Determination of pressure in aqueo-carbonic fluid inclusions at high temperatures from measured Raman frequency shifts of CO$_2$

XUEYIN YUAN$^{1,2}$, ROBERT A. MAYANOVIC$^3$, HAIFEI ZHENG$^{1,*}$, AND QIANG SUN$^1$

$^1$Key Laboratory of Orogenic Belts and Crustal Evolution, Ministry of Education, Peking University, Beijing 100871, China
$^2$MLR Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing 100037, China
$^3$Department of Physics, Astronomy and Material Science, Missouri State University, Springfield, Missouri 65897, U.S.A.

ABSTRACT

Due to the presence of additional volatiles and/or electrolytes in CO$_2$-H$_2$O fluids, the total pressure of many natural aqueo-carbonic fluid inclusions at high temperatures as determined using microthermometry is usually made with considerable uncertainty. In this paper, we present the results of our high $P$-$T$ in situ Raman scattering study of high-density aqueo-carbonic fluids, with and without a small amount of CH$_4$ and NaCl, whose objective is to derive a new method for pressure determination in aqueo-carbonic fluid inclusions at high temperatures. The measurement of the Fermi dyad bands at temperatures up to 400 °C and pressures up to 1200 MPa is described. The manner in which the frequency shifts and intensity of Raman bands are governed by pressure, temperature, presence of CH$_4$ in carbonic and NaCl in aqueous fluids is discussed. From the monotonic dependence of the frequency shifts of the lower Fermi dyad band $\nu_v$ and the Fermi resonant splitting $D$ ($D = \nu_v - \nu_r$) with pressure and temperature, the pressure (in MPa) in aqueo-carbonic fluid inclusions at elevated temperatures can be determined directly by using the following two polynomial equations:

\[ P \text{ (MPa)} = -16 + 1.232 \times T - 53.72 \times (\Delta \nu_v) - 1.83 \times 10^3 \times T^2 + 24.46 \times (\Delta \nu_v)^2 - 0.292 \times T \times (\Delta \nu_v), \]
\[ P \text{ (MPa)} = -26 + 1.501 \times T + 193.24 \times (\Delta D) - 1.61 \times 10^3 \times T^2 + 5.436 \times (\Delta D)^2 + 0.158 \times T \times (\Delta D), \]

where $T$ is in °C, $\Delta \nu_v$ and $\Delta D$ represent frequency shifts (in cm$^{-1}$) of the lower band and the resonant splitting relative to the reference values measured at 23 °C and 6 MPa, respectively. Based on the attainable accuracy of the fitted peak positions and the results from fitting of Raman frequency shifts’ dependence with pressure and temperature, the uncertainty in pressure determination is about 50 MPa for pressures determined from $\nu_v$ and 40 MPa from that determined from $D$.

Keywords: CO$_2$, Raman spectroscopy, pressure determination, HDAC, fluid inclusion

INTRODUCTION

Fluid inclusions containing H$_2$O-CO$_2$ fluids (aqueo-carbonic fluid inclusions) are very common and are often the dominant fluid inclusion type occurring in hydrothermal and medium- to high-grade metamorphic deposits (Chi et al. 2006; Lowenstern 2001; Mumm et al. 1997; Phillips and Evans 2004; Thomas and Spooner 1992; Tsunogae et al. 2002; Williams-Jones and Ferreira 1989; Xu and Pollard 1999). Determining the pressure of aqueo-carbonic fluid inclusions is of great significance both in understanding their thermodynamic properties and in constraining the depth of fluid activity and mineralization leading to trapping of the fluid inclusions. Presently, the principal method of estimating the pressure in aqueo-carbonic fluid inclusions is by microthermometry, which is based on measurements of two phase transition temperatures during heating (the liquid-vapor CO$_2$ homogenization temperature and the homogenization temperature of the immiscible-to-miscible aqueous and carbonic phase transition) and use of the known $P$-$V$-$T$-$x$ properties of the H$_2$O-CO$_2$ binary system (Bakker and Diamond 2000; Diamond 1996, 2001; Hurai 2010; Mao et al. 2009). However, due to the presence of additional volatiles in the carbonic or electrolytes in the aqueous phase in natural fluid inclusions (Berkesi et al. 2009; Bersani et al. 2009; Giorgetti et al. 1996; Li et al. 2014; Peng et al. 2014; Saltvioli-Mariani et al. 2015; Thomas et al. 1990; Wang et al. 2013; Zhu and Peng 2015), the phase transition temperatures in these aqueo-carbonic fluid inclusions could be apparently different from those of the H$_2$O-CO$_2$ binary system (Akinfiev and Diamond 2010; Aranovich et al. 2010; Hurai 2010; Mao et al. 2013; Shmulovich and Graham 1999, 2004; Thomas et al. 1990). In these cases, considerable errors in pressure estimation using microthermometry can occur.

The Raman vibrational modes of CO$_2$ have been measured and interpreted (Gordon and McCubbin 1966; Rosso and Bodnar 1995; Stojickeff 1958), and based on the experiments that were made in investigating the effects of temperature, pressure, or density on CO$_2$ Raman peaks (Fig. 1), the characteristic Fermi dyad bands ($\nu_v$ and $\nu_r$) shift to lower frequencies, the resonant splitting

* E-mail: hfhzheng@pku.edu.cn