



Measurement of volatile concentrations in volcanic glasses using thermogravimetric analysis: comparison with micro-analytical methods

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Thermogravimetric analysis-mass spectrometry (TGA-MS) is potentially a powerful tool for measurement of multi-species volatile concentrations in volcanic rock samples and characterisation of degassing patterns that relate to volatile speciation. Simultaneous differential scanning calorimetry (DSC) provides information on thermal transformations such as crystallisation or melting. However no study has addressed whether the TGA technique can be used to quantify water speciation or separate water from other volatile species such as halogens.

We have carried out TGA-DSC-MS experiments on a suite of compositionally homogeneous, variably-degassed rhyolitic obsidian samples from Blahnukur, Torfajökull, Iceland[1]. Sample water contents, as measured by infrared spectroscopy, range from 0.19–0.81 wt %; F and Cl concentrations, measured using electron microprobe, range from 0.26–0.35 and 0.18–0.22 wt % respectively. Other volatile species concentrations (e.g. CO₂, S) were beneath detection limits. The TGA results show an excellent correlation between the total volatile content measured using TGA (TVC_{TGA}) and the total volatile content ($H_2O_T + F + Cl$) measured by other techniques ($TVC_{TGA} = 0.992TVC_{FTIR,EPMA}$, with $R^2 = 0.94$). This shows that both water and halogen species are degassed during TGA measurements, even though halogen species are not detected through MS analyses.

Patterns of volatile release indicate a link between water speciation, as measured using FTIR, and the temperature of degassing, and allow identification of hydrated samples. There are strong correlations between TGA weight loss over the 250–550 °C interval and $[H_2O_m]$ concentration, and between weight loss >550 °C and the OH^- content. The total volatile loss above 550 °C far exceeds OH^- concentrations alone ($TGA_{>550} = 1.9126 [\text{OH}^-] + 0.1693$), but closely matches the sum of OH^- , F and Cl in glasses, with $TGA_{>550} = 1.02 [\text{OH}^- + F + Cl]$. This indicates that halogen release occurs at high temperatures and accompanies OH^- degassing. Simple models of diffusive degassing of powdered TGA samples corroborate the measured dTG profiles and illustrate that high-T temperature degassing (>1000 °C) cannot be dominated by water species. The temperature of maximum degassing rate (dTGA peak) consistently occurs ~ 10 °C higher than the onset of an endotherm attributed to melting. This indicates that melting and the onset of volatile advection play an important role in controlling the rate of volatile release, together with temperature-dependent diffusivity.

The results show that TGA indeed provides useful quantitative and qualitative information about the concentration and speciation of volatiles in volcanic glasses. However independent measurement of halogen concentrations is essential, especially for degassed samples, where the concentration of halogen species may greatly exceed that of water.

[1] Owen, J. et al, Bull. Volcanol., in revision.