

ATR-IR SPECTROSCOPY FOR *IN SITU* MINERAL ANALYSIS ON PLANETARY SURFACES: STEPS TOWARD A FORWARD MODEL. S. M. Chemtob¹, T. D. Glotch² and G. R. Rossman¹.
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Introduction: Attenuated total reflectance (ATR) is an infrared spectroscopic method that has potential as a tool for *in situ* quantitative mineralogical analysis on planetary lander missions. The sample of interest is placed in close physical contact with a crystal of high refractive index, such as Ge or diamond. Modulated infrared light from an FTIR interferometer enters the crystal at such an angle that when the light hits the interface with the sample, total internal reflection occurs. Light penetrates the sample via an evanescent wave that rapidly decays away from the interface. The beam is attenuated at frequencies corresponding to the fundamental vibrational modes and overtones of the sample crystal structure. The resultant ATR spectrum has similar peak positions as an equivalent transmission IR spectrum. ATR-IR potentially presents advantages over currently employed *in situ* planetary mineralogical methods, as it requires minimal sample preparation (grinding) and is effective with fine-grained materials.

ATR-IR has been used extensively in the study of polymers and organics ([1,2]) and in a few geological applications ([3,4]), typically for qualitative phase identification. ATR can be used to identify and distinguish between a variety of clays, sulfates and oxides of martian significance [5]. Few studies have attempted quantitative interpretation of ATR spectra of single-phase powders or mixtures [6]. We recently modeled ATR spectra of mineral mixtures using linear deconvolution [7]. Although the deconvolution algorithm was generally successful in identifying the component minerals, modeled proportions were often inaccurate; the spectra were dominated by non-linear grain size and interaction effects. Here we present new spectra of silicates and ongoing efforts to develop a forward model from first principles of ATR for geological samples.

Methods and Spectra: We analyzed powders of two minerals: San Carlos olivine (Fo₉₀) and quartz (var. rose, Riverside, CA). Minerals were ground and sieved to a series of grain sizes (<10 μm, 10-20 μm, 20-45 μm, 45-90 μm). Spectra were collected at Stony Brook University on a Nicolet 6700 FTIR spectrometer equipped with a SmartOrbit ATR accessory, a thermo-electrically cooled DLaTGS de-

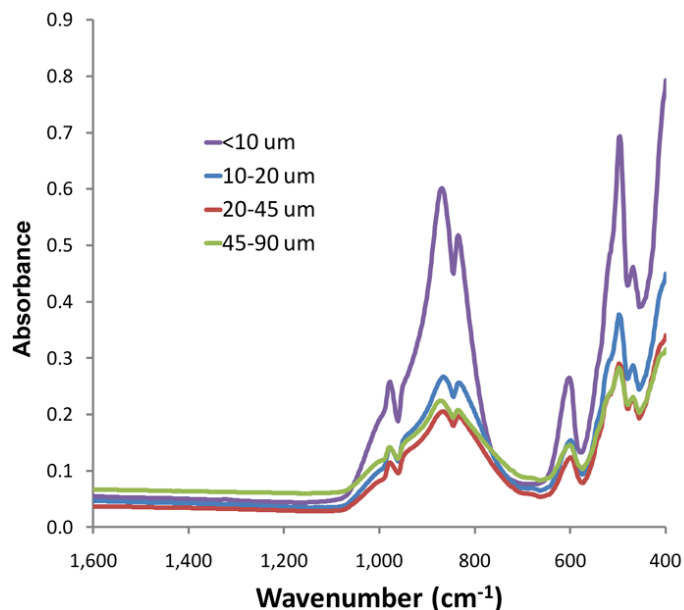


Figure 1. ATR-IR spectra of olivine powders of various grain size fractions.

tor with a KBr window (400-4000 cm⁻¹) and a KBr beamsplitter.

ATR spectra for olivine grain size separates are shown in Figure 1. Absorbance is shown to be strongly grain size dependent; finer powders can be packed closer than coarse powders in the region of the evanescent wave. Absorbance increases strongly for all grain sizes towards higher wavenumbers; the penetration depth (e-folding distance of evanescent wave, calculated as a function of n and k) scales with the wavelength. The positions of some peaks shift to higher wavenumber with increasing grain size, the result of changing penetration depth across the vibrational feature. A forward model should incorporate all of these observed spectral characteristics.

Description of forward model: We are developing a forward model to predict the ATR spectra of powder mixtures. The inputs to the model include the volume proportions of the constituent minerals and the optical constants and grain size distribution of each mineral, as well as experimental conditions ($n_{\text{diamond}} = 2.4$; $\theta_{\text{incident}} = 45^\circ$). Olivine mid-IR optical constants for a, b, and c axes are from [8], and quartz optical constants for the O- and E-ray are from [9]. Grains are assumed to be hard spheres and are assigned random orientations. A powder

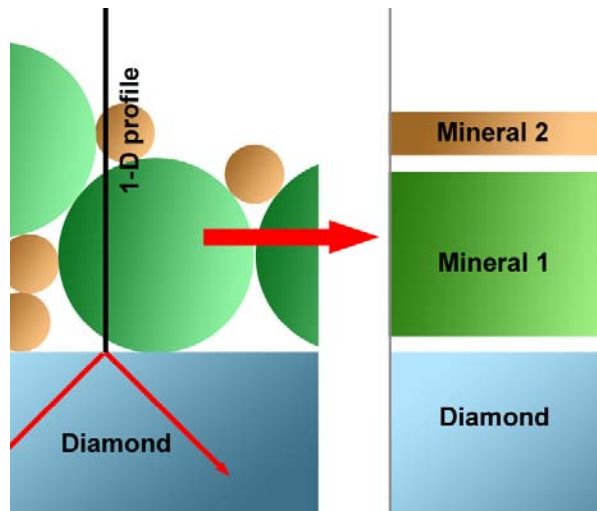


Figure 2. Schematic illustrating model assumption of slab model from a powder configuration.

configuration is achieved through Monte Carlo ray deposition and compression [10]. A random spot on the crystal-powder interface is selected, and the 1-D profile through the powder is selected. For each random spot, a slab geometry is assumed (Fig. 2); in making this assumption, we ignore intra-powder angles. Grains are oriented at various directions relative to the vertical profile; effective optical constants for each grain are determined using the indicatrix and averaging the slow and fast rays. The ATR spectrum is calculated using two sets of equations. If a grain is in direct contact with the diamond and its size is well above the wavelength, the complex Fresnel equations can be used to calculate the reflectance (separately for perpendicular and parallel polarizations) [1]. In the case of frustrated total reflection, where the diamond and mineral are separated by an air film of thickness comparable to the wavelength, reflectivity can be determined by solving a system of equations based on continuity conditions for electromagnetic waves [11]. The influence of slabs more distant to the interface is weighted by the penetration depth. The spectrum calculation is repeated for many random spots, and the model outputs the average of these calculations.

Model results: A comparison of the model output for olivine (avg. diameter = 10 μm) with acquired spectra of olivine is shown in Figure 3. The peak positions in the experiments generally matched those predicted by the model. There are several problems with the model output that must be addressed. First, the observed and modeled spectra differ in absolute absorbance (peak height). The low model absorbance may be the result of high model

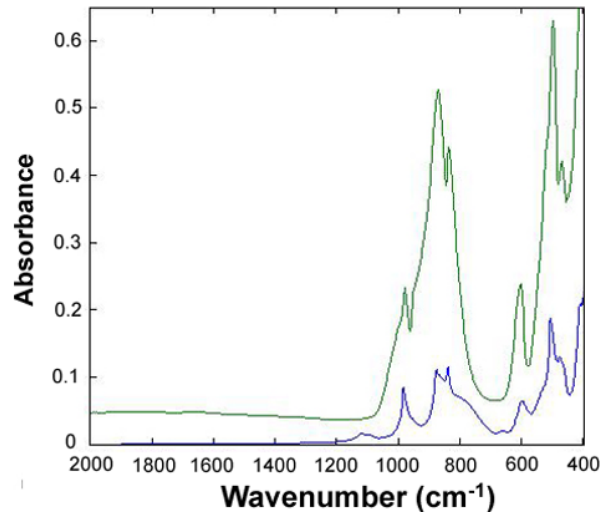


Figure 3. Comparison of forward model results (blue) with acquired spectrum for olivine (green).

porosity, as the method of [10] typically produces loosely packed powder configurations. Second, many peaks in the modeled spectrum are overly sharp compared to acquired spectra. These sharp peaks occur whenever $n_{\text{mineral}} = n_{\text{diamond}}$, in wavelength ranges where total internal reflection is not occurring. Finally, a peak appears in the model that is not observed in acquired spectra. The peak occurs where $n_{\text{mineral}} = 1$ and k is small ($\sim 1150 \text{ cm}^{-1}$ in olivine, $\sim 1350 \text{ cm}^{-1}$ in quartz), and is analogous to the Christiansen feature observed in mid-IR thermal emission and reflectance spectra. At present we cannot explain the absence of the Christiansen-like feature in the experimental spectra.

Planned improvements to the model include an expansion of the frustrated total reflection equations of [11] to solve for any general slab setup and a refined definition of penetration depth. Once the model more accurately matches observation, it will be employed to solve the inverse problem: determination of mineral abundances in an unknown powder.

References: [1] Harrick, N.J. (1967) Internal reflection spectroscopy, 327 p. [2] Urban, M.W. (1996) ATR spectroscopy of polymers, 256 p. [3] Johnston, C.T. and G.S. Premachandra (2001) *Langmuir*, **17**, 3712-3718. [4] Morlok, A. et al. (2004), *LPS XXXV*, #1622. [5] Glotch, T.D. et al. (2007) *LPS XXXVIII*, #1731. [6] Planinsek et al. (2006) *Int'l J. Pharmaceutics*, **319**, 13-19. [7] Chemtob, S.M. and Glotch, T.D. (2007) *LPS XXXVIII*, #1097. [8] Glotch, manuscript in prep. [9] Wenrich, M.L. and P.R.Christensen (1996) *JGR*, **101**(B7), 15921-15931 [10] Soppe, W. (1990) *Powder Tech.*, **62**, 189-197. [11] Young, T.R. and B.D. Rothrock, *J. Res. Nat'l Bur. Stds A.*, **67A**, 115-125.