

EFFECT OF SiO_2 , TOTAL FEO, $\text{Fe}^{2+}/\text{Fe}^{3+}$ AND ALKALIS IN GLASSES ON THERMAL INFRARED SPECTRA. P. L. King¹, C. D. M. Dufresne² and K. N. Dalby³, ¹Inst. Meteoritics, Univ. New Mexico, Albuquerque, NM 87131 USA, ²Dept. Earth Science, Univ. Western Ontario, London, ON N6A 5B7 Canada, ³Dept. Earth Sci., St. Francis Xavier University, Antigonish, NS B2G 2W5 Canada.

Introduction: Natural glasses are produced on planetary surfaces when melts cool rapidly (e.g., obsidians, quench rinds and glass within volcanic rocks); when rocks undergo shock metamorphism (e.g., impact breccias); or following lightning strikes on soil (fulgurites and Libyan desert glass). Glasses may therefore provide critical information on the igneous and shock history of a planetary surface such as the surface of Mars [e.g., 1-7].

Thermal (or mid-) infrared (TIR) spectroscopy is a useful technique for examining natural glasses because TIR photons interact with Si-O and Al-O species (abbreviated as Si-(Al)-O species). In particular, asymmetric stretching vibrations of Si-(Al)-O species contribute to at least five bands between ~ 700 and $\sim 1250 \text{ cm}^{-1}$ (~ 8 and $\sim 14.2 \mu\text{m}$) [8, 9]. The individual bands are difficult to discern in TIR spectra of glasses, but instead a broad peak is observed at $\sim 1100 \text{ cm}^{-1}$ ($\sim 9 \mu\text{m}$). As glass composition varies from mafic to felsic, the position of the peak in both emission and reflectance spectra shifts toward higher wavenumbers (shorter wavelengths) [e.g., 1, 4, 5, 8, 9] as a function of Si/O or Al/Si [1] or the mol% SiO_2 [9].

We investigated the detailed effects of changing SiO_2 wt. %, alkali content ($\text{Na}_2\text{O} + \text{K}_2\text{O}$), total Fe and $\text{Fe}^{2+}/\text{Fe}^{3+}$ on TIR spectra of glasses. Those elements vary substantially in natural rocks (especially basalts) and may affect the Si-(Al)-O species detected in TIR. It is necessary to relate the detailed TIR spectra of glasses to their composition to better understand the basic phenomena controlling glass IR spectra. Ultimately, such information could be used to create better spectral libraries of glass end members and to improve fitting procedures for TIR remote sensing data.

Methods: Thirty two glasses with compositions ranging from basalt to rhyolite were obtained or synthesized, and analyzed for their major element compositions (where necessary) using the electron microprobe (EMPA; 10-20 μm spot diam.). The glasses were then analyzed using micro-FTIR specular (bidirectional) reflectance spectroscopy ($\mu\text{R-FTIR}$; 100 μm spot diam.). Some basaltic glasses were synthesized in a gas-mixing furnace to produce samples with a range of total Fe, $\text{Fe}^{2+}/\text{Fe}^{3+}$ and alkali contents; the same location was analyzed with EMPA and $\mu\text{R-FTIR}$.

Byrnes et al. [1] showed that $\mu\text{R-FTIR}$ and emission TIR spectra in glasses are complementary, with the $\mu\text{R-FTIR}$ having higher spectral contrast and

higher signal-to-noise-ratio than emission IR. Micro-FTIR analyses were conducted at the University of Western Ontario using a Nicolet Nexus 670 FTIR with a Continuum microscope with a Globar source, XT-KBr beamsplitter and an MCT-A detector. The data were treated with the Kramers-Kronig (KK) transform to produce spectra in KK absorption units removing the effects of the refractive index [e.g., 9]. Such spectra may then be deconvolved to band positions that relate to the structural units in the silicate glass [9].

Results: Glass spectra show systematic changes in the Si-(Al)-O peak shape and position for natural glasses as a function of composition. Specifically, the $\sim 1100 \text{ cm}^{-1}$ ($\sim 9 \mu\text{m}$) and $\sim 1200 \text{ cm}^{-1}$ ($\sim 8.3 \mu\text{m}$) features decrease in wavenumber as mol% SiO_2 (or wt. % SiO_2) decreases (Fig. 1, 2A & B). The 1200 cm^{-1} ($\sim 8.3 \mu\text{m}$) IR shoulder position is particularly sensitive to SiO_2 content (Fig. 2B) and may be a valuable tool for determining glass composition.

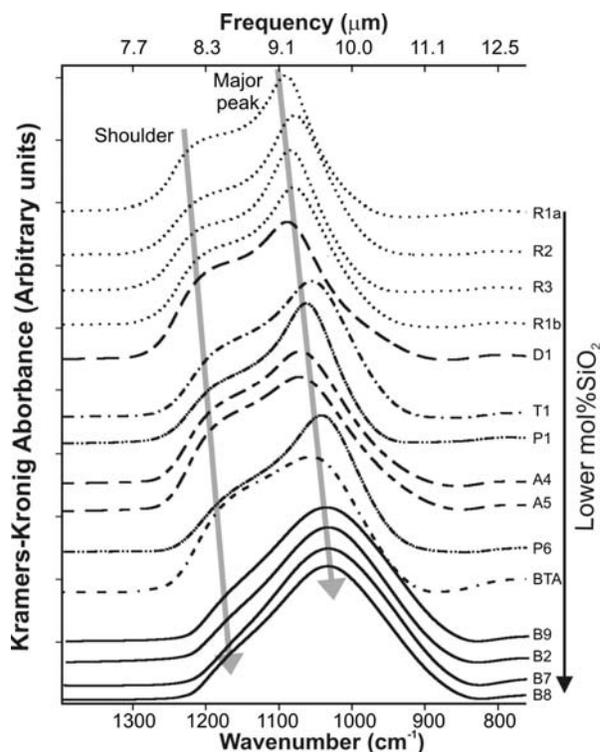


Figure 1: TIR spectra for a suite of glasses analyzed with $\mu\text{R-FTIR}$ and then transformed into absorbance units using the Kramers-Kronig transform. R- rhyolite; D- dacite; T- trachyte; P- phonolite; A- andesite; BTA

– basaltic trachyandesite; B- basalt, No.- sample number.

Because SiO_2 has a major influence on spectral features it is necessary to compare samples with a relatively constant SiO_2 content to determine the effects of total Fe and $\text{Fe}^{2+}/\text{Fe}^{3+}$. The latter variables have negligible effect on the glass spectra in the TIR. In contrast, alkalis, especially Na_2O , have a strong control on the TIR spectral features. As alkalis are added to a glass 1) the $\sim 1100\text{ cm}^{-1}$ ($\sim 9\text{ }\mu\text{m}$) peak broadens in full-width half-maximum (FWHM; Fig. 3, 4); 2) the $\sim 1100\text{ cm}^{-1}$ ($\sim 9\text{ }\mu\text{m}$) peak generally decreases in intensity (Fig. 4); and, 3) the wavenumber of the $\sim 1110\text{ cm}^{-1}$ ($\sim 9\text{ }\mu\text{m}$) peak remains essentially constant (Fig. 4).

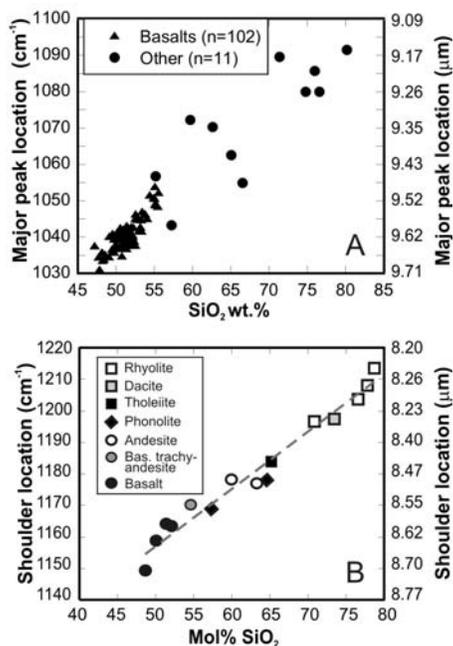


Figure 2: (A) Location of the major peak ($\sim 1100\text{ cm}^{-1}$, $\sim 9\text{ }\mu\text{m}$) in the μR -FTIR spectra as a function of wt. % SiO_2 and (B) the shoulder location ($\sim 1200\text{ cm}^{-1}$, $\sim 8.3\text{ }\mu\text{m}$) as a function of mol% SiO_2 .

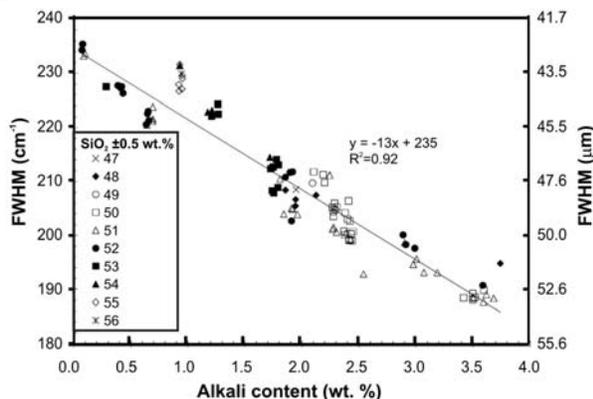


Figure 3: Full-width at half-maximum versus total alkali content ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) for basaltic glasses. Symbols indicate the SiO_2 content.

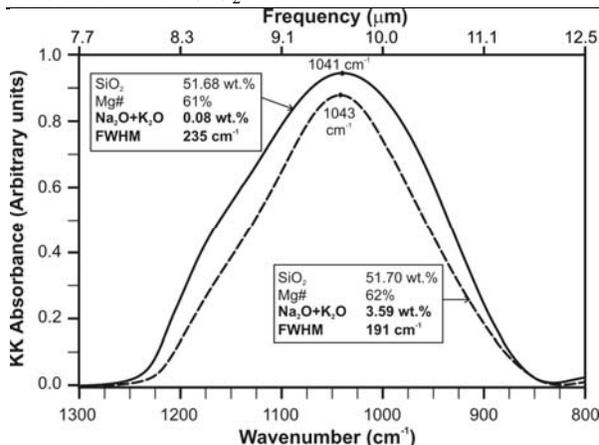


Figure 4: Absorbance units derived from the Kramers-Kronig transform of micro-reflectance data versus wavenumber for two glasses with very similar compositions excepting the alkalis. Note the FWHM and peak height difference, but similar peak position.

Conclusions: Our data may be used to predict the features of the $\sim 1100\text{ cm}^{-1}$ ($\sim 9\text{ }\mu\text{m}$) peak and $\sim 1200\text{ cm}^{-1}$ ($\sim 8.3\text{ }\mu\text{m}$) shoulder as a function of glass composition and vice versa. The peak and shoulder locations in the TIR depend on SiO_2 wt% and the FWHM depends on alkali wt%. The TIR spectra of basaltic glasses do not vary as a function of Fe_{total} and $\text{Fe}^{3+}/\text{Fe}^{2+}$.

The systematic changes in glass composition indicate that 1) changes in the Si-(Al)-O structural environment contribute to changes in glass composition; and 2) glass TIR spectra may be modeled empirically and used in fitting in spectral models of planetary surfaces.

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