



Raman quantitative measurement for carbon isotopic composition of CO₂: Theory and method

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ABSTRACT

Raman spectroscopy is an efficient non-contact and non-destructive method. It is a potential approach to quantitatively measure the carbon isotopic composition (¹³CO₂/¹²CO₂) of CO₂ in single fluid inclusion. Based on the theoretical analysis, Raman spectroscopy can reasonably be applied to measure the carbon isotopic composition of CO₂. It can theoretically be expressed as, $^{13}\text{CO}_2/^{12}\text{CO}_2 = (I_{13\text{CO}_2}/I_{12\text{CO}_2}) \cdot (\sigma_{12\text{CO}_2}/\sigma_{13\text{CO}_2})$, in which the ratio of cross section ($\sigma_{12\text{CO}_2}/\sigma_{13\text{CO}_2}$) is determined from Raman spectra of standard CO₂ sample. Therefore, Raman measurement process can be described as, from standard to analytical samples. In natural CO₂ sample, the ¹³CO₂ concentration is very low. Compared to ¹²CO₂, Raman intensity of ¹³CO₂ is much weaker. This greatly affects the accuracy and precision of Raman measurement on the ¹³CO₂/¹²CO₂. In this work, a method is provided in order to improve the accuracy and precision of measured ¹³CO₂/¹²CO₂.

1. Introduction

CO₂ has been identified as one of the most important compounds that exist in many geological environments (Lüders et al., 2012; Mironov et al., 2015; Tsunogae et al., 2008). In geological process, CO₂ can be trapped in fluid inclusions, which can be utilized to investigate the evolution of geological fluid. Because the carbon isotopic composition of CO₂ may provide important geological information on the origin and global circulation of CO₂ in the Earth's lithosphere, it has been attracting many attentions.

In general, the bulk minerals are cracked by mechanical crushing method or heating to a higher temperature to obtain carbon dioxide trapped in fluid inclusions. Then, the CO₂ may be measured by mass spectroscopy (MS) to obtain the carbon isotopic compositions of CO₂ in fluid inclusions (Deines, 2002). Compared with the bulk analysis of fluid inclusions, many attentions have been paid on single fluid inclusion because it can provide the details of geological fluid occurred in different time and space. In principle, Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) is available for extracting CO₂ from a fluid inclusion. However, it is impossible to measure the carbon isotopic composition of a fluid inclusion because of the detection limit of MS, which requires about 10⁻⁹ mol of CO₂ (Boutton, 1991). For a typical CO₂ fluid inclusion with 1 g/cm³ and 5 μm

in diameter, it corresponds to 10⁻¹¹ mol. Additionally, due to the destructive property of MS, this makes repeatable experimental measurement impossible to obtain further information. Therefore, it is necessary to develop a non-destructive method to measure the carbon isotopic composition of CO₂ in a fluid inclusion.

Raman spectroscopy is an efficient non-contact and non-destructive technique. This provides a potential approach to quantitatively measure the geochemical composition of a fluid inclusion. However, Raman scattering is more commonly associated with qualitative study, in which Raman shift ($\Delta\nu$) is utilized to differentiate the molecular species. In fact, this is mainly due to the fact that Raman spectra are obviously affected by the measurement conditions, such as scanning time, and accumulation times. Recently, some Raman quantitative measurements (Arakawa et al., 2008; Kawakami et al., 2003; Lamadrid et al., 2017; Sun et al., 2010; Sun and Qin, 2011; Takahata et al., 2014; Wang et al., 2011) have been conducted to measure the geochemical composition of a fluid inclusion, such as the salinity (Cl⁻ concentrations), CO₂ density.

Due to atom mass difference between ¹³C and ¹²C, Raman spectroscopy can be utilized to differentiate the ¹³CO₂ from ¹²CO₂ in CO₂ fluid inclusions. Therefore, Raman spectroscopy may be developed to quantitatively measure the carbon isotopic composition (¹³CO₂/¹²CO₂) of CO₂. So far, a few works (Arakawa et al., 2007; Li et al., 2016, 2018; Menneken and Geisler, 2009; Yokokura et al., 2020) have been carried

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out to measure the $^{13}\text{C}/^{12}\text{C}$ of CO_2 by Raman spectroscopy. In Arakawa et al. work (Arakawa et al., 2007), the micro-Raman spectroscopy is applied to determine carbon isotopic compositions of minute CO_2 fluid inclusions in minerals. They suggested that there was potential to use Raman spectroscopy to determine the carbon isotopic compositions of CO_2 inclusions. From Li et al. works (Li et al., 2016, 2018), a series of $^{12}\text{CO}_2/\text{N}_2$ and $^{13}\text{CO}_2/\text{N}_2$ binary mixtures with various molar fraction ratios were synthesized, and utilized to measure the carbon isotopic composition of CO_2 . Based on recent Yokokura et al. work (Yokokura et al., 2020), they examined the precisions of carbon isotopic ratios ($\delta^{13}\text{C}$) of CO_2 at constant room temperature and pressure of 10–150 MPa. In fact, due to the poor measurement accuracy and precision, this greatly restricts the Raman spectral applicability in measuring the $^{13}\text{CO}_2/^{12}\text{CO}_2$ of CO_2 . Therefore, it is very important to improve the accuracy and precision of Raman measurement on $^{13}\text{CO}_2/^{12}\text{CO}_2$.

In this study, Raman spectroscopy is applied to quantitatively measure the $^{13}\text{CO}_2/^{12}\text{CO}_2$ of CO_2 . Based on theoretical analysis, Raman quantitative measurement can be expressed as, $^{13}\text{CO}_2/^{12}\text{CO}_2 = (I_{13\text{CO}_2}/I_{12\text{CO}_2}) \cdot (\sigma_{12\text{CO}_2}/\sigma_{13\text{CO}_2})$, in which the ratio of cross section, $\sigma_{12\text{CO}_2}/\sigma_{13\text{CO}_2}$, can be determined through Raman spectra of standard CO_2 sample. Therefore, Raman measurement process can be described as, from standard to analytical samples. In natural CO_2 sample, the $^{13}\text{CO}_2$ concentration is very low. Compared to $^{12}\text{CO}_2$, the Raman intensity of $^{13}\text{CO}_2$ is obviously weak. Regarding to the accuracy and precision of Raman measurement, it is related to obtain the correct intensity of $^{13}\text{CO}_2$. In this work, a method is provided in order to improve the accuracy and precision of measured $^{13}\text{CO}_2/^{12}\text{CO}_2$.

2. Experiments

2.1. Samples

To measure the carbon isotopic compositions ($^{13}\text{CO}_2/^{12}\text{CO}_2$) of analytical samples, it is necessary to calculate the ratio of cross section ($\sigma_{12\text{CO}_2}/\sigma_{13\text{CO}_2}$). This can be determined by the measured Raman spectra of standard CO_2 sample, its $\delta^{13}\text{C}$ has been determined through MS measurement. In this work, standard sample is the pure CO_2 fluid inclusion, which is formed through fused silica capillary as described in anywhere (Chou et al., 2008; Lu et al., 2007) (Fig. 1). From the MS measurement, the carbon isotopic composition of CO_2 is -26.49% .

After the ratio of cross section ($\sigma_{12\text{CO}_2}/\sigma_{13\text{CO}_2}$) is determined from standard CO_2 sample, it can be utilized to quantitatively measure the carbon isotopic compositions of CO_2 of analytical samples. In this study, to evaluate the accuracy and precision of Raman measurement on $^{13}\text{CO}_2/^{12}\text{CO}_2$, the carbon isotopic compositions of CO_2 in analytical samples have also been measured by traditional MS method.

2.2. Raman spectroscopy

In this work, the unpolarized Raman spectra were recorded using a confocal micro-Raman system in a backscattering geometry (Renishaw inVia Reflex). A diode pumped solid state laser with an excitation wavelength at 532 nm was operated at 50 mW. The spectrometer with an entrance slit of 50 μm was used to collect the signals. The grating was 2400/mm, and the resolution was about 0.5 cm^{-1} . The spectra were collected in the range of 780.59 cm^{-1} to 1915.18 cm^{-1} . Each Raman spectrum was recorded in a 50 \times objective. To investigate the effects of measurement conditions on Raman intensity, the Raman spectra were recorded in different scanning time, and various accumulation times.

In this work, Raman spectra of liquid CO_2 are recorded, and utilized to determine the carbon isotopic composition ($^{13}\text{CO}_2/^{12}\text{CO}_2$) of CO_2 . To obtain the Raman intensity of measured CO_2 , Raman spectra were necessarily analyzed. In this study, the Raman spectra were analyzed by the Jandel Scientific Peakfit v4.04 program. Spectral smoothing may affect the measured Raman intensity, especially for weak peaks of $^{13}\text{CO}_2$. Therefore, no spectral smoothing was conducted on the

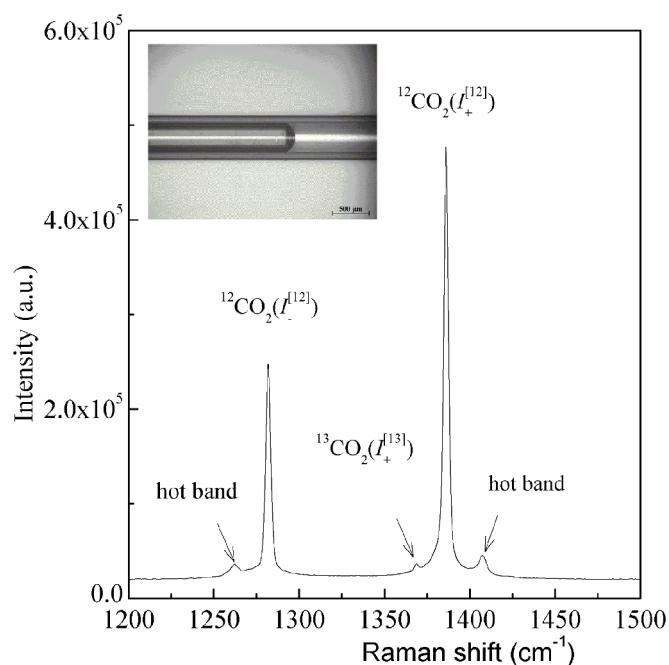


Fig. 1. Raman spectrum of liquid CO_2 at ambient conditions. Fermi diad of $^{12}\text{CO}_2$, denoted as $I_{-}^{[12]}$ and $I_{+}^{[12]}$, is situated at 1282 cm^{-1} and 1386 cm^{-1} . The two weak peaks at 1262 cm^{-1} and 1408 cm^{-1} are hot bands of $^{12}\text{CO}_2$. Regarding to Fermi diad of $^{13}\text{CO}_2$, one is located at 1369 cm^{-1} ($I_{+}^{[13]}$), the other at 1262 cm^{-1} is overlapped by the hot band of $^{12}\text{CO}_2$. In natural CO_2 sample, the concentration of $^{13}\text{CO}_2$ is greatly less than $^{12}\text{CO}_2$, Raman intensity of $^{13}\text{CO}_2$ at 1369 cm^{-1} is much weaker than $^{12}\text{CO}_2$ at 1386 cm^{-1} . Additionally, the Raman spectrum of $^{13}\text{CO}_2$ is located at the shoulder of $^{12}\text{CO}_2$ at 1386 cm^{-1} . The inlet shows the standard CO_2 sample.

measured Raman spectra of CO_2 . Regarding to Raman spectra of $^{12}\text{CO}_2$, the baselines were corrected by linear lines. Raman spectra of Fermi diad of CO_2 were fitted by Gaussian-Lorentzian functions to determine the spectral intensities of $^{12}\text{CO}_2$.

In comparison with $^{12}\text{CO}_2$, the $^{13}\text{CO}_2$ concentrations in natural CO_2 samples were very low. Therefore, Raman intensity of $^{13}\text{CO}_2$ was obviously weaker than that of $^{12}\text{CO}_2$. Regarding to the accuracy and precision of Raman measurement, it was seriously dependent on the spectral analysis of $^{13}\text{CO}_2$. This was related to not only Raman spectral measurement, but also the baseline subtraction of $^{13}\text{CO}_2$. These were discussed in the following discussion.

2.3. Mass spectroscopy

The carbon isotopic ($^{13}\text{CO}_2/^{12}\text{CO}_2$) measurements were conducted at the MRL Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resource, Chinese Academy of Geological Sciences. The CO_2 in the fluid inclusions was collected using thermal decrepitation method, the carbon isotopes (^{13}C) were measured on a MAT-253 mass spectrometer. The uncertainties of isotope measurements were 0.2‰. The variations of carbon isotopic compositions ($^{13}\text{C}/^{12}\text{C}$) were presented as the deviation from a standard by delta values, δ , in per mil (‰, or parts per thousand) units, $\delta^{13}\text{C} (\text{‰}) = ([^{13}\text{C}/^{12}\text{C}]_{\text{sample}}/[^{13}\text{C}/^{12}\text{C}]_{\text{PDB}} - 1) \times 1000$, $[^{13}\text{C}/^{12}\text{C}]_{\text{PDB}} = 0.0112372$. According to the international convention, $\delta^{13}\text{C}$ results were expressed relative to a calcium carbonate standard known as Pee Dee Belemnite (PDB).

3. Results

The vibrational spectra of CO_2 have been studied in great detail. Owing to the high symmetry of the molecule ($D_{\infty h}$), the infrared and Raman spectra are mutually exclusive and involve separate transitions

between vibrational states. For a linear CO₂, there are 4 fundamental modes of vibration. The normal modes can be described as follows: ν_1 (Σ_g^+), the symmetrical stretch at 1339.5 cm⁻¹, ν_2 (Σ_u^-), the doubly degenerate deformation mode at 667.3 cm⁻¹, and ν_3 (Σ_u^+), the anti-symmetric stretch at 2349.1 cm⁻¹. The modes ν_2 and ν_3 are infrared active, while ν_1 is Raman active. However, due to the Fermi resonance between $2\nu_2$ and ν_1 , this gives rise to a pair of bands of nearly equal intensity, usually denoted as ν^- and ν^+ .

At ambient conditions, Fermi diad of ¹²CO₂ is situated at 1282 cm⁻¹ (ν^-) and 1386 cm⁻¹ (ν^+), respectively (Fig. 1). With increasing pressure, both of them slightly move to lower wavenumber (Wang et al., 2011). In fact, the Raman spectrum of CO₂ is more complicated as it also exhibits the presence of several very weak satellite bands (Fig. 1), whose assignment is well known and has been extensively studied by Montero (Montero, 1983).

In theory, the frequency of harmonic vibration is closely related to reduced mass, which can be expressed as follows,

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (1)$$

where ν is molecular vibration frequency, k is bond force constant, and μ is reduced mass. Therefore, as reduced mass increases, this leads to vibrational frequency to move to lower wavenumber.

Based on the Raman spectrum of liquid CO₂, it can be found that, due to the difference of atom mass between ¹³C and ¹²C, the ¹³CO₂ is located at 1369 cm⁻¹ (ν^+) (Fig. 1). In fact, Raman spectrum of ¹³CO₂ may also be affected by Fermi resonance. However, the Raman intensity of symmetric peak at 1262 cm⁻¹ (ν^-) is weak, and easily overlapped by a hot band at the same position. Therefore, the 1369 cm⁻¹ peak is usually applied to differentiate ¹³CO₂ from ¹²CO₂. Additionally, it should be noted that the ¹³CO₂ peak is situated at the shoulder of the strong peak of ¹²CO₂ at 1386 cm⁻¹. This leads to the baseline of ¹³CO₂ peak to be inclined upward (Fig. 1). This makes the baseline subtraction of ¹³CO₂ peak to be very important in order to obtain the Raman intensity.

In this study, the Raman spectra of CO₂ are respectively recorded with different scanning time, accumulation times. With increasing scanning time (or accumulation times), these lead to the increase of measured Raman intensity (Fig. 2). However, due to the limit of CCD detector of Raman spectrometer, the ¹²CO₂ at 1386 cm⁻¹ becomes oversaturated as scanning time is 14 s (Fig. 3). In addition, with increasing Raman intensity, other hot bands can also be found. Therefore, the Raman spectral intensity is closely related to the measurement conditions.

Due to the difference of atom mass between ¹³C and ¹²C, Raman spectroscopy can be utilized to differentiate the ¹³CO₂ from ¹²CO₂. This means that Raman spectroscopy may be a potential approach to measure the carbon isotopic composition (¹³CO₂/¹²CO₂) of CO₂. However, it should be noted that the Raman spectra are obviously affected by the measurement conditions, such as scanning time, accumulation times. Before Raman spectroscopy can be applied to determine the ¹³CO₂/¹²CO₂ of CO₂, it is necessary to eliminate the effects of measurement conditions on Raman intensities.

4. Discussions

4.1. Theoretical analysis

In theory, Raman intensity of molecular vibration can be expressed as follows,

$$I = KN\sigma I_L \quad (2)$$

where I means the measured Raman intensity, k is proportionality coefficient, σ is cross section, N is the Raman active molecular number, and I_L is the intensity of excitation radiation, respectively. It seems that the

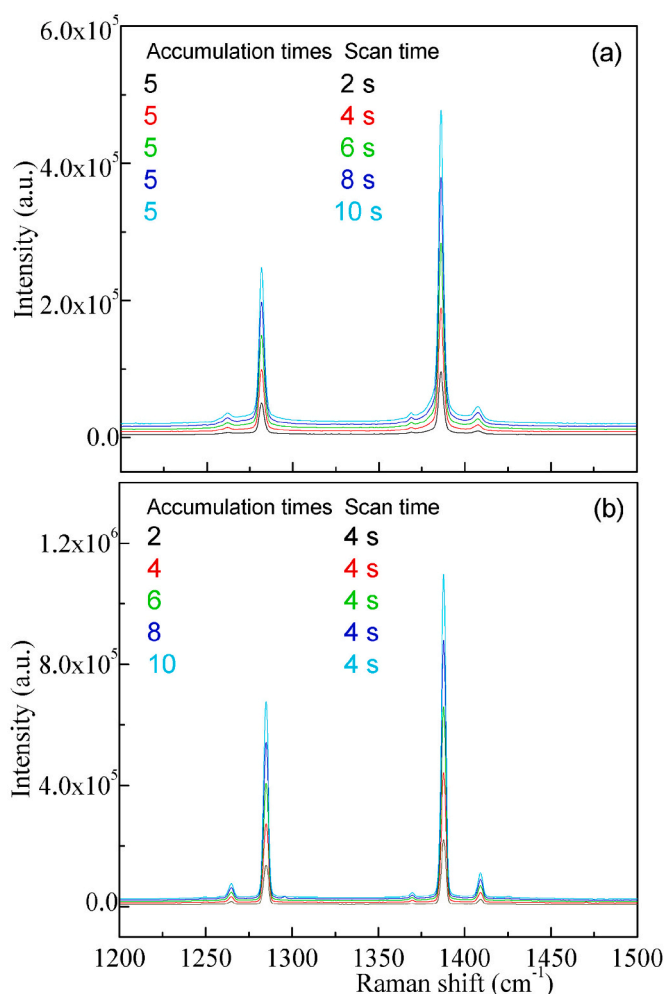


Fig. 2. Raman spectra of liquid CO₂ in standard sample under various measurement conditions. (a) With increasing scanning time, this increases the Raman intensities of ¹³CO₂ and ¹²CO₂. (b) Due to the increase of accumulation times, this also enhances the Raman intensities.

Raman intensity can directly be utilized to quantitatively determine the measured molecular number. However, the measured Raman intensity is related to not only the molecular number, but also the intensity of the incident light. The latter is closely related to Raman spectral measurement conditions, such as the power of the excitation source, the instrumental optical configuration, scanning time, accumulation times, and sample alignment. Therefore, Raman intensity may not be directly applied to quantitatively measure the molecular number.

Before Raman intensity can be used to quantitatively determine the molecular number, it is necessary to eliminate the influence arising from the measurement conditions. According to Eq. (2), it can be found that the intensity ratio (relative intensity) is an effective approach to meet the requirement. Based on the intensity ratio, it can be expressed as,

$$\frac{I}{I_R} = \frac{N}{N_R} \frac{\sigma}{\sigma_R} \quad (3)$$

where R is the reference system, its Raman spectrum should be measured under the same measurement conditions as the sample.

Raman quantitative measurements are reasonably based on the intensity ratio (relative intensity), which can be classified into external and internal standards (Aarnoutse and Westerhuis, 2005; Nah et al., 2007; Park et al., 2007; Sun and Qin, 2011). For external standard, it is necessary to respectively measure the Raman spectra of the corresponding standard and sample, the spectral collection of them is

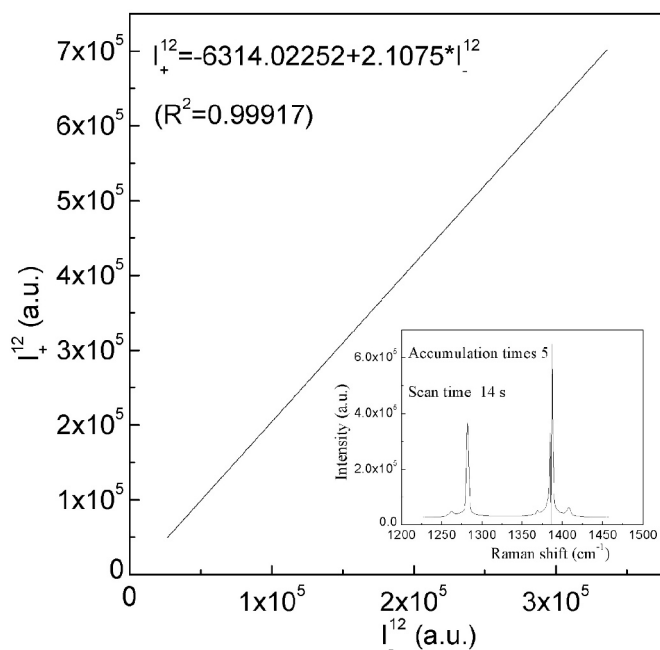


Fig. 3. Calculation of Raman intensity of $^{12}\text{CO}_2$ at 1386 cm^{-1} as being oversaturated. The Raman spectrum of $^{12}\text{CO}_2$ at 1282 cm^{-1} is used as the reference. Before the $^{12}\text{CO}_2$ at 1386 cm^{-1} peak is saturated, the Raman intensity ratio between them can be determined. It can be utilized to determine the corresponding intensity of oversaturated $^{12}\text{CO}_2$ at 1386 cm^{-1} . Inset shows that the Raman spectrum of $^{12}\text{CO}_2$ at 1386 cm^{-1} is oversaturated as scanning time reaches 14 s.

asynchronous. Of course, it is difficult to decide whether or not the sample is measured under the same conditions as the standard. An internal standard is a material that is added (or incorporated) into the sample. The measured Raman spectra include both internal standard and analytical sample, the non-overlapping band of internal standard can be utilized as the reference. Because the Raman spectral collection is synchronous for both internal standard and sample, this analytical method may be more appropriate for intensity correction of measured Raman spectra.

Due to the difference of atom mass between ^{13}C and ^{12}C , various vibrational peaks can be expected for $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$. To eliminate the influence of measurement conditions on Raman intensity, Raman quantitative measurement can be based on the intensity ratio between them. Therefore, Raman quantitative measurement of carbon isotopic composition of CO_2 can be expressed as,

$$\frac{N_{^{13}\text{CO}_2}}{N_{^{12}\text{CO}_2}} = \frac{I_{^{13}\text{CO}_2} \sigma_{^{12}\text{CO}_2}}{I_{^{12}\text{CO}_2} \sigma_{^{13}\text{CO}_2}} \quad (4)$$

where $I_{^{12}\text{CO}_2}$ and $\sigma_{^{12}\text{CO}_2}$ are the intensity and cross section of $^{12}\text{CO}_2$ at 1386 cm^{-1} , and $I_{^{13}\text{CO}_2}$ and $\sigma_{^{13}\text{CO}_2}$ are the intensity and cross section of $^{13}\text{CO}_2$ at 1369 cm^{-1} , respectively. Additionally, the Raman spectral collection of them should be synchronous.

According to Eq. (4), before the Raman intensities of $^{13}\text{CO}_2$ at 1369 cm^{-1} and $^{12}\text{CO}_2$ at 1386 cm^{-1} can be utilized to calculate the $^{13}\text{CO}_2/^{12}\text{CO}_2$, it is necessary to obtain the ratio of cross section between them, $\sigma_{^{12}\text{CO}_2}/\sigma_{^{13}\text{CO}_2}$. In fact, this can be determined through the measured Raman spectra of standard CO_2 sample, in which carbon isotopic composition ($\delta^{13}\text{C}$) of CO_2 has been determined by MS measurement.

In combination with the ratio of cross section ($\sigma_{^{12}\text{CO}_2}/\sigma_{^{13}\text{CO}_2}$) determined from standard CO_2 sample, Raman spectroscopy can reasonably be utilized to quantitatively measure the carbon isotopic composition of CO_2 . Regarding to the Raman measurement procedure of

carbon isotopic composition of CO_2 , it can be described from standard to analytical samples. In this work, the standard CO_2 sample is synthetic fluid inclusion, which is composed of pure CO_2 (Fig. 1). Based on the MS measurement, the $\delta^{13}\text{C}$ of CO_2 is -26.49‰ .

4.2. Measurement accuracy and precision

From Eq. (4), Raman spectroscopy is a potential approach to measure the $^{13}\text{CO}_2/^{12}\text{CO}_2$ of a fluid inclusion. So far, to determine the carbon isotopic composition of CO_2 , this is still carried out through destructive MS measurements on bulk fluid inclusions. This is mainly due to the poor accuracy and precision of Raman quantitative measurement on $^{13}\text{CO}_2/^{12}\text{CO}_2$, especially as compared with MS measurement. In Arakawa et al. work (Arakawa et al., 2007), Raman mass-spectrometric technique has an uncertainty above 20%. This greatly restricts widely application, and only meets the demand that discriminates whether the reservoir of CO_2 is organic or inorganic. Therefore, it is necessary to investigate the accuracy and precision of Raman measurement on $^{13}\text{CO}_2/^{12}\text{CO}_2$.

Before the measured Raman spectra of CO_2 are utilized to determine the $^{13}\text{CO}_2/^{12}\text{CO}_2$, the baselines of them should be corrected so that the Raman intensities of both $^{13}\text{CO}_2$ at 1369 cm^{-1} and $^{12}\text{CO}_2$ at 1386 cm^{-1} can be determined. Therefore, the spectral analysis is necessary for both standard and analytical CO_2 samples. This is related to the ratio of cross section ($\sigma_{^{12}\text{CO}_2}/\sigma_{^{13}\text{CO}_2}$) determined from standard CO_2 sample, and the calculated $^{13}\text{CO}_2/^{12}\text{CO}_2$ of analytical sample. In fact, as the baselines are corrected, this undoubtedly brings the uncertainties on the Raman intensities of CO_2 . Therefore, Eq. (4) can reasonably be revised as,

$$\frac{N_{^{13}\text{CO}_2}}{N_{^{12}\text{CO}_2}} = \frac{I_{^{13}\text{CO}_2}}{I_{^{12}\text{CO}_2}} F \quad (5)$$

where F is the quantitative factor, which is closely related to the ratio of cross section of CO_2 . In theory, the ratio of cross section ($\sigma_{^{12}\text{CO}_2}/\sigma_{^{13}\text{CO}_2}$) is constant. However, due to the spectral analysis of CO_2 , such as the baseline subtraction of CO_2 , this may bring the uncertainty on the ratio of cross section. In other words, this indicates that F may be affected by the spectral analysis of CO_2 .

In fact, the calculated $\delta^{13}\text{C}$ is closely related to the Raman intensity ratio between $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$ ($I_{^{13}\text{CO}_2}/I_{^{12}\text{CO}_2}$ or $I_{+^{13}}/I_{+^{12}}$). It can be found that the uncertainty of measured $I_{^{13}\text{CO}_2}/I_{^{12}\text{CO}_2}$ ($I_{+^{13}}/I_{+^{12}}$) must be less than ± 0.00005 so that the corresponding uncertainty of calculated $\delta^{13}\text{C}$ of CO_2 to be less than $\pm 5\text{‰}$. In other words, the uncertainty of Raman intensity of $^{13}\text{CO}_2$ must be less than 100 as the Raman intensity of $^{12}\text{CO}_2$ being 2,000,000, the uncertainty of Raman intensity of $^{13}\text{CO}_2$ is less than 50 as the Raman intensity of $^{12}\text{CO}_2$ being 1,000,000. Therefore, to weaken the effects related to the spectral analysis, it is important to increase the Raman intensity of CO_2 .

There are two types of CO_2 in natural samples, organic and inorganic (Liu et al., 2014). For the inorganic origin, it is related to rock metamorphism, the thermal decomposition of carbonate rocks, volcanomantle derived CO_2 and the meteorite impact sources (Dai et al., 2005; Zhang et al., 2008). It is found that the $\delta^{13}\text{C}$ value of mantle derived CO_2 is about -6‰ , while the $\delta^{13}\text{C}$ value of metamorphic CO_2 is approximate to that of sedimentary carbonates with $\delta^{13}\text{C}$ value greater than -8‰ . Generally, CO_2 is primarily from the biological and the thermal decomposition of organic matter during deep burial, and the organic sourced gas fields with $\delta^{13}\text{C}$ value less than -10‰ (Dai et al., 1996).

In nature, $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ account for 98.89% and 1.11%, respectively. Therefore, in comparison with $^{12}\text{CO}_2$, the $^{13}\text{CO}_2$ concentrations in natural samples are very low. From Eq. (4), Raman intensity is proportional to the molecular number. Regarding to the Raman spectrum of natural CO_2 sample, compared to $^{12}\text{CO}_2$ at 1386 cm^{-1} , the Raman intensity of $^{13}\text{CO}_2$ at 1369 cm^{-1} is obviously weak (Fig. 1).

To obtain the correct Raman intensities of $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$, the

baselines of measured Raman spectra are necessarily corrected. As the baselines are corrected, this undoubtedly brings the uncertainties on the Raman intensities of CO₂. Because the Raman intensity of ¹³CO₂ at 1369 cm⁻¹ is weaker than ¹²CO₂ at 1386 cm⁻¹ in natural CO₂ sample, obvious uncertainties can be expected for the ¹³CO₂ at 1369 cm⁻¹ during the baselines are corrected. Therefore, to improve measurement accuracy and precision, it is important to obtain the strong Raman intensity of ¹³CO₂ at 1369 cm⁻¹. This is related to not only Raman spectral measurement of CO₂, but also spectral analysis of ¹³CO₂.

In fact, with increasing measured Raman intensity, this may decrease the uncertainty as the baseline is corrected to obtain the Raman spectral intensity. With increasing the scanning time (or accumulation times), these lead to the increase of measured Raman intensity, which provides an approach to improve the measurement accuracy and precision. However, it should be noted that Raman quantitative measurement is based on the internal standard. Therefore, it is necessary that both of Raman spectra of ¹³CO₂ and ¹²CO₂ are synchronously recorded. Because the Raman intensity of ¹²CO₂ at 1386 cm⁻¹ peak is obviously stronger than that of ¹³CO₂, with increasing the measured Raman intensity of ¹³CO₂, this may lead to Raman spectrum of ¹²CO₂ at 1386 cm⁻¹ to be oversaturated (Fig. 3). Therefore, to improve the measurement accuracy and precision, it is necessary to build a method to determine the spectral intensity of ¹²CO₂ at 1386 cm⁻¹ as it becomes oversaturated.

In addition, the Raman spectra of ¹³CO₂ and ¹²CO₂ are respectively situated at 1369 cm⁻¹ and 1386 cm⁻¹. Due to the difference of atom mass between ¹³C and ¹²C, the ¹³CO₂ band is located at the shoulder of ¹²CO₂ peak (Fig. 1). This leads to the baseline of ¹³CO₂ to be inclined to high wavenumber (Fig. 1). From Fig. 4, no obvious difference can be found for various baselines of ¹³CO₂ at 1369 cm⁻¹. In fact, based on different baseline, this gives obvious difference on Raman intensity of ¹³CO₂ (Fig. 4), which greatly affects the calculated ¹³CO₂/¹²CO₂. Therefore, it is very important to find a method to determine the

reasonable baseline of ¹³CO₂.

It is important to improve the measurement accuracy and precision so that Raman spectroscopy can be applied to quantitatively measure the ¹³CO₂/¹²CO₂ in natural CO₂ sample. In fact, this is closely related to the weaker Raman spectrum of ¹³CO₂ than ¹²CO₂ because the ¹³CO₂ concentration is less than ¹²CO₂ in natural sample. Therefore, it is necessary to obtain the correct Raman intensity of ¹³CO₂. From this work, it can be found that it is related to not only Raman spectral measurement, but also the baseline subtraction of ¹³CO₂.

4.3. Method

To improve the measurement accuracy and precision, it is necessary to enhance the measured Raman intensity of ¹³CO₂ at 1369 cm⁻¹. Due to the limit of CCD detector, this may lead to Raman spectrum of ¹²CO₂ at 1386 cm⁻¹ to be oversaturated. Therefore, it is important to determine the corresponding intensity of ¹²CO₂ at 1386 cm⁻¹ as being oversaturated. In fact, other bands of ¹²CO₂ can be utilized to determine the Raman intensity of oversaturated ¹²CO₂ at 1386 cm⁻¹, such as the sub-band at 1282 cm⁻¹, hot bands of ¹²CO₂. In other words, they can be regarded as references just as discussed in internal standard. Of course, this means that the intensity ratio of ¹²CO₂ at 1386 cm⁻¹ to reference bands of ¹²CO₂ should first be determined before it is oversaturated.

In this work, to determine the Raman intensity of oversaturated ¹²CO₂ at 1386 cm⁻¹, the intensity of ¹²CO₂ at 1282 cm⁻¹ is used as the reference. Based on the measured spectra of standard CO₂ sample, the Raman intensity ratio of ¹²CO₂ at 1386 cm⁻¹ ($I_{+}^{[12]}$) to ¹²CO₂ at 1282 cm⁻¹ ($I_{-}^{[12]}$) can be determined (Fig. 3), which is expressed as follows,

$$I_{+}^{[12]} = -6314.02252 + 2.1075 * I_{-}^{[12]} \quad R = 0.99917 \quad (6)$$

From this, the Raman intensity of oversaturated ¹²CO₂ at 1386 cm⁻¹ can reasonably be determined from the corresponding intensity of ¹²CO₂ at 1282 cm⁻¹, and can be used to calculate the carbon isotopic composition of CO₂. In addition, hot bands of ¹²CO₂ may also be used to calculate the spectral intensity of ¹²CO₂ at 1386 cm⁻¹.

In fact, after the Raman spectra of standard and analytical samples are recorded, the baselines are necessarily corrected for them to obtain the Raman intensities. In natural CO₂ sample, Raman spectrum of ¹³CO₂ at 1369 cm⁻¹ is much weaker than that of ¹²CO₂ at 1386 cm⁻¹. Additionally, it is situated at the shoulder of Raman spectrum of ¹²CO₂ at 1386 cm⁻¹, which leads to the baseline of ¹³CO₂ to be inclined upward (Fig. 4). To improve the measurement accuracy and precision, it is very important that the baseline of ¹³CO₂ at 1369 cm⁻¹ is reasonably corrected. Of course, this is related to both standard and analytical CO₂ samples.

To measure the ¹³CO₂/¹²CO₂ of analytical sample, it is necessary to obtain the ratio of cross section, $\sigma_{12\text{CO}_2}/\sigma_{13\text{CO}_2}$, which is determined from standard sample. Based on Eq. (4), Raman spectra of analytical sample are recorded, and can be utilized to calculate the ¹³CO₂/¹²CO₂. In fact, it is assumed that the same ratio of cross section can be applied for standard and analytical samples. From the above, the ratio of cross section is mainly dependent on the baseline subtraction of ¹³CO₂. Therefore, it is necessary that the background of ¹³CO₂ spectra of standard and analytical samples may be close each other so that they give the same ratio of cross section. This indicates that the ratio of cross section can be utilized to calculate the ¹³CO₂/¹²CO₂ of analytical sample only the background of ¹³CO₂ of analytical sample is close to that of standard sample. In fact, this may be utilized to determine the baseline of ¹³CO₂ of analytical sample.

As the background of ¹³CO₂ of analytical sample being close to that of standard sample, both of them can be corrected with the same baselines. Of course, this provides a method to choose the reasonable baseline for ¹³CO₂ at 1369 cm⁻¹. In this work, the baseline of ¹³CO₂ is subtracted by a quadratic polynomial function to obtain its Raman intensity. This is carried out through the Jandel Scientific Peakfit v4.04

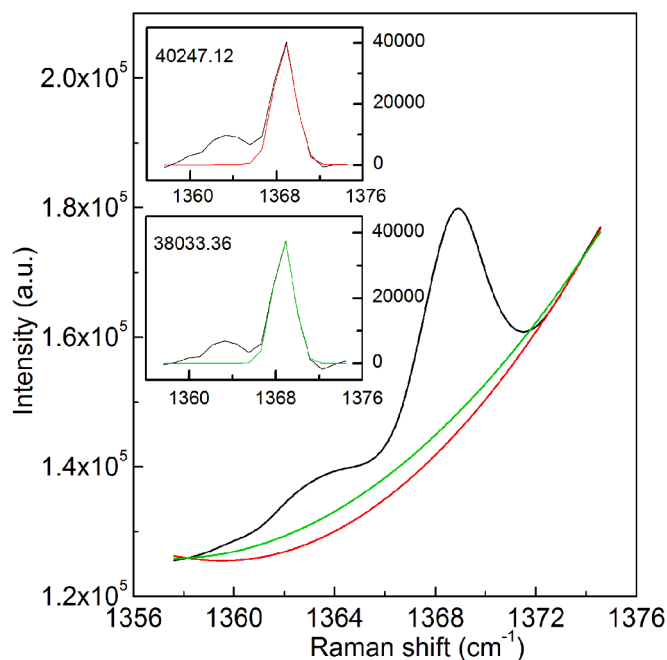


Fig. 4. The baseline subtraction of ¹³CO₂ at 1369 cm⁻¹. To obtain the Raman intensity of ¹³CO₂ at 1369 cm⁻¹, the baseline of Raman spectrum should be corrected. Based on various baselines, these give different Raman intensities of ¹³CO₂, which are shown in the inset. The corresponding Raman intensity of ¹²CO₂ at 1386 cm⁻¹ is 2,725,209. With reference to MS data, it is necessary for the uncertainty of ¹³CO₂ at 1369 cm⁻¹ to be less than 189.24 so that the deviation of calculated ¹³CO₂/¹²CO₂ ($\delta^{13}\text{C}$) is less than $\pm 5\%$. Therefore, the baseline subtraction of ¹³CO₂ greatly affects the accuracy and precision of the calculated ¹³CO₂/¹²CO₂.

program.

From the measured Raman spectra of CO₂, the Raman intensity ratio (I_+^{13}/I_+^{12}) between ¹³CO₂ and ¹²CO₂ can be determined. It can be found that the calculated I_+^{13}/I_+^{12} is dependent on the Raman intensity of ¹³CO₂ at 1369 cm⁻¹ (Fig. 5). Obvious uncertainties of I_+^{13}/I_+^{12} can be found as the Raman peak of ¹²CO₂ at 1386 cm⁻¹ is under saturated (Fig. 5). The corresponding standard deviation ($\sigma_{I_+^{13}/I_+^{12}}$) is calculated to be 0.00035315. As Raman intensity of ¹²CO₂ becomes oversaturated, this greatly lowers the uncertainty of calculated I_+^{13}/I_+^{12} . The corresponding standard deviation ($\sigma_{I_+^{13}/I_+^{12}}$) is calculated to be 0.00001118. With increasing Raman intensity of ¹³CO₂ at 1369 cm⁻¹, this decreases the uncertainties of I_+^{13}/I_+^{12} . Additionally, the calculated I_+^{13}/I_+^{12} becomes convergent with increasing the Raman intensity of ¹³CO₂. Therefore, to improve the measurement accuracy and precision, it is important to obtain the strong Raman signal of ¹³CO₂ at 1369 cm⁻¹ just as discussed above.

Based on the measured Raman spectra of natural fluid inclusions, they can be utilized to calculate the carbon isotopic compositions of CO₂. To determine the Raman intensities of ¹³CO₂ at 1369 cm⁻¹, the baselines of them are corrected with the same quadratic polynomial functions just as used in the baseline subtraction of standard sample (Fig. 6). Based on Eq. (4), the ¹³CO₂/¹²CO₂ can be determined. In combination with the MS data on the analytical sample, this can be applied to evaluate the reasonability of spectral analysis of ¹³CO₂. It can be found that, as the background of Raman spectrum of ¹³CO₂ is close to that of standard sample, the calculated ¹³CO₂/¹²CO₂ is close to MS data. This indicates that the above discussion on the baseline subtraction of ¹³CO₂ to be reasonable.

According to the Raman spectrum of standard sample, this can be used to determine the ratio of cross section, $\sigma_{12CO_2}/\sigma_{13CO_2}$. From Eq. (4), it is applied to measure the ¹³CO₂/¹²CO₂ of analytical sample as the background of ¹³CO₂ of analytical sample being close to that of standard sample. In this work, whether the ¹³CO₂ Raman spectra of standard and analytical samples can be corrected using same baselines, it is necessary for them to meet the following conditions, similar background, and high intensity (Fig. 6).

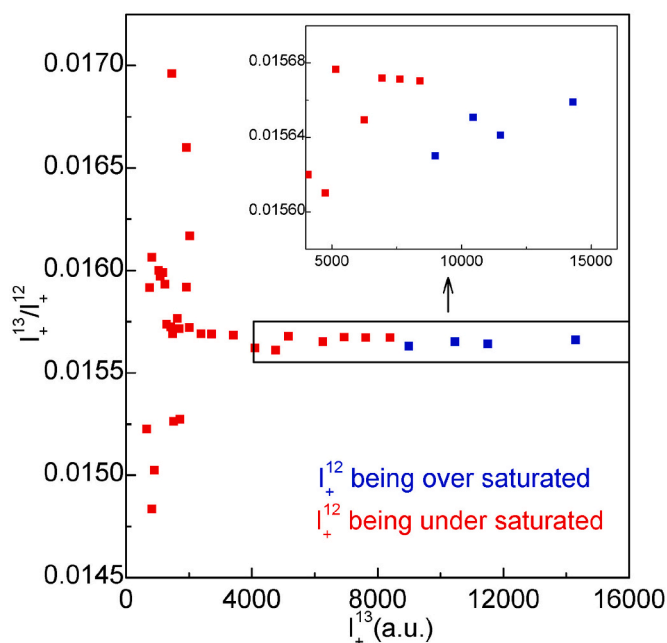


Fig. 5. The dependence of intensity ratio (I_+^{13}/I_+^{12}) on the intensity of ¹³CO₂ at 1369 cm⁻¹. Obvious uncertainties can be found on I_+^{13}/I_+^{12} as I_+^{12} being under saturated. As I_+^{12} being oversaturated, the I_+^{13}/I_+^{12} become stable. Due to the increase of Raman intensity of ¹³CO₂ at 1369 cm⁻¹, this lowers the uncertainty of calculated I_+^{13}/I_+^{12} .

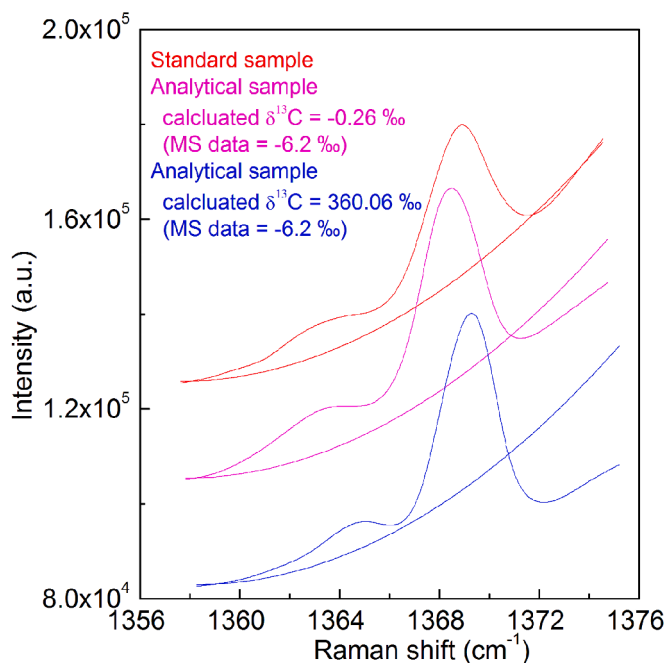


Fig. 6. The baseline subtraction of ¹³CO₂ spectra of standard and analytical samples. The background of ¹³CO₂ spectra of analytical sample should be close to that of standard sample so that they can be corrected using same method. In combination with the MS data on analytical sample, it can be utilized to evaluate the reasonability of baseline subtraction of ¹³CO₂. In this work, the baselines of ¹³CO₂ are subtracted by the quadratic polynomial functions to obtain the Raman intensities.

Based on the measured Raman spectrum of standard sample, this provides a method to choose the reasonable baseline for ¹³CO₂. Only the ¹³CO₂ Raman spectrum of analytical sample is close to that of standard sample, they can be analyzed with the same baselines. Of course, this restricts the Raman applicability on carbon isotopic composition measurement (¹³CO₂/¹²CO₂) of analytical sample. Therefore, it is necessary to build the Raman baseline database of standard ¹³CO₂ sample so that Raman spectroscopy can widely be utilized to quantitatively measure the carbon isotopic composition of CO₂. In this work, Raman spectra of liquid CO₂ in the standard sample ($\delta^{13}C = -26.49\text{‰}$) are recorded (Fig. 7), which can be used as references during the baselines of Raman spectra of ¹³CO₂ are corrected.

From the above discussion, Raman spectroscopy can reasonably be utilized to quantitatively measure the ¹³CO₂/¹²CO₂ of CO₂. Based on the relative intensity, Raman measurement can be expressed as, $^{13}CO_2/^{12}CO_2 = (I_{13CO_2}/I_{12CO_2}) \cdot (\sigma_{12CO_2}/\sigma_{13CO_2})$. To determine the ¹³CO₂/¹²CO₂, it is necessary to obtain the ratio of cross section between them, $\sigma_{12CO_2}/\sigma_{13CO_2}$, which can be calculated through the measured Raman spectra of standard CO₂ sample. Therefore, the Raman measurement procedure can be described as, from the standard to analytical samples (Fig. 8). Additionally, to improve the measurement accuracy and precision, it is important to obtain correct Raman intensity of ¹³CO₂ at 1369 cm⁻¹, which is respectively related to spectral measurement and spectral analysis of the sub-band.

5. Applications

Raman spectroscopy can be applied to quantitatively measure the ¹³CO₂/¹²CO₂ of analytical samples. From this study, Raman spectra of standard CO₂ sample are first recorded. In combination with the MS data, the ratio of cross section ($\sigma_{12CO_2}/\sigma_{13CO_2}$) can be determined. Based on Eq. (4), it can be utilized to calculate the ¹³CO₂/¹²CO₂ of analytical samples. In this work, to evaluate the accuracy and precision of Raman

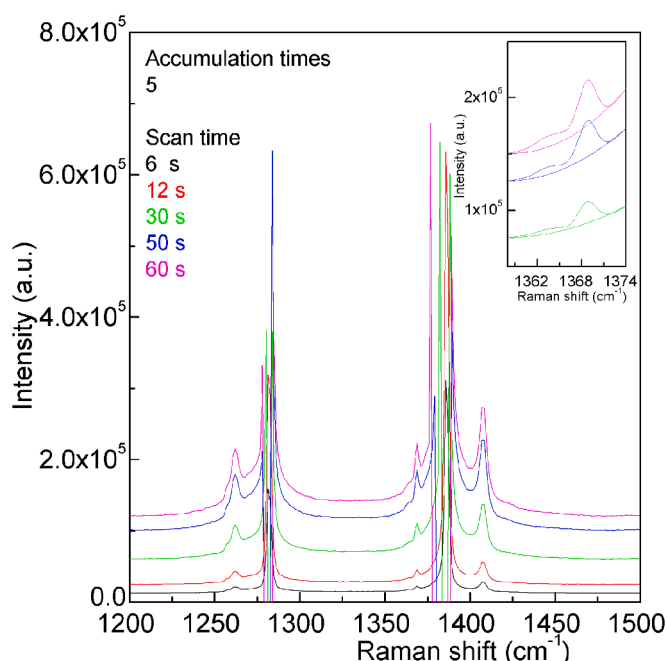


Fig. 7. The Raman spectra of liquid $^{13}\text{CO}_2$ in standard sample (-26.49%). They can be used as references during the baselines of Raman spectra of $^{13}\text{CO}_2$ are corrected.

measurement, the carbon isotopic compositions of analytical samples are also measured by MS.

5.1. Standard sample

In this study, pure CO_2 fluid inclusion is synthesized through fused silica capillary (Chou et al., 2008; Lu et al., 2007) (Fig. 1), which is utilized as the standard CO_2 sample. Both gas and liquid CO_2 phases can be found in CO_2 standard samples. The purity of CO_2 is 99.99%. Based on the MS measurement, the carbon isotopic composition ($\delta^{13}\text{C}$) is -26.49% .

With increasing scan time, this increases the measured Raman intensity of CO_2 (Fig. 2). As increasing scanning time up to 14 s, the Raman spectra of $^{12}\text{CO}_2$ at 1386 cm^{-1} is oversaturated (Fig. 3). Before Raman spectrum of $^{12}\text{CO}_2$ at 1386 cm^{-1} is saturated, Raman intensity ratio of 1282 cm^{-1} peak to 1386 cm^{-1} sub-band can be determined (Fig. 3). Based on Eq. (6), it can be used to determine the corresponding intensity as it is oversaturated.

For the Raman spectra of $^{13}\text{CO}_2$ at 1369 cm^{-1} , the baselines are corrected by the quadratic polynomial functions (Fig. 6). Then, they are fitted by Gaussian-Lorentzian functions to obtain the Raman intensities of $^{13}\text{CO}_2$ at 1369 cm^{-1} . In combination with the carbon isotopic composition measured by MS, the quantitative factor (F) can be determined.

5.2. Analytical samples

In combination with the quantitative factor (F), Raman spectroscopy can be utilized to measure $^{13}\text{CO}_2/^{12}\text{CO}_2$ of analytical samples. In this work, both synthetic and natural fluid inclusions are used as analytical samples. Additionally, both of them are also measured by MS to evaluate the reasonability of Raman quantitative measurements on $^{13}\text{CO}_2/^{12}\text{CO}_2$ of analytical samples.

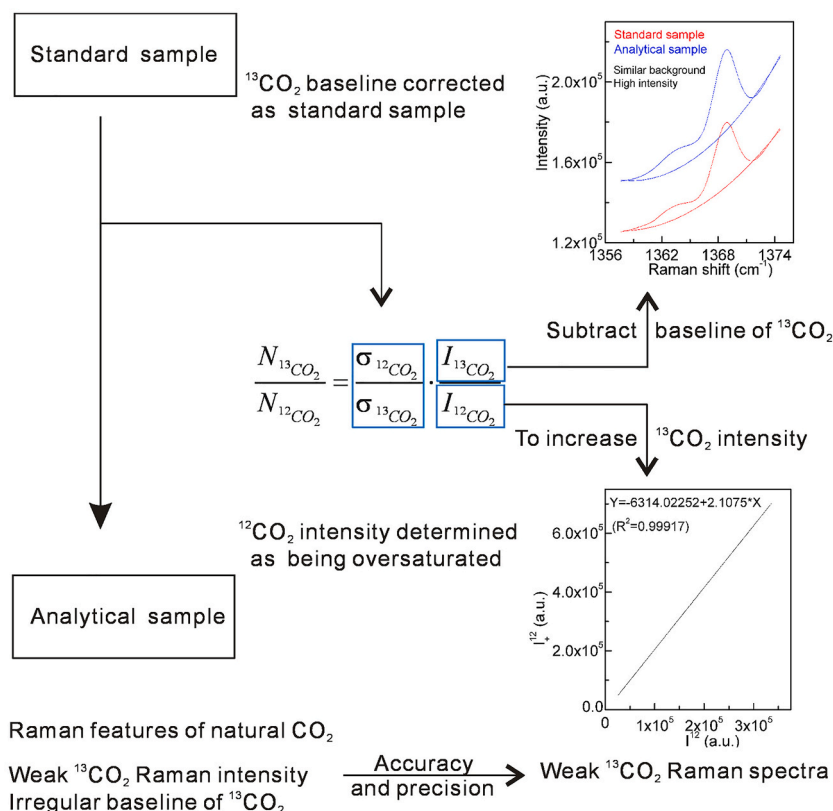


Fig. 8. The Raman measurement procedure can be described as, from the standard to analytical samples.

Regarding to cross section, it is the likelihood of light or other radiation being scattered by a particle, the scattering center. Therefore, the cross section may be closely related to the property of measured molecule. With increasing pressure (or CO₂ density), this may decrease the separation between CO₂. In other words, it decreases the molecular size of CO₂, which undoubtedly affects the cross section. Due to the increase of pressure (or CO₂ density), this may change the ratio of cross section between ¹²CO₂ and ¹³CO₂ ($\sigma_{12\text{CO}_2}/\sigma_{13\text{CO}_2}$). Of course, this is in agreement with Yokokura et al. work on CO₂ fluid (0.83–1.20 g/cm³), which means that the ratio of cross section ($\sigma_{12\text{CO}_2}/\sigma_{13\text{CO}_2}$) may be affected by the inner pressure of fluid inclusion (Yokokura et al., 2020). Before the measured ratio of cross section of standard CO₂ sample is applied to determine the carbon isotopic composition of analytical CO₂ sample, it is necessary to take into account the pressure effects on the ratio of cross section.

In this work, both gas and liquid CO₂ phases can be found in CO₂ standard and analytical samples. According to Lamadrid et al. work (Lamadrid et al., 2017), the CO₂ density of liquid phase can be determined to be 0.64 g/cm³ for standard sample, 0.71 g/cm³ for synthetic analytical sample, and 0.54 g/cm³ for natural sample. The corresponding pressures are 6.98 MPa, 6.43 MPa, and 7.34 MPa. The CO₂ densities are out of research range of Yokokura et al. work (Yokokura et al., 2020). Additionally, with reference to standard sample, the pressure differences between standard and analytical samples are small. Therefore, no pressure corrections on the ratio of cross section are carried out.

The synthetic analytical sample is pure CO₂ inclusion (Fig. 9(a, b)). It is also synthesized through fused silica capillary, but the CO₂ is different from the gas used in preparing standard CO₂ sample. The baseline of ¹³CO₂ at 1369 cm⁻¹ is corrected by the quadratic polynomial function just as standard CO₂ sample (Fig. 9(c)).

The quantitative factor (F) is mainly dependent on the baseline subtraction of ¹³CO₂. It is important to ensure the background of CO₂ sample to be similar to that of standard CO₂ sample. This can be carried

out to measure the deviation between the ends of measured ¹³CO₂ Raman spectra and the baselines vertically moved from the baseline of standard CO₂ sample (Fig. 9(c)). With decreasing the deviation, the background of sample becomes more similar to that of standard CO₂ sample. In this work, as the deviation being less than 1000, the background of ¹³CO₂ of analytical sample is regarded to be similar to that of standard CO₂ sample.

To evaluate the reliability of measured $\delta^{13}\text{C}$, several measurements have been conducted on analytical synthetic sample. These are listed as follows, -21.51‰, -19.48‰, -21.23‰, -21.46‰, and -20.97‰. From these measurements, the average of measured $\delta^{13}\text{C}$ is -20.93‰. For synthetic analytical sample, the MS data is -21.23‰. With reference to MS of CO₂, the absolute errors of $\delta^{13}\text{C}$ are -0.28‰, 1.75‰, 0‰, -0.23‰, and 0.26‰, respectively.

The natural fluid inclusions are taken from pegmatite, Abagong, Xinjiang province, China (Zhu et al., 2006). Based on the Rb–Sr isochrones, it gives the 218.4 ± 5.8 Ma for the pegmatite (Zhu et al., 2006). The baseline of ¹³CO₂ at 1369 cm⁻¹ is also corrected just as standard CO₂ sample (Fig. 10). The carbon isotopic composition from MS is -6.2‰, which is the average of bulk fluid inclusions. Therefore, various fluid inclusions have been measured by Raman spectroscopy to determine the carbon isotopic composition of CO₂. According to the measured Raman spectra of liquid CO₂, the calculated $\delta^{13}\text{C}$ is -9.05‰, -5.24‰, and -5.62‰, respectively. The average of measured $\delta^{13}\text{C}$ is -6.64‰. With reference to MS of CO₂, the absolute errors of $\delta^{13}\text{C}$ are -2.85‰, 0.96‰, and 0.58‰, respectively.

6. Conclusions

Raman spectroscopy is a non-contact and non-destructive method. It is a potential approach to quantitatively measure the carbon isotopic composition (¹³CO₂/¹²CO₂) of CO₂ in a fluid inclusion. From this work, the following conclusions can be derived,

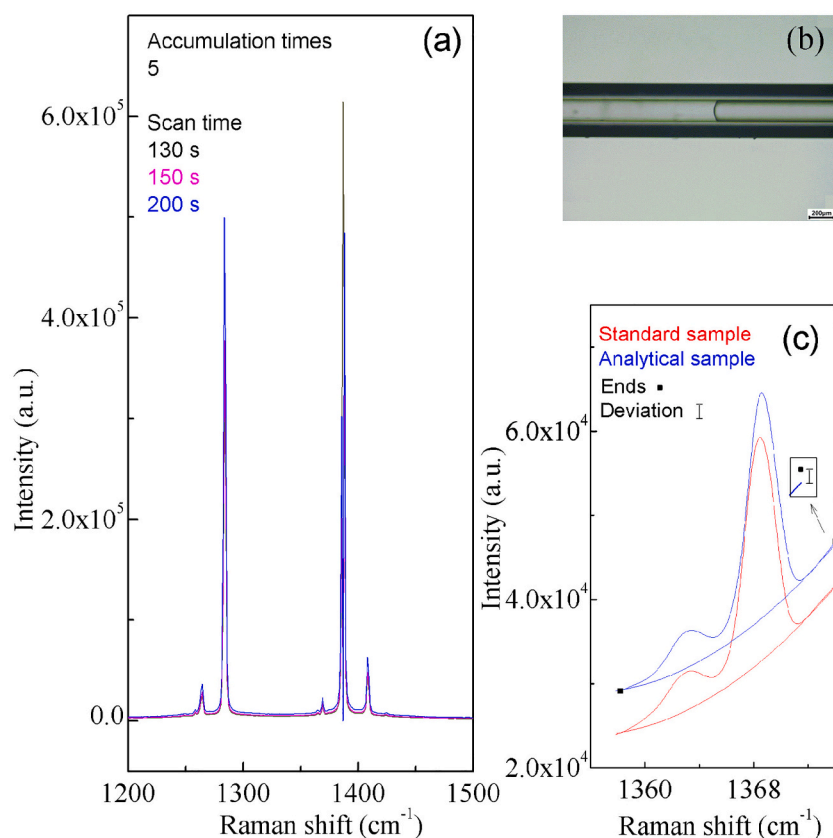


Fig. 9. (a) The Raman spectra of CO₂ of analytical sample (synthetic fluid inclusion). (b) It is a pure CO₂ inclusion. (c) The baseline of the ¹³CO₂ at the 1369 cm⁻¹ is corrected with the same quadratic polynomial function just as standard sample. It is important to ensure the background of CO₂ sample to be similar to that of standard CO₂ sample. This can be carried out to measure the deviation between the ends of measured ¹³CO₂ Raman spectra and the baselines vertically moved from the baseline of standard CO₂ sample. The calculated $\delta^{13}\text{C}$ is -21.51‰. The carbon isotopic composition from MS is -21.23‰.

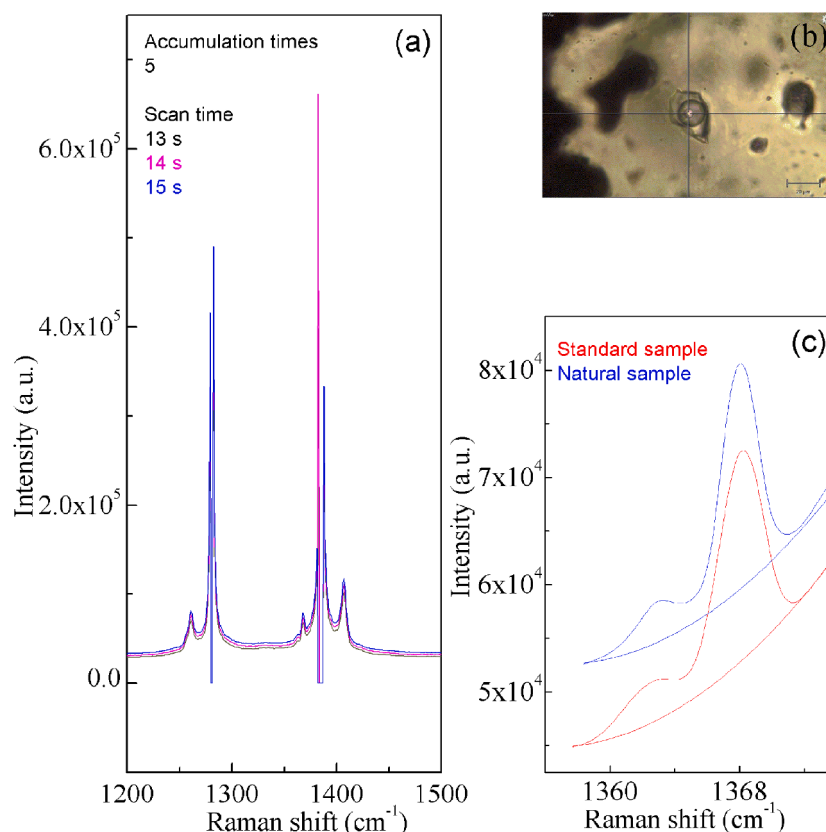


Fig. 10. (a) The Raman spectra of CO₂ of analytical sample (natural fluid inclusion). (b) It is composed of CO₂ and aqueous solutions. (c) The baseline of the ¹³CO₂ at the 1369 cm⁻¹ is corrected with the same quadratic polynomial function just as standard sample. The calculated δ¹³C is -9.05‰. The carbon isotopic composition from MS is -6.2‰.

- (1) Based on the theoretical analysis, Raman quantitative measurement may be carried out through relative intensity. To determine the carbon isotopic composition of CO₂, Raman measurement can be expressed as, $^{13}\text{CO}_2/^{12}\text{CO}_2 = (I_{13\text{CO}_2}/I_{12\text{CO}_2}) \cdot (\sigma_{12\text{CO}_2}/\sigma_{13\text{CO}_2})$. After the ratio of cross section is calculated from standard CO₂ sample, it can be applied to measure the $^{13}\text{CO}_2/^{12}\text{CO}_2$ of analytical sample. Therefore, Raman measurement process can be described as, from the standard to analytical samples.
- (2) In natural CO₂ sample, the concentration of ¹³CO₂ is very low. Therefore, compared to ¹²CO₂, the Raman intensity of ¹³CO₂ is much weaker. Regarding to the accuracy and precision of measured $^{13}\text{CO}_2/^{12}\text{CO}_2$, it is closely related to obtain the correct Raman intensity of ¹³CO₂. This is related to not only the spectral measurement, but also the baseline subtraction of ¹³CO₂. In this study, a method is provided to improve the measurement accuracy and precision.
- (3) It is necessary to build the spectral database of standard ¹³CO₂ baselines so that Raman scattering can be widely utilized to measure the carbon isotopic composition ($^{13}\text{CO}_2/^{12}\text{CO}_2$) of CO₂.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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