

ATTENUATED TOTAL REFLECTION AS AN *IN SITU* INFRARED SPECTROSCOPIC METHOD FOR MINERAL IDENTIFICATION. T. D. Glotch¹, S. M. Chemtob², and G. R. Rossman², ¹Jet Propulsion Laboratory, California Institute of Technology (tglotch@gps.caltech.edu), ²California Institute of Technology.

Introduction: Attenuated total reflection (ATR) is a spectroscopic method rarely used in the geological sciences that has the potential to be a useful *in situ* mineralogical analysis tool on planetary missions. The method takes advantage of the difference in refractive index between the sample being measured and a high-refractive index crystal such as ZnSe, Ge, or diamond. The sample is placed in contact with the crystal, and modulated infrared light from a Fourier Transform Infrared (FTIR) interferometer is allowed to enter the crystal. The light then penetrates into the sample via an “evanescent wave.” Specific frequencies of the incoming radiation, corresponding to the fundamental vibrational frequencies and vibrational overtones of the sample material are absorbed, and the rest of the light is reflected through the crystal and into a detector. A schematic of this process is shown in Figure 1.

ATR has primarily been used as a tool in inorganic and organic chemistry research [1], but this technique has also recently been used in some geological applications [2-4]. Current work by the mineralogy research group at Caltech [5] includes a study of the spectra of mixtures of mineral powders and the application of linear deconvolution techniques [6-7] to correctly determine modal mineralogy. Here we present ATR spectra of clay, sulfate, and oxide minerals, focusing on the fundamental vibrational absorption features from ~8-100 μm and the H_2O vibrational overtone near 3 μm . The great variety in spectral properties of minerals in these regions, and the ability to linearly deconvolve mineral mixtures makes ATR a potentially useful mineral analysis technique for future robotic missions to the moon, Mars, and other solar system objects.

Methods: Spectra were acquired on a Nicolet Magna 860 FTIR spectrometer fitted with a Thermo Spectra-Tech Foundation Series ATR attachment with a type IIA diamond ATR element. Sample grain sizes of < 10 μm were used to assure the best contact between the sample and the ATR element. Two spectra of each sample were collected and merged to create a final spectrum spanning 50-4000 cm^{-1} (2.5-200 μm). Mid-IR spectra from 400-4000 cm^{-1} were collected using a KBr beamsplitter and an uncooled deuterated triglycine sulfate (DTGS) detector with a KBr window. Far-IR spectra were collected from 50-600 cm^{-1} using a Thermo Nicolet solid substrate beamsplitter and a DTGS detector with a polyethylene window.

Results: We acquired ATR spectra of several clay, iron oxide, and sulfate minerals. As with other Mid-IR spectroscopic techniques (e.g. emissivity, specular reflectance, transmission), spectra of different mineral classes display fundamental vibrational bands at unique frequencies between ~100-2000 cm^{-1} . In addition, the vibrational overtone between 3000 and 4000 cm^{-1} due to bound water varies in shape, contributing the uniqueness of each spectrum (Figure 2). It should be noted that each spectrum displays spectral features of instrumental artifacts between ~1800-2200 cm^{-1} .

Minerals within each class also have distinct spectra. Figure 3 shows ATR spectra of 10 clay minerals described in detail by [8-9]. Spectra vary considerably both in terms of fundamental vibrational bands (Figure 3a) and in the 3000-4000 cm^{-1} overtone (Figure 3b). Significant variation is also seen in the iron oxide/oxyhydroxide spectra shown in Figure 4. In addition, there are indications that ATR spectra may be more sensitive to differences in crystal structure than specular reflectance or emissivity. Figure 4b shows an ATR absorbance spectrum and an inverted emissivity spectrum of a hematite that was derived from the heating of goethite at 400 °C [10]. While the emissivity spectrum shows no sign of spectral features attributable to residual goethite within the sample, the ATR spectrum contains weak features at ~1100 and 1200 cm^{-1} that are present in the precursor goethite spectrum.

Discussion and Conclusions: As with other common infrared spectroscopic methods used in the laboratory and for remote sensing applications, ATR spectroscopy is a useful tool for both the identification of the mineral class of a material as well as distinguishing between minerals within a given class.

Because the ATR technique measures sample absorbance, it does not suffer from the effects of multiple scattering due to fine sample particle size that can make interpretation of reflectance or emissivity spectra difficult. In fact, ATR is an ideal technique to determine the mineralogy of fine particulate samples because fine particulates provide the best contact between the sample and the ATR element.

Work is currently underway to determine to what degree ATR spectra of fine particulate mineral mixtures may be deconvolved, and the initial results are promising [5]. Future work will concentrate on analysis of complex mixtures with variable particle sizes

and hydration states, and determining and analyzing the sources of error associated with this technique.

Ease of sample preparation and the small volumes of sample required to make a measurement make ATR a useful tool to analyze geological materials in the laboratory. The ability to linearly deconvolve mineral mixtures and its usefulness in analyzing fine particulates make ATR an intriguing candidate for future development as a planetary *in situ* mineralogical analysis instrument.

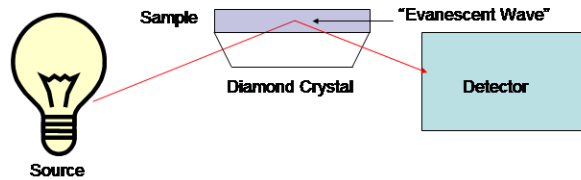


Figure 1. Schematic diagram of ATR assembly and sample measurement.

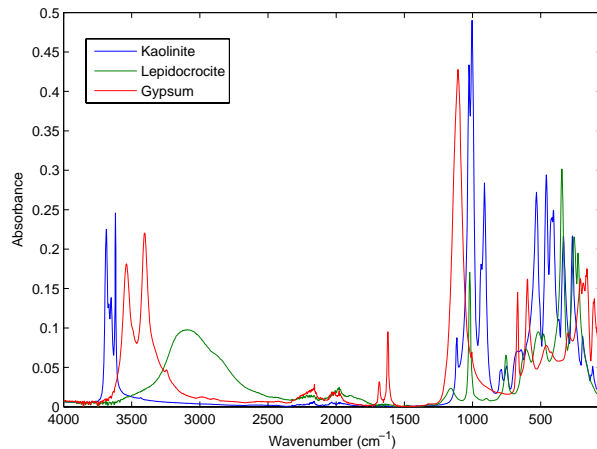


Figure 2. ATR spectra of clay, Fe-oxyhydroxide, and sulfate minerals. Spectra of different mineral classes are easily distinguishable in ATR spectra.

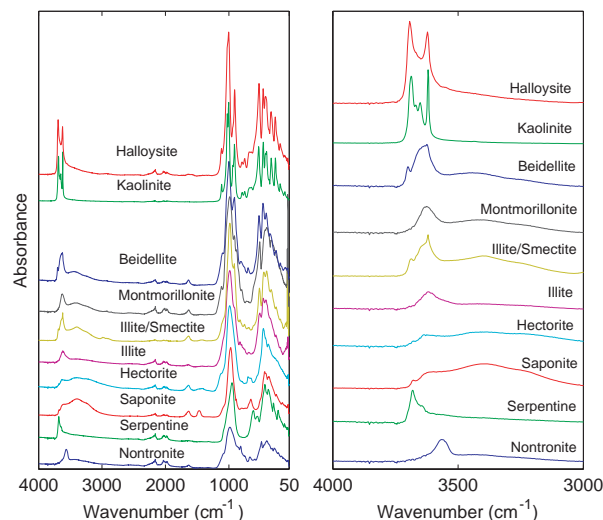


Figure 3. ATR spectra of clay minerals. a) Spectra covering the full available wavenumber range. b) Same spectra, zoomed into the 3000-4000 cm^{-1} to emphasize the variability of the hydration overtone feature.

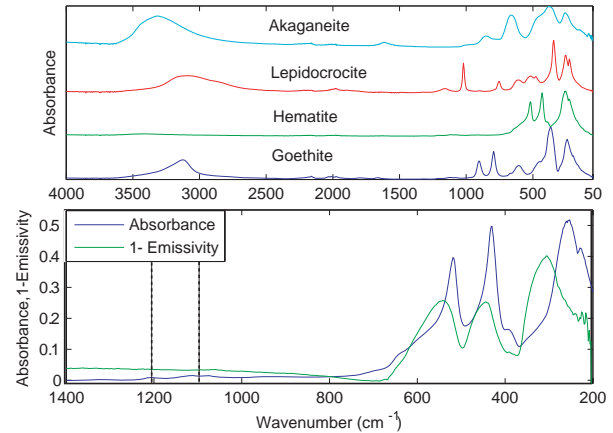


Figure 4. ATR spectra of iron oxides/oxyhydroxides. a) comparison of four iron oxides/oxyhydroxides. All spectra, including the hematite, display hydration overtone features between 3000 and 4000 cm^{-1} . b) Comparison of ATR (labeled absorbance) and emissivity spectra of a goethite-derived hematite. The ATR absorbance spectrum is sensitive to small features (marked by dashed lines) indicative of an incomplete transformation to hematite. These features are absent in the emissivity spectrum.

References: [1] Mirabella, M. F. (ed) (1998), *Modern techniques in applied molecular spectroscopy*, 410 p. [2] Johnston, C. T. and Premachandra, G. S. (2001) *Langmuir*, 17, 3712-3718. [3] Morlok, A. et al. (2004), *LPSC XXXV*, #1622. [4] Grigoriev, A. et al. (2004) 35th COSPAR Assembly, 2655. [5] Chemtob, S. M., and Glotch, T. D., this conference. [6] Ramsey, M.S. and Christensen, P.R. (1998) *JGR*, 103, 577-596. [7] Rogers, A. D. et al. (2006) *LPSC XXXVII*, #2273. [8] Michalski, J. R. et al. (2005) *Icarus* 174, 161-177. [9] Michalski, J. R. et al., *JGR*, 111, E03004. [10] Glotch, T. D. et al. (2004) *JGR*, 109, E07003.