Use of attenuated total reflectance (ATR) FTIR spectroscopy to measure H2O and CO2 in silicate glass

Jacob B Lowenstern, Bradley W Pitcher

U.S. Geological Survey, United States

E-mail: jlwnstrn@usgs.gov

Petrologists have long sought simple, rapid, and inexpensive techniques to quantify the amounts of H_2O and CO_2 dissolved in volatile-bearing silicate melts. We recently developed a calibration for Attenuated Total Reflectance (ATR) micro-FTIR that requires only a singly polished sample and applies to compositions ranging from basalt to rhyolite. A Ge ATR accessory makes direct contact with the sample to measure evanescent wave absorption within the hydrous glass. Absorbance at 3450 and 1630 cm^{-1} showed high correlation (r^2 = 0.98) with measured H_2O concentration in the glasses as determined by manometry and transmission FTIR spectroscopy. The calibration permits determination of H_2O concentration in singly polished glass samples with spot size down to 15 micrometers (for H_2O-rich samples) and detection limits of 0.1 wt.% H_2O. Accuracy is 6% relative at 1 wt.% H_2O and 3% relative at 6 wt.% H_2O (one sigma). Precision based on replicate analyses is similar. Results for basaltic and basaltic andesite glasses of known H_2O concentrations fall along a density-adjusted calibration, indicating that ATR spectra are relatively insensitive to glass composition. The technique can also be used to quantify dissolved carbonate in basalts with >100 ppm CO_2. We are still evaluating whether quantification of dissolved CO_2 in rhyolite (2350 cm^{-1}) is feasible.

The ATR micro-FTIR technique is less sensitive than transmission FTIR, but requires only a singly polished sample for quantitative results, thus minimizing time for sample preparation. Compared with specular reflectance, it is more sensitive and better suited for imaging of H_2O variations in heterogeneous samples such as melt inclusions. One drawback is that the technique can damage fragile samples and we therefore recommend mounting of unknowns in epoxy prior to polishing. Our calibration should hold for any Ge ATR crystals with the same incident angle (31°). Use of a different crystal type or geometry would require measurement of several H_2O-bearing standard glasses to provide a crystal-specific calibration.