American Mineralogist, Volume 108, pages 1346–1356, 2023

CO_2 quantification in silicate glasses using µ-ATR FTIR spectroscopy

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Abstract

A new method for measurements of high-CO_2 concentrations in silicate glasses was established using micro–attenuated total reflectance (µ-ATR) Fourier transform infrared (FTIR) spectroscopy in the mid-IR (MIR) region. We studied two glass/melt compositions, namely leucitite and granite, to cover samples in which CO_2 is dissolved as carbonate ions (CO_3^{2-}) or as CO_2 molecules (CO_2^{mol}). In the leucitite glasses a carbonate absorption doublet with maxima at 1510 and 1430 cm^{-1} has shown to clearly separate from aluminosilicate lattice vibrations at lower wavenumbers. Due to the lower sensitivity of the µ-ATR method, we were able to measure high-CO_2 contents (c_{CO_2} >0.5 wt%) in experimental silicate glasses that would only be measurable with great difficulties using established transmission MIR measurements due to detector linearity limit effects even with very thin sample wafers. The peak heights of the 1430 cm^{-1} ATR band (A_{1430}), normalized to the integral of the *T*-O lattice vibrations (T = Si, Al, Fe) at about 930 cm^{-1} (Int_{930}) show a linear trend with CO_2 contents in the range 0.2–4.3 wt%, yielding a linear correlation with c_{CO_2} (wt%) = 0.4394 ± 0.006·A_{1430}·10000/Int_{930}. The normalization of the CO_2 related band to a lattice vibration accounts for variations in the quality of contact between ATR crystal and sample, which has a direct effect on signal intensity.

In granitic glasses, where CO_2 is dissolved as CO_2^{mol} only, the asymmetric stretching vibration at 2350 cm^{-1} overlaps with the signal of atmospheric, gaseous CO_2. As the ATR signal of dissolved CO_2 is very weak, the atmospheric signal may dominate the spectrum. Since the absorbance spectrum is calculated by division of the single-channel sample spectrum by a single-channel reference spectrum measured in air, keeping the laboratory and spectrometer atmosphere as constant as possible during spectral acquisition can resolve the problem. Nonetheless, a procedure to subtract the signal of remaining atmospheric CO_2 may still be required for the spectral evaluation. We studied a series of 5 granitic glasses with CO_2^{mol} contents of 0.08 to 0.27 wt% and found an excellent linear relation between CO_2 concentration and lattice vibration normalized ATR intensity of the 2350 cm^{-1} band: c_{CO_2} (wt%) = 0.2632 ± 0.0016·A_{2350}·10000/Int_{990}. Although the CO_2^{mol} concentrations in our granitic glass series can still be analyzed without major difficulties by conventional transmission IR spectroscopy, our data demonstrate the potential of the ATR method for samples with higher CO_2 contents or for samples where a high spatial resolution is required (melt inclusions, vesicular or partially crystallized glasses). The lower limits of the ATR method are approximately 0.2 wt% CO_2 dissolved as carbonate groups or 0.1 wt% CO_2 (or slightly less) dissolved in molecular form.

Keywords: ATR-micro spectroscopy, ATR FTIR, silicate glasses, carbon dioxide, CO_2 quantification, CO_2