Iron-bearing minerals are a major component of planetary surfaces, and many can be identified by their characteristic absorption bands in the near-infrared (NIR). Here we present laboratory NIR spectra of a wide range of common Fe-bearing minerals (e.g., olivines, pyroxenes), glasses, and mineral/glass mixtures. We then use this suite of spectra to evaluate the effects of mixtures on mineral detection methods, including olivine and pyroxene spectral indices developed for the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) onboard Mars Reconnaissance Orbiter. We find that although these indices can be compromised by minerals with atypical compositions, mineral mixtures, and the presence of other ferrous minerals, these issues can generally be mitigated by visual inspection of the spectra. However, a special case occurs when the mineral or mixture in question is spectrally indistinguishable from a more common mineral. In particular, we show that spectra of high-calcium pyroxene mixed with Fe-bearing glass can be virtually indistinguishable from common Fe-bearing olivine compositions. This effect, combined with the fact that Fe-bearing glass is generally much more difficult to detect than other ferrous minerals, may be causing glass occurrences on planetary surfaces to be underreported. In support of this hypothesis, we use Mars Express OMEGA observations to show that previous olivine detections in the north polar sand sea on Mars are actually more consistent with local mixing of glass and pyroxene. To address these issues, we present an alternative ferrous mineral identification method based on the position and shape of the 1 and 2 μm iron absorption bands, which are sensitive to mineralogy, composition, and mineral mixtures in planetary surface spectra, including glass and mixtures with glass. Using Chandrayaan-1 Moon Mineralogy Mapper (M3) observations of Aristarchus Crater on the Moon, we show that these band parameters can reveal subtle spectral variations and can produce mineralogical maps at an exceptional level of detail.

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1. Introduction

Iron-bearing minerals are a major component of planetary surfaces, and dominate the visible (0.3–0.75 μm) and near-infrared (0.75–5 μm) spectra of low albedo regions on Mars (e.g., Soderblom, 1992; Mustard et al., 1997; Bell et al., 2004; Mustard et al., 2005; Poulet et al., 2007; Horgan and Bell, 2012), the Moon (e.g., Adams et al., 1974: McCord et al., 1981; Gaddis et al., 1985, 2003; Pieters, 1986; Hawke et al., 1989; Isaacson et al., 2011), the Earth (e.g., Guinness et al., 1997, 2007; Tirsch et al., 2012), and many small bodies (e.g., Gaffey, 1976; Feierberg et al., 1980; Cruikshank, 1991; Gaffey et al., 1993; DeMeo et al., 2009). Because identification of specific minerals on planetary surfaces provides insight into both their geochemical and geological history, extensive laboratory work has been done to understand the spectral characteristics of iron-bearing minerals, including olivines, pyroxenes, as well as Fe-bearing glasses (Adams, 1968, 1974; Adams et al., 1974; Hunt, 1977; Hazen et al., 1978; Cloutis et al., 1986; King and Ridley, 1987; Clark et al., 1990; Sunshine et al., 1990; Cloutis and Gaffey, 1991a, 1991b; Sunshine and Pieters, 1993; Cloutis, 2002; Schade et al., 2004; Klima et al., 2007, 2011b). However, these materials do not often occur in nature as concentrated deposits of pure phases, due to both primary crystallization processes and secondary sedimentary processes. This is particularly a problem in the latter case, as aeolian, fluvial, impact, and volcanic processes produce both areal and intimate mixtures of iron-bearing sediments, often derived from multiple sources,
complicating determination of their endmember compositions and separate transport histories. Thus, understanding the near-infrared spectral characteristics of physical mixtures of Fe-bearing minerals is necessary when using spectral analysis to interpret the geology of mafic planetary surfaces. To this aim, we provide a systematic evaluation of the laboratory spectra of ferrous mineral mixtures (Section 2), discuss the effect of mixtures on common spectral detection techniques (Section 3), and provide a new method for the detection of specific ferrous minerals as well as mixtures among minerals and glasses (Section 4). In order to demonstrate the utility of this new approach, we apply it to both lunar (M³; Section 5) and martian (OMEGA; Section 6) near-infrared datasets and compare our results to more standard techniques (Section 6).

2. Near-infrared spectra of ferrous minerals and mixtures

Here we present laboratory spectra of samples of a variety of ferrous (Fe²⁺) and ferric (Fe³⁺) minerals, along with two-component mixtures of olivines, orthopyroxenes (OPX), clinopyroxenes (CPX), and glasses. We have chosen these four classes to focus on because they are the most common ferrous phases observed in near-infrared (NIR) spectra of planetary surfaces (e.g., Gaffey et al., 1993; McCord et al., 1981; Mustard et al., 2005; Horgan and Bell, 2012). Previous laboratory studies of ferrous mineral mixtures have included various mixtures of these phases (Adams, 1974; Singer, 1981; Cloutis et al., 1986, 1990; Cloutis and Gaffey, 1991b; Sunshine et al., 1990; Burns, 1993; Sunshine and Pieters, 1993; Reddy et al., 2008), but systematic two-component mixtures of all four primary ferrous phases have not been presented together, and the effects of these mixtures on band properties and ferrous spectral indices has not been presented in a systematic fashion. For this study, we have focused on two-component mixtures of a subset of possible mineral compositions for simplicity. While many planetary materials are most likely composed of more than two components, the spectra shown here are representative of the general spectral trends that occur due to mixtures.

2.1. Acquisition of spectra

All pure mineral and glass spectra acquired or used in this study are shown in Figs. 1–3.1 The spectra used in this study cover the full range of major-element compositions within the pyroxene and olivine groups, and the Fe-bearing glass spectra range from ultramafic to felsic in composition. While we are not sampling the full range of compositional variability due to trace elements, spectral effects due to trace elements have been studied previously (e.g., Cloutis, 2002). When available, spectra of pure minerals were taken from public spectral libraries, including the Brown RELAB spectral catalog (Pieters, 1983), the MRO CRISM spectral library (Murchie et al., 2007), the USGS digital spectral library (Clark et al., 2007), and the University of Winnipeg Planetary Spectroscopy Facility (UWPSF) online database (e.g., Cloutis and Gaffey, 1991a). Glass spectra were also contributed from previous studies (Minitti et al., 2007). Additional pure mineral spectra and spectra of mineral mixtures were acquired at the UWPSF. For a list of all samples used in this study and their sources, see Tables A1–A5.

All samples were crushed and dry-sieved to grain size ranges within or near the sand range (tens to hundreds of μm). Mixtures were produced by varying the weight percent of the components. All mixtures were sampled at 25 wt.% intervals or less. In mixtures where the endmembers exhibit markedly different absorption strengths (e.g., all mixtures with OPX), additional higher resolution wt.% mixtures were created at very high and low abundances to capture the full range of spectral variation. To test our parameters for sensitivity to grain size, OPX–olivine and OPX–CPX intimate mixtures were created at several grain sizes ranging from <38 μm to 180 μm. Mixture endmembers included a forsterite olivine, enstatite and hypersthene OPX, diopside CPX, and a mafic glass, all with spectra typical of their group (Table A5).

Reflectance spectra of mineral mixtures and endmembers were acquired at i = 30° and e = 0° and under ambient conditions over the 0.35–2.5 μm range with an Analytical Spectral Devices Field-Spec Pro HR™ spectrophotometer. The spectral resolution of the instrument varies between 2 and 7 nm and spectral sampling is done at 1.4 nm intervals. The instrument internally resamples the spectra to 1 nm intervals (Cloutis et al., 2006, 2007). In total, the spectral database for this study contains 158 pure mineral/glass spectra and 149 mineral/glass mixture spectra.

2.2. Near-infrared properties of ferrous minerals

As shown in Figs. 1–3, both ferrous and ferric iron in minerals cause strong absorptions between 0.8 and 2.4 μm that can be used to identify trends in iron mineralogy (e.g., Adams, 1968, 1974; Cloutis and Gaffey, 1991a, 1991b; Burns, 1993). Ferric minerals most commonly exhibit an absorption band near 0.9 μm due to spin forbidden transitions in ferric iron (Fig. 3; e.g., Hunt, 1977; Morris et al., 1985). The strongest ferrous iron absorption band is usually centered near 1 μm, but varies between 0.9 and 1.4 μm. Additionally, many pyroxenes and Fe-bearing glasses also exhibit a second absorption band, which is usually centered near 2 μm, but varies between 1.8 and 2.4 μm.

In ferrous minerals, these absorptions are mainly due to crystal field effects in ferrous iron, which cause a split in the energy levels of the partially filled 3d orbitals (Burns, 1970a, 1970b, 1970c, 1993; Burns et al., 1972). Important factors in the energy of the electronic transitions that occur between these energy levels include crystal structure, the crystallographic site occupancy of the iron (M1 and M2 sites of Burns, 1970a, 1970b, 1970c), and the presence of other cations (Figs. 1–3; Burns, 1970a, 1970b, 1970c; Cloutis et al., 1986; Cloutis, 2002). Thus, the positions of the ferrous iron absorption bands are determined both by mineralogy and mineral composition.

OPX, which is usually classified compositionally as a low calcium pyroxene (LCP), exhibits a relatively narrow and symmetrical absorption band centered near 0.9 μm, as well as a broad absorption band centered near 1.9 μm, as shown in Fig. 1 (Adams, 1974; Cloutis and Gaffey, 1991a). Both of these bands are due to the high concentration of Fe²⁺ in the M2 crystallographic site, whereas the M1 site is mainly occupied by Mg²⁺ (Burns, 1970a, 1970b, 1970c). CPX, which is usually compositionally classified as high-calcium pyroxene (HCP), falls into two spectral categories (Adams, 1975). “Type-B” CPX exhibits a narrow, symmetrical absorption band centered near 1.05 μm as well as a broad absorption band centered near 2.2 μm (Adams, 1974; Cloutis and Gaffey, 1991a; Klima et al., 2007, 2011b). As in OPX, both of these absorptions are due to Fe²⁺ in the M2 site. “Type-A” CPX exhibits a complex absorption band near 1 μm, but no 2 μm absorption band. This spectral behavior is generally correlated with high calcium content, and has been attributed to Ca³⁺ cations partially or completely filling the M2 site, and forcing Fe²⁺ cations into the M1 site. The complex 1 μm band is actually a combination of two or three distinct bands centered near 0.94, 1.03, and 1.15 μm due to Fe²⁺ in both the M1 and M2 sites (Schade et al., 2004; Klima et al., 2007, 2011b). Other absorption bands centered between 0.7 and 0.8 μm occur in type-A CPX with minor Fe³⁺, and are due to Fe²⁺–Fe³⁺ charge transfers. Trace transition metals (e.g., Fe³⁺, Cr³⁺,
Ti$^{4+}$, and V$^{3+}$) in CPX can cause additional absorptions centered below 0.8 μm (Cloutis, 2002; Fig. 1). In OPX, higher iron contents tend to shift all bands to longer wavelengths, but the reverse is true for CPX (Burns, 1970a; Burns et al., 1972; Cloutis and Gaffey, 1991a). Some pyroxenes with high iron contents also exhibit a secondary absorption centered near 1.2 μm due to iron in the M1 crystallographic site that may be related to their cooling histories (Klima et al., 2008).

Olivine exhibits a broad and asymmetric absorption band centered near 1.05 μm, and no 2 μm band (Fig. 2). The 1 μm band is a combination of three bands centered near 0.85, 1.05, and 1.15 μm (Sunshine et al., 1990; Sunshine and Pieters, 1998), caused by Fe$^{2+}$ ions in both the M1 and M2 coordination sites in the olivine crystal lattice (Burns, 1970a, 1970b, 1970c). The wavelength position of the band generally increases with the fraction of Fe-rich olivine (fayalite) relative to the fraction of Mg-rich olivine (forsterite) in the sample (King and Ridley, 1987). More fayalitic olivines also tend to exhibit broader and more asymmetric bands (Fig. 2), but this is not a reliable indicator of composition, as band shape is also highly dependent on grain size (King and Ridley, 1987). Fe-bearing glass exhibits an absorption band at longer wavelengths, between 1.07 and 1.20 μm (e.g., Adams, 1974; Miniti et al., 2002), and sometimes exhibits a second absorption centered near 2 μm (Fig. 2). The effects of chemistry and structure on glass spectral characteristics, including the presence or lack of a 2 μm absorption band, has not yet been studied in detail.

Other Fe-bearing minerals also exhibit absorption bands near 1 μm (Fig. 3). For example, iron oxides, iron-bearing clays, and ferric sulfates often exhibit absorption bands near 0.9 μm, along with other diagnostic absorptions in the visible, due to spin-forbidden transitions in Fe$^{3+}$ (Morris et al., 1985; Bishop et al., 1993; Bishop and Murad, 1996; Cloutis et al., 2006). The iron sulfide pyrite exhibits a broad shoulder just beyond 1 μm, while pyrrhotite exhibits broad absorption bands centered near 1 and 2 μm, making it difficult to distinguish from pyroxenes based on NIR data alone (Hunt et al., 1971). Fe-bearing carbonates (including magnesite with very little Fe; Bishop et al., 2013a) exhibit a broad doublet of absorption bands centered near 1.05 and 1.2 μm, and while this could be misidentified as olivine, carbonates also exhibit other diagnostic absorptions near 2.3 and 2.5 μm due to C–O vibrational overtones (Hunt and Salisbury, 1971).

Plagioclase feldspar can also exhibit absorptions due to ferrous iron. While most plagioclase varieties do not exhibit NIR absorption bands, substitution of Fe$^{2+}$ for Ca in anorthite causes a broad absorption centered between 1.10 and 1.35 μm. The position and depth of this band generally correlates with Fe$^{2+}$ content (and thus often anorthite content as well), and bands centered below 1.2 μm are usually very weak (Adams and Goullaud, 1978). However, due

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Fig. 1. All near-infrared laboratory spectra of pyroxenes used in this study. (a) Orthopyroxenes exhibit two symmetrical absorption bands centered between 0.90–0.95 and 1.8–2.0 μm. (b) Clinopyroxenes (CPX) that exhibit absorption bands in the 1 μm region but not in the 2 μm region are referred to as “type-A”. Their primary absorption is usually a complex combination of three bands centered near 0.94, 1.03, and 1.15 μm. (c) CPX that exhibit a simple, symmetrical absorption between 1.00 and 1.05 μm and a second absorption band centered between 2.0 and 2.4 μm are known as “type-B”. All spectra are scaled and offset for clarity, and are sorted by increasing 2 μm band center position bottom to top (where no 2 μm band is present, the 1 μm band center is used), with a few exceptions for clarity. Narrow absorptions near 1.4, 1.9, and 2.2 μm are due to minor alteration. See Table A1 for sample information and calculated band positions.
to the low iron content, these plagioclase absorptions are generally very weak relative to other ferrous minerals, and are only observed when plagioclase is present at high abundances. This characteristic has been used to infer the presence of plagioclase-rich assemblages like anorthosite and granite on the Moon and Mars (e.g., Ohtake et al., 2009; Cheek et al., 2013; Carter and Poulet, 2013; Wray et al., 2013).

Grain size is also an important factor in the spectral characteristics of ferrous minerals. Larger grains generally produce deeper absorption bands (higher spectral contrast) due to less surface area (less first-surface scattering) compared to smaller grains of the same material (e.g., King and Ridley, 1987). However, the larger surface area of fine grains also means that fine grains tend to produce more reflectance (higher albedo), and therefore tend to dominate in mixtures with other grain sizes (e.g., Mustard et al., 1993).

2.3. Spectra of ferrous mineral mixtures

Figs. 4–6 show representative spectra for two-component mixtures of OPX, CPX type-B, olivine, and Fe-bearing glass. These results compare well with mixture spectra presented in other previous studies of olivine–pyroxene and pyroxene–pyroxene mixtures (Adams, 1974; Singer, 1981; Cloutis et al., 1986; Cloutis and Gaffey, 1991b; Burns, 1993), as well as pyroxene–glass mixtures (Cloutis et al., 1990). The mixture spectra for olivine and Fe-bearing glass also compare well with olivine-bearing glass spectra presented by Nicholis et al. (2006), suggesting that these overall trends are valid for intimate as well as inter-granular mixtures. Furthermore, while overall spectral contrast varies with grain size, the spectral shapes do not (Figs. 5 and 6). Thus, these spectra provide a good general reference for the types of spectral shapes produced by these mixtures even under varying grain sizes, mixtures types, etc., not exactly duplicated here. However, the presence of additional endmembers or possible variations in the spectral shape or spectral contrast of the endmembers due to grain size, composition, etc., do prevent these mixture spectra from being used to estimate quantitative mineral abundances in mixtures from near-infrared spectra alone.

The mixture spectra in Figs. 4a–6 show that OPX is a strong absorber, and can be clearly identified in mixture spectra even at low abundances (10–20 wt.%.) by the presence of band minima at ~0.9 and ~1.9 μm. Thus, OPX-bearing mixtures will tend to underrepresent the other component, as demonstrated for olivine–OPX mixtures by Cloutis et al. (1986). In a reverse effect, the mixture spectra in Fig. 4a, c, and d shows that Fe-bearing glass is a very weak absorber. The only major effect of glass at abundances below

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2 All mixture spectra are publically available at http://psf.uwinnipeg.ca/Sample_Database.html as well as in the Supplemental spreadsheet.
80 wt.% is to widen and skew the 1 μm absorption band toward longer wavelengths. Because this effect is subtle even at high abundances, this suggests that Fe-bearing glass could be present in large quantities on planetary surfaces and still not be readily detected using NIR spectroscopy. Furthermore, these particular mixtures of Fe-bearing glass and CPX type-B from approximately equal abundances to high glass abundances exhibit a 1 μm band that is asymmetric to longer wavelengths and no 2 μm band, perhaps due to the wide separation between the shallow glass and CPX 2 μm bands. These spectral characteristics are consistent with those usually assigned to olivine, and the mixture spectra look qualitatively very similar to spectra of pure olivine. Thus, while Fe-bearing glass is difficult to detect in general on a planetary surface, even at high abundances, it is also possible that some glass-rich deposits have been misidentified as olivine, as demonstrated for the martian north polar sand sea in Section 6.

3. Spectral identification of ferrous minerals

Many different methods have been developed for the identification of ferrous minerals in both laboratory and planetary surface near-infrared spectra, from full spectral modeling to simple arithmetic analyses. Here we summarize a selection of these methods and discuss their relative advantages and disadvantages.

3.1. Spectral modeling

Visible–NIR solar photons are observed by orbital spectrometers after reflection off the surface, and they often interact with more than one particle or surface before being scattered in the direction of the detector. Because each photon cannot usually be tied to a specific interaction, the resulting reflectance spectra are often a non-linear mixture of spectra from different minerals, and simple linear deconvolutions do not generally estimate mineral abundances accurately. More accurate non-linear deconvolution methods require mathematical models of photon-particle interactions and multiple scatterings (e.g., Hapke, 1981; Shkuratov et al., 1999). While these methods have the potential to provide quantitative abundance estimates from planetary surface spectra (e.g., Mustard and Pieters, 1987; Poulet and Erard, 2004; Poulet et al., 2008a, 2009a, 2009b), they require substantial assumptions. Specifically, non-linear models require assumptions about scattering parameters, optical constants, mineral assemblages, and grain sizes that may not be available for planetary surface spectra, and they often cannot account for more complicated spectral effects (e.g., coatings). Thus, non-linear spectral unmixing methods must be applied and interpreted with care.

Another commonly used approach is the Modified Gaussian Model (MGM; Sunshine et al., 1990; Sunshine and Pieters, 1993), which was developed specifically for analysis of ferrous absorption bands. In the MGM, each observed absorption feature is modeled as one or a combination of several overlapping modified Gaussian functions corresponding to individual absorption bands, which can then be assigned to absorptions due to specific minerals. The MGM can provide specific information on mineralogy as well as composition, and has been successfully applied both to laboratory and planetary surface spectra (e.g., Sunshine and Pieters, 1993; Isaacson and Pieters, 2010; Isaacson et al., 2011; Klima et al., 2011a). However, accurate modeling requires significant user feedback and manual adjustments to the number, strength, and position of bands, and therefore the MGM is most efficient when used on individual spectra, as opposed to a large dataset, like a spectral image cube or mosaic. While several efforts toward automation of the MGM and other curve-fitting techniques have been successful (Gendrin et al., 2006; Parente et al., 2011; Clénet et al., 2011), further work is needed to develop a fully automated routine...
that does not require prior knowledge of the mineralogy of the target spectra and is capable of differentiating among the full range of probable ferrous minerals.

3.2. CRISM spectral indices

The main drawback to any modeling approach for interpreting planetary surface spectra is that an accurate result requires knowledge of all minerals contributing to the spectrum. A simpler approach that is often used to simply detect the presence of any ferrous mineral is the calculation of simple spectral indices to detect the 1 and 2 nm bands, like the 1 and 2 nm integrated band depths (IBD) that are often applied to detect ferrous minerals in lunar spectra (e.g., Besse et al., 2011; Cheek et al., 2013) and, more rarely, in martian spectra (e.g., Pelkey et al., 2007). In lunar spectra, this approach is often used to identify regions of interest for detailed study with the MGM (e.g., Mustard et al., 2011; Whitten et al., 2011; Staid et al., 2011; Isaacson et al., 2011). However, because these indices are non-unique, they are not generally used to identify specific ferrous minerals.

An alternative approach that is commonly used in many Mars surface studies is to calculate spectral indices that are designed to detect contributions from specific ferrous minerals (e.g., Bell et al., 2000; Pelkey et al., 2007; Poulet et al., 2007; Salvatore et al., 2010). Spectral indices use arithmetic combinations of reflectance at specific wavelengths to gauge the shape of a spectrum, and are useful because they provide a quick method of determining spectral variations over a region (e.g., Poulet et al., 2007). However, the sensitivity of these spectral indices to variations in mineralogy and composition, the presence of other ferrous (or other) minerals, and mineral mixtures has not been fully tested. Using our set of ferrous mineral and mixture spectra, we can evaluate the effects of these variables on common spectral indices.

Two near-infrared spectrometers are currently operating at Mars: the Observatoire pour la Minéralogie, l’Eau, les Glaces et l’Activité (OMEGA) imaging spectrometer onboard Mars Express, and the higher-resolution Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) onboard Mars Reconnaissance Orbiter. Spectral indices have been developed for both datasets (e.g., Poulet et al., 2007), but here we focus on those developed for CRISM (Pelkey et al., 2007; Salvatore et al., 2010). The primary spectral indices used to detect ferrous minerals in CRISM spectra are LCPINDEX, HCPINDEX, and OLINDEX2, and all three are based on searching for lower reflectance in selected channels inside the absorption bands of their target minerals compared to reference channels outside of the absorption bands (Table 1). The LCPINDEX is designed to detect the 1 and 2 µm OPX absorptions via reduced reflectance at 1.08 and 1.82 µm relative to the value of the spectrum at the mid-band peak near 1.33 µm (Pelkey et al., 2007; Salvatore et al., 2010). 1.08 µm is used to detect the presence of a 1 µm band because this is the lowest reliable wavelength on the CRISM L (near-IR) detector. The HCPINDEX is similarly designed to detect CPX via reduced reflectance at 1.08 and 2.07 µm relative to the value of the spectrum at 1.47 µm (Pelkey et al., 2007; Salvatore et al., 2010). 1.08 µm is used to detect olivine (and other ferrous components) via reduced reflectance at 1.05, 1.21, 1.33, and 1.47 µm relative to the predicted value at those channels based on the average slope of the spectrum (Salvatore et al., 2010). These spectral indices do not give quantitative information on the abundance of a mineral in a scene, just on whether certain spectral characteristics are...
present in a given spectrum. This is useful because the index will
give a value greater than zero even in low spectral contrast or
dusty scenes or, in theory, even when the targeted mineral is pres-
ent as part of a mixture. Thus, the value of an index for a given
spectrum is not as critical as the combination of indices that give
positive values for that spectrum.

Ideally, a given ferrous mineral would only produce a positive
value for its associated spectral index but not the other two. This
is generally true, but not in every case, and the spectral indices of-
ten give positive values for other minerals as well. Fig. 7 shows the
CRISM ferrous spectral indices of all olivine, pyroxene, and glass
spectra in our sample set. In some ways, the olivines are the
best-behaved mineral group, as all of the olivines give positive val-
ues for OLINDEX2 but not HCPINDEX nor LCPINDEX (Fig. 7b). How-
ever, OLINDEX2 is also positive for the majority of the iron-bearing
minerals in our full sample set, with the exception of all of the OPX
spectra, less than half of the glass spectra, and two of the three
hematite spectra (c1jb129 and bbc17). So, while OLINDEX2 is often
strongest in olivines, it also functions as a general spectral in-
dex for ferrous (and some ferric) minerals (e.g. Bishop et al., 2008,
2013b). Thus, an elevated OLINDEX2 does not signify a unique
detection of olivine (Salvatore et al., 2010), even when the other
indices are not elevated.

Pyroxenes have more complicated effects on the spectral indi-
ces. All of the OPX spectra give positive values for LCPINDEX and
negative values for OLINDEX2 (below the range of Fig. 7c), but
many also give positive values for OLINDEX2 and LCPINDEX. Spec-
tral indices for CPX type-A are indistinguishable from those for the
olivines. As expected based on the shape of the spectrum, pyrrho-
tite also tends to give positive values for HCPINDEX (~0.99).

One drawback of spectral indices is that it is difficult to formu-
late an index that could consistently identify iron-bearing glass, in
part due to the variation in glass spectral shapes (Fig. 2). This is
demonstrated in the existing CRISM indices, as most but not all
glasses give positive values for OLINDEX2. This is a potential prob-
lem because even after inspection of the relevant spectra, some of
these glasses could easily be misidentified as olivine based on their
lack of a strong 2
\mu
m band. Glass is a significant component of both
impact and volcanic deposits, so another method is clearly needed
that can more uniquely identify glass on a planetary surface.

Fig. 8 shows the effects of mixtures on CRISM spectral indices.
Mixtures of CPX, olivine, and glass tend to produce relatively linear
variations in the spectral indices; however, OPX causes highly non-
linear trends, for several reasons. As discussed above, OPX is a
stronger absorber than the other minerals, so the LCPINDEX re-
mains high even at lesser abundances of OPX. Some of the non-
linearity is also due to using the 1.08
\mu
m channel to detect the
1
\mu
m band in both the HCPINDEX and LCPINDEX. This channel is
located so far from the center of the OPX absorption band at
0.9 \mu m that adding any phase with a longer-wavelength 1 \mu m
band (CPX, olivine, glass) increases the absorption at this
channel and the value of the index. This effect can be seen in the
OPX–olivine mixtures in Fig. 8e, in which the HCPINDEX increases
as the proportion of olivine increases, even though no CPX is
present in the system. Finally, the sensitivity of the HCPINDEX to

Fig. 5. Two component mixture spectra of OPX–CPX type-B mixtures for two different endmember sets: (a and b) hypersthene and endiopside, and (c and d) enstatite and
diopside. Mixtures in (a) and (c) made at 0–45 \mu m and 10 wt.% intervals; (b) and (d) at 90–180 \mu m and 20 wt.% intervals. Note that while the hypersthene/endiopside mixture linearly transitions between the two endmembers, the enstatite/diopside mixture does not. The enstatite dominates the spectrum much like in mixtures of OPX with olivine
or glass (Figs. 4 and 6), in all cases due to the greater absorption strength of the OPX relative to the other endmembers. Narrow ~1.4 and 2.2 \mu m absorption bands present in
some spectra are due to minor alteration. See Tables A4 and A5 for sample information.
composition is demonstrated in Fig. 8c. One of the CPX endmembers has a 2 μm band shifted to slightly longer wavelengths (Fig. 4a). This produces less absorption at the 2.07 μm channel used in the HCPINDEX, and thus a lower index value relative to more typical CPX. This means that the intermediate spectra in the mixture with 2 μm bands in between those of the CPX and OPX endmembers look more similar to typical CPX than the actual CPX endmember (Fig. 5a and b), and so these intermediate spectra also produce a much higher HCPINDEX (Fig. 8c and d).

Fig. 8c–f demonstrates that grain size is also a major influence on the value of spectral indices, because larger grains generally produce deeper absorption bands due to less surface area (less first-surface scattering and therefore more interaction with and more absorption by the volume of the material) compared to smaller grains of the same material (e.g., King and Ridley, 1987). While the major effect of larger grains is to exaggerate the values of all of the indices (thus neither the relative values of different indices nor the overall shapes of mixing trends are significantly affected), grain size variations within a scene could be misinterpreted as a change in the mineral abundance.

In most cases, these possible points of confusion regarding the CRISM spectral indices to identify ferrous minerals should be avoidable as long as all spectral index maps are confirmed with detailed spectral analysis, as suggested by previous studies (Salvatore et al., 2010). However, when a mineral mixture or entirely different ferrous mineral has both spectral index values and an overall spectral shape that is similar to an olivine or pyroxene, they will most likely be misidentified as those more commonly expected minerals. Examples that we have provided above include Fe-bearing glass, glass–CPX mixtures, and many other
4. A new method for detection of ferrous minerals and their mixtures

A different approach to identifying ferrous minerals is to use more detailed information about the position and shape of the 1 and 2 μm ferrous absorption bands, which have been well-characterized by previous laboratory studies (e.g., Adams, 1968; Cloutis and Gaffey, 1991b). While this approach is commonly used during analysis of individual planetary surface spectra, often in combination with MGM (e.g., Bell and Hawke, 1995; Mustard et al., 2005; Isaacson et al., 2011), robust imaging spectroscopy data sets have only recently become available for which such methods could be used to map mineralogy at the regional scale. Furthermore, previous laboratory studies have shown that physical mixtures of many ferrous minerals result in systematic and quantifiable changes to both absorption band position and shape (e.g., Singer, 1981; Cloutis et al., 1986; Cloutis et al., 1990; Cloutis and Singer, 1981; Cloutis et al., 1990; Cloutis and Gaffey, 1991b), suggesting that these properties could also be used to identify and map compositional mixing trends.

This approach combines several of the advantages of previous methods. Much like spectral indices, band center and shape parameters are simple arithmetic operations that can be applied to large data sets, and do not require prior knowledge of the mineral assemblage present for analysis. Much like MGM, these band center and shape parameters also allow estimation of endmember mineralogy and composition. Furthermore, a mapping approach based on band center, in particular, has significant advantages for detecting mineralogy over maps based only on simple spectral ratios (e.g., Weitz et al., 1998; Gaddis et al., 2003), as band center is not generally influenced by variations in overall spectral shape (Horgan and Bell, 2012). Spectral shape variations can be caused by atmospheric effects, coatings, space weathering, the spectral roll-off in Mars spectra beyond 2 µm due to the ~3 µm H₂O/OH fundamental absorptions, and spectral roll-offs in the visible due to transition metals, etc. Band center and shape are also both independent of band depth, allowing detection and characterization of shallow absorption bands, including the shallow absorption bands characteristic of iron-bearing glass. Indeed, the 1 µm band center was recently used to identify terrains rich in glass on Mars (Horgan and Bell, 2012).

Here we provide a new approach for identifying mixtures in planetary surface spectra, based on the shapes and positions of the 1 and 2 µm iron absorption bands. While characterizing the detailed position and shape of these bands in large spectral data sets presents some challenges for automation, such an approach yields the detailed analysis that simpler spectral indices alone cannot always provide. To determine how these parameters may aid in mineral identifications, we have derived parameters for our suite of ferrous and ferric iron-bearing minerals as well as mineral mixtures.
4.1. Spectral processing

Mineral absorption bands are superposed on the continuum of the spectrum, and for most techniques, the effects of this continuum must be removed before analysis of the bands can be completed (e.g., McCord et al., 1981; Clark and Roush, 1984; Clark et al., 2003). The continuum of a laboratory sample is due to a complex combination of influences, so modeling the exact shape of the continuum is difficult at best (e.g., Sunshine et al., 1990; Parente et al., 2011). For our laboratory spectra, we have assumed an upper convex hull – a linear continuum broken into three segments with adjustable tie points: one segment over the 1 μm absorption band, a connecting segment, and one segment over the 2 μm absorption band, as shown in Fig. 9 (Clark and Roush, 1984; Parente et al., 2011). The continuum (i.e., the tie points) was initially found by maximizing the band area around the spectral minima between 0.75–1.5 μm and 1.5–2.7 μm; if needed, the fit was manually adjusted. This approach allows for broad variation in the position and width of the 1 and 2 μm bands, where using set channels for the fit would not (e.g., a center tie point near 1.3 μm appropriate for most OPX would not be appropriate for many olivines, which can have 1 μm bands extending beyond 1.6 μm). A horizontal fit (a flat line) was assumed in cases of highly variable or non-linear continua in the region of the 1 μm band, usually in type-A CPX spectra, or in cases where the 2 μm band extended beyond the range of the spectrum, usually in type-B CPX spectra (Fig. 9b). The small fraction of spectra where a linear continuum could not adequately account for the actual continuum shape were not included in this study. The continuum was removed by dividing the derived linear segments out of the spectrum. Especially noisy
laboratory spectra (e.g., very low albedo glass and oxide spectra) were smoothed with a boxcar average of width $0.25 \mu m$ prior to continuum derivation and spectral analysis.

4.2. Definition of band parameters

Once the continuum has been removed from the spectrum, several band parameters can be derived, as shown in Fig. 9 (e.g., Clark and Roush, 1984; Cloutis and Gaffey, 1991b). The band minimum and center parameterize band position, while the band depth, area, and asymmetry parameterize band shape. Table 2 provides detailed definitions of these parameters. All parameters are derived from continuum-removed spectra. Band center differs from band minimum because it is the minimum of a polynomial fit to the absorption band, which allows for a better estimation of the true center of the band in noisy spectra, in spectra with narrow absorptions due to secondary minerals (Fig. 9d), and when the fit has a higher resolution than the spectrum. Thus, the band center allows for band characterization even in non-ideal circumstances. In smooth spectra, the band minimum and center should be the same or very similar (Fig. 9c). We have used a fourth-order polynomial to find the band center as opposed to a lower-order polynomial because it allows for the narrower band center characteristic of many pyroxenes.

4.3. Band parameters for mineral identification

Fig. 10 shows 1 and $2 \mu m$ band parameters derived from spectra of pure minerals. The band parameters that have most commonly been used in previous studies are the 1 and $2 \mu m$ band centers, as shown in Fig. 10a (e.g., Adams, 1974; Cloutis and Gaffey, 1991a; Klima et al., 2011a, 2011b). Pyroxenes exhibit an approximately linear trend of both 1 and $2 \mu m$ band centers increasing from OPX to CPX. The OPX and CPX spectra in this sample set separate into two regions; however, a full continuum exists between these groups, with the intermediate region (0.94–1.02 and 2.0–2.2 $\mu m$) mainly populated by CPX with both high iron contents (20–60% of total Ca/Mg/Fe) and significant trace metal contents (>1–5 wt.%), as well as by some pigeonites (Adams, 1974; Cloutis and Gaffey, 1991a; Klima et al., 2007, 2011b). The 1 and $2 \mu m$ band centers also clearly distinguish Fe-bearing glass from pyroxenes, as glass has a high 1 $\mu m$ band center and a low 2 $\mu m$ band center. However, this parameter space is only applicable for phases that exhibit both 1 and $2 \mu m$ absorptions, which means that only approximately half of the pyroxenes and glasses and very few of the olivines in our sample set can be evaluated using the 1 and $2 \mu m$ band centers.

Based on our analyses, the parameters that produce the most unique mineral identifications for our sample set are the 1 $\mu m$ band center and 1 $\mu m$ band asymmetry (Fig. 10b). The band center of the 1 $\mu m$ absorption alone allows broad discrimination of most ferrous minerals (e.g., Adams, 1974; Hunt, 1977; Singer, 1981; Cloutis and Gaffey, 1991b). However, the band centers of some minerals do overlap, such as CPX and olivine in the 1.02–1.08 $\mu m$ region. As shown in Fig. 10b, utilizing band center and band asymmetry together reduces most of this overlap in major rock-forming ferrous minerals. While there is still some overlap with other ferrous and ferric minerals, such as between OPX and oxides, CPX and Fe-sulfides, and olivine and Fe-carbonates (Fig. 10c), other diagnostic absorptions can be used to distinguish between these overlapping minerals (see Section 2.2).

The band center and asymmetry parameters are also useful for identifying mineral mixtures. Band parameters for our sets of

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See Tables A1–A3 for parameter values, which are also available in the Supplemental spreadsheet.
mixture spectra are shown in Figs. 11 and 12, and plot smoothly along characteristic mixing trend lines that are generally independent of grain size, and often fall outside of parameter regions expected for pure minerals. These trends are a quantitative representation of the mixture spectra shown in Figs. 4–6 and discussed in Section 2.3. For mixture spectra that vary smoothly between endmembers, the mixing trends are linear between endmembers (Figs. 11 and 12b), but when one endmember dominates over the other, the trends can be highly non-linear (Fig. 12a and c). The best examples of non-linear mixing trends are the mixtures of OPX with glass or olivine (Fig. 12a and c), where OPX controls the location of the band center up to high abundances (40–80 wt.% of the other endmember. This produces a highly asymmetric combined absorption band (Figs. 4a and 6) and pushes the band parameters into the upper left corner of Fig. 12 plot. Indeed, as little as 5 wt.% OPX is enough to push the band parameters outside of the region of the other endmember, so the presence of even minor OPX should be obvious when using this parameter space. The reverse is true for Fe-bearing glass, which is a weak absorber – mixtures with other ferrous phases only exhibit glass-like band centers and asymmetries when they contain more than 80–95 wt.% glass. So while glass is therefore difficult to detect, detection would imply very high glass abundances. This result has been used to infer very high Fe-bearing glass abundances in the northern lowlands of Mars, based on 1 μm band centers around 1.15 μm over a widespread region (Horgan and Bell, 2012).

The trends shown in Fig. 12 also demonstrate that mineral mixtures can produce spectral parameter values within the regions of other pure minerals, potentially leading to false mineral identifications. For example, both the OPX/CPX with glass mixtures trend through the olivine region, and follow a similar trend as the olivine with glass mixture into the glass region. To discriminate between these possible interpretations, the shape of the rest of the spectrum and the presence of other bands should be considered. However, as noted earlier (Section 2.3), the pyroxene and glass mixture spectra can look very similar to a subdued pure olivine spectrum.

On planetary surfaces, similar parameter trends should be apparent in situations where mixing trends are present across a region, such as mixing of sediments from separated sources, in sediments undergoing mineralogical maturation during transport due to chemical or mechanical weathering, and in cases where dust or sediments partially mask an underlying substrate. In the next section, we demonstrate these parameters in an example of the latter case, in which impact ejecta overlie pyroclastic deposits and mare flood basalts on the Moon.

5. Application: M3 spectra of the Aristarchus plateau on the Moon

Here we use near-infrared spectra from the Moon Mineralogy Mapper (M3; Green et al., 2011; Pieters et al., 2009) instrument on the Chandrayaan-1 lunar orbiter to demonstrate a generalized approach for identification of ferrous minerals and their mixtures using the 1 μm band parameters described above. The M3 dataset is ideally suited for our 1 μm analysis methods. The entirety of the M3 dataset is publicly available from the Planetary Data System, and here we have used Level 2 products, which have been corrected for thermal emission as well as topographic, photometric, and instrumental effects (Green et al., 2011; Clark et al., 2011; Hicks et al., 2011; Boardman et al., 2011; Besse et al., 2013). In orbits with low instrument temperatures, the quality of the data can be very high, and no major post-processing adjustments are required. The vast majority of the M3 dataset is the 140–240 m/pixel resolution global mapping data set, and the 82 spectral band global dataset is designed for 1 μm band analysis, with 2× higher spectral sampling in the 0.7–1.6 μm region.

For this demonstration, we have chosen the region proximal to Aristarchus Crater, based on the previously identified spectral diversity of the region and the presence of mixtures of impact and volcanic minerals and glasses. By applying band ratios, spectral unmixing, and band area calculations to M3 data, Mustard et al. (2011) identified strong signatures of olivine-bearing and glass-bearing impact melts, OPX-bearing basement materials, and CPX-bearing mare basalts in Aristarchus ejecta, which overlies the glass-rich pyroclastic deposits of the Aristarchus plateau (e.g., Gaddis et al., 1985; Lucey et al., 1986; Pieters, 1986). Previous multispectral visible/near-infrared analysis of the region also identified an anorthositic component within the crater central peak (Le Mouël et al., 1999; McEwen et al., 1994; Chevrel et al., 2009; Ohtake et al., 2009). Two M3 images cover this region, M3G20090209T054031 and M3G20090209T072710, which we have projected together into a cylindrical mosaic, as shown in Fig. 13.

Prior to band analysis, the continuum slope of the spectra must be removed or suppressed. In lunar spectra, the continuum slope is dominated by spectral reddening due to fine particle sizes and space weathering. This effect can be suppressed using a linear continuum (e.g., McCord et al., 1981; Bell and Hawke, 1995; Mustard et al., 2011), but in the presence of significant space weathering (Hiroi et al., 2010) or low albedo glasses, additional components are required. Thus, we have modeled the spectral continuum as a second order polynomial fit to local spectral maxima in the regions 0.5–1.0 μm, 1.15–1.8 μm, and 2.3–2.6 μm, with the latter boundary chosen to reduce the effects of thermal emission at long wavelengths. The fit iterates to refine the local maxima until the number of points in the spectrum that fall above the continuum is minimized (see Fig. 14 for examples of continua and continuum removed spectra). Effects from noise are reduced by smoothing each spectrum with a median filter followed by a boxcar smoothing filter, both with widths of five points. Once the continuum is suppressed, the 1 and 2 μm band parameters can be calculated. The analysis routines are modified only slightly from those used in analyzing the lab spectra above: the minimum of the 1 and

<table>
<thead>
<tr>
<th>Band parameter</th>
<th>Definition and restrictions</th>
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<tr>
<td>Minimum Center</td>
<td>Wavelength position of the channel with the minimum value between continuum segment endpoints</td>
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<tr>
<td>Depth Area</td>
<td>One minus the value of the polynomial fit at the band center</td>
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<tr>
<td>Asymmetry</td>
<td>Difference between the band area to the left and right of band center, as a percent of the total area. A symmetric band has an asymmetry of 0%, and positive asymmetries correspond to bands that have more area at longer wavelengths. The asymmetry is not calculated if the absorption extends beyond the range of the spectrum</td>
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Fig. 10. Band center vs. band asymmetry for laboratory spectra. (a) 1 μm vs. 2 μm band centers for primary rock-forming ferrous materials: pyroxenes (blue triangles), olivines (green circles), and glasses (red squares). Colored regions indicate characteristic parameter space identified for each material. Only minerals with 2 μm band depths greater than 2% are shown. (b) Band center vs. asymmetry for the 1 μm band, same symbols as (a). Unfilled symbols indicate spectra with no 2 μm band (band depth <2%), which are not shown in (a). 60% of olivine and CPX spectra fall within small regions (inner boxes), and samples that fall outside of this box are usually iron-rich. 10 of our CPX-type A spectra fall off this plot to the left because the shortest wavelength absorption in their 1 μm triplet (near 0.8–0.85 μm) is dominant. (c) 1 μm parameters for other iron-bearing minerals, compared to regions from (b). See Tables A1–A3 for sample information and exact parameter values. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2 μm bands are found between 0.8–1.4 and 1.6–2.5 μm in the continuum removed spectra, the band centers are the minimum of a third order polynomial fit to the spectrum within 0.1 μm of the minima, and band asymmetry is calculated relative to the band center.

Fig. 13b and c shows the 1 and 2 μm band parameters for Aristarchus visualized using a simple red–green–blue (RGB) stretch of various combinations of the 1 and 2 μm band centers, the 1 μm band area, and the 1 μm band asymmetry. This approach emphasizes subtle variations in mineralogy throughout the scene, and is useful for evaluating spectral diversity. Variations in pyroxene composition due to mixing between the OPX-bearing ejecta and HCP-bearing mare are clearly illustrated by comparing the 1 and 2 μm band centers (blue/yellow/green tones in Fig. 13b). Impact melt and pyroclastic deposits containing glass and olivine are identified by their high 1 μm band asymmetry (pinks and yellows in Fig. 13c), and glass can be differentiated from olivine based on a high 1 μm band center combined with a low 1 μm band area (magenta and orange tones in Fig. 13b). High 1 μm band centers are also associated with high concentrations of plagioclase, like the plagioclase-rich ejecta blocks and streamers in the NW portion of the Aristarchus ejecta.

In order to interpret this band parameter data, spectral endmembers must be identified. Because spectral mixing generally reduces spectral contrast (e.g., Mustard et al., 1993), endmember spectra can often be identified by their high band depths. In the Aristarchus scene, OPX, HCP, and olivine endmember spectra in Fig. 14 exhibit the highest band depths of all spectra with parameters that are possibly consistent with OPX, HCP, and olivine, based on the laboratory data shown in Fig. 10. The OPX, HCP, and olivine endmember spectra do not exhibit significant absorptions due to other minerals, confirming that these spectra are most likely endmembers that represent distinct geologic units. As shown in Fig. 15a–c, these endmember spectra have band parameters that place them clearly at the ends of regional mixing trends. These endmembers agree well with those presented for the eastern half of Aristarchus by Mustard et al. (2011).

However, if an endmember has an inherently low band depth compared to other endmembers in the scene, mixing can actually increase the band depth, so it can be difficult to identify based on high band depths alone. Instead, such endmembers can be identified by their position at the ends of regional or local mixing trends in band parameter space. For example, mixing between the OPX and HCP endmembers cannot explain the full observed variation in 2 μm band centers, as shown in Fig. 15b, suggesting that another phase with a 2 μm band is present – in this case, Fe-bearing glass. Fig. 16 shows local mixing trends from various parts of the Aristarchus scene, and several of these local trends have endmembers consistent with glass. Representative glass endmember spectra are shown in Fig. 14b and c. The impact glass endmember spectrum is observed within the ejecta blanket. A spectrum consistent with pure glass was not found in the pyroclastic deposits in the northern half of the scene; however, many of the spectra in this region are consistent with glass mixed with minor HCP, based on their band parameter values and local mixing trends, as shown in Fig. 16a, and their overall spectral shape, as shown in Fig. 14. Interestingly, the impact glass spectra exhibit elevated 2 μm band centers (closer to 2.1 μm) compared to both the set of mafic glasses in our laboratory study as well as the pyroclastic glass spectra in this scene (closer to 1.9 μm). This difference between the two glass endmembers is clearly illustrated by comparing the mixing trends in Fig. 16a and c. While we hypothesize that this difference in 2 μm band centers could be due to differences in glass composition, we cannot verify this, as systematic laboratory work on the spectral variations in glasses has not yet been conducted.

Fig. 16 also shows other local spectral mixing trends from around the scene, including examples of pyroxene mixing (Fig. 16b) and OPX–olivine mixing within the Aristarchus ejecta (Fig. 16d). These trends are very similar in parameter space to those derived from our lab mixture spectra above (Figs. 11 and 12), and demonstrate the ability of this method to detect glasses and to discriminate mixtures from pure minerals. Based on the shapes of the trends observed at local and regional scales, we can assign regions of the parameter space to specific minerals or
mixtures (Fig. 15d) and color-code the scene based on these regions (Fig. 15e). These interpreted parameter values are scene-dependent, and should not be uniformly applied to geologically disparate scenes.

One of the major advantages of this band parameter-based method is the detection of materials with very shallow absorption bands, such as glasses. The interpreted mineral map shown in Fig. 15e clearly shows the Aristarchus plateau pyroclastic glasses overprinting on HCP-bearing mare, which are overlain by OPX-bearing impact ejecta of younger craters. While glass-bearing materials are present throughout the pyroclastic materials, as expected, in addition, glass-bearing units on the floor of Aristarchus may correspond to pools of impact melt, and clear streamers of glassy melt are present in the SW region of the ejecta blanket. These results complement those from Mustard et al. (2011), who identified glass in a few local ejecta flows using spectral modeling techniques.

Space weathering also causes a shallowing of absorption bands, in addition to a overall darkening and reddening of spectra (e.g., Adams and Jones, 1970; Hapke et al., 1970). While many causes have been proposed for space weathering, laboratory experiments have shown that the most likely cause is irradiation of the lunar surface by the solar wind concurrent with micrometeorite impact vaporization, leading to the vapor deposition of coatings containing sub-microscopic metallic iron particles (e.g., Hapke et al., 1975; Hapke, 2001). In the Aristarchus scene, the majority of the surfaces (outside of recent crater ejecta) in the mare and pyroclastic deposits have been heavily space weathered, and exhibit very low band depths as a result. However, the band parameter technique successfully identifies the mineralogy of these areas, and pulls out subtle spectral variations, like the overprinting of Aristarchus ejecta on the mare to the south.

Finally, the Aristarchus scene also demonstrates how this band parameter method can be used to identify unexpected phases with

Fig. 11. 1 vs. 2 μm band centers for two component mixture spectra. (a) CPX–glass mixtures (squares) and OPX–glass mixtures (triangles) from Fig. 4a and c, at <45 μm grain size, 20 wt.% intervals. (b) OPX–CPX type B mixtures from Fig. 5, at <45 μm grains at 10 wt.% intervals, and 90–180 μm grains at 20 wt.% intervals. Open circles indicate the enstatite–diopside mixtures and filled circles indicate the hypersthene–endiopside mixtures (Fig. 5). The non-linear trend of the small open circles in (b) is due to wide separation of the OPX and CPX bands shown in Fig. 5c, which prevents the creation of an “intermediate” spectrum with OPX or CPX-like smooth absorption bands. Instead, one endmember always dominates over the other and the intermediate spectrum exhibits highly asymmetric bands. See Tables A4 and A5 for sample information.

Fig. 12. 1 μm band center vs. band asymmetry for two component mixture spectra. (a) Glass mixtures and olivine–CPX type-B mixture from Fig. 4, all <45 μm grain size, 20 wt.% intervals. (b) OPX–CPX type B mixtures from Fig. 5, all <45 μm grains at 10 wt.% intervals, and 90–180 μm grains at 20 wt.% intervals. Open and filled circles indicate two mixtures with different endmembers. (c) OPX–olivine mixtures from Fig. 6, a variety of grain sizes at 10 wt.% intervals. As in Fig. 10, the blue regions are pyroxene, the green region is olivine, and the red region is glass. Note that the parameter trends for all three glass mixtures pass through the olivine region, that as little as 5–25 wt.% OPX can place the parameter values well outside of the expected ranges for CPX, olivine, and glass, and that less than 20% of other minerals must be present for glassy spectra to enter the typical glass endmember region. See Tables A4 and A5 for sample information. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
parameters outside those of expected Fe-bearing minerals. The Aristarchus scene exhibited a class of spectra with no 2 \( \mu m \) bands and 1 \( \mu m \) bands centered at very long wavelengths (1.25–1.30 \( \mu m \); Fig. 14), consistent with Fe-bearing plagioclase feldspar in anorthosite. On further inspection, these spectra correspond to portions of the central peak and a sequence of ejecta blocks extending to the northwest, consistent with detections of anorthosite by previous multispectral studies listed above. As Mustard
et al. (2011) was unable to detect anorthosite in the same M^2 data with more traditional spectral analysis methods, this result also showcases the ability of our 1 and 2 μm band center and shape analysis methods to detect weak ferrous spectral signatures.

Previous multispectral studies also interpreted the light blue region NW of Aristarchus in Fig. 13b as an OPX–anorthosite mixture (Chevrier et al., 2009). This is also a plausible interpretation of our data, as anorthosite would also induce a strong asymmetry in the OPX 1 μm band (e.g., Cheek et al., 2013). However, because of the close proximity of the glass-rich pyroclastic deposits, we tend to favor an OPX–glass mixture instead. More detailed spectral analysis should help to resolve this ambiguity, as would future studies of plagioclase mixtures with other ferrous phases.

6. Application: OMEGA spectra of the martian north polar sand sea

Here we use near-infrared spectra from the Observatoire pour la Minéralogie, l’Eau, les Glaces et l’Activité (OMEGA) near-infrared spectrometer (Bibring et al., 2005) onboard the Mars Express spacecraft to demonstrate our 1 μm band analysis methods for a martian dataset, and to compare our results with the CRISM spectral indices discussed in Section 3.2. For this demonstration, we have chosen the north polar sand sea, which encircles the north polar cap (Planum Boreum; Fig. 17a) and is thought to be sourced from sedimentary units within Planum Boreum.

Our previous studies using this dataset in the north polar region and surrounding northern plains identified a widely distributed class of spectra with very high 1 μm band centers (1.10–1.16 μm) and a concave upward slope between 0.68 and 1.5 μm (Horgan and Bell, 2012). As shown above, the long 1 μm band center is consistent with iron-bearing glass, and the concave spectral slope is a unique spectral signature that is consistent with weathering rinds on glass that form under acidic leaching conditions (Minitti et al., 2007; Seelos et al., 2010). These glass signatures are strongest in the north polar dune fields between 250°E and 330°E, but are also detected throughout the low albedo northern plains, in total covering over 10 million square kilometers of the northern basin. However, the north polar sand sea also exhibits other mafic spectral signatures. Previous studies using OMEGA and CRISM data have identified clear pyroxene 1 and 2 μm absorption bands in the north polar sand sea (Fishbaugh et al., 2007; Poulet et al., 2008b), as well as a possible olivine component, based on strong olivine spectral index values and enhanced absorption longward of 1.1 μm (Poulet et al., 2008b). However, our laboratory work above has shown that mixtures of HCP and glass can mimic olivine, suggesting that this olivine detection may instead be due to mixing between the more confidently detected pyroxene and glass endmembers in the region.

6.1. OMEGA processing

Fig. 17a shows our mosaic of OMEGA visible (0.36–1.07 μm; 96 channels) and near-infrared (NIR; 0.93–2.5 μm; 113 channels) spectra in the martian north polar region. As described in Horgan and Bell (2012), this mosaic was constructed using a polar stereographic projection of all spectra from the first year of OMEGA observations above 70°N. The maps were limited to surface observations taken at phase angles <70° to minimize high-phase effects, and between LS = 90–135° to minimize surface frost and north polar hood clouds.

All spectra were calibrated to I/F using standard OMEGA calibration routines (SOFT4; Bellucci et al., 2006), and the NIR channels were atmospherically corrected using the volcano scan algorithm (e.g., Langevin et al., 2005; Horgan et al., 2009). Visible and atmospherically-corrected NIR spectra were separately converted to albedo (assuming a simple Lambertian phase function) and projected using each spectrometer’s individual pointing information before being joined at 0.97 μm. Many OMEGA spectra exhibit poor alignment between visible and NIR spectra even after the above corrections, especially bright surfaces and those close to strong albedo boundaries. Because our 1 μm band analysis routines would be affected by a discontinuity at 0.96 μm, the boundary between the visible and NIR detectors, spectra with poor alignments (>3% offset) were not included in the final mosaics. Spectra with minor offsets (<3%) were adjusted to improve alignment by linearly scaling the visible channels to match a value projected at 0.96 μm from adjacent NIR channels. To minimize the amount of atmospheric and surface dust contamination, each spectrum included in the final mosaics was chosen from the lowest albedo at 0.75 μm out of all available spectra at each location. After construction of the mosaics, saturated, null, and known bad channels (Bellucci et al., 2006) were replaced with interpolated values. Example estimated Lambert albedo spectra derived using these methods are shown in Fig. 18b.

In order to analyze the 1 μm band in the OMEGA spectra, first we must suppress contributions to the spectra from systematic instrumental and atmospheric artifacts, atmospheric and surface dust, and the overall continuum slope. The former two contributions may be suppressed by ratioing the spectra to a nearby “reference” area that shows little or no relevant spectral contrast, such as a dusty plains region (e.g., Bibring et al., 2005; Langevin et al., 2005). Here, we have used a regional average of all bright (0.3–0.35 estimated Lambert albedo at 0.77 μm) and ice-free spectra (1.5 μm ice band depth less than 1%) as a reference spectrum to suppress these effects (top spectrum in Fig. 18b). While this approach would not be appropriate for identifying narrow spectral features, we are focusing on broad features in smoothed spectra. Furthermore, many of the individual images in our maps are relatively dust-free and therefore do not contain appropriate reference spectra, so we have been able to produce greater consistency between images by using a regional average. Example ratioed spectra are shown in Fig. 18c.

Once the dust contribution is suppressed or removed, the overall continuum shape for most spectra is then dominated by the wings of the 3 μm water band, which cause a downturn at longer wavelengths. For simplicity, we model this downturn as a second
order polynomial. Spectra with strong concave slopes due to weathered glass have an additional component to their continua that is modeled well by a power law function with an exponent typically between \(-\frac{4}{7}\) and \(-\frac{2}{7}\), similar to Rayleigh or Tyndall scattering (e.g., He et al., 2009). Combining these models gives the following continuum function:

\[
\text{Continuum} = ax^b + cx^2 + dx + e
\]  

where \(a\) is positive and \(-7 < b < 0\). This continuum function is fit to a subset of channels between 0.75 and 0.96 \(\mu\)m and channels near 1.65 and 2.3 \(\mu\)m. This continuum function is effectively a version of the general continuum function suggested by Hiroi et al. (2000), modified to account for the unique shapes induced by leached glass and \(H_2O/OH\)-bearing martian materials. Once the ratioed spectrum is divided by the continuum function, the only remaining features are absorption bands. Example modeled
continuums are shown as dashed lines in Fig. 18c, and continuum removed spectra are shown in Fig. 18d. To further reduce noise and to emphasize broad iron absorptions, all spectra were smoothed with a boxcar smoothing algorithm with a width of $\sim 0.06 \mu m$, which is equivalent to 10 channels in the visible and 5 channels in the near-infrared. Smoothed spectra are represented by solid lines in Fig. 18b–d.

6.2. Mineralogy from spectral indices

Fig. 17b and c shows HCPINDEX and OLINDEX2 parameters calculated from estimated Lambert albedo spectra in our mosaic. While these parameters were originally designed for CRISM, here we have modified both parameters for use with OMEGA by choosing the closest corresponding OMEGA channels. These maps
generally correspond well to the OMEGA olivine and pyroxene spectral index maps used to infer the presence of olivine and pyroxene by Poulet et al. (2008b), as the OMEGA spectral indices used by Poulet et al. (2008b) search for similar spectral shapes as the CRISM indices. However, there are some differences between the maps that are the result of the different formulas used for the indices. For olivine, both indices look for enhanced absorption near $\lambda_{2400}$, although the wavelengths and weights used in the two indices are slightly different (Poulet et al., 2008; Salvatore et al., 2010). One key difference is that OLINDEX2 is less affected by spectral slopes – while OLINDEX2 evaluates absorption relative to a linear continuum, the OMEGA index uses set points near 1.55 and 1.70 $\mu$m for forsterite and fayalite, respectively. Thus, the OLINDEX2 exhibits positive values in some terrains with strong spectral slopes due to gypsum and weathered glass, where the OMEGA olivine index detections are more limited. Likewise, the OMEGA pyroxene index appears to be adversely affected by the presence of gypsum, as the HCPINDEX shows detections throughout eastern Olympia Undae where the OMEGA pyroxene index does not. Unlike the CRISM HCPINDEX/LCPINDEX, the OMEGA pyroxene index looks for enhanced absorption near 2.15 and 2.22 $\mu$m relative to 1.8 and 2.5 $\mu$m due to the pyroxene 2 $\mu$m band, but does not look for contributions from the 1 $\mu$m band. This index may be limited in the presence of gypsum by the 2.4 $\mu$m sulfate band, which would significantly reduce the reflectance at 2.5 $\mu$m.

Based on these spectral indices, a general interpretation of the mineralogy of the region would be a mixture of HCP and olivine, as previous workers have suggested. However, there are several...
regions within the dune sea that do not exhibit positive values of either index, including Siton Undae, Hyperborea Undae, Abalos Undae, and parts of Olympia Undae. As these regions are as low or lower in albedo than the rest of the dune sea, this cannot be due to dust cover, and so this lack of olivine or pyroxene detections suggests the presence of another component in these areas.

6.3. Mineralogy from 1 \textmu m band centers

The 1 and 2 \textmu m band parameters for the OMEGA dataset are calculated from smoothed, continuum-removed spectra using the same algorithm that was applied to the M"osaic mosaic in Section 5. However, a major additional challenge for interpreting the 1 and 2 \textmu m band parameters calculated from this particular mosaic is the presence of 1.38–1.48 \textmu m and 1.92–1.98 \textmu m OH/H$_2$O absorption bands due to hydrated sulfates and hydrated glass and/or silica in many locations throughout the north polar sand sea (e.g., Fig. 18). These absorption bands skew the area of the 1 \textmu m iron band toward longer wavelengths, and overprint on the 2 \textmu m iron band, making the 1 \textmu m band asymmetry and the 2 \textmu m band center more indicative of alteration than iron mineralogy. Thus, in the north polar region, the band parameter that is most representative of variations in iron mineralogy is the 1 \textmu m band center, as shown in Fig. 17d. The majority of band centers detected range from just below 1 \textmu m up to above 1.15 \textmu m, with a smooth transition within the range. As discussed above, the very high band centers (above 1.1 \textmu m) are consistent with iron-bearing glass, and are highly correlated with strongly concave spectral slopes, which are also consistent with weathered glass. Spectra with high HCPINDEX values correlate well with 1 \textmu m band centers between 0.99 and 1.04 \textmu m and exhibit clear 2 \textmu m bands, all consistent with HCP. Spectra with high OLINDEX2 values correlate well with 1 \textmu m band centers between 1.05 and 1.07 \textmu m, consistent with olivine. However, these potentially olivine-bearing locations are consistently located between HCP and glass-bearing regions. Fig. 18 shows spectra from a transect across western Olympia Undae, spanning from dunes with glass-like spectra on the north (bottom) edge of the dune sea, into dunes with HCP-like spectra on the southern (top) edge. The intermediate dunes exhibit elevated OLINDEX2 values and 1 \textmu m band centers consistent with olivine, but also clearly exhibit 2 \textmu m bands consistent with pyroxene. Thus, we interpret these intermediate spectra and the elevated CRISM/OMEGA olivine index values as indicating a region of mixing of glass-bearing sand and HCP-bearing sand within the dune sea, and not olivine.

Thus, the north polar dune sea provides a clear example of terrains where mixing between two minerals (glass and HCP) produces spectral signatures that can easily be confused for a completely different mineral (olivine), much as we showed using lab spectra above. Also as stated above, this suggests that there may be other locations on Mars with glass and HCP mixtures that have been misidentified as olivine.

7. Conclusions

Analysis of near-infrared spectra of ferrous minerals has shown that their spectral characteristics are directly related to the chemistry and crystal structure of the minerals, and that the spectra of ferrous minerals and glasses mix in well-defined ways. However, a possible pitfall in analysis of near-infrared spectra of ferrous minerals is that spectral shapes can be non-unique, especially in the case of mineral mixtures. This presents a problem for simple spectral index approaches, like the CRISM OLINDEX2/HCPINDEX/LCPINDEX spectral indices, which rely on spectral shape for mineral identification. We find that olivine is well-behaved in these indices, in that it only exhibits positive values for OLINDEX2 and not for HCPINDEX or LCPINDEX, but that OLINDEX2 gives positive values for nearly every other ferrous and ferric mineral in our sample set (except OPX). Thus, OLINDEX2 is most useful as a general indicator of iron-bearing minerals. Pyroxenes, on the other hand, are somewhat less well behaved, as
many OPX spectra give positive values for HCPINDEX, and vice versa, especially in the case of iron-rich OPX/CPX. Mixtures have a more complicated effect on these spectral indices. Because these indices search for an idealized pyroxene spectra shape, OPX–CPX mixtures can produce stronger LCPINDEX/HCPINDEX values than for either endmember if the endmembers differ from the expected spectral shape. OPX–olivine mixtures can also produce strong HCPINDEX values.

While most of these issues can generally be mitigated by manual investigation of the spectra, a special case occurs when the mineral or mixture in question is spectrally indistinguishable from a more common material. In particular, we have shown here that the spectra (and CRISM spectral indices) of CPX–glass mixtures can be virtually indistinguishable from pure olivine. In a practical example of this phenomenon, OMEGA spectra and spectral indices from the north polar sand sea of Mars have been previously interpreted as indicating CPX and olivine, but our analysis of these spectra indicate that the possible olivine is instead a mixture of CPX and glass. Because olivine is generally assumed to be more common than glass, it is plausible that some previously identified olivine deposits are instead mixtures of CPX and glass. This result suggests that glass may be substantially under-detected compared to other ferrous and ferric minerals on planetary surfaces. While the translucency of glass makes it generally difficult to detect in the near-infrared anyway, it is also plausible that glass deposits have been misidentified as either olivine (in the cases of glass without a 2 μm band or CPX–glass mixing) or CPX (in the case of glass with a stronger 2 μm band). However, glass does exhibit unique spectral characteristics that allow it to be identified. When glass is present at high concentrations (~80% or more), the 1 μm iron band is shifted to longer wavelengths (1.10–1.18 μm). In mixtures with other ferrous phases, moderate amounts of glass (~50% or more) skew the area of the 1 μm iron band to longer wavelengths, producing a highly asymmetric absorption band.

Partly motivated by these concerns, we have developed a new method for identifying and mapping ferrous minerals, glasses, and mixtures in planetary surface spectra using the position and shape of the 1 and 2 μm iron absorption bands. As demonstrated on M² spectra of Aristarchus Crater on the Moon, this band parameter approach reveals subtle spectral variations and can produce compositional maps at a very high level of detail. The strength of this approach is that the derived parameters provide detailed information on the mineralogy and composition of a surface, but are not limited by the assumptions and approximations required by other techniques. Possible future applications of this technique include studying impact and pyroclastic processes on the Moon, Mars, and small bodies, as well as aeolian and other sedimentary processes on Mars.

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Appendix A. Supplementary material

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References


