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Quantitative measurement of the concentration of sodium carbonate in the system of Na_2CO_3–H_2O by Raman spectroscopy

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ABSTRACT

Na_2CO_3 concentrations in three Na_2CO_3–H_2O systems($1.5\ mol \cdot L^{-1}$, $2.0\ mol \cdot L^{-1}$, and $2.5\ mol \cdot L^{-1}$) were studied by in situ Laser Raman scattering spectra in a moissanite anvil cell in order to develop a procedure to quantify the concentration of carbonate ion in fluid inclusion in bulk minerals. The relative concentration was obtained by the ratio of the Raman intensity of carbonate ion to that of water. The result shows that there is significant correlation between the ratios of Raman intensity and the concentrations, and the CO_3^{2-} concentration in Na_2CO_3–H_2O aqueous solution can be determined by the Raman intensity according to the equation $c(Na_2CO_3) = 426R_S/(87.3R_S + 1)$. $R_S = S(Na_2CO_3)/S(H_2O)$. Comparing with previous methods, it is a rapid and reliable one for determining the concentration of the sodium carbonate solution in Na_2CO_3–H_2O systems and in micro samples, such as those in fluid inclusions and in diamond anvil cells.

1. Introduction

The composition of fluid inclusion is of significance for understanding the genesis of minerals and the fluid evolution in Earth crust and upper mantle. However, it is not easy to determine with satisfactory accuracy the compositions of single fluid inclusions because of their small size. The common methods to determine the composition in fluid inclusions are crack extraction or direct extraction from a single fluid inclusion in bulk minerals. The former one is that the bulk mineral with fluid inclusion is cracked by heating the mineral to a higher temperature to obtain the volatile samples, which can be measured by quadrupole mass spectrometer or gas chromatography. The soluble substances in fluid inclusion can also be extracted by deionized water for further analysis. This method is only suitable for obtaining an average composition for large quantity of fluid inclusions and often inevitably introduces impurities that cause unpredictable error. The latter one resorts to laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), whose high accuracy, high sensitive and low detection limit is a prerequisite for high-quality analysis. One limitation of the method is its 20% error from impurities in main fluid inclusion and its internal standard—salinity—obtained by heating–cooling stage, which is not very exact. Another limitation is that the error will increase when the sample is too small (Sun and Zeng, 2000; Lu et al., 2004).

Carbonate widely exists in crust and upper mantle. Carbonate ion and carbon-bearing substances are important components in the hydrothermal fluids. It is important to study their behavior at the *T*–*P* condition of upper mantle and some scholars carried out related experiments under high pressure and high temperature. Davis studied the species in CO_2–H_2O system by Raman and infrared spectra (Davis and Oliver, 1972). Martinez et al. (2004) studied two aqueous solutions of sodium carbonate by in situ Raman spectroscopy in 1–30 GPa, 25–400 °C *P*–*T* range in DAC. One-molar solution of potassium carbonate was investigated by Raman spectroscopy from 22 to 550 °C and 1 to 2 kb (Frantz, 1998).

Since the fluid inclusion must be destroyed by both methods, it is necessary to find a new non-destructive method for measurement. Microscopic Laser Raman Spectrum technique has provided a potential way to solve the aforementioned problem. For example, Chou and Burruss (2002) used Raman spectroscopic method to determine the solubility of methane in water at room temperature and from 0.5 to 68 MPa. Liu et al (2004) measured the percentage of gas components of synthetic carbonate fluid inclusions by Laser Raman quantitative factorial formula; Wu et al (2007) used water as an internal standard to measure the concentrations of glucose solutions by the intensity of Raman peak. However, their strategy requires the establishment of a working curve for every experiment. Furthermore, an accurate result is unattainable for solutions with high concentration that fall beyond the linear portion of the working curve. Zhang et al (2006) also employed water as an internal standard to

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calibrate semi-quantitative working curves for measuring the concentration of anions, by the integrated area of Raman peak at −170 °C. Recently, we investigated the relationship between the Raman peak and the concentration of carbonate ions in sodium carbonate aqueous solution. This paper is the report of the study.

2. Experimental methods

Even at ambient temperature, fluid inclusions have a variable internal pressure. In order to observe the influence of pressure on the measuring accuracy, moissanite anvil cell (MAC) was employed as the sample chamber. The gasket is stainless steel foil with 0.5 mm thickness and a hole 300 μm in diameter. Three different concentrations of solution samples, which were fixed into volumetric flasks of 50 mL, are prepared to be measured and listed in Table 1.

The internal pressure of the system is determined by the relationship between the pressure and the Raman shift of quartz (Schmidt and Ziemann, 2000):

$$p(\mathrm{MPa}) = 0.36079 \times \left(\Delta\nu_p\right)^2_{464} + 110.86 \times \left(\Delta\nu_p\right)_{464} \tag{1}$$

where $(\Delta\nu_p)_{464}$ is the difference of Raman shift at high pressure and 20 °C relative to that ($464\ \mathrm{cm}^{-1}$) at ambient temperature and pressure ($0<(\Delta\nu_{464})\leq 20\ \mathrm{cm}^{-1}$). The pressure determined by this method has an uncertainty of ±50 MPa.

The Raman spectra are collected by a Raman microspectrometer (Renishaw system RM-1000, Renishaw Group, Gloucestershire, United Kingdom). The excitation wavelength is a 514.5 nm line of an argon ion laser operated at 20 mW. The slit width is 50 μm. The objective is a Leitz 20× with a long working distance. Collection times for Raman spectra are one accumulation of 10 s each, and the range of wavenumber region is 200–4000 cm^{-1}. The corresponding spectral resolution is $\pm 1\ \mathrm{cm}^{-1}$. All of the measurements are performed at ambient temperature (~22 °C).

After the quartz grain and solution sample were loaded into the sample chamber, the Raman spectra of quartz and the aqueous solution were measured respectively. During the measurement, we allowed a three-minute interval after the force on the sample was increased before measuring the Raman spectra in order to keep the sample in an equilibrium state. The parameters of the peaks were fit by Peakfit4 software.

3. Result and discussion

The Raman spectra (Fig. 1) of carbonate ion were collected from 200 to 4000 cm^{-1}. It can be seen that there is a single observable Raman band at 1066 cm^{-1}, which is assigned to the symmetric stretching mode of carbonate ions (Oliver and Davis, 1973), and an envelope band from 3000 to 3700 cm^{-1} which is assigned to H–O vibration in the water molecule (Walrafen, 1964, 1967).

Intensity of Raman band is proportional to the amount of molecules or ions and it may theoretically serve as a plausible parameter for quantitatively determining their concentrations. However, the effect of any fluctuation in the laser position and intensity, the time of scanning, scattering cross sections of the sample would cause unpredictable variations of Raman intensity, which would render it unreliable and therefore unsuitable as a quantitative descriptor of concentration.

Table 1
The concentrations of the experiment samples.

	1	2	3
Na2CO3/g	7.95	10.63	13.18
[Na2CO3]/mol L^{-1}	1.50	2.006	2.487

For two Raman active species *a* and *b* in a fluid phase, relative concentrations *C* (e.g., molar or mol%) are related to their Raman peak areas (Wopenka and Pasteris, 1986) *S* which could be expressed by:

$$S_a / S_b = (C_a / C_b)(\sigma_a / \sigma_b)(\eta_a / \eta_b) = (C_a / C_b)(F_a / F_b) \tag{2}$$

where σ, η, and *F* are the Raman scattering cross-section, instrumental efficiency, and Raman quantification factor, respectively. This approach has been successfully applied to a CH_4–H_2O system in aqueous solution (Lu et al., 2006, 2008).

Sodium chloride in inclusions was used as an internal standard to measure the fluid composition by LA-ICP-MS. The sodium chloride concentration is determined from the freezing temperature (Lu et al., 2004). However, determining the salinity would cause error when setting sodium chloride as the internal standard. In this study, we used water as the internal standard for Raman analysis, because the ratio of water and carbonate ions will not be changed by the influence mentioned above (Zhang et al., 2006).

The fitted and calculated results are listed in Tables 2, 3 and 4. Fig. 2 is a diagram of the ratios of R_S versus pressure. It can be seen that the ratio becomes large as the pressure increases, indicating that the pressure would influence the ratios. It can also been seen that for higher concentration solution the pressure has greater affect on the ratio R_S. By comparison, the relative error of the ratio is more than 20% within the pressure condition.

Since the internal pressures in fluid inclusions are lower, it is reasonable to have the ratios at lower pressure or zero pressure (Kawakami et al., 2003; Kagi et al., 2006). In this study, the values of intercepts of the fitted straight line were taken as the parameter R_S. In addition, the components in fluid inclusion are generally measured at ambient pressure.

For the Na_2CO_3–H_2O system, there are two variables, the amounts of sodium carbonate ion and the water molecule. The molar concentration of water is 55.4 mol L^{-1} at ambient pressure and 22 °C. The molar concentration of water would decrease as the concentration of sodium carbonate increases, which will cause the Raman intensity of carbonate ions to increase and that of water to decrease. Obviously, the relationship between R_S and the concentration of sodium carbonate would not be linear and could be described by

$$c(H_2O) = 55.4 - a \times c(Na_2CO_3) \tag{3}$$

and R_S can be deduced from Eq. (2)

$$R_S = \frac{c(Na_2CO_3)}{c(H_2O)} \times \frac{F(Na_2CO_3)}{F(H_2O)} = b \times \frac{c(Na_2CO_3)}{55.4 - a \times c(Na_2CO_3)}. \tag{4}$$

The data fitting is by following the equation:

$$y = \frac{x}{A + Bx}. \tag{5}$$

For pure water, the parameter R_S is equal to zero since Raman peak area of sodium carbonate is zero. Now we can fit four set data to Eq. (5) by the software OriginLab7.5. The result is shown in Fig. 3 and the equation is expressed as follows:

$$R_S = \frac{c(Na_2CO_3)}{426 - 87.3c(Na_2CO_3)} = 0.130 \times \frac{c(Na_2CO_3)}{55.4 - 11.4c(Na_2CO_3)}, r = 0.9996. \tag{6}$$

The high correlation coefficient indicates that the measured data is well consistent with the theoretical model. The concentration of sodium carbonate solution could be calculated by

$$c(Na_2CO_3) = 426R_S / (87.3R_S + 1). \tag{7}$$