An equation for determining methane densities in fluid inclusions with Raman shifts

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ABSTRACT

Raman shift of the C-H symmetric stretching band (ν_1) of methane can be used to calculate the pressure and density of methane in fluid inclusions. However, previous numerical functions for Raman band shifts and methane density are only suitable for methane with densities lower than 0.3 g/cm³. In this study, Raman shifts for pure CH₄ were systematically measured at 25 °C and pressures up to 150 MPa. Parameters of the long range attractive forces were fitted, and Raman shifts of CH₄ were calculated with hard sphere model for density up to 0.55 g/cm³. Based on experimental data and theoretical calculation, a unified equation was established to calculate the density of methane gas from Raman shifts over a wide density ranges up to 0.55 g/cm³:

$$D = \nu_d - \nu_o = 211.3\rho^4 - 73.238\rho^3 + 24.477\rho^2 - 29.0632\rho$$

23 Where ρ represents the density of methane in g/cm^3 ; $D(\text{cm}^{-1})$ is the difference between the measured
24 peak position of methane in the fluid inclusion (ν_d) and the known peak position of methane at quite
25 low density (ν_o). The equation will work regardless of which machine the measurements of Raman
26 shifts are done on, as long as the user knows or finds the zero-density peak position.

27 *Keywords:* Fluid inclusion; Methane density; Raman shifts; Unified equation; Pb-Zn deposit.

28 **1. Introduction**

29 Raman spectroscopy is a non-destructive technique to study individual fluid inclusions
30 (Roedder, 1990), especially small fluid inclusions ($\leq 3\mu\text{m}$) which are difficult to analyze with the
31 micro-thermometry technique (Wopenka et al., 1990). The presence of water in methane-rich
32 inclusions could cause the difficulty in methane density determination with micro-thermometry: at
33 low temperature water forms ice or clathrate, modifies the density of the methane-bearing phase, and
34 it is difficult to get an accurate homogenization temperature when ice or clathrate occurs in the vapor
35 phase in small inclusions. Raman parameters, such as peak intensity (area) ratio, peak width ratio,
36 and peak position, can be used to determine the properties of CH_4 -bearing fluid inclusions, for
37 example, compositions in gas mixtures of $\text{CH}_4\text{-CO}_2$ and $\text{CH}_4\text{-N}_2$ system (Seitz et al., 1993, 1996),
38 concentration of dissolved methane in water solution (Dubessy et al., 2001; Guillaume et al., 2003;
39 Lu et al., 2006), and the pressure of methane (Fabre and Couty, 1986; Fabre and Oksengorn, 1992;
40 Hansen et al., 2001; Lin et al., 2007; Lu et al., 2007).

41 Lu et al. (2007) established a unified equation for calculating methane pressures in the
42 $\text{CH}_4\text{-H}_2\text{O}$ system from Raman shifts for the C-H symmetric stretching band of methane. However,
43 the pressure range of most previous measurements is just from 0 to 70 MPa, and the corresponding
44 methane densities are lower than 0.3 g/cm^3 , so their equations do not apply to the inclusions with
45 density higher than 0.3 g/cm^3 .

46 In this study, we measured Raman shifts of pure methane at pressures up to 150 MPa at 25 °C.
47 With the new data and theoretical calculation, we established an equation which could be also
48 applied in other laboratories for determining the density of methane in pure CH_4 fluid inclusions. The
49 new equation was effectively applied to determine the density of four typical pure CH_4 inclusions in
50 two samples obtained from a MVT-Pb-Zn deposit in mid-south China.

51 **2. Methods**

52 **2.1 Experimental apparatus and procedures**

The apparatus and procedures are similar to those used in the study of Lu et al. (2007) (Fig. 1). Experiments were carried out with a capillary high-pressure optical cell (HPOC; Chou et al., 1990, 2005). After the capillary cell and pipeline were evacuated, methane (99.99%, Air Products) was loaded into the cell and Raman spectra were collected under high pressures gradually up to 150 MPa. The methane pressure in the optical cell was adjusted by a high pressure generator and monitored by an Omega PX91N0-50KSV digital pressure transducer (on a full scale of 400 MPa, accurate to ± 0.5 %). The temperature in the cell was controlled by a Linkam CAP 500 heating-cooling stage with an accuracy of ± 0.1 °C at 25 °C (Lu et al., 2013).

2.2. Spectra collection and calibration

Raman spectra of gas were collected with a JY/Horiba LabRam HR 800 system provided with 532.06 nm laser (Nd: YAG) which produces approximately 15 mW laser excitation on the surface of the sample cell. The detector is an electronically-cooled CCD detector, operating normally at -70 °C. An 1800 groove/mm grating with a spectral resolution of about 0.65 cm^{-1} , a narrow slit (50 μm) and an Olympus $50 \times$ objective with a numerical aperture of 0.5 were used. Raman spectra were collected from 2750 to 3050 cm^{-1} , simultaneously with two emission lines from a neon lamp as calibration reference at 626.56 nm (2836.9888 cm^{-1}) and 633.36 nm (3008.1274 cm^{-1}), respectively. Each Raman peak wave number ν_{true} for the symmetric stretching bands of CH_4 was calibrated with the following equation (Kim et al., 1986):

$$\frac{\nu_{true}-2836.9888}{\nu_1-Ne_1} = \frac{3008.1274-2836.9888}{Ne_2-Ne_1} \quad (1), \frac{\nu_{true}-2836.9888}{\nu_1-Ne_1} = \frac{3008.1274-2836.9888}{Ne_2-Ne_1} (1)$$

Where, ν_1 is the observed wave number of methane, Ne_1 and Ne_2 are two measured lines corresponding to the neon lamp scattering bands on 626.56 nm and 633.36 nm, respectively.

2.3 Theoretical calculation

There have been a lot of experimental studies on the relationship between Raman peak position and methane density. All nine data sets collected from the literature and from this study indicate that peak positions of CH₄ shift to lower relative wave numbers as a function of increasing density (Fig. 2). Theoretically, the trends of these data sets are same, though the instrumental parameters vary in different laboratories.

Molecular vibrations in methane gas are influenced by its surrounding composition and density (Seitz et al., 1996; Hansen et al., 2001). Isolated molecule often becomes closer to each other at increased densities or pressures, and an average force exerted by its surrounding molecules causes a frequency shift of the molecular vibrations. On the basis of a theoretical model—the perturbed hard sphere model, developed by Schweizer and Chandler (1982), the density dependence of Raman shifts of simple molecules had been studied since the 1980s, such as benzene (Zakin et al., 1985), pyridine (Zakin et al., 1986), methanol (Zerda et al., 1987) in solutions; and nitrogen (Devendorf and Ben-Amotz, 1993), methane, ethane (Ben-Amotz et al., 1992) in supercritical fluids.

Generally, in hard sphere model, a solute stands for an approximate pseudo-diatomic molecule, composed of two hard spheres (diameters of σ_1 and σ_2 respectively) and a bond length r_{12} . It is dissolved in a hard sphere solvent (infinite dilution; diameter σ_s) with the density of ρ (g/cm³). However, for pure fluids, the solute and solvent molecules are the same. According to hard sphere model, the frequency shift resulted from the symmetrical stretching vibration of the “diatomic” solute dilute in a solvent is a sum of the two contributions (Ben-Amotz et al., 1992):

$$\Delta\nu = \Delta\nu_R + \Delta\nu_A \quad (2)$$

where $\Delta\nu$ stands for total frequency shifts, $\Delta\nu_R$ and $\Delta\nu_A$ represent frequency variations caused by the repulsive force (close-range) and attractive force (long-range), respectively. The frequency shift contribution of repulsive force can be calculated by the following function:

$$\Delta v_R = v_0 \frac{F_R}{f} \left[-\frac{3g}{2f} f_1(\kappa) + \frac{G_R}{F_R} f_2(\kappa) \right] \quad (3)$$

where v_0 is the unperturbed vibrational frequency shift of single solute (pure CH₄ fluid) in low density vapor phase; f and g represent the intra-molecular quadratic force-constant (harmonic vibration) and the cubic force-constant (anharmonic vibration), respectively, which can be obtained from measured vibrational frequencies and bond lengths with extended Barger's rule correlations (Herschbach et al., 1961). $f_1(\kappa)$ and $f_2(\kappa)$ are the modified Morse coefficients for anharmonic vibrations (Buckingham et al., 1958). As a function of the solute bond length, constants F_R and G_R represent the linear and quadratic coefficients of the potential energy of mean force, respectively.

For the case of diatomic solute, the attractive force frequency shift Δv_A is proportional to the force (F_A) along the bond, because F_A is relatively varying slowly when the density is lower. And according to the state of equation of van der Waals, Δv_A is as a linear function of methane density. However, the attractive force contribution of C-H stretching vibration should be approximately quadratic rather than linear dependence on methane density (Ben-Amotz and Herschbach, 1993). The quadratic function is extrapolated as follows (Fig. 3):

$$\Delta v_A = \Delta v - \Delta v_R = a\rho^2 + b\rho \quad (4)$$

where Δv is the measured total frequency shifts, Δv_R is the repulsive force frequency shift calculated with Eq.3. Parameters a and b can be fitted with the vibrational frequency shifts measured in this study, as other molecular parameters (Table 1) can be quoted from the literature (Buckingham, 1958; Ben-Amotz et al., 1992). The relationship between frequency shifts and fluids densities at high pressure conditions can be predicted with this model.

3. Results and discussion

3.1 Unified equation for near room temperature

With the new data and theoretical calculation, we can establish an equation which could be applied in all laboratories for determining the density of methane. Following the procedures of Lu et al. (2007), we fitted the relationship between $D_{k,j}$ (the difference between the measured shift $\nu_{k,j}$ of k th data point of the j th data set, and the Raman position $\nu_{o,j}$ near zero-density of the j th data set) and density $\rho_{k,j}$. The measured data in this study were used to derive the initial coefficients C_i ($i=1-4$) of a four-order polynomial function:

$$D_{k,j} = \nu_{k,j} - \nu_{o,j} = \sum_{i=1}^4 C_i \rho_{k,j}^i, \quad j = 1, 2, 3, \dots, 10 \quad (5)$$

We repeatedly fitted the data to Eq. (5), until the relation between deviation $D_{k,j}$ (cm^{-1}) and density $\rho_{k,j}$ (g/cm^3) of all data sets can fit the polynomial equation. Data up to 0.55 g/cm^3 used in the fitting were calculated values from the hard-sphere model. We got the following polynomial equation to calculate the density of pure CH_4 with Raman shifts (Fig. 4):

$$D = \nu_d - \nu_o = 211.3 \rho^4 - 73.238 \rho^3 + 24.477 \rho^2 - 29.063 \rho \quad (6)$$

with $R^2 = 0.9988$, where $D(\text{cm}^{-1}) = \nu_p - \nu_o$ represents the difference between the peak positions at increasing densities (ν_p) and near zero density (ν_o); ρ is the density of pure CH_4 . The peak positions for some data sets near zero density ν_o (Table 2) were calculated using the similar procedures in Lu et al. (2007). The density-depended Raman shifts (D s) calculated with this polynomial equation, can reproduce both experimental data and values predicted from theoretical hard sphere model (Fig. 4), including high density region ($>0.4 \text{ g/cm}^3$) where experimental data are not covered.

Once the frequency shift ν of methane in fluid inclusion is measured in a lab, D value in Eq. 6 could be obtained if the peak position near zero density ν_o for the Raman system was calibrated with a referenced methane-bearing sample (details were described in Lu et al., 2007), the density of methane in the inclusion can be conveniently determined from Fig. 4 and Eq. 6, e.g., using half-interval search method. It is worth noting that, for a specific D ,

there could be two possible values of density in the range of $0 \sim 0.55 \text{ g/cm}^3$ which satisfy the Eq. 6, one solution is smaller than 0.37 g/cm^3 and the other solution is larger than 0.37 g/cm^3 . To determine the right solution, the value of full width at half height (FWHH) of methane ν_1 band could be used as a reference, since the value of full width at half height is increase with the density of methane (Fig. 5). But one should be keep in mind that, the FWHH of methane is not only the function of density, but also changes with the instrumental seting, e.g., the wavelength of the laser, the numerical aperture of objective, the slit width, the groove density of grating, the resolution of CCD detector used, and so on.

3.2 Error analysis

Accuracy of the CH_4 density inside a natural inclusion determined with measured Raman shift with Eq. 6 will be affected by two factors. One is the accuracy of the measurement of CH_4 peak position, the other is the accuracy of the calculation using Eq. 6.

For the accuracy of the measurement of CH_4 peak position, it usually depends on the resolution of Raman spectrometer, as Dubessy et al. (2012) noted that “The spectral resolution of a Czerny-Turner spectrometer does not only result from the groove density and focal distance of the spectrometer, but also from the width of the entrance slit and the diameter of the confocal hole”. He also pointed out the spectral resolution depends on both the excitation wavelength and Raman shift (Dubessy et al., 2012). In order to achieve a maximum precision, a high resolution grating (e.g., 1800 groove/mm) and a narrow slit (e.g., $50 \mu\text{m}$) should be used during the measurement. Besides, peak positions were determined by fitting the summed Gaussian-Lorentzian curve to each CH_4 peak and calibrated with the neon emission lines. The error of CH_4 peak positions resulted from peak fitting ($\pm 0.01 \text{ cm}^{-1}$) and calibration ($\pm 0.02 \text{ cm}^{-1}$) is within a maximum value about $\pm 0.03 \text{ cm}^{-1}$.

The accuracy of the CH_4 density in pure CH_4 inclusions calculated from eq. 6 can be evaluated by the following derivation analysis:

$$\frac{dv}{d\rho} = 4a\rho^3 + 3b\rho^2 + 2c\rho + d \quad (7a)$$

where, $a= 211.3$; $b=-73.238$; $c= 24.477$; $d=-29.063$.

$$\frac{d\rho}{dv} = \frac{1}{4a\rho^3 + 3b\rho^2 + 2c\rho + d} \quad (7b)$$

As in figure 6, the error of density was plotted with increasing density in the range 0 ~ 0.55 g/cm³, with a high accuracy ($\pm 0.03\text{cm}^{-1}$) and a lower one ($\pm 0.3\text{cm}^{-1}$) of CH₄ peak position, respectively. The density error of methane is quite small when the accuracy of CH₄ peak position is as small as $\pm 0.03\text{cm}^{-1}$ (full line, Fig. 6) in the ranges of 0 ~ 0.32 g/cm³ and 0.4 ~ 0.6 g/cm³. The density error is relatively bigger (about 10%) in the range of 0.1 ~ 0.32 g/cm³ when the accuracy of CH₄ peak position is $\pm 0.3\text{cm}^{-1}$ (dashed line, Fig. 6). However, in the range of 0.32 ~ 0.40 g/cm³, the error is large, and the accuracy of density calculated with Eq. 6 is much lower.

3.3 The effect of temperature on CH₄ (ν_1) peak position shifts

The above Eq. 6 is obtained from and suitable for near room temperature studies. In order to investigate the temperature effect on the Raman shifts of CH₄, Raman spectra of pure CH₄ fluid (in a HPOC) were collected from 25 to 200 °C at pressures up to 140 MPa. And the neon emission lines were collected simultaneously with each CH₄ spectra throughout the analytical session. The result shows that the CH₄ (ν_1) peak position shifts to the higher wavenumbers as the temperature increases at constant pressure (Fig. 7) and density (Fig. 8). The temperature effect becomes larger at higher density or pressure, which agree with the previous observations (Shang et al., 2014). As temperature increases from 25 to 100 °C, D in Eq. 6 decreases 0.47 cm⁻¹ at density of 0.06 g/cm³, and 0.96 cm⁻¹ at 0.30 g/cm³. We can deduce that, for room temperature study, the difference between D at 20 °C and D at 25 °C is from 0.031 to 0.064 cm⁻¹ for density in the range from 0.06 to 0.30 g/cm³, such difference has very small effect on the density calculation. However, the effect of temperature should be taken into account at high temperatures.

4. Applications

Microthermometry coupled with thermodynamic modeling and Raman spectroscopy are complementary and efficient methods in the study of fluid inclusions (Roedder, 1980; van den Kerkhof, 1990; Wopenka et al., 1990; Burke, 2001), parameters of methane fluid inclusions obtained from micro-thermometry and Raman spectroscopy can be used to reconstruct the P-T conditions of methane-bearing fluid migration in sedimentary basins (Roedder E., 1990; Pironon et al., 2000; Dubessy et al., 2001) and metamorphic environments (Crawford et al., 1981).

4.1 Determination of density of pure CH₄ inclusions with Raman shifts

Quartz or fluorite in MVT deposit often trapped inclusions with hydrocarbons (Roedder et al., 1984). We observed some CH₄ fluid inclusions (typically 5-20 μm in the maximum dimension, Figs 9&10) hosted within a quartz vein and a fluorite vein from ore samples of a MVT Pb-Zn deposit in Sangzhi & Shimen synclinorium tectonic district, north of Hunan province, China.

Four individual fluid inclusions, CH₄-A and CH₄-B in quartz (Fig.9) and the other two CH₄-C and CH₄-D in fluorite (Fig.10) from the two samples were studied with Raman spectroscopy. Firstly, a 300 groove/mm grating and a spectral window of 0 ~ 4000 cm⁻¹ by Raman spectroscopy were adopted to check whether the gas inside the inclusions was pure CH₄ or not. The Raman spectra (Fig.11) indicated that the four individual inclusions are pure methane inclusions. Secondly, the inclusions were both studied with a 1800 groove/mm grating and a spectral window of 2750 ~ 3050 cm⁻¹ and a narrow slit around 50 μm, calibrated with the neon lamp at 25 °C (Fig.12).

Using the unified equation (Eq.6), we calculated the internal density of these four inclusions ρ_1 (A: 0.2719 g/cm³, B: 0.2712 g/cm³; C: 0.026 g/cm³, D: 0.0249 g/cm³) from the measured peak position and with reference to the peak width of CH₄ (Table 3).

4.2 Low temperature phase transition analysis of pure CH₄ inclusions

For comparison, we also observed the phase transitions of natural pure CH₄ fluid inclusions at low temperatures controlled by the Linkam CAP 500 heating-cooling stage. Figure 13 illustrates the phase transition process of pure CH₄ fluid inclusions in quartz at low temperatures in details. Inclusion A and B homogenized to the liquid phase; while C and D homogenized to the vapor phase. It is apparent that the homogenization temperature (Table 4) of each CH₄ inclusion is far below the critical point of CH₄ at -82.1 °C (van den Kerkhof, 1990) or -82.599 °C (Friend et al., 1989). The corresponding bulk density of the four inclusions ρ_2 (Table 4) were calculated from the computer programs for fluid inclusions studies FLUIDS (Bakker et al., 2003), using equation of state of Setzmann & Wagner (1991).

4.3 Comparison between Raman spectroscopy and micro-thermometry

It is obvious that the densities of CH₄ inclusion A and B are much higher than the critical density of methane (0.163 g/cm³); while the densities of C and D are much lower than it. But on the whole, the densities of the four pure CH₄ fluid inclusions calculated with Raman shifts agree with the values from micro-thermometry (Table 3, Table 4).

According to the error analysis, the achievable maximum precision of measured CH₄ peak position is $\pm 0.03 \text{ cm}^{-1}$, the corresponding accuracy of density of the fluid inclusions should be $\pm 0.0025 \text{ g/cm}^3$. For the temperature below the critical point of CH₄ at -82.1 °C, the accuracy of measurements of the heating-cooling stage is about ± 0.5 °C, the corresponding accuracy of the calculated density is about $\pm 0.0034 \text{ g/cm}^3$. It can be seen that methane density calculated with Raman shifts has a similar accuracy to that calculated with micro thermometry. Similar to the accuracy of Raman spectroscopic method we discussed above, the accuracy of micro-thermometry method depends on not only the accuracy of measurements of homogenization temperature, but also the thermodynamic model (Equation of state) used to calculate the methane density at the homogenization temperature. Since

methane density near the critical density (0.163 g/cm^3) is very sensitive to the homogenization temperature, it is difficult to accurately determine the sample density from 0.09 to 0.163 g/cm^3 via micro-thermometry; however, Raman spectroscopic method can give a satisfied result.

5. Conclusions

This paper presents a unified equation to determine methane densities up to 0.55 g/cm^3 in fluid inclusions with measured Raman shifts, based on experimental data and theoretical calculation. The key advantage is that the proposed equation will work regardless of which machine the measurements are done on, as long as the user knows an estimate for the zero-density peak position. The equation was successfully applied to calculating the densities of two individual natural methane inclusions in quartz vein with high densities and fluorite vein with low densities in a MVT mineral deposit. Unfortunately, at present we did not get a good sample to demonstrate using the equation to calculate the density of methane higher than 0.3 g/cm^3 , but we believe that the equation can also be applied to those fluid inclusions formed in deep geological environments, for example, the inclusions in mantle minerals such as olivine, diamond. Sachan et al. (2007) observed some inclusions in harzburgite, which preserved methane generated during serpentinization of upper mantle rocks, the density is 0.473 g/cm^3 for one observed inclusion with homogenization temperature of -160°C . In such cases, Raman spectroscopic method can be used to get accurate density information.

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383

FIGURE CAPTIONS

Fig.1 Schematic diagram of the experimental system (modified from Lu et al., 2007).

Fig.2 Raman shift position of C-H symmetric stretching band (ν_1) of methane from 10 available data sets as a function of density. The density of methane is calculated from the computer program of Mao et al. (2010).

Fig.3 The measured total frequency shift $\Delta\nu$ in this study, the repulsive force frequency shift $\Delta\nu_R$ calculated with hard sphere model, and the derived attractive force frequency shift $\Delta\nu_A$, as a function of density of methane.

Fig.4 The polynomial equation fitted from ten data sets and theoretical calculation of the Raman shift.

Fig.5 CH₄ peak width at half height measured in this study at 25 °C, and the values observed by Fabre et al., (1986) at 19.85 °C.

Fig. 6 Error of the calculated density (a) and the relative uncertainties (b), plotted with density of methane, for the different values of accuracy of CH₄ peak position of 0.03 cm⁻¹ (full line) and 0.3 cm⁻¹ (dashed line).

Fig. 7 Raman spectra of methane at 80 MPa from 25 to 200 °C.

Fig.8 Raman position shift of methane at 25, 100, 160, and 200 °C, together with previous study of Lu et al.(2007) at 100 and 200 °C, and Shang et al.(2014) at 100 °C.

Fig. 9 Photograph of natural CH₄ fluid inclusions (A and B in the square frame) in quartz from a MVT-Pb-Zn deposit basin under an Olympus 20 × objective.

Fig. 10 Photographs of natural CH₄ fluid inclusions (C and D) in fluorite from a MVT-Pb-Zn deposit under an Olympus 50 × objective.

Fig. 11 Raman spectra of four natural fluid inclusions, collected with 300 groove/mm grating.

Fig.12 Raman spectra of four individual natural fluid inclusions collected with an 1800 groove/mm grating.

Fig. 13 Illustrations of low-temperature phase transition under an Olympus 50 × objective (inclusions A and B). (a) Single -phase CH₄ inclusions at 25 °C; (b) Bubbles appeared when frozen to -101.5 °C; (c) Bubbles got bigger in size at -125 °C; (d) Bubbles remained constant at -193.3 °C; (e) Bubbles decreased in size when heated from -193.3 °C to -112.5 °C; (f) Bubbles became smaller (-101 °C); (g) Bubbles almost disappeared (-99.2 °C); (h) Bubble in A disappeared at -98.1 °C; (i) Bubble in B disappeared at -97.9 °C. Both of inclusions A and B homogenized to the liquid phase.

Table 1 Parameters used in hard sphere model for calculating density-depended Raman shifts.

mol	bond	T	r_e	σ_1	σ_2	σ_{HS}	ν_{vib}	f	g	a	b
		(°C)	(Å)	(Å)	(Å)	(Å)	(cm ⁻¹)	(dyne)	(dyne)	(cm ⁻¹ / g/cm ³)	(cm ⁻¹ / g/cm ³)
CH ₄	C-H	25	1.091	3.53	2.22	3.585	2916.5	0.005049	-0.01047	-4.92	-34.43

r_e —bond lengths, in low density vapour phase;
 σ_1, σ_2 —pseudo-atomic hard sphere diameters;
 σ_{HS} —effective molecular hard sphere diameter;
 ν_{vib} —vibrational resonance frequency in the low density vapor phase;
 f, g —force constants are obtained from vibrational frequencies and extended Bager’s rule correlations;
 a, b —attractive force parameters are obtained by fitting the hard fluid model to high density frequency shifts measured in this study.

Table 2

Table 2 methane ν_1 band position near zero pressure (ν_0) fitted for ten data sets of peak positions.

	This study	Hansen 2001	Seitz 1996	Fabre 1986	Thieu 2000	Lin 2005	Lu 2007	Shang 2014	Jager*	Hester*
T (°C)	25	22	23	19.85	24.85	22	22	22	24	30
ν_0	2917.58	2916.96	2916.56	2916.52	2918.46	2917.62	2918.28	2918.24	2918.63	2917.33

*Original data of Jager and Hester of Colorado School of Mines are cited from Table 1b of Lu et al. (2007).

Table 3 Results of Raman analysis for the four pure CH₄ fluid inclusions at 25 °C.

Inclusion	Hosted Mineral	ν_{true} (cm ⁻¹)	D (cm ⁻¹)	Peak Width at half height	ρ_1 (g/cm ³)
A	Quartz	2911.17	-6.41	4.95	0.2719
B	Quartz	2911.18	-6.40	4.98	0.2712
C	Fluorite	2916.84	-0.74	2.51	0.026
D	Fluorite	2916.87	-0.71	2.40	0.0249

ν_{true} (in cm⁻¹) is the calibrated peak position of sample fluid inclusion measured by Raman spectroscopy.

D (in cm⁻¹) represents the deviation of the measured peak posion of sample fluid inclusion from near zero density ν_0 .

Peak width at half hight is the measured Raman parameter, which can be used to determine the approximate range for methane density in fluid inclusions.

ρ_1 (in g/cm³) stands for the calculated density of each natural CH₄ fluid inclusion with the unified equation established in this study.

Table 4 Results of micro-thermometry analysis for the four fluid inclusions.

Inclusion	Hosted Mineral	<i>Th</i> (°C)	Homogenization (phase)	ρ_2 (g/cm ³)
A	Quartz	-98.1	Liquid	0.2948
B	Quartz	-97.9	Liquid	0.2941
C	Fluorite	-116	Vapor	0.0224
D	Fluorite	-117.2	Vapor	0.0213

Th (°C) is the homogenization temperature of each fluid inclusion measured with the heating-cooling stage.

ρ_2 was inferred from the homogenization temperature of methane with the computer programs FLUIDS for fluid inclusion studies developed by Bakker (2003).

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