

Quantification of dissolved CO₂ in silicate glasses using micro-Raman spectroscopy

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ABSTRACT

This study investigates the potential use of confocal micro-Raman spectroscopy for the quantification of CO₂ in geologically relevant glass compositions. A calibration is developed using a wide range of both natural and synthetic glasses that have CO₂ dissolved as carbonate (CO₃²⁻) in the concentration range from 0.2 to 16 wt%. Spectra were acquired in the 200 and 1350 cm⁻¹ frequency region that includes the ν₁ Raman active vibration for carbonate at 1062–1092 cm⁻¹ and the intensity of this peak is compared to various other peaks representing the aluminosilicate glass structure. The most precise and accurate calibration is found when carbonate peaks are compared to aluminosilicate spectral features in the high-frequency region (HF: 700–1200 cm⁻¹), which can be simulated with several Gaussian peaks, directly related to different structural species in the glass. In some samples the “dissolved” CO₃²⁻ appears to have two different Raman bands, one sharper than the other. This may be consistent with previous suggestions that CO₃²⁻ has several structural environments in the glass, and is not related to any precipitation of crystalline carbonate from the melt during quenching. The calibration derived using the HF peaks appears linear for both the full range of glass composition considered and the range of CO₂ concentrations, even when multiple carbonate peaks are involved. We propose the following, compositionally independent linear equation to quantify the CO₂ content in glass with micro-Raman spectroscopy

$$\text{wt\% CO}_2 = 15.17 \times \text{CO}_3/\text{HF}$$

where CO₃/HF is the area ratio of the fitted ν₁ carbonate peak(s) at 1062–1092 cm⁻¹ to the remaining area of the fitted aluminosilicate envelope from 700–1200 cm⁻¹. This is similar to the Raman calibration developed for water, but is complicated by the overlapping of these two fitted components. Using error propagation, we propose the calibration accuracy is better than ±0.4 wt% CO₂ for our data set.

The ν₁ Raman peak position for carbonate is not constant and appears to be correlated with the density of the melt (or glass) in some way rather than the chemical composition.

Keywords: Raman spectroscopy, CO₂ content, silicate glass, melt density, CO₃ molecules Raman shift