A re-evaluation of the effects of temperature and NaCl concentration on quantitative Raman spectroscopic measurements of dissolved CH$_4$ in NaCl aqueous solutions: Application to fluid inclusion analysis

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A B S T R A C T

We re-evaluated the effects of temperature and NaCl concentration on quantitative Raman spectroscopic measurements of dissolved CH$_4$ in NaCl aqueous solutions with the newly developed Unsaturated Homogenized Solution Method (UHSM). The Raman peak area ratios (PARs) of the symmetric stretching vibrational mode of methane (at ~2917 cm$^{-1}$) to the OH stretching band of water in homogeneous CH$_4$-containing aqueous solutions were obtained at temperatures from 273.15 to 603.15 K, pressures from 0 to 120 MPa, and NaCl concentrations from 0 to 5 mol/kg H$_2$O. The pressure and concentration of CH$_4$ (mCH$_4$) have little effect on the Quantitative Factor (QF = PAR / mCH$_4$). However, the QF shows both temperature and NaCl concentration dependencies; QF increases linearly with temperature from 273 to 603 K at constant NaCl concentration, and the rate of increase of QF to temperature decreases with NaCl concentration. After normalization to QF at 298.15 K, the QF at elevated temperature (T, in K) and NaCl concentration (mNaCl, in mol/kg H$_2$O) can be represented as a function of temperature and mNaCl:

$$QF[T, mNaCl] / QF[298.15 K, mNaCl] = f_\theta (T, mNaCl) = a_\theta T + b_\theta$$

where $a_\theta = -4.898E-04 \times mNaCl^{1/2} + 2.011E-03$ and $b_\theta = 1.377E-01 \times mNaCl^{1/2} + 4.042E-01$. This function has been applied successfully to determine the methane concentration in natural fluid inclusions in quartz, and it can be used in other laboratories for CH$_4$–NaCl–H$_2$O ternary systems, where QF at 298.15 K is the only parameter that needs to be obtained for the quantitative analyses of dissolved CH$_4$ in NaCl aqueous solutions.

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1. Introduction

Raman spectroscopy is becoming a powerful tool for the quantitative analysis of aqueous solutions in geochemical environments with various temperature, pressure, and salinity. For example, Raman spectroscopy has been applied to study the submarine hot hydrothermal vent and cold seep systems (Pasteris et al., 2004; Brewer et al., 2004; White, 2010) and quantitative analysis of the concentration of dissolved species in individual aqueous fluid inclusions (Dubessy et al., 2001, 2002; Guillaume et al., 2003; Pironon et al., 2003; Azbej et al., 2007; Caumon et al., 2013, 2014) at or above the liquid–vapor homogenization temperature, where the fluids in the inclusion become homogeneous. However, accurate calibration of a Raman system for analysis of dissolved gases in brines in a wide temperature range (e.g., 273 to 573 K) is still a challenge (Guo et al., 2014a). The calibrations of Raman spectroscopy systems for the determination of the CH$_4$ concentration in a NaCl aqueous solution have been mainly carried out by using the synthetic inclusion method (SIM) (Dubessy et al., 2001, 2002; Guillaume et al., 2003; Pironon et al., 2003; Faulstich et al., 2013) and the saturated concentration method (SCM) (Lu et al., 2008; White, 2010; Caumon et al., 2014); however, the effects of temperature and salinity on the measurements of dissolved CH$_4$ in these solutions are still not well defined. For example, Guillaume et al. (2003) and Faulstich et al. (2013) observed the dependency of the estimated CH$_4$ concentration on salinity, but no such salinity effect was observed by White (2010) and Caumon et al. (2014).

The focus of this work is to determine the effects of temperature, NaCl concentration, and pressure on the calibration of a Raman spectroscopic system for the determination of dissolved CH$_4$ in NaCl aqueous solutions. Recently, we developed an “unsaturated homogenized solution” method (UHSM) to accurately calibrate the quantitative relationship between dissolved gas composition and Raman peak intensity.
(area) ratios between dissolved gas and water to determine the solubilities of carbon dioxide and methane in pure water from 273 to 603 K and from 10 to 120 MPa. Functions for Quantitative Factor (QF = PAR/\(m_{CH_4}\)) to temperature \((T)\), NaCl concentration \((m_{NaCl})\) and pressure \((P)\) were established and can be used in all laboratories, after normalization, for quantitative analyses of dissolved \(CH_4\) concentrations in NaCl aqueous solutions.

2. Experimental

2.1. Materials

The methane (99.99%) used in this study was supplied by Air products, sodium chloride (99.95%) was purchased from Shanghai Shanpu Chemical Co., Ltd., and water was ultra-purified with a resistivity of 18.24 M\(\Omega\)·cm. Solutions of various NaCl concentrations (0, 0.62, 1.03, 2.00, 2.09, 3.00, 3.01, 4.50, 5.00 and 5.70 mol/kg H\(_2\)O) were prepared.

2.2. Apparatus and sample preparation procedures

The Chou–Burruss–Lu-type high pressure optical capillary cell (HPOC) (Chou et al., 2005; Lu et al., 2006, 2008), combined with a Linkam CAP500 heating–cooling stage (Chou, 2012; Lu et al., 2013; Guo et al., 2013; Caumon et al., 2014), was used to prepare homogeneous aqueous solutions containing \(CH_4\) and NaCl for in situ Raman measurements. The HPOC functions as the equilibrium cell in this study, which is like a “micro” version of the Cailletet apparatus (De Loos et al., 1986). The procedures were similar to those described by Guo et al. (2014a), including the following steps: (1) load an aqueous solution column (~20 cm long) into a large capillary tube with one end closed (665 \(\mu\)m OD, 300 \(\mu\)m ID for pressure less than or equal to 50 MPa; 665 \(\mu\)m OD, 150 \(\mu\)m ID for pressure greater than 50 MPa; approximately 30 cm in length); (2) connect a small round tube (200 \(\mu\)m OD, 75 \(\mu\)m ID for a tube with a 300 \(\mu\)m ID; 90 \(\mu\)m OD, 20 \(\mu\)m ID for a tube with a 150 \(\mu\)m ID; approximately 50 cm in length) to a \(CH_4\) source and adjust the rate of \(CH_4\) flow; (3) insert the small tube into the large tube until it reaches the solution surface in the large tube and hold for several minutes to expel air; (4) insert the small tube to a certain length (0.7–2 cm) away from the closed end of the large tube to inject \(CH_4\) and wait until a certain volume of \(CH_4\) has been injected.

Table 1

<table>
<thead>
<tr>
<th>Soln.</th>
<th>(m_{NaCl}) (mol/kg H(_2)O)</th>
<th>(P) (MPa)</th>
<th>(T) (K)</th>
<th>(L_{CH_4}^{a}) (mm)</th>
<th>(L_{soln}^{b}) (mm)</th>
<th>(V_{m,CH_4}^{c}) (cm(^3)·mol(^{-1}))</th>
<th>(\rho_{soln}^{d}) (kg·m(^{-3}))</th>
<th>(m_{CH_4}) (mol/kg H(_2)O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0</td>
<td>0.1</td>
<td>298.15</td>
<td>17.6</td>
<td>7.708</td>
<td>24,748</td>
<td>997.05</td>
<td>0.093</td>
</tr>
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<td>S2</td>
<td>0</td>
<td>0.1</td>
<td>293.45</td>
<td>31.7</td>
<td>10,000</td>
<td>24,355</td>
<td>998.14</td>
<td>0.120</td>
</tr>
<tr>
<td>S3</td>
<td>0</td>
<td>0.1</td>
<td>293.95</td>
<td>27.8</td>
<td>8,505</td>
<td>24,397</td>
<td>998.04</td>
<td>0.134</td>
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<td>S4</td>
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<td>0.1</td>
<td>295.85</td>
<td>42.5</td>
<td>10,573</td>
<td>24,356</td>
<td>997.61</td>
<td>0.164</td>
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<td>S5</td>
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<td>0.1</td>
<td>286.65</td>
<td>44.0</td>
<td>6,966</td>
<td>23,787</td>
<td>999.31</td>
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<td>S6</td>
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<td>290.65</td>
<td>210.3</td>
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<td>24,121</td>
<td>998.09</td>
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<td>290.65</td>
<td>352.4</td>
<td>10,150</td>
<td>24,121</td>
<td>998.69</td>
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<tr>
<td>S8</td>
<td>0.62</td>
<td>0.1</td>
<td>290.55</td>
<td>49.7</td>
<td>13,922</td>
<td>24,113</td>
<td>1023.97</td>
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<td>24,080</td>
<td>1024.06</td>
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<td>15.3</td>
<td>7,360</td>
<td>24,748</td>
<td>1105.75</td>
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<td>25,174</td>
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<td>289.45</td>
<td>16.1</td>
<td>14,442</td>
<td>24,021</td>
<td>1170.67</td>
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<tr>
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<td>0.1</td>
<td>291.45</td>
<td>47.0</td>
<td>15,306</td>
<td>24,188</td>
<td>1169.66</td>
<td>0.140</td>
</tr>
</tbody>
</table>

\(^a\) Length of \(CH_4\) column in the fused silica capillary at 0.1 MPa measured by a ruler with accuracy of 1 mm.

\(^b\) Length of solution in the fused silica capillary at 0.1 MPa measured by a screw micrometer with accuracy of 0.01 mm.

\(^c\) Molar volume of the solution calculated from http://models.kf-ed.ac.cn/models.htm.

\(^d\) Density of the solution calculated from Mao and Duan (2008).
accumulated between the retained solution column and the pushed solution column; (5) quickly pull out the small tube; (6) inject a mercury column (approximately 1 cm in length) into the CH4 column in the large tube to form a closed system (Fig. 1); (7) measure the length of the solution section (Lsoln) and CH4 section (LCH4) sealed by mercury at one atmosphere pressure and room temperature (Table 1), where the molar volume and density of the solution are well known; (8) connect the sampled tube with a pressure line and insert the tube horizontally into the Linkam CAP500 heating-cooling stage; (9) slowly pressurize the line (usually over 10 MPa) until CH4 has completely dissolved in the aqueous solution to form a homogeneous solution; and (10) mount the sample already in the heating-cooling stage on a microscope stage to collect Raman spectra of the homogeneous aqueous solution at 273.15–603.15 K and 10–120 MPa between 1200 and 4000 cm\(^{-1}\) to cover the Raman band of dissolved CH4 near 2917 cm\(^{-1}\) and the water band near 3425 cm\(^{-1}\).

Thirteen CH4 homogeneous aqueous solutions were prepared and kept under high pressure conditions with no immiscibility so that the concentrations of CH4 remained unchanged under all studied temperatures. Dissolved CH4 concentrations (in mol·kg\(^{-1}\), \(m_{\text{CH}_4}\)) in these samples were calculated based on the measured initial length of CH4 and the initial length of the aqueous solution column loaded under a certain condition of temperature and pressure:

\[
m_{\text{CH}_4} = \frac{n_{\text{CH}_4}}{m_{\text{H}_2\text{O}}} = \frac{\pi \cdot r^2 \cdot L_{\text{CH}_4} / V_{m,\text{CH}_4}}{1000 \cdot L_{\text{soln}} / \rho_{\text{soln}}} = \frac{1000 \cdot L_{\text{soln}} / \rho_{\text{soln}} - [1000/(1000 + M_{\text{NaCl}} - m_{\text{NaCl}})]}{1000 \cdot L_{\text{CH}_4} / V_{m,\text{CH}_4}}
\]

where \(m_{\text{CH}_4}\) (in mol/kg H\(_2\)O) is the concentration of CH4 in the solution; \(n_{\text{CH}_4}\) is the number of moles of CH4 dissolved in the total volume of

![Fig. 2.](image-url) In situ Raman spectra of symmetric stretching vibration of methane and OH-stretching vibration of water molecules collected from CH4-bearing NaCl aqueous solutions at various pressures, temperatures, and NaCl concentrations.
solution; \( m_{\text{H}_2\text{O}} \) is the mass of \( \text{H}_2\text{O} \); \( r \) is the radius of the cell, which is assumed to be constant; \( L_{\text{CH}_4} \) (in cm) is the length of the \( \text{CH}_4 \) column; \( V_m, \text{CH}_4 \) (in cm\(^3\)·mol\(^{-1}\)) is the molar volume of \( \text{CH}_4 \); \( \rho_{\text{soln.}} \) (in g·cm\(^{-3}\)) is the density of the solution; \( M_{\text{NaCl}} \) (in g·mol\(^{-1}\)) is the molar mass of \( \text{NaCl} \); \( m_{\text{NaCl}} \) (in mol/kg \( \text{H}_2\text{O} \)) is the \( \text{NaCl} \) concentration of the solution.

The descriptions and calculated \( \text{CH}_4 \) concentrations of the 13 samples homogenized at high pressures are listed in Table 1.

2.3. Raman spectra collection

Raman spectra were collected by using a JY/Horiba LabRam HR800 Raman system equipped with a frequency doubled Nd:YAG laser (532.06 nm), whose output laser power is 45 mW, and a 50× long-working-distance Olympus objective with a 0.5 numerical aperture. The aperture of the confocal hole was set to 200 \( \mu \)m. Raman peak position calibration was verified regularly with the ~520.7 cm\(^{-1}\) band of a polished silicon wafer. A 300 groove/mm grating was used to obtain spectra of the \( \text{CH}_4 \) homogeneous solutions and the liquid phase of the fluid inclusions. Spectra were collected in the range of ~1200–4000 cm\(^{-1}\) (Fig. 1). The acquisition time was approximately 100 s, with two accumulations for each spectrum to maintain a high signal-to-noise ratio. The Raman peak area ratio (PAR) and peak intensity ratio (HR) of the symmetric stretching vibrational mode of methane (at ~2917 cm\(^{-1}\)) to the OH stretching band of water (range of 2650 to 3900 cm\(^{-1}\)) were obtained using the software GRAMS/AI (Thermo Galactic). Three to five spectra were usually collected for each temperature–pressure condition. The average values of PAR and HR were used, although the deviations of the observations were generally very small (~1%). A 1800 groove/mm grating was used to acquire spectra of the methane vapor at clathrate melting temperatures to calculate pressures in the inclusions with measured Raman shifts (Lu et al., 2007). The emission lines of the neon (Ne) laser at 626.65 nm (2836.99 cm\(^{-1}\)) and 633.44 nm (3008.13 cm\(^{-1}\)) were collected simultaneously with the Raman spectra. The method of calibration of the methane peak position described by Wang et al. (2014) was used. The accuracy of the peak position in wavenumber scale was approximately ±0.2 cm\(^{-1}\), resulting in an accuracy of approximately 1 MPa for pressure estimation.

3. Results and discussion

3.1. Temperature, pressure, and salinity effects on PAR/m\( \text{CH}_4 \)

According to Placzek’s ratio method (Chou et al., 1990 and references therein; Lu et al., 2008), for two Raman active species \( a \) and \( b \) in a fluid phase, their relative concentrations, \( C_s \) (e.g., mole or mol %), are related to their Raman peak areas, \( A_s \), by the formula:

\[
\frac{A_a}{A_b} = \frac{C_a}{C_b} \left( \frac{\sigma_a}{\sigma_b} \right) \left( \frac{\eta_a}{\eta_b} \right) \left( \frac{F_a}{F_b} \right) \quad (2)
\]

where \( \sigma \), \( \eta \) and \( F \) are the Raman scattering cross-section, instrumental efficiency, and Raman quantification factor, respectively. For \( \text{CH}_4 \)-containing aqueous solutions, the OH stretching band of water was taken as an internal standard (Guillaume et al., 2003; Pironon et al., 2003; Azbej et al., 2007; Lu et al., 2008; Sun and Qin, 2011). Based on Eq. (2) above,

\[
A(\text{CH}_4)/A(\text{H}_2\text{O}) = \frac{m(\text{CH}_4)/m(\text{H}_2\text{O})}{m(\text{H}_2\text{O})/m(\text{CH}_4)} \times \frac{F(\text{CH}_4)/F(\text{H}_2\text{O})}{F(\text{H}_2\text{O})/F(\text{CH}_4)}. \quad (3)
\]
Therefore,

\[
\text{PAR} = \frac{[m \text{CH}_4]/(1000/MW(H_2O))] \times [F(\text{CH}_4)/F(H_2O)]}{QF}
\]

where \(MW(H_2O)\) is the molecular weight of \(H_2O\), and the \(QF\) used in this study can be represented by

\[
QF = \frac{\text{PAR}}{m(\text{CH}_4)} = \frac{[F(\text{CH}_4)/F(H_2O)]}{[1000/MW(H_2O)]}.
\]

The Raman spectra of thirteen \(\text{CH}_4\) homogeneous aqueous solutions (\(\text{NaCl}\) concentrations from 0 to 5 mol/kg \(H_2O\) and \(\text{CH}_4\) concentrations from \(-0.05~to~1.44\) mol/kg \(H_2O\)) under 273.15–603.15 K and 10–120 MPa were collected. Note that some of the measurements were performed on the samples in the \(P-T\) stability field of methane hydrate under metastable equilibrium conditions without the presence of hydrate. Fig. 2 shows the evolutions of Raman spectra with temperature at constant \(\text{NaCl}\) concentrations. The results of \(\text{PAR}/m\text{CH}_4\) are shown in Fig. 3. The average absolute deviations (AAD) of \(\text{PAR}/m\text{CH}_4\) are generally smaller than 1.6% at a constant temperature and \(\text{NaCl}\) concentration, indicating that pressure and \(\text{CH}_4\) concentration show little effect on \(QF\). \(\text{PAR}/m\text{CH}_4\) increases linearly with temperature from 273.15 to 603.15 K when the \(\text{NaCl}\) concentration is constant. Thus, they can be fitted to functions (6-1) to (6-4) regardless of pressure and \(\text{CH}_4\) concentration:

\[
0~\text{m} : QF = 3.673E-05 \times T + 7.143E-03; r^2 = 0.995 (n = 235)
\]

(6-1)

\[
0.62~\text{m} : QF = 2.934E-05 \times T + 9.105E-03; r^2 = 0.993 (n = 48)
\]

(6-2)

\[
3~\text{m} : QF = 2.046E-05 \times T + 1.155E-02; r^2 = 0.986 (n = 44)
\]

(6-3)

\[
5~\text{m} : QF = 1.398E-05 \times T + 1.282E-02; r^2 = 0.963 (n = 32)
\]

(6-4)

where \(T\) is temperature in K. As seen from the functions, \(QF\) increases with temperature linearly from 273 to 603 K when the \(\text{NaCl}\) concentration is constant, and the rate of increase of \(QF\) to temperature decreases with \(\text{NaCl}\) concentration, indicating that both \(\text{NaCl}\) concentration and temperature do affect the calibration curve. Considering the effects of temperature and \(\text{NaCl}\) concentration on \(\text{PAR}/m\text{CH}_4\), these functions can be represented as follows:

\[
QF = \frac{\text{PAR}}{m(\text{CH}_4)} = f(T, m(\text{NaCl})) = aT + b.
\]

(7)

The slope \((a)\) and intercept \((b)\) of functions (6-1) to (6-4) depend on the square root of \(m(\text{NaCl})\) (Fig. 4) and can be represented by:

\[
a = -1.001E-05 \times m(\text{NaCl})^{1/2} + 3.703E-05; R^2 = 0.996
\]

(7-1)

\[
b = 2.546E-03 \times m(\text{NaCl})^{1/2} + 7.128E-03; R^2 = 0.999
\]

(7-2)

where \(m(\text{NaCl})\) is the \(\text{NaCl}\) concentration in mol/kg \(H_2O\).

The Raman quantification factor is affected by Raman cross-sections \((\sigma_i)\) and the instrumental factor \((\eta_i)\) (White, 2010). To apply these relationships to all laboratories, we normalized the \(\text{PAR}/m\text{CH}_4\) of each temperature (\(QF[T, m(\text{NaCl})]\)) by using \(\text{PAR}/m\text{CH}_4\) at 298.15 K (\(QF[298.15\text{K}, m(\text{NaCl})]\)) of the corresponding \(\text{NaCl}\) concentration. The results can be represented by the following equations (Fig. 5):

\[
0~\text{m} : QF[T, m(\text{NaCl})]/QF[298.15\text{K}, m(\text{NaCl})] = 2.030E-03 \times T + 3.948E-01
\]

(8-1)

\[
0.62~\text{m} : QF[T, m(\text{NaCl})]/QF[298.15\text{K}, m(\text{NaCl})] = 1.643E-03 \times T + 5.100E-01
\]

(8-2)

Furthermore, these equations can be represented by Eq. (9), where the slope \((a_n)\) and intercept \((b_n)\) can be represented by Eqs. (9-1) and (9-2), respectively.

\[
QF[T, m(\text{NaCl})]/QF[298.15\text{K}, m(\text{NaCl})] = f_n(T, m(\text{NaCl})) = a_nT + b_n
\]

(9)

\[
a_n = -4.898E-04 \times m(\text{NaCl})^{1/2} + 2.011E-03; R^2 = 9.989E-01
\]

(9-1)

\[
b_n = 1.377E-01 \times m(\text{NaCl})^{1/2} + 4.042E-01; R^2 = 9.989E-01
\]

(9-2)

If \(QF[298.15\text{K}, m(\text{NaCl})]\) for a particular Raman spectroscopic system is obtained, the concentration of dissolved \(\text{CH}_4\) at a certain temperature can be calculated from the measured \(\text{PAR}\) through Eq. (7) and the corresponding \(QF[T, m(\text{NaCl})]\).

3.2. Comparison with previous studies

In this study, we observed that both temperature and salinity affect the peak area ratio (\(\text{PAR}\)) between the stretching bands of methane and water, as shown in Figs. 6 and 7, respectively. Furthermore, as shown in Fig. 3, the effect of \(\text{NaCl}\) concentration (0–5 mol/kg \(H_2O\)) on \(\text{PAR}/m\text{CH}_4\)
is small at low temperatures (with deviations of less than 5% below 318 K), but it becomes more obvious with increasing temperature (with a deviation of up to 39% at 603 K). This is in contradiction to the results of other studies, which showed that salinity and temperature had no or only minor effect on the derivation of dissolved methane in saline solutions, even though all studies agreed that pressure had negligible effect.

Fig. 8 shows a comparison of our results with those of similar Raman studies. As shown in Fig. 3, the Quantitative Factors ($QF_s$) at 273.15 K with various salinities are essentially the same, shown in Fig. 8 as a solid line. However, the rate of increase of $QF_s$ to temperature decreases with salinity, as demonstrated in Fig. 8 by the difference in slopes for 0 (long dashed line), 0.62 (dotted line), 3 (dash-dot-dot line), and 5 m (short dashed line) at 603.15 K. Although all data points are located in the range of this study, except two data points of Dubessy et al. (2001), the effects of temperature and salinity on the quantitative relationship are not well revealed. Caumon et al. (2014) calibrated the Raman signal of CH$_4$ as a function of solubility over a wide range of temperature (60–180 °C), pressure (30–1000 bar) and salinity (0–4 m NaCl) and considered that the calibration curve is not salinity- and temperature-dependent. However, the differences of CH$_4$ concentrations calculated from their calibration curve at their temperature, salinity and CH$_4$ concentration ranges were approximately 2.6–9.3% in comparison to this study, and the differences will be greater when applied to higher temperatures. Lu et al. (2008) reported a linear relationship between PAR and the dissolved methane concentration in pure water at temperatures from 274.15 to 373.15 K. The maximum difference in PAR / mCH$_4$ at this temperature range is approximately 17%. They both used the saturated concentration...
method, and the solubilities of methane were calculated using thermodynamic models. The uncertainties of their determinations include the relative uncertainties of the thermodynamic model for calculating CH4 solubility in a NaCl aqueous solution and the experimental/analytical uncertainties of pressure, temperature, and salinity. Guillaume et al. (2003) and Faulstich et al. (2013) observed a variation in the calibration curve as a function of salinity. This is consistent with our study. White (2010) noted that pressure has little effect and salinity has a small effect on the Raman spectrum of water when comparing the spectrum to determine the ice-melting temperatures that relate salinity and freezing point depression (Bodnar, 1993, 2003). However, in some cases, this technique cannot be applied. For example, salinities of the aqueous phase estimated from ice-melting temperatures are higher than the actual salinity of the aqueous phase if ice melting occurs before the final dissolution of clathrate (Fall et al. 2011; Caumon et al. 2014). Fall et al. (2011) developed a technique to determine the salinity of CO2-bearing aqueous inclusions based on measured clathrate melting temperatures and CO2 pressures obtained from Raman analyses. This method can be extended to CH4-bearing inclusions, but the premise is that the bubble is large enough for pressure determination, allowing the collection of a good Raman signal for an accurate determination of the CH4 concentration in a NaCl solution at a specific temperature, we first need to determine its salinity. The general approach used to determine the salinity of an aqueous solution is to use microthermometry to determine the ice-melting temperatures that relate salinity and freezing point depression (Bodnar, 1993, 2003). However, in some cases, this technique cannot be applied. For example, salinities of the aqueous phase estimated from ice-melting temperatures are higher than the actual salinity of the aqueous phase if ice melting occurs before the final dissolution of clathrate (Fall et al. 2011; Caumon et al. 2014). Fall et al. (2011) developed a technique to determine the salinity of CO2-bearing aqueous inclusions based on measured clathrate melting temperatures and CO2 pressures obtained from Raman analyses. This method can be extended to CH4-bearing inclusions, but the premise is that the bubble is large enough for pressure determination, allowing the collection of a good Raman signal for an accurate determination of the CH4 concentration in a NaCl solution at a specific temperature.

4. Application

After careful calibration, Raman spectroscopy can be applied to accurately measure the dissolved methane in the submarine hot hydrothermal vent and cold seep systems and also the concentration of methane in individual aqueous fluid inclusions. In this study, the calibration was applied to a set of H2O–CH4–NaCl ternary natural fluid inclusions in a quartz vein (Fig. 9).

4.1. Geological context and description of the samples

The samples came from Longmaxi Formation of the Jiaoshiba shale gas field, located in the Fuling District, Chongqing City. It is a part of the Jiaoshiba structure of the Baoying–Jiaoshiba Anticline in the Eastern Sichuan Fold Belt, located in the western part of the Qiyueshan fault (Guo et al., 2014b), and formed during periods of global transgression (Zhu et al., 2010; Slatt and O’Brien, 2011). The shale layer containing inclusions in quartz vein is found in Hirnantian (Upper Ordovician) and Rhuddanian (Lower Silurian). The lithology is mainly composed of dark carbonaceous shale and dark silty carbonaceous shale. Drilling results show that organic-matter-rich shales are common and vary in thickness from 80 to 120 m, with a current depth of 2300–2595 m (Guo et al., 2014b, Guo and Zhang, 2014; Gao et al., 2015). The shale gas is mainly composed of methane (97.22–98.47%). The homogenization temperatures of gas–liquid inclusions are concentrated in the range of 488 to 528 K, and the densities of the coexisting pure methane inclusions range from 0.254 to 0.290 g/cm3, reflecting the trapping pressures of 102.6–137.3 MPa. (Gao et al., 2015).

4.2. Determination of the NaCl concentration in aqueous fluid inclusions

As previously described, the Quantitative Factor PAR / mCH4 is a function of NaCl concentration and temperature. To accurately determine the CH4 concentration in a NaCl solution at a specific temperature, we first need to determine its salinity. The general approach used to determine the salinity of an aqueous solution is to use microthermometry to determine the ice-melting temperatures that relate salinity and freezing point depression (Bodnar, 1993, 2003). However, in some cases, this technique cannot be applied. For example, salinities of the aqueous phase estimated from ice-melting temperatures are higher than the actual salinity of the aqueous phase if ice melting occurs before the final dissolution of clathrate (Fall et al. 2011; Caumon et al. 2014); Fall et al. (2011) developed a technique to determine the salinity of CO2-bearing aqueous inclusions based on measured clathrate melting temperatures and CO2 pressures obtained from Raman analyses. This method can be extended to CH4-bearing inclusions, but the premise is that the bubble is large enough for pressure determination, allowing the collection of a good Raman signal for an accurate determination of the CH4 shift of the symmetric stretching vibration of water, has been developed as an alternative (Dubessy et al., 2002; Caumon et al., 2013) due to the interaction of solutes with water molecules through the solvation of ions, causing a modification of the structure of liquid water and, therefore, the vibrational spectra of the water molecules (Dubessy et al., 2002; Furič et al., 2000; Mernagh and Wilde, 1989; Georgiev et al., 1984; Walrafen, 1962). Caumon et al. (2013) used the fused-silica capillary capsule (FSCC) method to prepare synthetic fluid inclusions for calibrating the Raman signal of water toward chlorinity and found that the molalities (mol/kg H2O) of NaCl solutions in FSCCs, measured using LabRAM HR, are second-order polynomial fit functions of the Raman intensity ratio I3425/I3260 (the signal intensities at 3425 cm−1 and 3260 cm−1 are denoted as I3425 and I3260, respectively), laser radiation, and grating groove density. They noted that the Raman signal intensity is also influenced by the excitation radiation, the grating efficiency (which also depends on the excitation radiation), and possibly the CCD efficiency. Therefore, the Raman signal of water must be calibrated for each spectrometer for corresponding salt with various concentrations. The spectra of solutions of various NaCl concentrations (0, 0.62, 1.03, 2.00, 2.09, 3.00, 3.01, 4.50, 5.00, and 5.70 mol/kg H2O) acquired at 298.15 K were treated according to the data process of Caumon et al. (2013). The correlation
curve of $m\text{NaCl}$ (in molal scale) vs. $I_{3425}/I_{3260}$ is shown in Fig. 10, consistent with the five data sets of Caumon et al. (2013). The relation can be represented as Eq. (10). The precision of $m\text{NaCl}$ is ±0.1 mol/kg H$_2$O or ±0.4 mass% NaCl when the noise level of the Raman spectra is low (≤1%).

$$m\text{NaCl} = -0.116(I_{3425}/I_{3260})^2 + 5.805(I_{3425}/I_{3260}) - 6.933 \quad R^2 = 0.998$$

(10)

As shown in Fig. 9, the gas bubbles in inclusions “a–c” are large enough for pressure determination. When the inclusions were cooled to 243 K, inclusions “a” and “b” nucleated CH$_4$ clathrate and ice, but inclusion “c” did not nucleate CH$_4$ hydrate. Thus, both the clathrate melting method by Fall et al. (2011) and the Raman method by Caumon et al. (2014) were used to determine the NaCl concentrations of inclusions “a” and “b” for comparison, but only the Raman method by Caumon et al. (2014) was used for inclusions “c–f”. It was recognized that the birefringence of quartz, a common host for fluid inclusions, can influence the Raman OH stretching bands because the depolarization ratio of the OH-stretching massif of water in aqueous solution is not constant over this entire band and probably varies with the NaCl concentration (Dubessy et al., 2002; Baumgartner and Bakker, 2009). However, the polarization effects, due to the birefringence of quartz, can be treated by positioning the crystal at the extinction angle or by using an unpolarized laser radiation (Dubessy et al., 2002; Caumon et al., 2013). To avoid the deformation of the water band shape with crystal orientation, unpolarized laser radiation was used in this study. The Raman intensity ratios $I_{3425}/I_{3260}$ of the six natural inclusions determined at
298.15 K range from 1.263 to 1.341, and the calculated NaCl concentrations range from 0.21 to 0.64 mol/kg H2O (1.2 to 3.6 mass% NaCl) (Table 2). For the case of the clathrate melting method, we determined the pressures at the clathrate melting temperatures based on the Raman shifts of CH4 vapor in the inclusions and then used them along with the P–T–X data to calculate the NaCl concentration of the aqueous phase in the inclusions. Fig. 9g gives an example of Raman spectra of CH4 in inclusion “a”, showing the clathrate melting process. The clathrate dissociation temperatures (Td) of inclusions “a” and “b” were 292.5 and 291.2 K, respectively. The measured methane peak positions at the clathrate dissociation temperatures were corrected using the Ne lamp reference shifts and the following equation (Kim et al., 1986):

$$\nu_{\text{true}} - 2836.9888 = \frac{3008.1274 - 2836.9888}{N_2 - N_1}$$ (11)

where $\nu_{\text{true}}$ is the corrected wavenumber of the symmetric stretching bands and $\nu_1$ is the acquired wavenumber along with the Ne lamp reference. Then, the pressures of the methane inclusions could be calculated using the following equation (Wang et al., 2014):

$$P = -0.0148 \times D^2 - 0.1791 \times D^4 - 0.8479 \times D^3 - 1.765 \times D$$

(12)

where $D$ (cm$^{-1}$) is the difference between the measured peak position of methane in fluid inclusion ($\nu_{\text{true}}$) and the known peak position of methane near zero density ($\nu_0$) ($D = \nu_{\text{true}} - \nu_0$). The lab reference shift $\nu_0$ for our laboratory was 2917.849 cm$^{-1}$ (Wang et al., 2014). The calculated D were $-5.11$ cm$^{-1}$ and $-4.63$ cm$^{-1}$ for inclusions “a” and “b”, respectively, and the corresponding pressures (P) were 26.5 and 22.7 MPa (Table 2). Finally, the NaCl concentrations could be calculated from Td and P based on phase equilibria in the system CH4–NaCl–H2O according to Sun and Duan (2005). The NaCl concentrations of inclusions “a” and “b”, determined by using the clathrate melting method, were 0.57 and 0.63 mol/kg H2O, respectively, which are consistent with the results determined by using the Raman spectra of water (0.55 and 0.64 mol/kg H2O, respectively).

### 4.3. Determination of the CH4 concentration in aqueous fluid inclusions

The measurement of the amount of dissolved gas after homogenization is one of the ways to constrain the actual bulk composition of a fluid inclusion. Obviously, the effects of temperature and salinity on quantitative Raman spectroscopy measurements of dissolved CH4 cannot be neglected. For example, the QF of dissolved CH4 in pure water at 527 K is approximately 1.21 times that at 400 K, and if the QF at 400 K is well defined, then using QF at 400 K to calculate the methane concentration at 527 K without considering the temperature effect will yield an ~21% overestimation for fluid inclusions with low NaCl concentration. Thus, to accurately determine the CH4 concentration in individual NaCl aqueous inclusions, we not only need to obtain a high signal-to-noise ratio spectrum of aqueous inclusion at temperatures above the homogenization temperature, but we also need to find the accurate QF of the Raman system at these temperatures and NaCl concentrations.

The inclusions “a” and “b” decrepitated when heated to approximately 503 K due to high internal pressures. The homogenization (to liquid) temperatures of the other four inclusions were from 485 to 549 K (Table 2). To test the effect of temperature, the concentration of dissolved methane in each inclusion was measured at two temperatures; one is a few degrees above its homogenization temperature and the other is at 553 K (Table 2). The concentration of dissolved methane at each temperature was calculated with Eqs. (7), (7-1) and (7-2). Our results show that the differences of mCH4 determined at the two temperatures for each inclusion were less than 3%, indicating that our

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**Table 2**

Homogenization temperature (T$_h$), NaCl concentration (mNaCl), and CH4 molality (mCH4) of natural fluid inclusions (FI).

<table>
<thead>
<tr>
<th>FI</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T$_h$ (K)</td>
<td>D (cm$^{-1}$)</td>
<td>P (MPa)</td>
<td>mNaCl (mol/kg H2O)</td>
<td>I$<em>{3425}$/I$</em>{3260}$</td>
<td>mNaCl (mol/kg H2O)</td>
<td>T$_h$ (K)</td>
<td>mCH4 (mol/kg H2O)</td>
<td>mCH4 (mol/kg H2O)</td>
</tr>
<tr>
<td>a</td>
<td>292.5</td>
<td>-5.11</td>
<td>26.5</td>
<td>0.57</td>
<td>1.324</td>
<td>0.55</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>b</td>
<td>291.2</td>
<td>-4.63</td>
<td>22.7</td>
<td>0.63</td>
<td>1.341</td>
<td>0.64</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>c</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.316</td>
<td>0.51</td>
<td>540</td>
<td>0.66</td>
<td>0.65</td>
</tr>
<tr>
<td>d</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.274</td>
<td>0.28</td>
<td>485</td>
<td>0.56</td>
<td>0.57</td>
</tr>
<tr>
<td>e</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.263</td>
<td>0.21</td>
<td>539</td>
<td>0.99</td>
<td>1.00</td>
</tr>
<tr>
<td>f</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.293</td>
<td>0.38</td>
<td>546</td>
<td>0.92</td>
<td>0.94</td>
</tr>
</tbody>
</table>

1. T$_h$, clathrate dissociation temperature.
2. D (cm$^{-1}$) is the difference between the measured peak position of methane in fluid inclusion ($\nu_{\text{true}}$) and the known peak position of methane near zero density ($\nu_0$).
3. Pressure (P) in fluid inclusion at T$_h$, calculated from D according to Wang et al. (2014).
4. Calculated from T$_h$ and P according to Sun and Duan (2005).
5. Calculated from the Raman spectra of water at 298.15 K according to Eq. (7).
6. T$_h$, homogenization temperature in K.
7. Concentrations of dissolved CH4 in the inclusions measured at few degrees above the homogenization temperatures; (c) 538 K; (d) 493 K; (e) 543 K; (f) 548 K.
8. Concentrations of dissolved CH4 in the inclusions measured at 553 K.
calibration procedures can be used to accurately determine the dissolved CH$_4$ in aqueous fluid inclusions.

5. Conclusions
The effects of temperature and salinity on quantitative Raman spectroscopy measurements of dissolved CH$_4$ in a CH$_4$-NaCl-H$_2$O ternary system were studied at temperatures from 273.15 to 603.15 K, pressures from 10 to 120 MPa, and NaCl concentrations from 0 to 5 mol/kg H$_2$O. Our results show that the Quantitative Factor PAR / mCH$_4$ is both temperature- and NaCl concentration-dependent. It increases with temperature linearly from 273 to 603 K when the NaCl concentration is constant. The rate of increase of PAR / mCH$_4$ to temperature decreases with NaCl concentration.

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Appendix A. Supplementary data
Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.chemgeo.2015.09.018.

References
Brewer, P.G., Malby, E.G., Pasteris, J.D., White, S.N., 2010. Qualitative and quantitative analysis of CO$_2$ and CH$_4$ dissolved in water from 273.15 to 573.15 K and from 10 to 120 MPa Fluid Phase Equilib. 382, 70–79.
Ou, W., Peng, L., Lu, W., Guo, H., Qu, K., Mao, P., 2015. Quantitative Raman spectroscopic investigation of geo-fluids high-pressure phase equilibria: part II. Accurate determination of CH$_4$ solubility in water from 273 to 603 K and from 5 to 140 MPa and refining the parameters of the thermodynamic model. Fluid Phase Equilib. 391, 18–30.
Wang, M., Lu, W., Li, L., Qiao, S., 2014. Pressure and temperature dependence of the Raman peak intensity ratio of asymmetric stretching vibration (v$_3$) and asymmetric bending overtone (2v$_1$) of methane. Appl. Spectrosc. 68 (5), 536–540.