

UNDERSTANDING THE COMPOSITION AND THERMAL HISTORY OF SILICIC GLASSES THROUGH THERMAL INFRARED SPECTROSCOPY. W. A. McCutcheon¹, P. L. King^{1, 2}, R. J. Lee³, and M. S. Ramsey³, ¹Inst. Meteoritics, Univ. New Mexico, Albuquerque NM, 87131 USA (wamcc@unm.edu), ²Research School of Earth Sciences, Bldg 61, Mills Road, Acton ACT 0200 Australia, ³Dept. Geol. & Planet. Sci., Univ. Pittsburgh, Pittsburgh PA 15260 USA.

Introduction: Glasses, produced by volcanism, impacts and other processes, are common on planetary surfaces and contribute to data collected through remote sensing. Unfortunately, the spectral peculiarities of varying glass compositions remain relatively poorly understood because the spectra depend on glass composition, mineral %, surface roughness, grain size and temperature. To adequately evaluate remote sensing data containing glasses it is important to examine their spectral variations using laboratory techniques.

Thermal infrared (TIR) spectroscopy has been used extensively to examine glasses because it is sensitive to the asymmetric stretching of Si-O-Si bonds. These vibrations produce a distinctive band at $\sim 10\mu\text{m}$ (or $\sim 1050\text{ cm}^{-1}$) and a shoulder at $\sim 8\mu\text{m}$ ($\sim 1200\text{ cm}^{-1}$) that are easily measured and can be compared using different laboratory and remote sensing IR techniques [1-3].

This contribution examines the thermal emission and $\mu\text{R-FTIR}$ spectra of a range of synthetic quartzofeldspathic and natural dacitic-rhyolitic glasses. We focus on felsic glasses because 1) they form in explosive and effusive volcanism or during impact; and 2) their TIR spectra vary in shape and intensity, thus, spectral analysis tools developed for them are likely applicable to more mafic glasses also. The reflectance spectra are further examined for trends relating to composition and fictive temperature.

Methods: Synthetic quartzofeldspathic and natural dacitic-rhyolitic glasses were obtained from [2] or naturally-occurring samples. Synthetic glasses were dominated by SiO_2 , Al_2O_3 , CaO , Na_2O with minor K_2O , and SiO_2 ranging from 55.16 to 87.54 wt.%. The natural dacitic-rhyolitic glasses, collected from Big Glass Mountain lava flow at Medicine Lake volcano California, range from 57.83 to 74.61 wt% SiO_2 . Glass compositions and microlite abundances were determined using the JEOL 8200 electron microprobe at the University of New Mexico. Micro-Fourier Transform specular (bidirectional) reflectance ($\mu\text{R-FTIR}$) spectra were obtained using a Nicolet Nexus 670 FTIR and a Continuum microscope with a Globar source, XT-KBr beamsplitter and an MCT-A detector ($4000\text{-}400\text{ cm}^{-1}$, 8 cm^{-1} resolution, 300 scans, and $100\times 100\text{ }\mu\text{m}$ spot except $40\times 40\text{ }\mu\text{m}$ in microlite-rich glasses). Thermal infrared (TIR) emission spectra were collected at the University of Pittsburgh ($4000\text{-}400\text{ cm}^{-1}$, 4 cm^{-1} resolution and 256 scans).

Results: *Compositional Effects on Si-O Band Position in $\mu\text{R-FTIR}$:* Spectra of both the quartzofeldspathic and Medicine Lake glasses show an increase in the wavenumber (cm^{-1}) position of both the $\sim 1050\text{ cm}^{-1}$ (main band) and $\sim 1200\text{ cm}^{-1}$ (shoulder) as a function of increased SiO_2 content (Figs. 1 and 2). The natural glasses show similar trends to those observed for the synthetic glasses but the change in wavenumber with SiO_2 content is more muted (Fig. 2).

Discussion: The $\mu\text{R-FTIR}$ major band position is related to the average Si-O bond length in the glass and is therefore a strong indicator of SiO_2 content, particularly if the alkali content of the glass is known [4, 5]. We hypothesize that the Si-O bond length in the Medicine Lake samples varies less as a function of SiO_2 than in the synthetic glasses because the Medicine Lake samples are much more complex glasses with significant Fe, Ti, Al and K affecting the glass structure.

Another hypothesis is that other parameters, such as temperature [6] cause the glass IR spectra from the two sample sets to differ. One of the major differences between the synthetic quartzofeldspathic glasses and the natural glasses is the cooling rate. The synthetic samples were quenched from high temperature, thus retaining the structure of the glass at that high temperature. In contrast, the natural glasses cooled in a lava flow and therefore may have a more complex cooling history. Glasses that are cooled rapidly typically retain a structure that is representative of the glass transition temperature (T_g). Glasses that are annealed at temperatures below T_g for prolonged periods of time undergo structural relaxation and reflect the new, lower temperature, known as the fictive temperature (T_f) [5, 7].

Investigation of the effect of temperature: Eight of the synthetic quartzofeldspathic glasses, ranging in SiO_2 content from 62.44 to 85.29 wt%, were heated for 20 min. at temperatures below the projected T_g . The glasses were drop-quenched into an ice bath and $\mu\text{R-FTIR}$ spectra were taken. The process was repeated in descending increments of 25°C until crystallization or 1000°C was reached.

Six (3, 8, 19a, 20a, 21 & 24) of the eight samples show an increase in wavenumber of the major Si-O band position with decreasing temperature (Fig. 3). As expected [6], the most depolymerized glasses 3 and 8 with the lowest SiO_2 contents (62.44 and 70.53 wt. % respectively) demonstrate the most dramatic increase in IR band position. In those glasses with the highest SiO_2 contents the trend is more subtle.

Our results show that high SiO₂ glasses show little shift in μ R-FTIR band positions when the glass is annealed at a lower temperature. In contrast low-moderate SiO₂ show a significant shift to higher wavenumbers. Industrial glasses show similar behavior [5, 7] and this has been interpreted to indicate that low-moderate SiO₂ glasses have structures that are readily rearranged. Such glasses have an increase in average Si-O bond distances with annealing, resulting in a higher μ R-FTIR band position.

Conclusions: The μ R-FTIR major band position may be a valuable tool for assessing the approximate SiO₂ content of simple glasses, particularly if the alkali content is known. However, samples with mafic to intermediate compositions may undergo significant structural rearrangement upon annealing, making the IR main spectral band at ~ 1050 cm⁻¹ indistinguishable from felsic glasses. In sum, natural glasses with varying compositions and thermal histories may contribute significant challenges to spectral deconvolution methods and mapping with remote TIR spectra. TIR spectra of explosive volcanic rocks are likely further complicated by surface texture and grainsize effects [8].

References: [1] Byrnes, J. M. et al. (2007) *GRL*, 34, doi:10.1029/2006GL027893. [2] Lee, R. J. et al. (2010) *JGR*, 115, doi:10.1029/2009JB006672. [3] Minitti, M.E. and Hamilton, V.E., 2010. *Icarus*, 210, 135-149. [4] Dufresne, C.D.M. et al. (2009) *Amer. Mineral.*, 94, 1580-1590. [5] King P. L. et al. (2004) *Mineral. Assoc. Canada, Short Course Series*, 33, 93-133. [6] King, P.L et al. (2011) *Lunar Planet. Sci. Conf.*, 42, Abstr. #2069. [7] Koike, A & Tomozawa, M. (2006) *J. Non-Crystal. Solids*, 352, 3787. [8] Ramsey, M.S. and Fink, J.H. (1999) *Bull. Volc.* 61, 32-39.

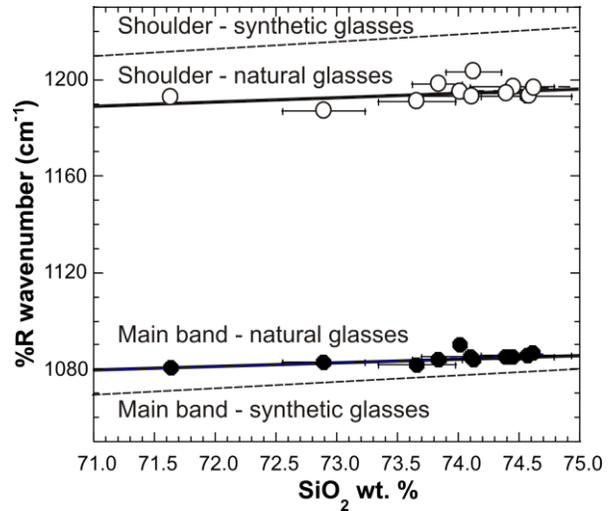
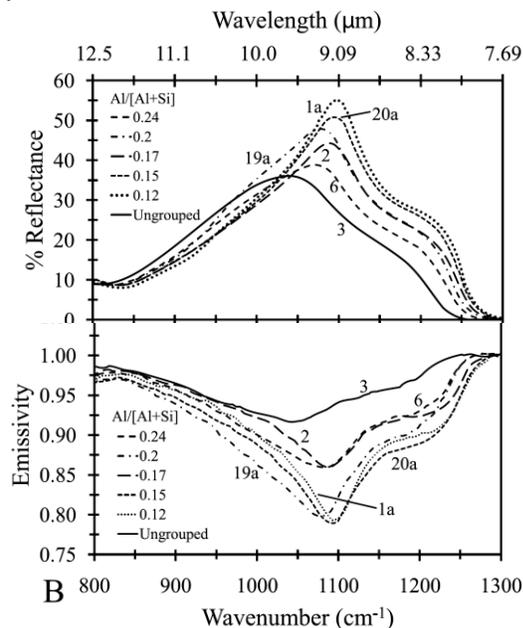


Figure 2: Comparison of μ R-FTIR spectral band position for Medicine Lake glasses relative to the fit observed for quartzofeldspathic glasses.

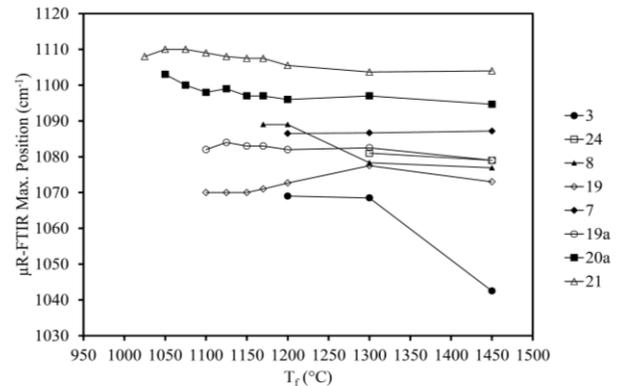


Figure 3: μ R-FTIR major band position as a function of fictive temperature.

TO LEFT:

Figure 1: μ R-FTIR vs. TIR of quartzofeldspathic glasses from R.J. Lee et al (2010) [2].