



Near-infrared spectra of ferrous mineral mixtures and methods for their identification in planetary surface spectra



Briony H.N. Horgan^{a,c,*}, Edward A. Cloutis^b, Paul Mann^b, James F. Bell III^a

^a School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85282, United States

^b Department of Geography, University of Winnipeg, Winnipeg, Manitoba R3B 2E9, Canada

^c Department of Earth, Atmospheric, and Planetary Sciences, Purdue University, West Lafayette, IN 47907, United States

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ABSTRACT

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 (M^3) 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,

* Corresponding author. Present address: Department of Earth, Atmospheric, and Planetary Sciences, Purdue University, 550 Stadium Mall Drive, West Lafayette, IN 47907, United States. Fax: +1 765 496 1210.

E-mail address: briony@purdue.edu (B.H.N. Horgan).

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 $i = 30^\circ$ and $e = 0^\circ$ 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 Ca²⁺ 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⁺,

¹ All spectra are publically available from sources listed in Tables A1–A3, as well as in the Supplemental spreadsheet.

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