Characterization of the 1.2 µm M1 pyroxene band: Extracting cooling history from near-IR spectra of pyroxenes and pyroxene-dominated rocks

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(Received 25 October 2007; revision accepted 20 April 2008)

Abstract–The 1.2 μ m band in near-infrared spectra of pyroxenes results from Fe²⁺ in the M1 crystallographic site. The distribution of Fe and Mg between the M1 and M2 sites is in part a function of the cooling rate and thermal history of a pyroxene. Combining near-infrared and Mössbauer spectra for a series of compositionally controlled synthetic Mg, Fe, Ca pyroxenes, we quantify the strength of the 1.2 μ m band as a function of Fe²⁺ in the M1 site. Near-infrared spectra are deconvolved into component absorptions that can be assigned to the M1 and M2 sites using the modified Gaussian model. The relative strength of the 1.2 μ m band is shown to be directly related to the amount of Fe²⁺ in the M1 site measured by Mössbauer spectroscopy. The strength of the 1.2 μ m band relative to the combined strengths of the 1.2 and 2 μ m bands, or the M1 intensity ratio, is calculated for 51 howardite, eucrite, and diogenite (HED) meteorites. Diogenites and cumulate eucrites exhibit the lowest M1 intensity ratios, consistent with their formation as slowly cooled cumulates. Basaltic eucrites exhibit a large range of M1 intensity ratios, all of which are consistently higher than the diogenites and cumulate eucrites. This example illustrates how the M1 intensity ratio can be a used as a tool for characterizing the cooling history of remotely detected pyroxene-dominated rocks.

INTRODUCTION

Pyroxene is one of the most abundant and spectrally distinctive minerals in the solar system. Characterizing the specific pyroxene mineralogy of a planet's surface allows us to address questions about the magmatic evolution and cooling history of the pyroxene-bearing rocks. In laboratory studies, the chemistries of coexisting pyroxenes have been used to characterize the phase equilibria of igneous systems, which can be used for geothermometry (Lindsley 1983). Detailed analyses of Mg-Fe²⁺ ordering between crystallographic sites in a pyroxene provide further constraints on the cooling rates and history of pyroxene-bearing rocks (e.g., Virgo and Hafner 1970; Saxena et al. 1974; Anovitz et al. 1988; Molin and Zanazzi 1991). Pyroxene compositions and site preferences inferred from remotely detected spectra can thus be used to address important petrologic questions. To do so requires a detailed understanding of how pyroxene spectra vary with mineral chemistry and how uniquely coupled these two variables are.

Laboratory studies of natural pyroxenes have provided a foundation for near-infrared spectral analyses (e.g., Adams 1974; Hazen et al. 1978; Rossman 1980; Cloutis and Gaffey

1991a; Burns 1993; Sunshine and Pieters 1993). Methods have been developed to estimate mafic mineralogy of asteroids and planets from reflectance spectra using the positions of absorption bands and their relative band areas (Cloutis et al. 1986; Cloutis and Gaffey 1991b; Gaffey et al. 2002), or by deconvolving near-infrared spectra into their component absorption bands (Sunshine et al. 1990; Sunshine and Pieters 1993). The majority of spectroscopic studies of pyroxenes have focused on characterizing the positions of the strong spin allowed crystal field absorption bands centered near 1 and 2 µm as a function of Ca and Fe content (Adams 1974; Hazen et al. 1978; Cloutis and Gaffey 1991a). An example of a typical pyroxene spectrum is presented in Fig. 1. Both the 1 and 2 µm bands of pyroxenes move regularly to longer wavelengths with increasing Fe and/or increasing Ca content. Despite these compositional trends, extracting geothermometric information from a the measurement of the 1 and 2 µm band minimum has been shown to be impossible (Cloutis and Gaffey 1991a) because the contours of band position on the pyroxene quadrilateral are roughly orthogonal to geotherms.

In addition to the 1 and 2 μm absorption bands, pyroxenes also exhibit a weaker absorption band at 1.2 μm



(Fig. 1) (e.g., Sunshine et al. 1990; Burns 1993; Klima et al. 2007). This absorption is best defined in Ca-saturated pyroxenes, particularly those belonging to type A in the nomenclature of Adams (1975) and Cloutis and Gaffey (1991a). The 1.2 μ m band is also prominent in high Fe orthoand clinopyroxenes. Many low-Fe pyroxenes have been shown to require an absorption band at 1.2 μ m when deconvolved by methods such as the modified Gaussian model (MGM) (e.g., Sunshine et al. 1990; Sunshine and Pieters 1993; Klima et al. 2007), even when such a band is not visually obvious.

The area and strength of the 1.2 μ m band provides additional information about the distribution of Fe²⁺ within the pyroxene, and, in orthopyroxenes, has been shown to correlate with the amount of Fe²⁺ in the M1 octahedral cation site as determined from Mössbauer spectroscopy (Besancon et al. 1991; Burns et al. 1991; Klima et al. 2007). Because the distribution of Fe²⁺ between cation sites is a function of the thermal history of a pyroxene, Fe-Mg ordering provides an additional constraint for assessing the cooling history of a pyroxene-bearing planetary body or surface unit observed by near-infrared remote sensing.

Though the 1 and 2 μ m pyroxene absorption bands have been extensively studied, the behavior of the 1.2 μ m band as a function of major cation chemistry has not been fully documented. This is in part due to the fact that many natural terrestrial pyroxenes (particularly orthopyroxenes) have cooled slowly or been metamorphosed, driving Fe²⁺ from the M1 cation site and consequently weakening the 1.2 µm band. Band relationships and strengths in natural pyroxenes are further complicated by the presence of minor elements such as Ti, Al, Na, and Mn. Klima et al. (2007) used the MGM to quantify the band parameters of the 1, 1.2, and $2 \mu m$ bands in a series of synthetic orthopyroxenes containing only Mg and Fe^{2+} in the octahedral cation sites. These orthopyroxenes, equilibrated at around 900 °C and then guenched, exhibit well-defined 1.2 µm bands that increase in strength as the total Fe²⁺ in the pyroxene increases. Building on the detailed orthopyroxene study and an expanded suite of Ca-bearing synthetic clinopyroxenes, in the discussion below we further quantify the behavior of the 1.2 µm band with compositions throughout the pyroxene quadrilateral. As an application, we demonstrate how the strength of the 1.2 µm band relative to the 2 µm band can be used to differentiate between quickly and slowly cooled materials on the HED (howardite, eucrite, and diogenite) meteorite parent body.

BACKGROUND

Fe²⁺-Mg Ordering in Pyroxenes

Pyroxenes are single-chain silicates containing cations in tetrahedral and octahedral sheets. Both monoclinic (clino) and orthorhombic (ortho) pyroxenes have two distinctive octahedral sites, M1 and M2. The M2 site is larger and more distorted than the M1 site in both ortho- and clinopyroxenes, and thus contains large cations such as Ca²⁺. When Fe²⁺ and Mg are present, Fe²⁺ prefers the M2 site over the M1 site both because Fe²⁺ is slightly larger than Mg²⁺ and because the distortion in the M2 site results in a greater crystal field stabilization energy for Fe²⁺ cations (Burns 1993). However, this preference is not absolute, and the amount of Fe²⁺ partitioned into the M1 and M2 sites depends on the bulk composition of the pyroxene, temperature and pressure of formation, cooling rate, and subsequent metamorphism (e.g., Virgo and Hafner 1970; Saxena and Ghose 1971). A pyroxene in which a large proportion of the Fe²⁺ resides in the M2 site is considered well ordered, while one with a closer to random distribution of Mg and Fe²⁺ between the M1 and M2 sites is considered more disordered.

The thermodynamics and kinetics of Mg-Fe²⁺ orderdisorder in orthopyroxenes (e.g., Evans et al. 1967; Anovitz et al. 1988; Stimpfl et al. 1999), pigeonites (Saxena et al. 1974; Pasqual et al. 2000; Domeneghetti et al. 2005) and clinopyroxenes (Hafner et al. 1971; Molin and Zanazzi 1991) are the focus of a large body of literature. In brief, pyroxenes that crystallize at high temperatures and cool quickly, such as volcanic tuffs or surface lava flows, show the highest concentrations of Fe²⁺ in the M1 site, or the highest degrees of disorder. Fe²⁺-Mg exchange in pyroxenes is relatively rapid



compared to most other cations. Experimental studies have shown that it is even difficult to quench Fe^{2+} -Mg distributions that are representative of true high-temperature equilibria (e.g., Zhang 1994). For example, reaction rate coefficients for the order-disorder reaction increase with increasing Fs content (Kroll et al. 1997). Thus in natural systems, Fe^{2+} and Mg can easily re-equilibrate between the M1 and M2 sites during cooling. So, slowly cooled intrusive igneous rocks and metamorphic rocks generally contain well-ordered pyroxenes.

Several examples of M1 and M2 site occupancies for terrestrial and extraterrestrial pyroxenes from the literature (as determined by Mössbauer spectroscopy and X-ray diffraction) are presented in Table 1, and a review of site occupancy with respect to the interpretation of asteroid spectra can be found in Hardersen et al. (2006). Samples in Table 1 are separated into extraterrestrial and terrestrial; each subgroup is listed in order of increasing total Fe. On average, approximately 20% of the total Fe resides in the M1 site. For very high-Fe or high-Ca samples (SC6C and XYZ), the percentage is necessarily higher, as the M2 sites are almost completely filled by Fe or Ca, forcing large amounts of Fe into the M1 site. Samples with less than 10% of the total Fe in the M1 site are either metamorphosed (274) or slowly cooled cumulates (Johnstown). In the case of samples 68671 and HK56071001, both of which have the same $Fe^{2+}/(Fe^{2+} + Mg)$ ratio, the metamorphic granulite is significantly more ordered (15% of Fe in M1) than the more rapidly cooled dacite (25% of Fe in M1).

Determination of Site Occupancy in Pyroxenes

The M1 and M2 site occupancy of Fe²⁺ in pyroxenes can be quantitatively determined using Mössbauer spectroscopy. Mössbauer spectra measure absorptions caused by nuclear energy transitions, and are sensitive to the valence state of iron, the symmetry of the cation site, the surrounding anion environment and the presence or absence of magnetic ordering (Dyar et al. 2006). An example of a Mössbauer spectrum for the En40Fs60 synthetic orthopyroxene is presented in Fig. 2. A Mössbauer doublet can be described by its isomer shift, caused by the difference in the s-orbital electron density between the nuclei of the ⁵⁷Co source and the sample, and its quadrupole splitting. The quadrupole splitting, or the distance between the two peaks in a doublet, is a result of the splitting of the nuclear quadrupole moment by the local ligand field (Dyar et al. 2006). The differing environments around Fe²⁺ in the M1 and M2 sites result in each site having slightly different Mössbauer parameters. The inner doublet is assigned to the M2 site, and the outer doublet is assigned to the M1 site (Fig. 2)(e.g., Bancroft et al. 1967; Evans et al. 1967; Saxena and Ghose 1971).

The areas of the doublets that comprise a Mössbauer spectrum are proportional to the relative number of atoms of the species represented by the doublet, i.e., the relative amount of Fe²⁺ in the M1 and M2 sites or the proportion of Fe²⁺ (or Fe³⁺) relative to the total Fe content (e.g., Preston et al. 1962; Bancroft et al. 1967; Bancroft 1969). A quantitative determination of number of moles of Fe²⁺ per site requires a correction for thickness (Rancourt et al. 1993) and for the recoil-free fraction (*f*) for the M1 and M2 sites (work currently in progress).

An alternative method to quantitatively determine the concentration of Fe²⁺ in the M1 and M2 crystallographic sites from polarized near-infrared absorption spectra of orthopyroxene crystals has also been developed (Goldman and Rossman 1979). Goldman and Rossman suggest using the 2 μ m M2 band in the β polarization direction, because its absorbance is shown to vary linearly with concentration of Fe²⁺ in the M2 site as determined by Mössbauer spectroscopy.

Relating absorbance to the amount of Fe in a crystallographic site requires a precise knowledge of the thickness and orientation of the orthopyroxene crystal. This cannot be directly applied to reflectance spectra of bulk samples, because light traveling through the grains is multiply scattered and the grains are randomly oriented. Nevertheless, the relative strengths of the 1.2 µm M1 and 2 µm M2 sites in a powdered sample are still related to the populations of Fe²⁺ in each site. Burns et al. (1991) heated natural pyroxenes to a series of different temperatures to observe the disorder as measured by the change in relative areas of the M1 and M2 Mössbauer doublets (Besancon et al. 1991; Burns et al. 1991). Near-infrared reflectance spectra were also measured, and the modified gaussian model (MGM) was used to separate the pyroxene spectra into component absorptions that could then be assigned to the M1 site (1.2 μ m band) and the M2 site (2 μ m band). For each absorption, the MGM outputs a continuumremoved band intensity (similar to band depth but usually calculated as natural log reflectance), band width (full width at half maximum), band center and band area. Burns et al. (1991) compared the percent area of the 1.2 μ m band relative to the sum of the areas of the 1.2 and 2 μ m bands to the area of the M1 Mössbauer doublet and concluded that despite the effects of unknown crystal orientation and surface scattering, the two methods were linearly related. Although this relationship was developed using Mössbauer data that were not corrected for thickness and differential recoil-free fraction effects, those corrections are expected to be small, are (probably) linear with composition, and thus would affect the slope of the relationship only slightly.

Here, we define the M1 area ratio as:

M1 Area Ratio =
$$\frac{\text{Area }_{1.2\mu\text{m}}}{\text{Area }_{1.2\mu\text{m}} + \text{Area }_{2\mu\text{m}}}$$
 (1)

For comparison, MGM M1 area ratio values in Burns et al. (1991) are given as percentages rather than fractional ratios as in this work.

Klima et al. (2007) showed that for a suite of synthetic Ca-free orthopyroxenes, a linear relationship also exists

*	10 0	,	N	11		M2				
Sample name	Source	Туре	Mg	Fe	Mg	Fe	Ca	Fe_{M1}/Fe_{tot}	Method	Refs
Extraterrestrial										
Hallingeberg	L chondrite	OPX	0.960	0.040	0.830	0.170	n.a.	0.19	Mössbauer	1, 2
Sharps	H chondrite	OPX	0.920	0.080	0.800	0.200	n.a.	0.29	Mössbauer	1, 2
PCA82506-3	Ureilite	CPX	0.915	0.049	0.562	0.305	0.117	0.14	XRD	3
Carraweena	L chondrite	OPX	0.930	0.070	0.670	0.330	n.a.	0.18	Mössbauer	1, 2
Johnstown N.15	Diogenite	OPX	0.939	0.027	0.482	0.463	0.054	0.05	XRD	4
12021,150-P1	Apollo 12 basalt	СРХ	0.879	0.121	0.305	0.521	0.176	0.19	Mössbauer	5
Terrestrial										
SC6C	Salina lava flow	CPX	0.815	0.105	0.083	0.155	0.754	0.40	XRD	6
N-5	Stillwater norite, Montana	OPX	0.963	0.037	0.494	0.506	n.a.	0.07	Mössbauer	2
274	Silicate from iron formation, Quebec	OPX	0.978	0.022	0.678	0.322	n.a.	0.06	Mössbauer	2
BTS308 N.35	Paraná rhyodacite	CPX	0.776	0.196	0.144	0.636	0.191	0.24	XRD	7
N103/719138 #12	Hatepe Lapilli	OPX	0.724	0.276	0.276	0.724	0.050	0.28	Mössbauer	8
68671	Granulite, Ceylon	OPX	0.836	0.164	0.101	0.899	n.a.	0.15	Mössbauer	2
HK56071001	Dacite, Sidara Japan	OPX	0.736	0.264	0.195	0.805	n.a.	0.25	Mössbauer	2
XYZ	Granulite, West Greenland	OPX	0.216	0.784	0.030	0.970	n.a.	0.45	Mössbauer	2

Table 1. M1 and M2 site occupancies of Mg and Fe^{2+} in natural extraterrestrial and terrestrial pyroxenes as determined by Mössbauer spectroscopy and X-ray diffraction (XRD).

¹Dundon and Walter 1967; ²Virgo and Hafner 1970; ³Pasqual et al. 2000; ⁴Zema et al. 1971; ⁵Hafner et al. 1971; ⁶Molin and Zanazzi 1991; ⁷Domeneghetti et al. 2005; ⁸Johnston and Knedler 1979. Refs = references.



Fig. 2. 80K Mössbauer spectrum of a synthetic orthopyroxene with a composition of $En_{40}Fs_{60}$. The model fit is shown as a thin black line, with the M1 doublet component in grey and the M2 doublet in black. Data points are plotted as error bars representing the standard error.

between the Mössbauer M1 area and the band intensities of the 1.2 and 2 μ m bands. The advantage of using the M1 Intensity Ratio, where:

M1 Intensity Ratio =
$$\frac{\text{Intensity}_{1.2\mu\text{m}}}{\text{Intensity}_{1.2\mu\text{m}} + \text{Intensity}_{2\mu\text{m}}}$$
(2)

is that the intensity of an absorption is directly controlled by the probability of a crystal field transition occurring, which in turn depends on the site symmetry/ligand environment and the concentration of Fe^{2+} in the site. Band area incorporates band width, which is not strictly a function of the cation concentration, and may vary with temperature or other factors (Burns 1993). Deconvolution of reflectance spectra with very weak bands may also result in abnormally wide, shallow bands, with unrealistically larger than normal band areas.

Ca-Fe-Mg Synthetic Pyroxenes

To isolate the systematics of the M1 1.2 μ m band as a function of quadrilateral pyroxene chemistry and Fe²⁺ site occupancy, we focus on a subset of a suite of synthetic pyroxenes synthesized by Don Lindsley and colleagues between 1972 and 2007. Natural Ca-bearing pyroxenes often contain a significant number of non-quadrilateral components, such as Al or Cr, as well as some portion of Fe³⁺. By using synthetic pyroxenes, we can control not only the composition and oxidation state of the pyroxenes, but also the synthesis pressure, temperature, and cooling history.

Syntheses used procedures described in Turnock et al. (1973) with minor variations. All samples were prepared from reagent grade chemicals. Specific methods vary by composition, and were chosen to prevent nucleation of pyroxenoids and produce a single, homogeneous pyroxene. Hydrothermal syntheses were controlled to have fO_2 below FMQ (fayalite-magnetite-quartz) by dissociation of oxalic acid. Samples made in Fe capsules had fO_2 's below IW (iron-wüstite) but above IQF (iron-quartz-fayalite). The end result was that no Fe³⁺ was observed in any of these samples.

All samples were cooled to room temperature from 900– 1500 °C in water, so cooling times are estimated to be less than 1–2 min., but this is probably not fast enough to quench their high-temperature Fe^{2+}/Mg equilibria. The effect of quenching rate on the Fe distribution will probably be more severe for higher-Fe samples content as a result of the dependence of rate constants on Fe content (Kroll et al. 1997; Wang et al. 2005). However, all the samples were quenched in the same fashion, and the important thing for the present study is that the quenched distributions measured by Mössbauer and FTIR are the same. It is also important to note that our quench rates are likely to be orders of magnitude faster than cooling rates in planetary bodies because of their small sample sizes. Pyroxene compositions and space groups were confirmed by electron microprobe and X-ray diffraction.

Shown in Fig. 3 is a pyroxene quadrilateral representing the compositions of pyroxenes included in this study. Small black dots represent pyroxenes published in Klima et al. (2007), while large black dots represent pyroxenes that have been chosen for this study. Synthetic pyroxenes with evidence for exsolution were excluded from this work, because we are interested in the intensities of the 1.2 μ m and 2 μ m bands for single-phase pyroxene. Although the MGM allows deconvolution of multiple pyroxenes, we first seek to isolate the trends associated with crystal structure, composition, and site occupancy before considering the effect of exsolution.

Howardite, Eucrite, and Diogenite (HED) Meteorites

The HED meteorites, thought to originate on the asteroid 4 Vesta, can be broadly subdivided into basaltic and cumulate rocks. Diogenites are cumulates, consisting primarily of orthopyroxene with some finely exsolved augite (~10s of nm wide lamellae) (e.g., Mittlefehldt et al. 1998). Eucrites contain plagioclase and low-Ca pyroxene, and may be either cumulate or basaltic (e.g., Mittlefehldt et al. 1998). Howardites are physical mixtures of these lithologies. In general, HEDs are spectrally dominated by pyroxene, as is asteroid 4 Vesta.

Diogenites are nearly pure pyroxene, but eucrites and howardites contain a significant component of plagioclase. If Fe²⁺ is incorporated into the plagioclase crystal structure, as is the case for lunar plagioclase, a crystal field absorption band occurs near 1.2 µm. For plagioclase collected at the Luna 20 landing site, the strength of this absorption band has been shown to relate linearly to the amount of iron in the plagioclase (Bell and Mao 1973). The amount of iron in the plagioclase of typical eucrites is generally lower than in lunar plagioclase. There is also evidence that in eucrites where the bulk plagioclase contains as much as 0.12-0.13% Fe²⁺, this Fe²⁺ may not be incorporated into the plagioclase crystal structure. Plagioclase mineral separates extracted from cumulate eucrite Yamato (Y-) 980318 were found to contain an average of 0.13% Fe²⁺ (comparable to 0.12% Fe²⁺ in Serra de Magé plagioclase). Individual analyses, however, ranged from 0.03% to 0.28% Fe^{2+} , and likely suggest that the iron is present as inclusions in the plagioclase (Hiroshi Takeda, personal communication). The spectrum of the plagioclase



Fig. 3. Compositions of pyroxenes used in this study. Grey dots indicate the compositions of orthopyroxenes published by Burns et al. (1991), and small black dots indicate pyroxenes previously described by Klima et al. (2007). Also indicated are the general regions of pyroxene compositional space for diogenite (D), eucrite (E) and cumulate eucrite (CE) meteorites.

mineral separate of Y-980318 exhibits no absorption band at 1.2 μ m, though the bulk meteorite and pyroxene mineral separate spectra show a clear 1.2 μ m band (Pieters et al. 2005). To confirm this result, a second suite of mineral separates was prepared from the eucrite Y-980433. Spectra of the bulk meteorite, plagioclase, and pyroxene are presented in Fig. 4. As was observed for Y-980318, the plagioclase spectrum is almost completely flat through the near-infrared, and the only clear effect of the plagioclase on the bulk meteorite spectrum is an overall increase in albedo. Because the iron in HED plagioclase does not appear to be spectrally significant, we will treat HEDs as pyroxene-dominated rocks and assume that the 1.2 μ m band is entirely due to Fe²⁺ in the M1 site of pyroxene.

Several examples of HED spectra are presented in Fig. 5. Diogenites and basaltic eucrites can be distinguished from one another spectrally on the basis of the position of the 2 μ m band, which moves to longer wavelengths with the addition of Ca and Fe²⁺ (both of which are higher in eucrites than diogenites, see Fig. 3). However, for HEDs of similar bulk composition but different cooling history, such as the more Mg-rich basaltic eucrites and more Fe-rich cumulate eucrites, the 2 μ m band is insufficient to distinguish between the spectra. The relative strengths of the 1.2 μ m and 2 μ m bands also vary among the HEDs. Diogenites exhibit the weakest 1.2 μ m bands relative to the 2 μ m bands, while eucrites generally exhibit stronger 1.2 μ m bands.

SPECTROSCOPIC METHODS

Near-Infrared Spectroscopy and Modeling

Near-infrared spectra were collected using the Bidirectional Reflectance Spectrometer (BDR) at the NASA/ Keck Reflectance Experiment Lab (RELAB) at Brown University. Synthetic pyroxene samples were sieved to a grain



Fig. 4. Bulk rock and mineral separate spectra of cumulate eucrite Y-980433. The weak absorption near 1 μ m in the plagioclase is due to minor amounts of pyroxene contamination on the plagioclase grains. This contamination may also account for the minor inflections in the plagioclase spectrum near 1.2 and 2 μ m, though these features are too weak to reliably assign to either plagioclase or the trace of pyroxene.

size of <45 µm although the actual grain size is much smaller. Forty-nine HED spectra (<25 µm grain size) which were originally analyzed by Hiroi et al. (1994; 1995; 2001) were acquired from the RELAB database. An additional two cumulate eucrites (Y-980433 and Y-980318) were measured and published in a more recent study (Pieters et al. 2005). Spectra from the heating-induced disordering experiments conducted by Burns et al. (1991) were also obtained from the RELAB database. All samples were measured with an incidence angle of 30° and an emission angle of 0° over the wavelength range of $0.3-2.6 \mu m$ (5 nm sampling resolution). Raw data were ratioed with a spectrum of a calibrated halon reference standard to produce reflectance values.

All spectra were modeled using the MGM. The MGM deconvolves a spectrum into a continuum slope and a series of bands that can be directly linked to the crystal field absorptions that produce them (Sunshine et al. 1990; Sunshine et al. 1999). The MGM also outputs a wavelength-dependent RMS error, allowing the user to analyze whether additional absorptions are not being accounted for in a given fit. For synthetic pyroxenes, a continuum slope that is linear in wavelength space was chosen, but the slope and offset were allowed to vary freely. The visible region was modeled using 2–3 bands to account for oxygen-metal charge transfers.

Four spin-allowed crystal field transitions are predicted to occur in the near-infrared: one near 1 μ m and one near 2 μ m for the M2 site, and one near 1 μ m and one near 1.2 μ m for the M1 site. For low-Ca pyroxenes, the higher energy



Fig. 5. Example spectra of howardites, eucrites and diogenites. The wavelength position of the 2 μ m band relates to the amount of Mg, Fe²⁺, and Ca in the pyroxenes, moving to longer wavelengths for meteorites with higher Fe and Ca. The 1.2 μ m band also varies between the meteorites, and is generally visibly stronger in eucrites than in diogenites (after Pieters et al. 2005).

absorptions (~1 μ m) due to Fe²⁺ in the M1 and M2 sites occur at very similar wavelengths (e.g. Burns 1993) and are generally modeled as one band. For low-Ca, low-Fe pyroxenes where most of the Fe²⁺ is in the M2 site, this does not produce significant RMS error, but for pyroxenes with >50% Fe²⁺/(Fe²⁺ + Mg), an increase in RMS error around 1 µm becomes apparent (Klima et al. 2007). Caundersaturated pyroxenes can thus be modeled effectively with three spin-allowed crystal field absorption bands, but high-Ca pyroxenes require four distinct absorption bands. Because our goal is to characterize the intensity and behavior of the 1.2 µm band, MGM fits using four bands were used throughout the quadrilateral. For all pyroxenes beneath the diopside-hedenbergite join, three-band fits were also produced for comparison. The band area ratios (Equation 1) and band intensity ratios (Equation 2) were calculated using both the three- and four-band fits to determine whether the fitting method for the 1 µm band affected these ratios. For most pyroxenes, the ratios were equivalent for both fitting methods, with a maximum difference of 2%.

HED spectra were modeled with a continuum that was constrained to have a nearly flat ($\sim -10^{-10}$) slope. Although many of the HED spectra are actually mixtures of different pyroxene compositions, either due to mechanical mixing in regolith breccias or intimate mixing resulting from exsolution, we have chosen to model their spectra as single (three-band) pyroxenes. The choice of a flat slope and three

modified Gaussian curves to represent the crystal field absorptions is a simplification that will allow broader applications of absorption bands present. Our goal is to test whether the M1 intensity ratio can be simply applied to a suite of natural samples to differentiate, to first-order, between slowly cooled and rapidly cooled (on geological time scales, not those of the laboratory) pyroxene-dominated rocks.

A simplified MGM deconvolution can be applied to successfully derive basic parameters. However, a full MGM fit allowing for a sloped continuum and multiple pyroxenes, such as is used by Mayne et al. (2006) and Mayne (2008) should be used if quantitative petrologic information is desired. A comparison between a fit using our simplified three band deconvolution and a full two-pyroxene five band fit for the monomict eucrite Bouvante is shown in Fig. 6. A reasonable fit with low overall RMS error is derived using a flat continuum and a single pyroxene (Fig. 6a). In the 2 µm region, the best-fit modified Gaussian curve has a center wavelength that is slightly offset from the apparent band minimum. When a two-band pyroxene mixture is considered (Fig. 6b), the RMS error near 2 µm is reduced significantly (Fig. 6c). The MGM fit in Fig. 6b was derived using a straight line continuum in wave number space, a 1 and 2 µm band for each pyroxene, and one 1.2 µm band. The energies at which the 1.2 µm M1 absorption occurs in low- and high-Ca pyroxenes are very similar, making deconvolution of the bands into two physically meaningful bands near 1.2 µm impossible without imposing additional constraints on the MGM.

The single pyroxene fit depicted in Fig. 6a produces average pyroxene parameters that are comparable to those needed for analyses using band area and band center, such as those developed by Gaffey et al. (2002). A two-pyroxene fit, as in Fig. 6b, enables determination of relative amounts of coexisting pyroxenes (Sunshine and Pieters 1993). Using the calibration curves of Sunshine and Pieters (1993) and the relative strengths of the low- and high-Ca pyroxene 1 and $2 \mu m$ bands, we estimate that Bouvante contains roughly 33% high-Ca pyroxene and 66% low-Ca pyroxene. This result is consistent with the petrographically determined modal abundances reported by Delaney et al. (1984). They report that of the pyroxene, 31% is augite, 18% is orthopyroxene, and 51% is pigeonite.

Mössbauer Spectroscopy and Modeling

Mössbauer spectra were collected at Mount Holyoke College using a WEB Co. model W100 spectrometer with a 45 mCi ⁵⁷Co in Rh source. Samples were run at a series of temperatures ranging from room temperature to 4 K. For each spectrum, the fraction of the baseline due to the Compton scattering of 122 keV gammas by electrons inside the detector was determined by measuring the count rate with and without a 14.4 keV stop filter (~2 mm of Al foil) in the gamma beam. Compton-corrected absorption was calculated for each



Fig. 6. MGM fits for the monomict eucrite Bouvante. a) Simplified MGM fit using a flat continuum and one (three-band) pyroxene. b) MGM fit using a straight line slope in wave number space and two pyroxene mixture. c) Comparison of the RMS error for each fit as a function of wavelength.

individual spectrum using the formulation A/(1 - b), where *b* is the Compton fraction and *A* is the uncorrected absorption. This correction does not change the results of the fits per se but does allow accurate determination of % absorption in the spectra. It is necessary because the range of energy deposited in the detector by Compton events extends from 0 keV to

40 keV, overlapping both the 14 keV and 2 keV energies deposited by the 14 keV gammas. Compton-corrected spectra were collected in 1048 channels and corrected for nonlinearity via interpolation to a linear velocity scale defined by the spectrum of the 25 μ m α -Fe foil used for calibration. Data were then folded before fitting.

Data were modeled using an in-house program generously made available to us by Eddy De Grave and Toon Van Alboom at the University of Ghent, in Belgium. The Dist3e program models spectra using quadrupole splitting or hyperfine field distributions for which the subspectra are constituted by Lorentzian-shaped lines; it uses velocity approximations rather than solving the full Hamiltonian. This program does not presume any particular shape of the distribution, in contrast to other distribution programs (e.g., Recoil). A starting isomer shift and line width at half maximum for each doublet is input into the model, along with a range of quadrupole splitting values. Starting parameters were adjusted until the model produced an acceptable fit with all variables unconstrained. Errors on isomer shift and quadrupole splitting are ± 0.02 mm/s, and errors on peak areas are $\pm < 1\%$ absolute. Extrapolation of our peak areas to true site occupancies is not possible at this time because the corrections for recoil-free fraction are not yet known. However, this makes it possible to directly compare our results to those of Burns et al. (1991) and Besancon et al. (1991).

Each Mössbauer spectrum was fit with two doublets, one for the M1 and one for the M2 sites (Fig. 2). The total area of a spectrum, or the sum of the areas of the M1 and M2 doublets, of each pyroxene is normalized to 100%. Thus, the M1 Mössbauer Area is defined as the percent area of the Mössbauer spectrum contributed by Fe^{2+} in the M1 site. For comparison with previous studies fitting 77 K Mössbauer spectra (e.g., Burns 1991; Besancon 1991), we chose to fit spectra collected at 80 K. By way of comparison, data from Klima et al. 2007 were derived from room temperature Mössbauer spectra. Although the percent areas of the M1 and M2 doublets should remain consistent (within ~2–3%) at all temperatures, the individual doublets are more easily resolved by fitting programs at lower temperatures.

RESULTS

Isolation of the M1 1.2 μ m Band

Ca-bearing pyroxenes containing near 50% Ca/(Ca + Mg + Fe²⁺) have been divided into two spectral groups by Adams (1975) and later by Cloutis and Gaffey (1991a): type A, which exhibit bands near 0.9 μ m and 1.2 μ m and no 2 μ m band, and type B, which exhibit the more commonly observed 1 μ m and 2 μ m pyroxene bands. Both the high-Ca pyroxenes measured by Cloutis and Gaffey, as well as those analyzed by Schade et al. (2004) contain significant quantities of non-

quadrilateral elements, such as Cr, Al, Mn and Fe³⁺. The addition of transition elements other than Fe^{2+} , in particular, leads to very strong absorption bands at visible wavelengths for many natural type A pyroxenes.

To quantify the behavior of the 1.2 µm band in a pure system, we examined two synthetic hedenbergites of the same elemental composition (Wo₅₀Fs₅₀ or CaFeSi₂O₆) but slightly different site occupancy. Both are Fe³⁺-free as determined by Mössbauer spectroscopy, but one would be classified as type A and one type B. MGM fits of the two hedenbergites are presented in Fig. 7. The type A hedenbergite spectrum (Fig. 7a) exhibits a broad multicomponent band that appears to be composed of two roughly equal bands. Though MGM input parameters began with two bands of equivalent strength, the model iterations consistently resulted in a 1.2 μ m band that was more intense than the band at 0.9 µm. No model fit could be derived that would allow both bands to have near-equal intensity. MGM fits performed by Schade et al. (2004) for natural high-Ca pyroxenes also resulted in the 0.9 µm band being weaker than the 1.2 µm band. Absorption bands were also added to the model near 1 and 2 m to account for any Fe²⁺ present in the M2 site. A weak band was necessary at 2 µm, suggesting that a trace amount of Fe²⁺ does reside in the M2 site. This amount of Fe²⁺ was below the detection limits of even low-temperature Mössbauer measurements, suggesting that near-infrared spectra are extremely sensitive to very small amounts of Fe²⁺ in the M2 site. In addition to the crystal field bands predicted for Fe2+, fits require a modified Gaussian curve near 0.75 µm (dashed band in Figs. 7a and 7b). This is also consistent with MGM deconvolutions performed by Schade et al. (2004). A similar feature was observed in transmission spectra of high-Ca clinopyroxenes (e.g. Burns 1993). Although it has been suggested that this feature could be caused by an intervalence charge transfer (IVCT) between Fe²⁺ and Fe³⁺, Fe³⁺ was not detected, even by low-temperature Mössbauer spectroscopy of our samples.

Using the parameters for the two M1 bands near 0.9 and 1.2 μ m as starting parameters, an MGM fit can be derived for the type B hedenbergite (Fig. 7b). In addition to the M1 bands, weak M2 bands near 1 and 2 μ m are required for this sample. Shown in Fig. 7c is a comparison of the deconvolved crystal field bands for the type A and type B hedenbergite. The M1 bands are slightly weaker, as expected, in the type B hedenbergite. The separation between the 0.9 μ m and 1.2 μ m bands is greater in the type A hedenbergite than in the type B. The difference in intensities between the bands in the type A and type B hedenbergites correspond to a difference of 3% Fe²⁺ peak area as calculated from Mössbauer fits of 80 K spectra.

MGM fits of the remaining Ca-undersaturated pyroxenes indicate that with decreasing Ca, the separation between the two M1 bands continues to decrease. The intensity of the 1.2 μ m band is a function of both the total Fe²⁺ and total Ca in the pyroxene. This is expected, because



Fig. 7. MGM fits for a synthetic type A and type B hedenbergite. The type B hedenbergite contains 3% Fe²⁺ in the M2 site, while Fe²⁺ in the M2 site of the type A hedenbergite is below the detection limits of Mössbauer spectroscopy. a) MGM fit of the type A hedenbergite. b) MGM fit of the type B hedenbergite. c) Comparison of M1 and M2 crystal field bands for the type A and type B hedenbergites.

high concentrations of Ca occupy the M2 sites and force Fe²⁺ into the M1 site.

Derivation of Site Occupancy of Fe²⁺ Using NIR Spectra

An accurate quantitative measurement of the site populations of Fe^{2+} using Mössbauer spectra requires that the recoil-free fraction of a mineral be measured. In previous studies, the ratio of the recoil-free fraction of the M1 and M2 pyroxene sites has generally been assumed to be near unity (e.g., Burns et al. 1991). However, temperature-series measurements of pyroxenes indicate that the ratio of the recoil free fraction of the M1 and M2 sites ranges from at least 0.93 to 1.25 (De Grave and Van Alboom 1991; Eeckhout and De Grave 2003). For consistency and easy comparison with work published by previous authors, we here use the area of the M1 doublet in a Mössbauer spectrum, with the total spectrum area normalized to 100, as a proxy for the amount of Fe^{2+} in the M1 site (refer to Fig. 2 for an example of the M1 and M2 doublets for a Mössbauer spectrum). In future work (in progress), we will incorporate Mössbauer measurements of the synthetic pyroxenes acquired over the requisite temperature range so as to directly measure the recoil-free fraction and calculate the actual "true" site occupancies (also correcting for thickness).

Shown in Fig. 8 is a comparison of the M1 Mössbauer area to the MGM-based M1 area ratio derived for spectra of the synthetic pyroxenes using Equation 1. Also included are data collected by Burns et al. (1991) and data for nine synthetic orthopyroxenes from Klima et al. (2007)



Fig. 8. M1 area ratio derived from equation 1 compared to the M1 Mössbauer area for pyroxenes in this study. Natural pyroxenes (triangles) are from MGM fits performed by Burns et al. (1991) and open circles were previously discussed in Klima et al. (2007).

(compositions indicated in Fig. 3). Burns et al. measured the Mössbauer and near-infrared spectra of five natural pyroxenes, and then heated them to 500 °C and 700 °C at a controlled oxygen fugacity to disorder the Fe^{2+} into the M1 site (Burns et al. 1991; Besancon et al. 1991). Both the unheated and heated data (11 total) are included in Fig. 8.

For all pyroxenes, the M1 Area ratio is strongly correlated to the M1 Area measured by Mössbauer spectroscopy. The M1 area ratio is less than 50 for all pyroxenes except for those that are nominally Ca-saturated pyroxenes ($Wo_{50}En_{10}Fs_{40}$, M1 Area Ratio = 78 and the type B $Wo_{50}Fs_{50}$, M1 Area Ratio = 85). This is a result of the difference in the asymmetry of the M1 and M2 sites. Fe²⁺ in the M2 site, which is more distorted than the M1 site, produces broader, stronger absorption bands than Fe²⁺ in the M1 site. Thus, the 2 µm (M2) band does not become significantly weaker than the 1.2 µm (M1) band until it is almost completely occupied by Ca and contains only small amounts of Fe²⁺.

The systematic relationship between the M1 intensity ratio and the M1 Mössbauer area more closely approaches a 1:1 line than does the M1 area ratio relative to the Mössbauer area, as illustrated in Fig. 9. A 1:1 correlation between the M1 intensity ratio and the M1 Mössbauer area would be expected if both were perfect measures of the Fe²⁺ present in the M1 site. If the M1 site occupancy derived by Dyar et al. (2007), which *is corrected* for thickness effects and differential recoil-free fraction, is used for the synthetic orthopyroxenes instead of simply the M1 area, those data points shift slightly to the left on the diagram, closer to the ideal 1:1 line. Similarly, conversion of infrared spectra to single-scattering albedo using Hapke modeling (Hapke 1993) rather than natural log reflectance should better approximate absorbance,



Fig. 9. M1 intensity ratio derived from Equation 2 for synthetic pyroxenes and natural orthopyroxenes compared to the Mössbauer M1 area. Symbols are the same as those in Fig. 8.

moving the data points up on the diagram and closer to a 1:1 relationship with the molar occupancy determined by Mössbauer.

For powdered pyroxene samples, the consistency of the relationship between the Mössbauer measured Fe^{2+} site occupancy and the MGM-derived M1 intensity ratio indicates that site occupancy can be approximated from laboratory reflectance spectra (Fig. 9). For high spectral resolution remotely sensed near-infrared spectra, derivation of the M1 intensity ratio for pyroxene-rich lithologies can provide a relative measure of site occupancy (and thus cooling history) from orbit.

Application to the HED Meteorites

As discussed above, the M1 intensity ratio is directly related to the proportion of Fe²⁺ in the M1 site, which in turn depends in part on the thermal history of a pyroxene. The M1 intensity ratio has been derived for the spectra of 51 HED meteorites to evaluate how well the M1 intensity ratio can be used to differentiate between slowly and rapidly cooled natural pyroxene-bearing rocks. The meteorite spectra taken from the RELAB database have been classified broadly as eucrites, howardites, or diogenites. The petrology of some of the meteorites has not been described formally, and eucrites are not classified into basaltic or cumulate subgroups in the database. The eucrites that are known to be cumulates, including Y-980318 and Y-980433 have been grouped as such for this analysis. For global-scale mapping, it is essential that any parameter be easy to apply to large amounts of data with minimal user interaction. We have thus applied the simplified MGM fitting scheme, using



Fig. 10. M1 intensity ratios for the HED meteorites studied. a) M1 intensity ratios for the individual HED meteorite suite studied. Arrows indicate the meteorites plotted in (b) and meteorites with letters above the bars indicate that they have anomalous ratios that are described in detail in the text. b) Comparison of two eucrites that would be mapped as the same lithology if only the 2 μ m band position were used. The M1 intensity ratio for the cumulate eucrite, Serra de Magé, is significantly lower than that of the basaltic eucrite Pasamonte. c) M1 intensity ratio as a function of the wavelength position of the 2 μ m band. The M1 intensity ratio allows the meteorites to be distinguished by cooling regime, while the 2 μ m band separates them by average pyroxene composition. Anomalous meteorites are marked by letters, which correspond with the letters in (a).

a flat continuum and parameters for only one three $(1, 1.2, and 2 \mu m)$ band pyroxene, to the HEDs. We expect that for both our HED meteorites and for much of the surface of Vesta, the 1.2 μm band will be reasonably strong. This is because most of the surface is likely to consist of rapidly cooled basaltic material, or mixtures containing a large amount of a basaltic component. For exposed slowly cooled cumulates, the 1.2 μm band would be weaker. Our choice of a flat continuum may slightly overestimate the M1 intensity ratio if a spectrum is slightly red-sloped. By erring on the side of a stronger M1 intensity ratio, we can be more confident that any meteorites (or surface units mapped) with

a low M1 intensity ratio will be well-ordered, slowly cooled cumulates (or mixtures with a large portion of cumulate material in them).

The M1 intensity ratios derived for the HEDs are presented in Fig. 10. Shown in Fig. 10a are the M1 intensity ratios for the HED meteorite groups including the specific meteorite names. The diogenites, which are presumably the most slowly cooled, have the lowest M1 intensity ratio of 0.14 \pm 0.05. Using the relationship in Fig. 9, we can estimate that this corresponds to around an average of 9% of the total Fe²⁺ residing in the M1 site. Cumulate eucrites cluster very tightly around an M1 intensity ratio of 0.18 \pm 0.01, or contain

Table 2. Average M1 intensity ratios and predicted M1 site occupancy for eucrites, diogenites, and selected synthetic pyroxenes.

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Sample/group	Fs	M1 intensity ratio	Fe _{M1} /Fe _{tot}
Diogenites (avg) Cumulate Eucrites (avg)	25 ¹ 45 ¹	0.14 0.18	0.09^2 0.16^2
Eucrites (avg)	55 ¹	0.26	0.33 ²
Synthetic OPX 026	30	0.20	0.19 ³
Synthetic OPX 004	50	0.23	0.26 ³
Synthetic CPX 011	54	0.31	0.39 ³

¹Fs content for each meteorite group is an approximation of the mean based on elemental analyses published in Mittlefehldt et al. (1998). ²Fe²⁺ in M1 site as predicted by a linear regression of data from Fig. 9. Ca-saturated pyroxenes were excluded from the regression. ³Fe²⁺ in M1 site as predicted by Mössbauer doublet area.

roughly 16% of the total Fe²⁺ in the M1 site. The M1 intensity ratios of the eucrites as a group (most of which are probably basaltic) average 0.26 ± 0.07 , or between approximately 20–40% of the total Fe²⁺ in the M1 site. Howardites, as expected for mixtures of eucrites and diogenites, scatter between the other meteorite types. Since the simplified MGM fitting scheme that we used for the HED spectra was designed to err on the side of stronger M1 intensity ratios, the estimated M1 site occupancy is an upper limit. The M1 intensity ratios and predicted M1 Fe²⁺ occupancy for average diogenites, cumulate eucrites, and eucrites are presented in Table 2. These values are consistent with the M1 site occupancies for intrusive and extrusive natural pyroxenes summarized in Table 1. For comparison, the M1 intensity ratios and M1 Fe²⁺ occupancy (measured by Mössbauer) for synthetic pyroxenes of similar composition to each meteorite group are also included in Table 2. As expected, the synthetic pyroxenes, which were quenched from temperatures ranging from 900-1300 °C, are more disordered than the HEDs.

Several of the M1 intensity ratios calculated appear to be anomalous on the basis of the generally designated meteorite type, and are marked by letters in Fig. 10a and 10c. Asuka (A-) 881819 has not been formally described, and only is classified broadly as a eucrite in both the Meteoritical Bulletin Database and the Catalogue of Meteorites at the Natural History Museum of London. The spectrum of A-881819 has the lowest M1 intensity ratio of all of the non-cumulate eucrites and exhibits an M2 band at just under 2 μ m, consistent with other spectra of cumulate eucrites. It is thus likely that A-881819 is a cumulate, rather than basaltic, eucrite.

Two diogenites have M1 intensity ratios greater than 0.19: Johnstown (J) and Yamato-75032. Johnstown has a lower albedo than many of the other diogenites measured (~half as bright; see Fig. 5 for example), and its continuum is slightly red-sloped. Although there is no obvious reason for the anomalous M1 intensity ratio, a more rigorous MGM fit of the Johnstown spectrum using a sloped continuum drops the M1 intensity ratio to 0.14, which is consistent with those calculated for other diogenites.

The albedo of Y-75032 is similar to that of Johnstown, and also exhibits a slightly red slope. However, a full MGM fit of Y-75032 results in a 1.2 μ m band that is still significantly stronger than the other diogenites. This suggests that the "anomalous" M1 intensity ratio may indicate a real petrologic difference between Y-75032 and the other diogenites measured. As described by Takeda and Mori (1981), Y-75032 is a breccia that consists of 0.2–7 mm sized fragments of pyroxene in a glassy matrix. The pyroxene grains are heavily shocked, exhibiting deformation of exsolution textures and glassy haze within individual pyroxene crystals. It is highly likely that the shock history of Y-75032 has resulted in a disordering of Fe²⁺ between the M1 and M2 sites, as suggested by the high M1 intensity ratio.

Fig. 10b highlights the usefulness of the M1 intensity ratio for pyroxenes of similar composition. Both Pasamonte and Serra de Magé exhibit M2 (1 and 2 µm) bands almost exactly at the same wavelength. If the band position alone was used to distinguish these meteorites (or similar lithologies on Vesta), they would appear to be essentially identical. However, if the M1 intensity ratio is calculated, Pasamonte can be easily categorized as basaltic and Serra de Magé as cumulate. This is further illustrated in Fig. 10c, where the 2 μ m band position can be thought of as a proxy for pyroxene composition, and the M1 intensity ratio can be considered a proxy for cooling regime. With the exception of the meteorites described above and marked by letters in Fig. 10c, the slowly cooled diogenites and cumulate eucrites cluster tightly in composition and cooling history groups. The eucrites, which cooled at varying rates, show a larger diversity in M1 intensity ratio. As expected, the howardites, which are mixtures of eucrites, cumulate eucrites, and diogenites, also show a range of M1 intensity ratios and 2 µm band positions. Binda (B), though not anomalous in M1 intensity, is highlighted because it has been classified both as a cumulate eucrite and a howardite. It is nevertheless anomalous because it appears extremely Mg-rich relative to cumulate eucrites, as indicated by the observed position of the 2 µm band (Fig. 10c).

Band parameters and M1 intensity ratios calculated using a simplified MGM fitting scheme allow compositions and cooling histories for the HED meteorites to be estimated from near-infrared reflectance spectra. Basaltic eucrites can be easily differentiated from cumulate eucrites and diogenites on the basis of their M1 intensity ratio, independent of the position of the 2 μ m band. A similar fitting routine, applied to hyperspectral remotely sensed data (100s of spectral channels), will allow cumulate and basaltic lithologies to be distinguished and mapped on a pyroxene-dominated planetary surface.

CONCLUSIONS

The 1.2 μ m band in near-infrared spectra of pyroxenes results from Fe²⁺ in the M1 crystallographic site and its intensity is related to the thermal history of the pyroxene. To quantify the behavior of the 1.2 μ m band as a function of Fe²⁺ M1 site occupancy, we have integrated analyses of near-infrared and Mössbauer spectra for a suite of Ca-bearing synthetic clinopyroxenes. The strength of the 1.2 μ m band relative to the 2 μ m band, or the M1 intensity ratio, was derived for the spectra of 51 HED meteorites using the MGM to evaluate how well the M1 intensity ratio can be used to differentiate between slowly and rapidly cooled natural pyroxene-dominated rocks.

Specific key results include:

- 1. Deconvolution of pure Ca-Fe synthetic hedenbergite indicates that the M1 absorption bands occur near 0.9 and 1.2 μ m. The 1.2 μ m band is significantly stronger than the 0.9 μ m band. The separation between these bands and the strengths of both bands decrease with decreasing amounts of Fe²⁺ in the M1 site. An additional absorption band, currently unassigned, occurs near 0.75 μ m in Ca-saturated pyroxenes.
- 2. The strength of the 1.2 μ m M1 band relates directly to the amount of Fe²⁺ measured in the M1 site using Mössbauer spectroscopy. Deconvolution of near-infrared reflectance spectra with high band-to-band precision can be used to estimate the site occupancy of Fe²⁺. For all pyroxenes except those that are Ca-saturated, the 2 μ m M2 band is significantly stronger than the 1.2 μ m M1 band, and the M1 intensity ratios generally range from 0.1–0.4. Pyroxenes with a M1 intensity ratio greater than ~0.6 are likely to be Ca-saturated.
- 3. The M1 intensity ratio can be used to differentiate between rapidly and slowly cooled HED meteorites and thus can be used to assess the cooling history of lithologies exposed on the surface of the HED parent body (Vesta).

Acknowledgments—Many thanks to Ed Cloutis and an anonymous reviewer for their thoughtful reviews of this manuscript. We are extremely grateful to Don Lindsley and Al Turnock for providing us these pyroxene samples. We thank Taki Hiroi for his dedication and care in measuring these samples in RELAB and Eli Sklute for her help in running the Mössbauer spectra. Partial support for this project was provided by UCLA subcontract 2090 GFC198 of NASA grant NNM05AA86C and grants NNX07AP41G, EAR-0439161, and NNG06G130G.

Editorial Handling-Dr. Michael Gaffey

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