PREDICTING THE MODAL MINERALOGY OF HOWARDITES AND BRECCIATED EUCRITES USING VIS-NIR REFLECTANCE SPECTROSCOPY. E.A. Fisher[1], R.E. Milliken[1], S. Li[1], and K. Robertson[1], [1]Dept. Earth, Env., and Planetary Sciences, Brown University, Providence, RI 02912, elizabeth_fisher1@brown.edu

Introduction: Howardite-eucrite-diogenite (HED) meteorites are widely believed to originate from Vesta and thus record important information about early solar system processes [1,e.g.]. Eucrites are primarily basalts emplaced at/near the surface whereas diogenites represent deeper cumulate rocks; howardites are complex breccias of these two lithologies [2, e.g.]. A previous study has indicated that radiative transfer modeling (RTM) techniques applied to visible-near infrared (VIS-NIR) reflectance spectra of unbrecciated eucrites and diogenites are capable of predicting the modal mineralogy of these samples to within ~5-10% [3].

However, the majority of Vesta's surface is dominated by howardite-like VIS-NIR spectra, consistent with brecciation by impacts, that obscures the true distribution of eucrite and diogenite-like components [4,5]. Brecciated materials present unique challenges to RTMs due to the potential presence of amorphous components/glass, shocked phases (spectral masking of plagioclase), exotic impactor-derived components (e.g., metal), and wide ranges in particle size [6,7]. This study builds upon the previous modeling efforts of Li & Milliken [3] to test their technique on more complex brecciated eucrites and howardites. The the modal mineralogy of a suite of three howardites and three brecciated eucrites is estimated from the Hapke model and compared with modal values determined by modeling of X-ray diffraction patterns for these samples.

Methodology. *Radiative Transfer Theory.* VIS-NIR reflectance spectra were measured for chips, <125 µm powders, and <45 µm powders for a suite of 6 meteorites (Fig. 1) at the NASA RELAB facility at Brown University. Spectra were measured from from 0.3-25 µm and modeled over the range 0.73 – 2.5 µm in order to avoid spectral effects due to terrestrial weathering (e.g., Fe-oxide features at VIS wavelengths)[8]. The Hapke-based RTM [9] developed by [3,10] was used to predict the abundances of 13 mineral end-members, including 6 clinopyroxene, 5 orthopyroxene, one olivine, and one plagioclase end member, because this spectral library was determined to be the most efficient set for robust modeling of unbrecciated eucrites and diogenites [3]. Inputs to the model were optical constants for these endmembers and outputs were abundance and grain size for each mineral. A single effective grain size was calculated for each spectral fit based on the average of each end-member's modeled grain size, weighted by end member-abundance.

XRD Analysis. Powder diffraction patterns were measured from 10-90° 2-theta at a resolution of 0.02° with a dwell time of 15 seconds (4 samples) or 9 seconds (2 samples) using Bruker D2 Phaser with a Cukα X-ray source and a Lynx-eye detector. Two analytical methods were employed to derive the relative modal abundances of orthopyroxene, clinopyroxene and plagioclase for each sample. First, all patterns were modeled using the LeBail whole pattern decomposition method [11] using Topas 4.2. The LeBail method refines the unit cell parameters, instrumental parameters, and peak intensities to extract the intensities of each hkl reflection (a proxy for mineral abundance). All fits employed hkls for augite, enstatite, and labradorite. The intensity of labradorite's [2 0 -1] reflection was ratioed to the combined intensity of augite's [2 -2 1] reflection and enstatite's [2 2 1] reflection to produce a measure of plagioclase abundance relative to total pyroxene (PLAG/PX). The intensities of augite's [2 -2 1] reflection and enstatite's [2 2 1] reflection were ratioed to produce an estimate of orthopyroxene abundance relative to clinopyroxene (OPX/CPX). These PLAG/PX and OPX/CPX abundance metrics were then compared with ratios of these phases determined from the Hapke RTM that was applied to the corresponding spectra (<45 µm fractions).

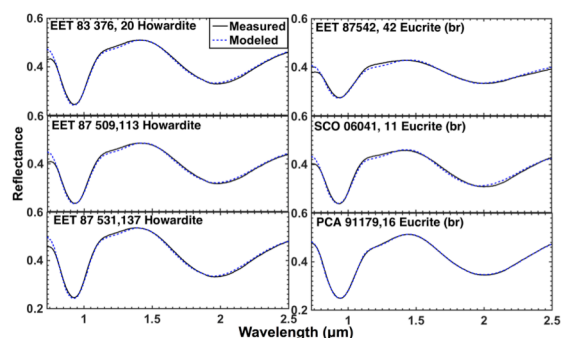

Figure 1. RELAB spectra of the <45 um size fraction of 3 howardites and 3 brecciated eucrites plotted with spectral fits from the RTM developed in [3].

We also performed preliminary Rietveld refinements using Topas 4.2 to identify both major minerals and terrestrial alteration phases, as well provide an estimate of modal mineralogy. Ongoing work will apply these refinements to all samples for a more robust estimation of modal values for major and minor phases.

Results. The quality of spectral fit for the <125 and ≤45 µm size fractions (Fig. 1) are in line with those reported by Li & Milliken 2015 for unbrecciated eucrites and diogenites; residuals for both howardite and brecciated eucrite samples are similar in magnitude. Additionally, particle sizes reported by the model are within expected ranges for both particle size suites. The largest spectral misfit occurs at <~0.73 µm, possibly due to the presence of terrestrial alteration products, especially Fe-oxides [8,12]. This is consistent with XRD patterns that indicate alteration products such as kaolinite and calcite.

Preliminary XRD Rietveld refinement results indicate that all major phases and the majority of minor phases can be successfully modeled using a library containing augite, enstatite, labradorite, forsterite, calcite, magnetite, kaolinite, and kamacite. As expected, orthopyroxene, clinopyroxene and plagioclase dominate the samples [4]. These results are in agreement with the results of the LeBail method, where low error values of ~1.5 rms and reasonable fits were achieved using only orthopyroxene, clinopyroxene and plagioclase as end members.

Discussion. PLAG/PX and OPX/CPX ratios derived from XRD data and the RTM (Fig. 2a) are highly correlated (with the exception OPX/CPX value for one eucrite), suggesting the RTM is able to accurately predict the relative proportion of these phases. However, XRD patterns systematically produce lower ratios of plagioclase relative to pyroxene than the Hapke RTM. This difference could be due issues caused by plagioclase's spectrally neutral nature relative to pyroxene [4]. Figure 2b shows that both XRD and spectral modeling techniques systematically predict more OPX than CPX in all meteorite samples, and that spectral modeling systematically produces a higher abundance of OPX relative to CPX than XRD peak ratios. The higher OPX/CPX values for howardites is consistent with the presence of a diogenitic component.

The goodness of spectral fit suggests the end member library used in the RTM is broadly capable of predicting the modal mineralogy of brecciated howardites and eucrites. However, both trends in Fig. 2 show the presence of outliers, indicating there might be a disagreement in estimated modal mineralogy between these two methods. This will be explored further by carrying out full quantitative refinements on XRD patterns to improve modal esimates and by measuring additional howardite and brecciated eucrite samples. Additionally, current XRD pattern fitting relies on only two pyroxene end members, augite and enstatite, whereas the spectral library utilized in this study contains 11 pyroxene compositions. Ongoing work includes adapting the RTM to include additional mineral endmembers that have been identified in howardites via XRD, including kamacite, clays, and carbonates.

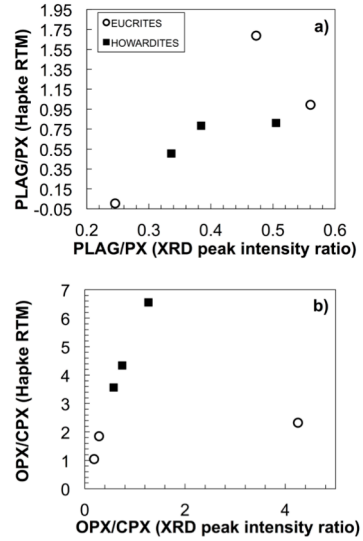

Figure 2. Mineral ratios from spectral RTM compared with proxies from XRD patterns for a) $PLAG/PX_{total}$ and **b)** OPX/CPX. The outlier eucrite sample may contain significant terrestrial alteration products.

Conclusions. Spectral and XRD modeling of data for three howardites and three brecciated eucrites shows promising results for using RTMs to predict modal mineralogy of these meteorites. Spectral fits with low RMS can be achieved with a limited spectral library that includes pyroxenes, olivine, and plagioclase, but residuals at certain wavelengths and estimates of modal mineralogy are likely to improve by adding new endmembers based on phases identified in XRD patterns. Kamacite, for instance, has been observed in several samples and will affect spectral properties such as albedo and slope. Howardites are further complicated by the presence of terrestrial weathering products, and though such phases may be volumentrically minor they can have large spectral effects (e.g., Fe oxides). Ongoing work will continue to test the efficacy of RTMs for HED breccias, including more robust estimates of modal mineralogy from XRD data. Ultimately, being able to map even the relative proportions of PLAG/PX and OPX/CPX across the surface of Vesta with Dawn VIR data can provide new insight into the distribution of basaltic (eucrite) and orthopyroxenite (diogenite) lithologies within the vestan crust.

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