A new reflectance IR spectroscopy method for analyzing H_2O in rhyolitic to basaltic glasses

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To model volatile processes in magma chamber processes and apply 'geospeedometers' it is necessary to measure volatile species in glasses. Fourier Transform infrared (IR) spectroscopy provides information on the volatile species in glasses such as OH^- and molecular H_2O. Transmission IR (T-IR) is used; however it is difficult to prepare the thin samples required for melt inclusion analysis. Also, to obtain quantitative data with T-IR it is necessary to use extinction coefficients that have large errors; likely due to the fact that glasses used in calibrations were prepared at different pressures and temperatures. Standard reflectance IR (R-IR) has large uncertainties associated with the baseline position and no calibrations are available for H_2O in basalt.

We have calibrated a new method for R-IR using the Kramers-Kronig (KK) algorithm. The raw R-IR data (5400 - 650 cm^{-1}) was smoothed to a ~40.5 cm^{-1} window before calculating a KK-absorbance (KK-Abs.) spectrum that corrects for optical dispersion effects due to a specular component. The KK-Abs. was measured from a linear baseline ($1\sigma < 5\%$ for 3-4 replicates on samples with > 1 wt. % total H_2O), and the ~3550 cm^{-1} band KK-Abs. = 0.045 units for total H_2O wt.% = 6.7 wt.%. The total H_2O wt.% = m * (3550 cm^{-1} band KK-Abs.), where m changes as a function of composition. The following are compositions/m/r^2 of the fit: rhyolite/204/0.99; Mascota andesite/156/0.99; Mt. Hood andesite/154/0.93; and basalt/125±15/0.92. Samples with compositions slightly different from our calibration standards will only have a small error in H_2O_{total} wt.%, but errors increase in glasses with total H_2O < ~1 wt.% ($1\sigma <$ 20%), suggesting a minimum detection limit. For andesite glasses we found the following relation: molecular H_2O=417*(1635 cm^{-1} KK-Abs.), r^2=0.88.

We are investigating depth of penetration issues with R-IR because doubly-polished andesite glasses <~100 μm thick produce mixed reflectance-transmission spectra.

In addition to variations in the bands associated with H-O species, the Si-O band widths vary as a function of H_2O content due to modification of the Si-O network and these variations may influence estimates of glass composition with remote sensing data.

Experimental determination of hydrogen partitioning between melts and nominally anhydrous minerals: Consequences for melting and H storage capacity in the upper mantle

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The small amounts of H dissolved in nominally anhydrous mantle minerals (NAMMs) have significant influence on the melting behavior of the mantle. Unfortunately, direct experiments determining the effect of H in NAMMs on the peridotite solidus temperature are intractable and thermodynamic calculations are impeded by a lack of available calibration data. However, mineral/melt partition coefficients can be used to model the effect of H on the peridotite solidus using a cryoscopic approximation. Recent determinations of H partitioning between NAMMs and silicate melt by newly developed low blank SIMS techniques (Koga et al., 2003; Aubaud et al., 2004) yield a bulk $D^{peridotite/melt}$ of 0.009, consistent with estimates based on analogies to LREE in oceanic basalts (e.g., Michael, 1988). Tests of the cryoscopic approximation in simple systems (forsterite-H_2O, enstatite-H_2O, diopside-H_2O) reproduce melting behavior for modest amounts of H_2O (<10 wt.%) in the liquid. Applied to peridotite, this approach indicates that 50–200 ppm H_2O causes melting beneath ridges 5–20 km deeper than intersection with the dry peridotite solidus. Beneath plumes, where the H_2O content may be 500–1000 ppm, the predicted increase is 60–100 km.

The H storage capacity is the maximum H that can be stored in solid peridotite at a given T and P without stabilization of a hydrous fluid or melt. Solubility measurements of individual NAMMs provide some evidence of peridotite storage capacities, but a critical additional constraint is equilibrium partitioning of H between coexisting peridotitic minerals. Experiments indicate values of $D^{pyx/ol}$ of ~10±1 (n=6) at modest pressure (1–2 GPa). Combined with solubility measurements of H in olivine (Kohlstedt et al. 1996; increased by 3 X: Bell et al., 2003, Koga et al., 2003), this suggests that the storage capacity of H_2O in the upper mantle is at least 0.4 wt.% at 410 km. This challenges the view that the storage capacity of the upper mantle is small and that hydrous material advected from the transition zone will likely melt.