

A GENETIC ALGORITHM APPROACH FOR OBTAINING WAVELENGTH DEPENDENT MID-IR INFRARED OPTICAL CONSTANTS (5-25 μm) OF SILICATE GLASSES. I. Varatharajan¹, E. Sklute^{2,3}, T. D. Glotch¹, M. D. Dyar^{2,3}, ¹Department of Geosciences, Stony Brook University, Stony Brook, NY11794 (indhu.varatharajan@stonybrook.edu), ²Dept. of Astronomy, Mount Holyoke College, South Hadley, MA 01075, ³Planetary Science Institute, Tucson, AZ, 85719 (ecksklute@psi.edu).

Introduction: Silicate glasses on planetary surfaces occur as fine particulates in volcanic ash, as fine-grained regolith, and as droplets or even bombs [e.g., 1-3]. Volcanic glass composition holds clues to primary melt compositions and the volatile species in those melts [4]. Thus, characterizing glass composition and abundance is crucial for understanding the chemical makeup of planetary interiors and their thermal evolution. Impact glasses, on the other hand, are produced through remelted crustal/surface materials and, therefore, have more complicated chemistries. Impact glasses may hold clues to the composition of the target and the impactor materials [5]. For both types of glasses, understanding composition, distribution, and abundance is integral to interpreting planetary evolution.

At mid-infrared wavelengths ($\sim 5\text{-}25\ \mu\text{m}$), spectral mixing is non-linear for fine particulates, and radiative transfer (RT) theory is required to model the spectral features to extract the compositions and abundances of glasses from the spectra of mixtures [6]. However, the RT-based modeling approach requires known wavelength dependent optical constants (real and imaginary indices of refraction, n and k) of each component in the mixture (e.g., [7, 8]) and optical constants for silicate glasses of varying compositions are still lacking.

To begin to fill this gap, we derived MIR optical constants of well-characterized planetary-relevant synthetic glasses, including andesite, rhyodacite, and two dacites as well as three natural samples including basaltic volcanic glass from Hawaii, rhyolitic volcanic glass from Mexico, and obsidian volcanic glass from Lassen, California.

Micro-FTIR spectroscopy of glasses: Because glasses are optically isotropic, a single sample need not be oriented to determine optical constants; instead, spectra for those calculations can be obtained from randomly selected fragments polished along any direction. For this study, glass fragments were mounted on a slide and the exposed top surface was polished to an evenly leveled and smooth ($< 1\ \mu\text{m}$ roughness) surface. Micro-FTIR spectra of the polished glasses were then collected using a Nicolet iN10MX FTIR microscope with a deuterated triglycine sulfate (DTGS) detector in the Center for Planetary Exploration at Stony Brook University. Point spectra covering $400\text{--}2000\ \text{cm}^{-1}$ ($5\text{--}25\ \mu\text{m}$) with a spectral sampling of $4\ \text{cm}^{-1}$ were

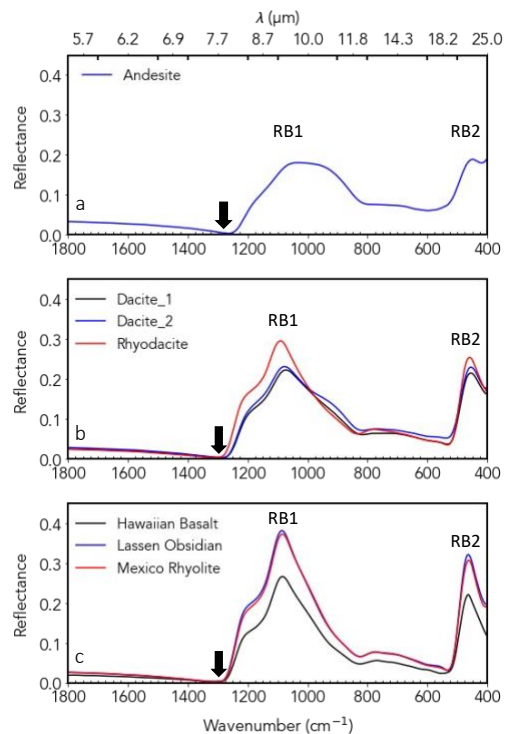


Figure 1. Micro-FTIR spectra of glasses studied. Black arrow indicates position of Christiansen Feature (CF). RB1 and RB2 indicate positions of the two Reststrahlen bands.

collected with a $300 \times 300\ \mu\text{m}$ spot size for at least three different spots of the same sample. Sample spectra (Fig. 1) were referenced to a gold mirror using the same spot size and acquisition times as samples; a reference was taken before each sample measurement.

Modeling optical constants – Genetic Algorithm approach: The wavelength-dependent optical constants of a material can be modeled by comparing the measured laboratory spectra of a material against the reflectance spectra modeled by combining the mathematical expressions of classical dispersion theory [7, 9-11] and a simplified Fresnel reflectance model for normal incidence [12]. The mathematical relationship between total vibration of a mineral and the sum of two or more individual harmonic oscillators within the mineral is given by classical dispersion theory. Each model harmonic oscillator within a mineral is defined by three oscillation parameters: center of frequency of the oscillation (ν), band strength ($4\pi\rho$), and band width (γ), along with an additional non-oscillator dependent

term, high frequency dielectric constant (ϵ_0), which is a bulk-mineral property that can be estimated from n_{vis}^2 measured in the visible part of the spectrum [10]. In this study, we adopted the Spitzer and Kleinman [9] formulation of the classical dispersion theory, which is expressed in wavenumber space.

This project improves on previous Lorentz-Lorenz based models with the implementation of a genetic algorithm (GA) to automatically find the natural oscillators responsible for spectral features in the measured reflectance spectrum of glasses; this optimizes the frequencies (ν), band width (γ), band strength ($4\pi\rho$), and dielectric constant (ϵ_0) of the oscillators. GA is one of the most widely used global, robust, and stochastic search algorithms that is modeled on the concept of natural selection and evolution. GA searches the wide domain space for all possible solutions (a population of individuals or ‘chromosomes’) of the given problem [13]. Each chromosome is an array of ‘genes’ that are the basic building blocks of GA. In this study, the genes are the oscillator parameters (ν_j , $4\pi\rho_j$, γ_j) and ϵ_0 . Therefore, each chromosome is a $j \times 4$ matrix of possible solutions of ν_j , $4\pi\rho_j$, γ_j , ϵ_0 for j number of oscillators. The GA-found oscillator frequencies and their parameters are further fine-tuned using a nonlinear least squares routine (LSQ) [7]. Without the GA-routine, the initial guesses of the number of oscillators and their parameters are chosen manually, a subjective step that can significantly affect the modeled optical constants.

Results: MIR spectra of the glasses measured at normal incidence are shown in Fig. 1. Irrespective of the variations in their composition, the measured spectra of all silicate glasses studied possess similar spectral shapes, with broad and smooth spectral features. Two diagnostic spectral features of all the silicate glasses studied are the Christiansen feature (CF) and Reststrahlen bands (RB). The Christiansen CF occurs near $8 \mu\text{m}$ (1250 cm^{-1}) and is indicated by black arrows in Fig. 1. This feature is an emissivity maximum (or minimum in reflectance) and is an indicator of silicate composition [14, 15]. It is not affected by variations in grain size, crystal orientation, or the crystallinity under ambient measurement conditions. The two RBs arise from fundamental molecular vibrations [16]. The broad RB at $8.5\text{--}12 \mu\text{m}$ ($\sim 800\text{--}1100 \text{ cm}^{-1}$) results from asymmetric stretching vibrations of SiO_4 units and is marked as RB1 in Fig. 1. This RB band position shifts to lower wavenumbers as a glass becomes depolymerized [17, 18]. A second RB peak appears near $20\text{--}25 \mu\text{m}$ ($400\text{--}500 \text{ cm}^{-1}$), resulting from the SiO_4 bending vibrations, and is marked as RB2 in Fig. 1. The modeled values of n and k derived from the GA-driven LSQ optimization approach of the dispersion analysis

for all glasses studied are shown in Fig. 2 along with their respective silica content (SiO_2 wt%).

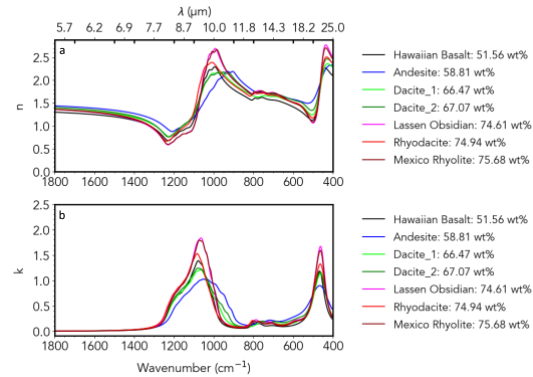


Figure 2. Modeled n and k values of the glasses studied are shown in (a) and (b) respectively. SiO_2 wt% of the glasses studied are added in the legend.

Modeled refractive indices of the studied glasses display common features; a) there is no variation in n and k in the regions up to $8 \mu\text{m}$ (1250 cm^{-1}) irrespective of the glass compositions, b) the similar trend for n and k is observed for all the studied glasses (except for andesite) between $8\text{--}25 \mu\text{m}$ but significant variations for larger wavelengths. The general shape of the refractive indices of obsidian, basalt, and andesite agrees with the previous studies [19, 20]. Unlike for bulk crystal mineralogy, weak correlation between silica content of glasses and refractive indices for peak positions, strengths, and widths in the regions $9\text{--}11 \mu\text{m}$ and $20\text{--}25 \mu\text{m}$ is observed for both n and k [20, 21] this could be due to chemical heterogeneity unlike crystals. The derived MIR optical constants can further be used in the light scattering models to quantify the mineral abundances of the volcanic surfaces from the orbit. The code and the modeled n and k values will be made available in a public repository.

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