the selection of the analysis environment and to correct the measurement data. However, the data obtained in this study represent only a few of the important host minerals for inclusion studies, and it will be necessary to determine the laser heating coefficients for many more host minerals in the future. The laser heating coefficients for olivine, orthopyroxene, and clinopyroxene obtained in this study were accompanied by relatively large errors. The errors in the laser heating coefficients can generally be reduced by extending the laser power range and the analysis time. Accurate determination of the laser heating coefficients will lead to the elucidation of the composition and wavelength dependence of the heating coefficients, and will allow more accurate estimation of the inclusion temperature during analysis.

In Chapter 1, the existence of laser heating was clarified. However, the extent to which such unintentional heating affects the measurement results in actual analysis is largely unknown. This is because the influence of laser heating on the results obtained by Raman spectroscopy depends on the temperature dependence of the calibration curve, which relates Raman spectral properties to physical properties, however, little research has been performed on the temperature dependence of the calibration curve. Therefore, in Chapter 2, I focused on the Raman CO₂ densitometer, which is relatively well studied, and investigated the temperature dependence of the calibration curve using a high-temperature and high-pressure cell. As a result, it was found that the fluid density was always underestimated when the inclusion was heated by laser during the analysis. To verify whether the predicted underestimation is also observed in natural samples, an experiment using natural fluid inclusions was conducted. The results showed that even a laser power of 15 mW, which is typical for inclusion analysis, can underestimate the density of inclusions by about 15%. Therefore, at least in the

Raman CO₂ densimeter, laser heating can affect the measured density. Combining the results of the present study with those of the previous study, the temperature dependence of the Raman CO₂ densimeter was found to cover most of the density range that can be encountered in natural fluid inclusions from 0.001–1.2 g/cm³. In the future, the temperature dependence of the calibrations should be investigated for other calibrations that relate Raman spectral properties to physical properties as well.

In Chapter 3, I showed that the density of fluid inclusions in mantle xenoliths is mineral species- and size-dependent. In particular, the tendency of fluid inclusions to become less dense with decreasing inclusion diameter observed in orthopyroxene, clinopyroxene, and Cr-spinel was a possible new finding that has not been reported before. However, these dependencies may have been artificially induced by the temperature dependence of the Raman CO₂ densimeter and the laser heating during the analysis, as revealed in Chapters 1 and 2. In this chapter, based on the results of Chapters 1 and 2, I clarified that the observed mineral species and size dependence were not caused by laser heating. Now that I have eliminated laser heating as a factor causing the dependence, I can investigate other factors with more confidence. Other factors that may cause the dependence include thermoelastic deformation, plastic deformation, diffusion, and phase separation. In the future, I will investigate these factors one by one to determine the causes of the mineral species and size dependence of the density of inclusions in mantle xenoliths, and to develop an accurate geobarometer using the density of fluid inclusions.

Acknowledgements

I would like to first thank the members of my dissertation committee - not only for their time and extreme patience, but for their intellectual contributions to my development as a scientist. To Dr. Hisayoshi Yurimoto, I thank for his consistent support and recommendations on this dissertation as Chair of my dissertation committee. I would also like to express my deep appreciation to Dr. Takaya Nagai, Dr. Junji Yamamoto, and Dr. Kenichi Bajo, the vice chair of my thesis committee, for sharing his experience with me. I would also like to thank Dr. Yasuhiro Iba for setting up the venue and schedule for my presentation in spite of the difficult circumstances caused by the outbreak of COVID-19.

Next, I also wish to express my gratitude to my collaborators for their advice and support during the course of my research because this thesis is the result of many experiences I have encountered from several remarkable individuals during my six years as a researcher.

I would like to express my sincere gratitude to my advisor Dr. Junji Yamamoto for the continuous support of my Ph.D study and research, for his patience, motivation, enthusiasm, and immense knowledge. His guidance helped me in all the time of research and writing of this thesis. I am also grateful for the exclusive use of the Raman spectrometer for several months, without which I would not have been able to accomplish this research project.

I had the precious opportunity to stay at the Mineral Physics laboratory of the University of Pavia for 90 days from September 21, 2021 to December 18, 2021, through the Young Scientists Overseas Challenge Program. I would like to express my gratitude to Dr. Matteo Alvaro, my host professor, for all the help he has given me during the period from my first contact with him in January 2020, just before COVID-19, to the moment of my departure, in terms of research plans and travel procedures. He taught me not only about his research, but also about Italian customs and the diversity of its food culture. I am very grateful to him for accepting me with open arms and for being so friendly, even though I could only speak poor English.

I am also very grateful to Ross John Angel who, together with Dr. Alvaro, introduced me to the fun of Mineral Physics during my stay in Italy. In his classes and in discussions with him, he taught me very carefully, using clear and memorable examples and tools. I am very surprised myself that I, as an almost beginner in mineral physics, could get to the level of knowledge to write a paper on equations of state in just three months of my stay, and the work I did here in Italy would not have been possible without his support. In particular, I was happy to have the opportunity to learn how to use Eosfi7c and its family of software directly from its developer, Dr. Angel.

I would like to express my gratitude to Dr. Kenta Yoshida. He has supported my research through numerous discussions, sometimes as one of the few colleagues on fluid inclusions research in Japan, sometimes as a reviewer, and sometimes as a collaborator. He also provided financial support through the Joint Usage/Research Program of ERI, including travel and open access fees. In addition, he also helped me with Raman spectroscopy at JAMSTEC and allowed me to use a newly purchased laser power meter to accurately measure the laser power, which enhanced the reliability of my research.

I would like to thank Dr. Akira Yoneda for his guidance on finite element methods (FEM) at Institute for Planetary Materials, Okayama University on December 17–20, 2018 and August 5–9, 2019. This method made it possible for me to carefully investigate the effects of parameters on laser heating that are difficult to investigate experimentally, which greatly improved the quality of this study. In addition, FEM can be used not only for the simulation of heat conduction, which was used in this research, but also for the simulation of various physicochemical phenomena such as diffusion, deformation, and fracture, which will lead to the expansion of my possibilities as a researcher.

I appreciate Mr. Junji Torimoto for assisting me with the Raman spectroscopic analysis at JAMSTEC, and for providing me with quartz containing pure CO₂ fluid inclusions. Since most fluid inclusionists focus on inclusions in quartz, the results of the temperature increase per unit laser power of inclusions in the quartz have increased the impact of this work on the international community on fluid inclusions.

I gratefully acknowledge the work and support of past and present members of our laboratory. My appreciation also goes out to my family for their encouragement and support all through my studies.

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Figures of Supporting Information (Chapter 1)

FigureS1-1 Raman spectra of CO₂ fluids containing the two main bands of the Fermi diad of ¹²CO₂ ($\nu\text{F.D.}-$ and $\nu\text{F.D.}+$) and the hot bands ($\nu\text{H.B.}-$ and $\nu\text{H.B.}+$). The peak at 1369.4 cm^{-1} is attributed to the ¹³C¹⁶O₂ isotopic species (¹³ $\nu\text{F.D.}+$). Temperature effects on Raman spectra of CO₂ at constant pressure, 21.8 MPa. Intensity of both $\nu\text{H.B.}-$ and $\nu\text{H.B.}+$ increase monotonically with temperature. 50

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