THE EFFECT OF GRAIN SIZE ON THE VIS-SWIR SPECTRUM OF OLIVINES: AN EXPLORATION OF STANDARD, MODIFIED AND EXPONENTIAL GAUSSIANS FOR DETERMINATION OF CRYSTAL CHEMISTRY. J. Buz[1] and B. L. Ehlmann[1,2], [1]Department of Geological and Planetary Sciences, California Institute of Technology (jbuz@gps.caltech.edu) [2]Jet Propulsion Laboratory, California Institute of Technology

Motivation: Mafic minerals such as olivine and pyroxene are prevalent on the surface of Mars, main-belt asteroids, and other solar system bodies [1]. Both of these minerals are part of solid solution series and their particular composition is indicative of their formation. On Earth, olivine is predominantly found with a highly magnesian composition, following the mantle olivine composition of Fo89-90. However, on Mars a wider range of compositions has been found, including outcrops as low as Fo40 [2]. The Fo# of the olivine is an indicator of the composition of the melt and the temperature at which the melt solidified, with lower Fo# indicating lower melting temperature. Olivine is thus an indicator of fractionation as well. The additional diversity in olivine composition on Mars as well as its ubiquitous presence in many areas makes it an important mineral for reconstructing the history of the Martian crust. Additionally, olivine composition can be mapped and used as an indicator of sediment source.

The electronic transition absorptions for these minerals lie in the visible/shortwave infrared (VSWIR) and are due to electron transfer in Fe^{2+} between the various d-orbitals in the distorted octahedral sites. The number of absorptions expected depends on the degree of distortion in the metal sites [3]. At least three absorptions have been observed (two from the M1 site and one from the M2 site) but more are possible (a maximum of ~5 lie in the VIS-SWIR range). The position and shape of these absorptions is influenced by their particular composition [4]. Complicating the characterization of this compositional influence is the overlapping nature of the multiple electronic transition absorptions [3], thus deconvolution of the spectra is necessary to infer any trends. Multiple deconvolution algorithms have been constructed to attempt this goal, all based off the Gaussian function to fit the absorption shape [3, 5-7]. The Modified Gaussian Model (MGM) [5], has demonstrated trends in absorption properties with changes in olivine iron content [8] and has since been applied to orbital data (e.g. [9]).

In addition to the influence of iron content on the spectrum of olivines, grain size has also been shown to affect their reflectance by deepening and broadening the 1-μm absorption [10]. This effect is not explicitly taken into consideration in the MGM algorithm, which used olivines of grain sizes <60 μm [8]. In particular, grain sizes larger than 250 μm show a large deviation from the previously established trends [10]. Work from orbital and rover data have shown that grain sizes larger than 250 μm make up a detectable fraction of particles in Martian sand dunes [11, 12]. The goal of this study is to characterize the effect of grain size on the reflectance spectra of mafic minerals, in particular olivine, in order to continue use of deconvolution techniques on remotely sensed spectra for Mars and other planetary bodies.

Methods: *Acquisition of an olivine suite.* We sought to acquire a suite of olivines that sampled the solid solution series as well as included grains between 25 μm and 2 mm. As previously stated, on Earth olivine is predominantly Mg-rich, thus acquiring this suite has not been feasible. Our suite currently contains the following Fo#s: 90, 88, 82, 1. The grains selected for the spectroscopic study were hand-picked to remove any grains with noticeable inclusions. We then sieved each sample into the following grain size bins: <45 μm, 45-75 μm, 75-125 μm, 125-250 μm, 250-500 μm, 500-1000 μm, and 1000-2000 μm. Reflectance spectra were acquired for each separate using an Analytical Spectral Devices Field Spectrometer. The composition of the olivines was determined via electron microprobe analysis; simultaneously, the degree of zoning was assessed for the largest grain sizes.

Spectral Deconvolution. In order to explore the entire parameter space we developed a Markov Chain Monte Carlo (MCMC) algorithm to determine the best fit for a given spectrum. We choose the MCMC algorithm because of the small dependence on the input parameters and its ability to also return information on model result uncertainties, sensitivities, and correlations. We model the spectra using standard Gaussian functions, modified Gaussians [5], and exponential Gaussians [6, 7]. The parameters which we allowed to vary are: absorption center, width, strength, and continuum position. Additionally, we explore the appropriate number of absorptions necessary to accurately model the given spectrum (i.e. how many electronic transition absorption bands make up the broad 1-μm feature of the olivine spectrum, and how many absorptions should be used to model the unrelated charge transfer absorptions at shorter wavelengths). Following the work of Sunshine [5], we use a flat line continuum, hence the continuum value is simply an offset from unity. Because the addition of parameters, e.g. 5 per absorptionin the exponential Gaussian vs. 3 in the standard Gaussian, will tend to increase the quality of

the fit we also assess the suitability of each fit using the Bayesian Information Criterion (BIC).

Results: *Olivine Compositions and Spectra*. Electron microprobe analyses of the olivines revealed that other transition metals were present only in minute qualities (<0.03 formula units). We did not find any detectable zoning in the olivine crystals suggesting that they are of approximately uniform composition throughout each separate. The fayalitic end member in our suite was found to be heavily oxidized, displaying absorptions attributed to alteration, and thus was excluded from the remainder of the study. As an example, the spectra obtained for the Fo90 olivine sample are shown in Figure 1, showing the expected 1-µm feature deepening and broadening with grain size increase.

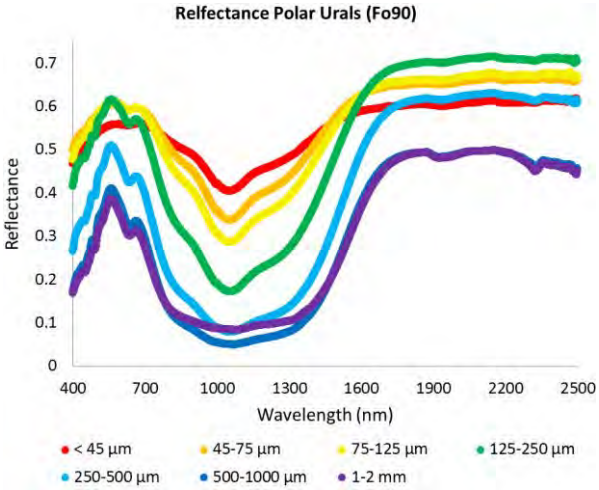

Figure 1: Reflectance spectra of Fo90 olivine demonstrating that larger grain sizes have a broader and flatter 1-µm absorption.

Spectral Deconvolution As a test, we reproduced the results of Sunshine et al. [8] using the freely available MGM software [13]. We also reproduce the results of [10] showing that grain sizes larger than 250 µm deviate from the trends established by Sunshine [8]. For comparison we also attempted to reproduce these trends using our MCMC routine: while the algorithm converges to a best fit model of comparable residual error, the resulting final parameters do not always match those given by Sunshine [8] (i.e. sometimes the fit is non-unique). We are capable of modeling the spectra using all three forms of the Gaussian absorption though the physical significance of the results is not yet understood without first determining the proper modeling procedure.

We calculated the BIC on our deconvolution of a single pyroxene absorption from Sunshine et al. [5] using all three absorption types and found that the exponential Gaussian had the lowest BIC, suggesting it most accurately models the absorptions; the modified Gaussian had the largest BIC.

Preliminary Conclusions: It is possible to model the electronic transition absorptions using a variety of forms of the Gaussian equation. The modeling does not always yield physically realistic results and thus care must be taken in using the outputs of the various fitting routines. The MCMC algorithm is a suitable method for determination of the best fit model for a given spectrum. While currently the BIC suggests that the exponential Gaussian best characterizes the electronic transition absorption, further analysis will be necessary to observe which if any of the functions produce trends with mineral composition and grain size. As previously demonstrated, large grain sizes can be confounding when doing compositional analysis of mafic minerals using spectral deconvolution.

Future Work: Exploring the full parameter space remains a work in progress. It is imperative to determine which of the forms of the Gaussian, if any, are most appropriate for modeling the electronic transition absorption. We will assess the difference in RMS error, the availability of observable trends, and the physical meaning of each equation to evaluate which model is most realistic. We must then determine the correct number of absorptions in the 1-µm region. Once the correct modeling procedure is determined we will systematically model changes with grain size to seek any trends. We are working on further optimization of the MCMC routine to reduce the processing time. We continue to seek olivines of intermediate iron compositions to augment our existing olivine suite. We have thus far focused our study on the reflectance spectrum of olivine, however, the effects of grain size on pyroxenes will also be necessary to characterize.

References: [1] Mustard, JF *et al.* 2005 *Science* 307 1594-7 [2] Koeppen, WC & Hamilton, VE 2008 *J Geophys Res* 113 [3] Burns, R 1970 *American Mineralogist* 55 1608-32 [4] Cloutis, EA *et al.* 1986 *J Geophys Res* 91 11641-53 [5] Sunshine, J *et al.* 1990 *J Geophys Res* 95 6955-66 [6] Pompilio, L *et al.* 2010 *Icarus* 208 811-23 [7] Pompilio, L *et al.* 2009 *Icarus* 201 781-94 [8] Sunshine, JM & Pieters, CM 1998 *J Geophys Res* 103 13675-88 [9] Skok, JR *et al.* 2010 *J Geophys Res* 115 [10] Clénet, H *et al.* 2011 *Icarus* 213 404-22 [11] Edgett, KS & Christensen, PR 1991 *J Geophys Res* 96 22765-76 [12] Lapotre, MGA *et al.* 2016 *Science* 353 55-8 [13] Sunshine, J *et al. LPSC* 1999