## Laboratory TIR Emission Spectroscopy of Silicic Melts

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### Introduction

Silicic glass is ubiquitous in volcanic environments, and is known to affect TIR remote sensing data. Glasses display similar TIR spectral features regardless of composition, making them difficult to distinguish spectrally [3,4], and their features vary with physical state [1,2]. To quantify these spectral changes, and provide calibrated laboratory melt data, a custom-built micro-furnace has been developed for use with a Nexus 670 FTIR spectrometer. It has been used to collect the very first *in-situ* laboratory TIR emissivity spectra of actively melting/cooling rhyolitic to dacitic compositions.

#### Methods

Absolute emissivity spectra were acquired using an empty Ptlined furnace cavity as the blackbody calibration source. Crushed synthesized glass (1 to 2g) was placed into Pt crucibles in the micro-furnace. Emissivity spectra were acquired in 100°C intervals to the melting point temperature (MPT). To mimic the cooling behavior of lava, data were also acquired at 100°C intervals as the melt cooled. Spectra of seven glasses were taken at 20°C intervals from MPT to ~1100°C, to determine the approximate glass transition (Tg).

#### **Results and Conclusions**

Changes in the position, depth and spectral morphology of the absorption band with physical state have been quantified. Significant findings include a reduction in average melt emissivity, and identification of  $\sim$  Tg. Preliminary results show this approach is applicable to melt petrology and could be used with remote sensing data to better characterize and map glassy volcanic environments.



Figure 1: Glass emissivity spectra from 700C to 1100C, showing changes in spectral morphology with physical state.

[1] Dalby and King (2006) *Am. Mineral.*, **91**, 1783-1793. [2] Lee et al. (2010) *J. Geophys. Res.*, **115**, B06202. [3] Minitti et al. (2007) *J. Geophys. Res.*, **112**, E05015. [4] Wyatt et al. (2001) *J. Geophys. Res.*, **106**, 14711-14732.

# In-situ observations of the formation of a single-layer gibbsite-like phase on the muscovite (001) surface

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Hydrolysis of a multivalent cation in aqueous solutions often precedes secondary reactions such as oligomerization. It is known that such reactions can be controlled by the presence of solid surfaces [1]. Previous work showed that crystalline Al-hydroxide phases formed on the surface of muscovite mica with an apparent epitaxial relationship to the underlying surface [2], but the molecular-scale interfacial processes that initiate the reactions are not well understood. We investigated the formation of an Al-hydroxide phase on the basal surface of single crystal muscovite by monitoring changes in muscovite-solution interfacial structure using in-situ high resolution x-ray reflectivity. Experimental solutions were prepared with a fixed total Al content (1 mM) as a function of pH. At pH 4, we observed sorbed Al<sup>3+</sup> species formed an approximately 2Å thick film. The thickness and the vertical structure of the film matches those of a single Al dioctahedral sheet, i.e., gibbsite, Al(OH)3, phase. The films formed at lower pH (2 and 3) are structurally more disordered and are less dense (i.e., covered a smaller fraction of the surface) than that formed at pH 4. These observations can be attributed to decrease in the concentration of hydrolyzed Al species with decreasing pH, both in the solution and at the surface. No film formation was observed at alkaline conditions (pH 9-12) where Al3+ occurs primarily as an anionic species, Al(OH)4. The difference implies that the formation of the film is initiated by adsorption of positively-charged Al species at the negatively charged surface.

The results demonstrate that the growth of secondary minerals and the structural control of underlying substrates can be investigated in situ, in real time, and with a molecular-scale resolution. The results also suggest a new capability to characterize the reactivity of nanomineral films [3] with a high resolution.

[1] Scheidegger et al. (1998) Geochim Cosmochim Acta **62** 2233-2245.

- [2] Nagy et al. (1999) Geochim Cosmochim Acta 63 2337-2351.
- [3] Hochella et al. (2008) Science **319** 1631-1635.