

LINEAR DECONVOLUTION OF ATTENUATED TOTAL REFLECTANCE INFRARED SPECTRA OF FINE-GRAINED MINERAL MIXTURES. S. M. Chemtob and T. D. Glotch. Division of Geological and Planetary Sciences, California Inst. of Technology, Pasadena, CA 91125.(chemtob@gps.caltech.edu)

Introduction: Attenuated total reflectance (ATR) is a spectroscopic method frequently used in conjunction with infrared spectrometers. The method involves placing a powdered sample in close physical contact with a crystal of high refractive index. When IR source radiation enters the crystal, a total internal reflection occurs. The radiation interacts with the sample in contact with crystal, and the radiation is attenuated at frequencies corresponding to the fundamental vibrational modes of the sample crystal structure. The resultant spectrum has the same peak positions but different relative peak intensities as an equivalent absorbance IR spectrum. ATR-IR spectroscopy has been used extensively in inorganic and organic chemistry, but only in a handful of studies with geological or planetary applications (e.g. [1-4]). Because of its ease of sample preparation, effectiveness with small grain sizes, and ability to cover a broad spectral range ($100\text{-}11000\text{ cm}^{-1}$), ATR-IR has potential as an *in situ* method for quantitative determination of mineralogy on future Mars or lunar lander missions. To assess this potential, it is necessary to understand how well we can use deconvolution algorithms to model the composition of mineral mixtures from their ATR spectra. Here we present findings determining how well modeled compositions of ATR spectra of mixtures match their known proportions, using methods developed in previous studies of IR emissivity spectra (e.g. [5,6]).

Methods: Powders were prepared from four end-member samples: San Carlos olivine (Fo_{90}), bytownite (An_{70}), gypsum, and calcite. Each pure sample was ground into a fine powder ($<100\text{ }\mu\text{m}$) using a Spex Industries shatterbox. Mixed powders of known volumetric proportions were prepared from two, three or four end-members. Spectra of end-members and mineral mixtures were acquired using a SensIR Durascope ATR accessory plate with a Nicolet Magna-IR spectrometer, an uncooled pyroelectric deuterated triglycine sulfate (DTGS) detector with a KBr window ($400\text{-}4000\text{ cm}^{-1}$), and a KBr beamsplitter. End-member spectra were grouped in a spectral library. Spectra of the mineral mixtures were modeled using the deconvolution

method of [7], which was based on the Non-Negative Least Squares Algorithm outlined in [8]. Modeled compositions were then compared to known compositions.

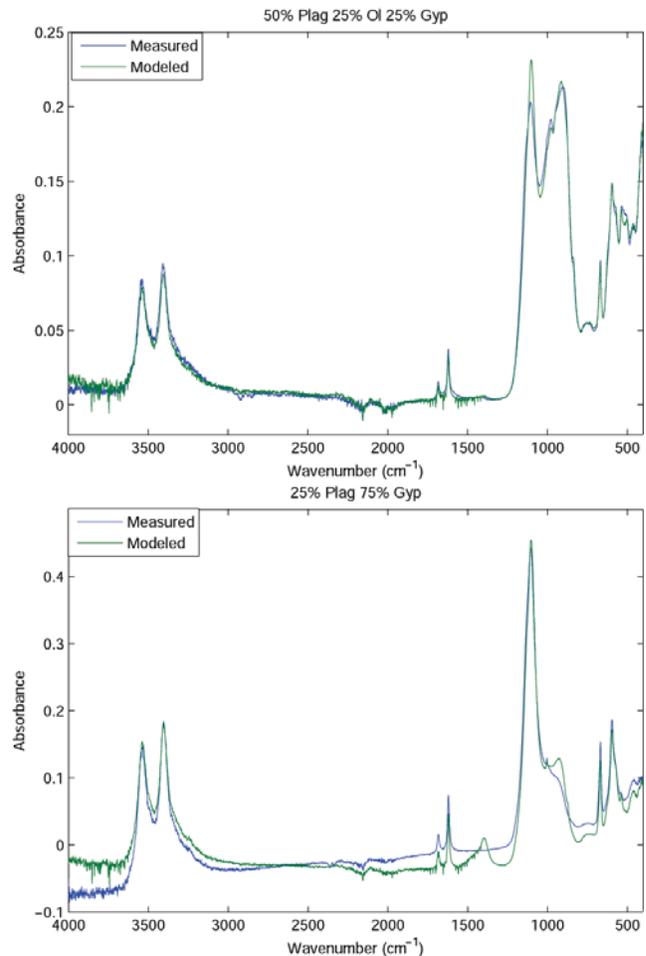


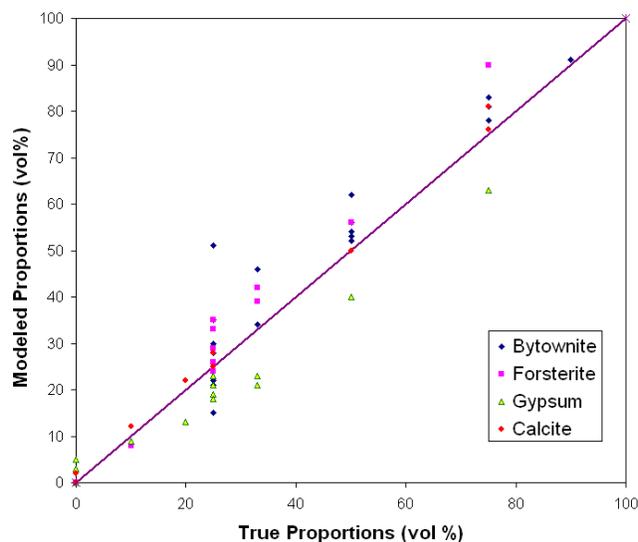
Figure 1. Measured and modeled spectra for two mineral mixtures. a) 50% bytownite, 25% olivine, 25% gypsum. Modeled spectra is very close to measured. b) 25% bytownite, 75% gypsum. Modeled spectra includes erroneous calcite peaks at 1400 and 900 cm^{-1} .

Results: Figure 1 illustrates examples of recorded and best fit modeled spectra for two of the prepared powders. These examples illustrate that some spectra were matched well, while some suffered from poor peak matches and false identifications. Initial examination of trends of modeled vs. actual volume proportions (Fig. 2) indicates that linear deconvolution of the ATR spectra is gener-

ally reliable to within ~10 vol. %. In some cases, there is significant deviation from the 1:1 line, indicating the modeled spectra are not perfect. The deviations are not randomly distributed. In our experiments, the proportion of gypsum was consistently underestimated, and the degree of underestimation increased with increasing proportion of gypsum. Bytownite and olivine were nearly always overestimated. In addition, unnormalized modeled compositions often produced totals above 100 percent. These deviations occasionally led to erroneous models. In the worst case, our mixture #15, composed of 25 vol% bytownite and 75 vol% gypsum, was modeled as 50% bytownite, 62% gypsum and 5% calcite.

There are several likely sources of error that may account for deviations. One source is grain size effects; while shatterbox preparation tends to produce homogenous and small grain sizes, variations from homogeneity could have a large impact on the deconvolution models. In previous studies of IR emissivity spectra, the assumption of linear mixing was shown to hold only for certain grain sizes [5]. In addition, gypsum, the only hydrous mineral studied, tended to clump together, forming a larger effective grain size; this may account for the consistent underrepresentation of gypsum.

Another potential source of error is differences in background intensity. Some of the spectral end-members had variable spectral background levels, which may have contributed to poor matches between measured and modeled spectra. The potential for mismatch in the background is evident in the 3500-4000 cm^{-1} spectral region of Fig 1b.



A third source of error is the potential that the assumption of linear spectral mixing is not correct for the entire spectral range studied. It has been previously shown that in the visible/near-IR region, where gypsum's H_2O peaks can be found, reflectance spectra may add nonlinearly [5]. To test this possibility, the deconvolution algorithm was run again on mixture #15 with a reduced spectral range of 400-2000 cm^{-1} . The resulting model produced 35% bytownite and 65% gypsum, an improvement on the original model.

Based on these preliminary results, we conclude that deconvolution of ATR-IR spectra can, at the very least, qualitatively predict the composition of mineral mixtures. Sources of error in the measurements have been identified. In future work, mineral mixtures will be prepared with more end-members and more strict control of grain size. Such work will likely better demonstrate the quantitative analytical capacity of ATR-IR.

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References: [1] Johnston and Premachandra (2001) *Langmuir*, **17**, 3712-3718. [2] Morlok, A. et al. (2004), *LPSC XXXV*, #1622. [3] Grigoriev et al. (2004) 35th COSPAR Assembly, 2655. [4] Glotch et al., this conference. [5] Ramsey, M.S. and Christensen, P.R. (1998) *JGR*, **103**, 577-596. [6] Feely, K.C. and Christensen, P.R. (1998) *JGR*, **104**, 24195-24210. [7] Rogers, A. D. et al. (2006) *LPSC XXXVII*, #2273. [8] Lawson, C.L. and Hanson, R.J. (1995) *Solving Least Squares Problems*, SIAM.

Figure 2. Model results for the entire set of mineral mixtures. Note that while the data points fit a linear trend ($R^2=0.946$), there is considerable spread, and gypsum proportions are consistently modeled below true values.