CO₂ quantification in silicate glasses using µ-ATR FTIR spectroscopy

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Abstract

A new method for measurements of high-CO₂ 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 CO₂ is dissolved as carbonate ions (CO₃²⁻) or as CO₂ molecules (CO₂⁰). In the leucitites a carbon 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-CO₂ contents (c_CO₂ >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 (A₁₄₃₀), normalized to the integral of the T-O lattice vibrations (T=Si, Al, Fe) at about 930 cm⁻¹ (Int₉₃₀) show a linear trend with CO₂ contents in the range 0.2–4.3 wt%, yielding a linear correlation with c_CO₂ (wt%) = 0.4394 ± 0.006·A₁₄₃₀·10000/Int₉₃₀. The normalization of the CO₂ 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 CO₂ is dissolved as CO₂⁰ only, the asymmetric stretching vibration at 2350 cm⁻¹ overlaps with the signal of atmospheric, gaseous CO₂. As the ATR signal of dissolved CO₂ 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 CO₂ may still be required for the spectral evaluation. We studied a series of 5 granitic glasses with CO₂⁰ contents of 0.08 to 0.27 wt% and found an excellent linear relation between CO₂ concentration and lattice vibration normalized ATR intensity of the 2350 cm⁻¹ band: c_CO₂ (wt%) = 0.2632 ± 0.0016·A₂₃₅₀·10000/Int₉₃₀. Although the CO₂⁰ 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 CO₂ 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% CO₂ dissolved as carbonate groups or 0.1 wt% CO₂ (or slightly less) dissolved in molecular form.

Keywords: ATR-micro spectroscopy, ATR FTIR, silicate glasses, carbon dioxide, CO₂ quantification, CO₂

Introduction

Besides water, carbon dioxide is the second most abundant volatile in magmatic systems (e.g., Anderson 1975; Symonds et al. 1994; Johnson et al. 1994). Silicate melts play a fundamental role in transporting carbon from the Earth’s interior to its surface. However, in most silicate melts CO₂ solubility is one to two orders of magnitude lower than the solubility of water under equivalent conditions (e.g., Mysen et al. 1976; Blank et al. 1993; Holloway and Blank 1994; King and Holloway 2002; Lesne et al. 2011a, 2011b; Iacono-Marziano et al. 2012; Shishkina et al. 2014; Fanara et al. 2015; Schanofski et al. 2019). Several analytical methods exist to quantify CO₂ concentration in silicate glasses: Infrared and Raman spectroscopy, elemental carbon analysis and secondary ion mass spectrometry.

The most frequently used spectroscopic method to analyze CO₂ concentration in silicate glasses is Fourier-transform infrared (FTIR) spectroscopy (see Ni and Kepler 2013, for review and references). It is a vibrational spectroscopic technique recording the interaction of electromagnetic radiation with structural units at the molecular level, more specifically, the absorption of the infrared radiation. In the case of silicate glasses, the asymmetric stretching vibrations of CO₂ dissolved in the molecular form (CO₂⁰) and as carbonate groups (CO₃²⁻) are well separated from the absorbance bands of the glass matrix (e.g., Mysen et al. 1976; Fine and Stolper 1985; Blank and Brooker 1994). The quantification of CO₂⁰ and CO₃²⁻ is done by correlating the baseline subtracted absorbance (measured in transmission on doubly polished sections with known thickness) to the concentration using the Lambert-Beer law. This method however requires a calibration by an independent ab-