Pressure dependence of micro-Raman mass spectrometry for carbon isotopic composition of carbon dioxide fluid

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Micro-Raman spectroscopy can find the carbon isotopic ratio of CO_2 fluid from the ratio of intensity or area of a $^{13}CO_2$ peak to that of a $^{12}CO_2$ peak. We exam- ined the precisions of carbon isotopic ratios (δ^{13} C) of CO_2 at constant room temperature and pressure of 10–150 MPa. Measurement of the intensity ratio has precision of 2.8–8.7‰, which is better than that of the area ratio of 4.5–14.7‰. We also investigated the pressure dependence of the Raman inten- sity ratios and area ratio by changing fluid pressure. When changing fluid pres- sure from 10 to 150 MPa, the ratios of intensity and area both show negative correlation with fluid pressure (CO_2 density). Pressures of two types affect the Raman spectrum of CO_2 peaks, affecting the peak position and peak shape. To evaluate effects on the peak position, we repeatedly measured the intensity ratio at constant CO_2 pressure (10 MPa) with movement of the grating center position, which is defined as the center value of the analyzed wave number range. Although we moved the grating center position from 1248.5 to 1251.5 cm^{-1}, no significant correlation was observed for either ratio of inten- sity or area. The pressure effect on the ratios can be corrected by ascertaining the CO2 pressure. Combination with the Raman spectroscopic barometry for CO_2 enables analyses of δ^{13}C of CO_2 respectively using the intensity ratio and the area ratio of CO_2 Raman peaks within 8.7 and 14.7‰.

Keywords: carbon isotope ratio, Micro-Raman spectroscopy, CO2 fluid, fluid inclusion

