Near- and mid-infrared microspectroscopy of the Ronda peridotite

Rachel L. Klima and Carlé M. Pieters
Department of Geological Sciences, Brown University, Providence, Rhode Island, USA

Received 18 July 2005; revised 11 October 2005; accepted 17 October 2005; published 20 January 2006.

[1] Microspectroscopy is a potentially useful tool for planetary applications, as individual mineral grains can be targeted and measured in situ. A series of closely coupled experiments was designed to investigate and compare the laboratory measurement of optical properties of a peridotite sample in the macroscale and microscale. The Ronda peridotite consists largely of olivine with significant orthopyroxene and minor clinopyroxene and serpentine. Microscopic transmission spectra of unmounted thin sections produce strong, well-defined absorption features in the near infrared, and band positions can be directly compared to macroscopic and microscopic reflectance spectra. For near-infrared reflectance, where photons are multiply scattered by different grains, measurement of a microscopic target means most photons are scattered out of the field of view and few photons return to the detector from the target area. This precludes most microspectroscopic reflectance measurements of small features in the near infrared. In the mid-infrared, where reflectance measurements involve only surface interactions, microspectrometric measurements detect well-defined absorption features for most samples. Although the intensity of absorption features varies between grains, band positions are consistent with macroscopic diffuse reflectance and emittance measurements of bulk samples, and can be used to extract general chemical information such as iron/magnesium ratios of olivines.


1. Introduction

[2] Optical spectroscopy is a widely used remote sensing tool for characterizing the composition and mineralogy of planetary surfaces. At visible and near-infrared wavelengths, a portion of light incident on a surface diffuses into the body of the material, inducing electronic transitions in the minerals present that absorb photons and produce diagnostic absorption bands in the reflected spectrum [Burns, 1993a]. In the mid-infrared there is typically no body component and molecular vibrations in the mineral lattice produce absorption features, measured remotely as emission from a planet’s surface [e.g., Kahle et al., 1993; Salisbury, 1993]. Although the interactions of light with a pure mineral are understood in principle, minerals on a planet’s surface are intimately mixed with other minerals and/or are altered by a variety of physical and chemical processes causing complex variations in the observed spectrum.

[3] Interpretation of remotely sensed extraterrestrial spectra has often involved measurement of spectral libraries of known rocks and minerals in the laboratory to be used as end-members in spectral mixture analysis. Current spectral libraries consist of end-member rock and mineral spectra collected using standard macrospectroscopic techniques such as bidirectional reflectance, diffuse reflectance, hemispherical reflectance, or thermal emission. Such macroscopic techniques measure the sample with beam widths on the order of millimeters to centimeters, and thus require relatively large amounts of samples.

[4] Analysis of minerals using microspectroscopy offers opportunities beyond those provided by standard reflectance or emission spectroscopy. Infrared microspectrometers are also being considered in designs of in situ experiments on planetary missions. Using either transmitted or reflected light, microspectrometers can target and measure spectra of individual mineral grains as small as 10 to 50 μm in diameter. This is particularly important for minor mineral phases and for precious samples that cannot be ground and separated by mineral. Under reflected light, samples can be measured completely noninvasively, preserving precious extraterrestrial samples for future investigations. Additionally, grains on a sample can be measured with spatial relationships preserved, for example allowing investigation of how spectra vary in zoned minerals or across grain boundaries [Dalton and Bishop, 2003; Klima and Pieters, 2004].

[5] Despite such advantages, studies have only recently begun applying microspectroscopy to extraterrestrial minerals [Bukovanska et al., 1998, 2000; Palomba et al., 2000; Dalton and Bishop, 2003; Klima and Pieters, 2004; Morlok et al., 2004] and few have involved measurement of cut samples that preserve the original spatial context of mineral grains [Dalton and Bishop, 2003; Klima and Pieters, 2004]. As documented in subsequent sections, this is in part due to...
inherent limitations of microscope systems and the physics of the interaction of light on a submillimeter scale target. In transmission experiments, standard thin sections cannot be studied in the infrared owing to the opacity of glass and epoxy [e.g., Moses, 1971]. Doubly polished thin sections may be prepared, but the necessary thickness varies based on the minerals present, and sample preparation becomes complicated in more friable samples. In contrast, for reflectance experiments, light must interact with the target and then scatter into the range of angles collected by the detector. Both transmission and reflectance measurements are also subject to artifacts and light loss due to diffraction when the aperture or grain size approaches the wavelength of light being measured [Hofmeister, 1995].

If microspectroscopy is to be used in conjunction with traditional macroscopic laboratory spectra and remotely sensed data, it is imperative that the strengths as well as limits and any systematic variations caused by physical properties, viewing geometry and grain orientation are recognized. A peridotite from the Ronda massif in Spain was selected for this study on the basis of the presence of olivine and pyroxene, common constituents of extraterrestrial material. A series of closely coupled experiments was designed to investigate and compare the laboratory measurement of optical properties in the macroscale and microscale and also to specifically address the following questions concerning the used of microspectroscopy. (1) How accurately can quantitative information, for example volatile content or Mg/Fe ratios, be extracted from microspectroscopic measurements? (2) What is an appropriate thickness for transmission microspectroscopic analysis of unmounted thin sections containing olivine and pyroxene? (3) Can reflectance from cut slabs provide reliable measurement of absorption features at all wavelengths? (4) How highly polished does a thin section or slab need to be to produce reliable data? (5) Are there recognizable anomalies or artifacts in spectra collected using a microscope when compared with those collected using macroscopic techniques?

2. Background

Shown in Figure 1 are typical macroscale laboratory spectra of silicate minerals from the Ronda peridotite. Diagnostic absorptions arise from several causes. When light is incident on a mineral, it is either reflected at the surface boundary, transmitted through the crystal, and/or absorbed by the crystal. If a photon is transmitted into a crystal, it is refracted based on the complex index of refraction,

$$n = \frac{1}{k}$$

where $n$ is the index of refraction and $k$ is the extinction coefficient. Values of $n$ and $k$ vary by mineral and are wavelength dependent, as illustrated for olivine in Figure 2. At short wavelengths where $k$ is near zero, $n \approx \frac{1}{k}$ and photons are transmitted readily into the body of the crystal. Small variations in $k$ over a significant path length produce observed absorptions in the transmitted (or body) component. Common absorptions in the near infrared are due to electronic transitions of d-orbital electrons in ions affected by the surrounding crystal field [Burns, 1993a]. These crystal field transitions produce distinctive absorption bands at visible and near-infrared wavelengths in transition metal bearing minerals. The energy at which specific absorption features occur is inversely related to the interatomic distance between the cation and the surrounding oxygen ions. Substitution of different sized cations such as Fe$^{2+}$, Mg$^{2+}$ and Ca$^{2+}$ into the crystal lattice will slightly change the size
of the ion site and thus cause a shift in the wavelength (energy) of diagnostic absorptions [Burns, 1993a, 1993b]. For example, in Figure 1a, two distinctive absorption features in the orthopyroxene spectrum are located at ~0.9 μm and ~1.7 μm. Comparable absorption features in clinopyroxene, which contains more of the large Ca²⁺ ion, are located at ~1.0 μm and ~2.3 μm.

[8] In the mid-infrared, fundamental molecular vibrations of the silica tetrahedra produce very strong absorption features in silicate minerals. Substitution of larger cations into the crystallographic sites changes the site sufficiently to alter the vibrational frequencies of the SiO₄ tetrahedra and hence the position and relative strengths of mid-infrared absorption features. This effect has been observed and quantified for Fe-Mg substitution in olivine [Sasenka, 1961; Duke and Stephens, 1964; Burns and Huggins, 1972; Hamilton, 2000; Hoefen et al., 2003]. In pyroxenes, cation substitution also affects the positions of the mid-infrared absorption bands although the vibrational frequencies associated with specific modes are less well defined [Hamilton, 2000].

[9] At all wavelengths, an observed reflectance spectrum is a combination of specular (Fresnel) reflectance, surface scattering and volume scattering. A schematic diagram of the interaction of light with a surface is presented in Figure 3. Fresnel reflectance (Figure 3a) often dominates a reflectance spectrum when the surface is smooth relative to the wavelength of the incident light (any transmitted component is either absorbed or never returns to the surface).

[10] If a particulate sample consisting of many (~10³ to 10⁴) grains is fully illuminated with visible to near-infrared radiation (Figure 3b), light is scattered both between and within many grains, and a portion of the transmitted (body) component of light is reflected out of the grains at the surface. This interaction typically involves 10’s of grains before light is scattered out [Pieters, 1983]. In contrast, if only a single particle is illuminated with visible or near-infrared radiation (Figure 3c), most of the light is scattered out of the field of view and little, if any, is scattered into the field of view. When fine-grained (<45 μm) particulate material is measured on a macroscopic scale using bidirectional or diffuse reflectance, the targeted area is typically on the order of ~5 mm diameter; however, microspectroscopy targets an area roughly two orders of magnitude smaller and the field of view is typically a single grain. As is discussed below, this difference in scale presents an important constraint on microspectroscopic reflectance measurements in the near infrared.

[11] In the mid-infrared, the extinction coefficient (k) is typically orders of magnitude larger than in the near infrared, causing surface interactions to dominate. Because light only has to interact with the surface of a material to produce a viable mid-infrared reflectance signal, it is able to follow a more direct path from the target to the detector (Figure 3d). Consequently, even illumination of a single submillimeter particle can produce a strong reflectance signal in the mid-infrared.

3. Experimental Methods

3.1. Ronda Peridotite

[12] Previous geochemical and petrologic analyses suggest that the Ronda represents the residue of a rising diapir of fertile upper mantle which underwent varying degrees of decompression melting [Frey et al., 1985]. Bulk magnesium numbers across the ~300 km² massif range between roughly 89–91 [Frey et al., 1985]. The specific peridotite sample used in this study is a spinel harzburgite, containing 67–73% olivine, 15–20% orthopyroxene, 4–5% clinopyroxene, 1–2% spinel and 5–6% serpentine based on point counting using an optical microscope and image analysis of a scanned thin section. Olivine and pyroxene compositions were determined using a CAMECA SX-100 electron microprobe.

Figure 2. Typical index of refraction (n) and extinction coefficient (k) of olivine [after Mustard and Hays, 1997].

Figure 3. Diagram illustrating the interaction of light with (a) a smooth and (b, c, d) a particulate surface. When light hits an optically smooth surface, Fresnel reflectance dominates the spectrum (Figure 3a). Macroscopic spectroscopic techniques illuminate a large number of particles fully, allowing near-infrared light to scatter between and through grains (Figure 3b). When a single particle is illuminated in the near infrared, a majority of light is transmitted into the material (Figure 3c). In contrast, in the mid-infrared the extinction coefficient (k) is high, and light is reflected more directly from the surface of the particles (Figure 3d).
Table 1. Average Chemical Composition of Olivines and Pyroxenes

<table>
<thead>
<tr>
<th></th>
<th>OLV</th>
<th>OPX</th>
<th>CPX</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>41.03</td>
<td>55.40</td>
<td>51.95</td>
</tr>
<tr>
<td>TiO₂</td>
<td></td>
<td>0.02</td>
<td>0.08</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td></td>
<td>3.64</td>
<td>4.65</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.00</td>
<td>0.63</td>
<td>1.09</td>
</tr>
<tr>
<td>FeO</td>
<td>8.95</td>
<td>5.95</td>
<td>2.39</td>
</tr>
<tr>
<td>MnO</td>
<td>0.14</td>
<td>0.14</td>
<td>0.09</td>
</tr>
<tr>
<td>MgO</td>
<td>50.04</td>
<td>33.56</td>
<td>16.51</td>
</tr>
<tr>
<td>MnO</td>
<td>0.41</td>
<td>0.76</td>
<td>22.95</td>
</tr>
<tr>
<td>Na₂O</td>
<td></td>
<td>0.02</td>
<td>0.53</td>
</tr>
<tr>
<td>K₂O</td>
<td></td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Mg</td>
<td>90.88</td>
<td>90.95</td>
<td>92.48</td>
</tr>
</tbody>
</table>

Table 2. Summary of Experiments

<table>
<thead>
<tr>
<th>Approach</th>
<th>Sample</th>
<th>Analysis</th>
<th>Instrument</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compositional</td>
<td>thin section 1</td>
<td>petrography: Olv, Op, Cpx</td>
<td>Petrographic Microscope Electron Microprobe</td>
</tr>
<tr>
<td>Spectroscopy</td>
<td>bulk powder (125–250 μm)</td>
<td>reflectance, 0.3–2.6 μm</td>
<td>RELAB Bidirectional Spectrometer</td>
</tr>
<tr>
<td>Standard</td>
<td></td>
<td>reflectance, 1.3–25 μm</td>
<td>Nicolet 870 Spectrometer + Pike Diffuse</td>
</tr>
<tr>
<td>(Macro)</td>
<td>mineral separates (125–250 μm):</td>
<td></td>
<td>Reflectance Accessory</td>
</tr>
<tr>
<td></td>
<td>Olv, Op, Cpx</td>
<td></td>
<td>RELAB Bidirectional Spectrometer</td>
</tr>
<tr>
<td>Microspectroscopy</td>
<td>mineral separates (125–250 μm):</td>
<td></td>
<td>Nicolet 870 Spectrometer + Pike Diffuse</td>
</tr>
<tr>
<td></td>
<td>Olv, Op, Cpx</td>
<td>reflectance, 1–14 μm</td>
<td>Reflectance Accessory</td>
</tr>
<tr>
<td></td>
<td>cut slabs 2–6 (400 grit)</td>
<td>reflectance, 8–14 μm</td>
<td>Nicolet 870 Spectrometer + Continuum Microscope</td>
</tr>
<tr>
<td></td>
<td>cut slab 7 (polished)</td>
<td>transmission, 1–4 μm</td>
<td>Nicolet 870 Spectrometer + Continuum Microscope</td>
</tr>
<tr>
<td></td>
<td>thin sections A–E (400 grit)</td>
<td>transmission, 1–4 μm</td>
<td>Nicolet 870 Spectrometer + Continuum Microscope</td>
</tr>
<tr>
<td></td>
<td>thin section 7 (polished)</td>
<td>transmission, 1–4 μm</td>
<td>Nicolet 870 Spectrometer + Continuum Microscope</td>
</tr>
</tbody>
</table>

3.2. Sample Preparation

[13] Coordinated spectroscopic and petrologic analyses of the Ronda peridotite are summarized in Table 2. A single hand sample of Ronda peridotite was selected and cut into seven ~1 cm³ cubes, each of which was divided into a thin section and matched slab. A summary of the slabs and associated thin sections is presented in Table 3. The first thin section was prepared on glass using epoxy, at the standard thickness of 30 μm. Five sections were cut with thicknesses ranging from ~20 to 25 μm roughness) to mimic typical cut surfaces with minor processing that might be produced robotically for in situ analysis. The sections were mounted by crystal bond during preparation, which was then dissolved using acetone so that they could be removed from the glass. For comparison, an additional thin section was prepared at a 300 μm thickness, with a 0.3-μm polish on both sides. The slabs corresponding to the first six thin sections were also polished with 400-grit corundum, and the seventh slab was polished to 0.3 μm. An example of a typical portion of the highly polished thin section showing the distribution of minerals within the sample is shown in Figure 4. Each thin section was cut from the cube and prepared so that the thin section would contain the minerals most spatially similar to those on the surface of the slab.

[14] A portion of the remaining hand sample was powdered and sieved to ~75 μm, 75–125 μm and 125–250 μm. Mineral separates of olivine, orthopyroxene and clinopyroxene were hand-picked under a binocular microscope by color and cleavage from the 125–250 μm size fraction. The mineral separates were sonicated in distilled water to remove serpentine and other contamination, and then decanted and dried in a desiccator for 72 hours.

3.3. Spectroscopic Measurements

3.3.1. Macroscopic Bidirectional and Diffuse Reflectance

[15] The Keck/NASA Reflectance Experiment Laboratory (RELAB) bidirectional reflectance spectrometer is specifically designed to mimic the viewing geometry of telescopic or orbital based remote measurements and allows both the incident and emission angles to be adjusted [Pieters and Hiroi, 2004]. An incidence angle of 30° and an emission angle of 0° were selected for bidirectional measurements. Spectra of 125–250 μm and <125 μm bulk sample and 125–250 μm mineral separates were measured relative to a halon reference standard over the wavelength range of 0.3–2.6 μm and corrected for the spectral properties of halon. Diffuse reflectance spectra of the bulk sample and mineral separates were collected in a purged (H₂O and CO₂ free) environment using a Thermo-Nicolet Nexus 870 spectrometer with an off-axis biconical geometry with a KBr beamsplitter and a thermoelectrically cooled deuterated triglyceric sulfate (DTGS-TEC) detector for the wavelength range of 1.3–25 μm. Raw data were ratioed to a diffuse gold reference standard to produce spectra.
3.3.2. Microspectroscopy

3.3.2.1. Transmission

[16] Transmission measurements of individual olivine and pyroxene grains within the 400-grit and highly polished thin sections (Table 3) were collected using a Nicolet Continuum infrared microscope attached to the Nexus 870 spectrometer with a CaF$_2$ beamsplitter and mercury cadmium telluride (MCT-A) detector. Transmission measurements were collected with a spot size of 70 $\mu$m. Raw data of thin sections A, B, C and 7 were ratioed against a background measurement collected through an empty hole to remove instrumental effects and any residual atmospheric absorptions. Thin sections D and E had to be supported on a KBr window and were therefore ratioed against a background measurement collected through the KBr.

3.3.2.2. Reflectance

[17] The Continuum microscope uses a Cassegrain objective, which illuminates a sample over a range of incident angles from 15° to 30° from the vertical. Reflected radiation from the target follows a similar path to the detector, as illustrated in Figure 5. The geometry of illumination spot size and the detector field of view are thus the same. A target as small as 10 $\mu$m wide can be illuminated; however, at near-infrared wavelengths, most of the photons that enter the body of the sample scatter out of the small spot viewed by the detector. For the smallest spot sizes, the signal reaching the detector is on the order of 1000x lower than the signal measured in the biconical diffuse reflectance system. A larger aperture improves the signal slightly.

[18] Reflectance measurements were collected using a KBr beamsplitter and MCT-A detector. A 150-$\mu$m spot size was used for reflectance measurements to maximize the signal at all wavelengths and to avoid diffraction artifacts as the aperture size approaches the wavelengths of light being measured [Hofmeister, 1995; Hofmeister et al., 2000]. Spectra collected from 400-grit surfaces were ratioed with a 400-grit diffuse gold standard, and spectra from highly polished samples were ratioed using a gold mirror standard. This procedure avoids detector nonlinearities caused by large intensity variations between samples and background measurements. At some wavelengths, differences in surface scattering caused the sample to have a higher total reflectance than the gold standard, producing a ratio greater than one. Reflectance in the following sections should thus be regarded as relative rather than absolute reflectance.

4. Results

4.1. Bidirectional and Diffuse Reflectance

[19] Bidirectional reflectance measurements of the bulk peridotite and mineral separates are presented in Figure 1. Fe$^{2+}$ absorptions due to olivine dominate the 1 $\mu$m region of the bulk peridotite spectrum with minor contributions from orthopyroxene. The Fe$^{2+}$ absorption near 2 $\mu$m is primarily associated with orthopyroxene, but may be slightly shifted toward longer wavelengths due to the presence of small amounts of clinopyroxene. The relatively high chromium content of the clinopyroxenes (Table 1) can be seen in the clinopyroxene spectrum as two crystal field bands centered at 0.45 $\mu$m and 0.65 $\mu$m. These bands are minimal in the bulk spectrum due to the low (≤5%) concentration of clinopyroxene.

[20] In the mid-infrared, the bulk spectrum is dominated by olivine, though the presence of pyroxene causes a shift in the Christiansen feature from around 9.0 $\mu$m to roughly 8.5 $\mu$m. Studies of olivine spectra in mid-infrared transmission indicate that the position of a small absorption band, centered just before 12 $\mu$m, can be used to determine the magnesium number for olivine [Duke and Stephens, 1964; Burns and Huggins, 1972]. This feature is easily seen in reflectance spectra of both the bulk sample and the olivine separate in Figure 1b. With high iron to magnesium ratios, this band shifts to longer wavelengths and shorter frequencies, and with higher magnesium ratios it moves to shorter wavelengths [Duke and Stephens, 1964; Burns and Huggins, 1972]. The band center for the Ronda olivine separate occurs at 11.93 $\mu$m or 838 cm$^{-1}$. Mid-infrared band

![Figure 4. Subsection of the highly polished Ronda peridotite thin section (TS7). The hand sample is dominated by olivine (OLV) and orthopyroxene (OPX), with some serpentinization.](image)

![Figure 5. Diagram of microscope optics for the Continuum IR microscope system. Light illuminates the sample with a cone of light ranging from 15° to 30° incident angles, and emitted light is collected within the same cone angles.](image)
positions are not necessarily the same in transmission and reflectance measurements. However, the best-fit polynomial for determining forsterite content ($Fo$) from the frequency of the 12 $\mu$m band ($\nu$) measured in units of cm$^{-1}$ as derived by Burns and Huggins [1972],

$$\nu = 826.78 + 0.124*Fo,$$

predicts a forsterite content of 90.5% when calculated using the reflectance band center, in good agreement with our microprobe average forsterite content of 90.9%.

### 4.2. Microspectroscopy

#### 4.2.1. Transmission

[21] Examples of transmission spectra for individual mineral grains in the first series of thin sections (TS A–E) are presented in Figure 6. Although the 400-grit surface is uniform between thin sections, surface scattering reduces the transmitted signal and produces a strong red slope to the resulting spectrum, which is most evident in the thinnest sections (TS C, D, E). Ferrous absorption features superimposed on this scattering continuum are discernable for each of the minerals at all thicknesses. The 3-$\mu$m O-H stretching modes are also evident, but as expected are most prominent in the thicker (>200 $\mu$m) sections (TS A, B). In contrast to the 400-grit thin sections, surface scattering is minimal for the polished thin section (TS 7), as the surface roughness (0.3 $\mu$m) is less than the wavelengths of light observed. As illustrated in Figure 7, spectra of the polished section indeed exhibit much stronger and well-defined absorption features. For comparison, also shown is the spectrum of the same minerals acquired for the 400-grit thin section of comparable thickness. The ratio of transmitted light to air for some of the pyroxene measurements of the polished thin section is greater than unity. This is likely due to light loss when the background was collected, as the condenser height was optimized for the ~300-$\mu$m-thick thin section.

#### 4.2.2. Reflectance

##### 4.2.2.1. Near Infrared (1.0–9.0 $\mu$m)

[22] Microspectroscopic reflectance measurements were conducted of both slabs and particulate mineral separates in the near infrared. Because of the relative sizes of the particles (125–250 $\mu$m) and the width of the incident beam (150 $\mu$m), each spectrum observed likely represents the interaction of light with a small number of grains. Examples of near-infrared microscopic reflectance spectra of particulate mineral separates are shown in Figure 8. An average spectrum is also presented, as the absolute reflectance and absorption strengths of measured absorption features vary significantly between measurements of different areas of the same sample. For slabs, only specular (Fresnel) reflectance

---

**Figure 6.** Transmission spectra for thin sections (A–E) of varying thickness, polished with 400 grit. All spectra exhibit a strong red slope due to surface scattering.

**Figure 7.** Transmission spectra of several grains on the fully polished thin section (TS7) (shaded line) compared with the same minerals measured in 400-grit thin section A (black line). Both sections are roughly 300 $\mu$m thick.
was detected over the same wavelengths, providing no useful compositional information. Light that entered into the rock was either transmitted deep into the surface and absorbed or scattered out of the necessary cone of collection.

[23] The near-infrared reflected signal received from the orthopyroxene separates was typically stronger and showed more definitive absorption features than that for the clinopyroxene or the olivine separates. The 2-\mum pyroxene Fe\textsuperscript{2+} absorption and the 3-\mum O-H stretching modes are discernible for both types of pyroxene, though the intensity of each measurement varies widely from spot to spot. In some cases, Si-O overtone bands around 5 \mum are also visible. A comparison of absorption features measured of particulate samples in reflectance with those of individual mineral grains measured in transmission is presented in Figure 9. Features in the reflectance spectra are \sim 10x weaker than those measured by transmission of the 300-\mum-thick doubly polished thin section (TS 7).

4.2.2.2. Mid-Infrared (8.0–14 \mum)

[24] Measurements in the mid-infrared produce good signal on particulate, polished and unpolished surfaces. Individual and average reflectance spectra of particulate mineral separates and cut slabs in the mid-infrared are presented in Figure 10. Slab measurements produce an average signal that is 5 to 10 times stronger than the particulate surface average although the grain-to-grain intensity of features is still highly variable. The shape and position of absorption bands is relatively constant for olivine and clinopyroxene.

[25] The orthopyroxene spectra of individual grains, however, can be separated into two distinct groups. The majority of orthopyroxene slab measurements display a large reflectance peak near 1100 cm\textsuperscript{-1} (Figure 10, Slab I) which is not evident in the other group (Figure 10, Slab II) nor in the macroscopic or microscopic reflectance measurements of particulate orthopyroxene (Figures 1b and 10). Further examination of grain orientation of orthopyroxenes within these samples reveals that those spectra that were collected perpendicular or near perpendicular to a cleavage surface (or the c-axis) exhibit the three-peaked spectrum seen in slab group II. The similarity of the spectra measured for particulates of orthopyroxene to those of slab group II suggests that the orthopyroxene grains may have been preferentially aligned on their cleavage surfaces owing to their tabular nature. A preferred orientation of the grains...
was confirmed by inspecting the sample through a binocular microscope, as shown in Figure 11. In contrast, cut slabs preserve the random grain orientation present in the original igneous texture, producing a greater number of “Slab I” spectra when numerous grains are measured.

A comparison of mid-infrared reflectance spectra of the macrospectroscopic and microspectroscopic measurements for the three minerals (particulate and slabs) is presented in Figure 12. Both the features and intensity of the averaged microscopic spectra of the mineral separates are comparable with spectra of the same bulk sample measured using the macroscopic reflectance system. The absolute value of measured reflectance depends on the texture of the gold reference. Mid-infrared microscopic spectra of both the 400-grit and polished slabs exhibit almost an order of magnitude greater reflected signals than the particulate samples produce when measured by either the infrared microscope or macroscopic diffuse reflectance. In some cases the reflected signal from the polished sample was more intense than that from the gold mirror reference standard. When the spectra are scaled to allow features to be compared, the band positions and overall spectral character are consistent between the microscopic measurements and macroscopic diffuse reflectance. Some variation in relative band strengths is observed; this is attributed to varying amounts of specular reflectance.

One notable variation between macroscopic diffuse reflectance spectra of particulate mineral separates and spectra measured using the Continuum microscope is an observed shift in the Christiansen feature. Particulate spectra collected as macroscopic diffuse reflectance exhibit a reflectance minimum at roughly 0.2-μm shorter wavelengths than spectra collected from slabs and particulates using the Continuum microscope. The position of the Christiansen

Figure 10. Mid-infrared reflectance spectra of particulate mineral separates and cut slabs. Average values for each are shown in black, and shaded lines show the range in spectra observed. Orthopyroxene slab measurements have been separated into two end-members, one of which was encountered in 75% of measurements. Reflectance is inverted for easier comparison with emission spectra.
feature for samples measured with the Continuum microscope is similar to the frequency of the Christiansen features of minerals of roughly equivalent composition measured through emission spectroscopy for the TES library [Christensen et al., 2000].

5. Discussion

5.1. Transmission Microspectroscopy

[28] Transmission measurements are not identical to reflectance measurements, either from the laboratory or remote sensing, as they rely only on the extinction coefficient ($k$) and not the refractive index ($n$) [Wooten, 1972]. However, in the near infrared, where $k$ is very small and allows a relatively long path length through the material, positions of vibrational features and bands caused by electronic transitions are observed at the same wavelength in both bidirectional reflectance measurements and microspectroscopic transmission measurements.

[29] Transmission measurements are well suited for detailed spectroscopic analyses of submillimeter-sized samples in the near infrared. Both polished and unpolished...
thin sections produce well-identified absorption features that are consistent with bidirectional measurements of the same minerals. However, spectra of 400-grit polished samples exhibit a strong red slope due to wavelength dependent scattering from the surface of the thin section. Highly polished thin sections are much preferred and produce the only data that can be directly analyzed with Beer’s law for relative values of extinction coefficient. Although thicknesses from 40 to 350 μm all produce measurable absorption features, thicknesses around 300 μm produced the best spectral contrast for measurement of electronic transition and vibrational bands for all three minerals studied.

5.2. Reflectance Microspectroscopy

[30] Reflectance spectra collected for small individual grains in the near infrared using the Continuum microscope provide a generally weak signal, and absorption features due to electronic transitions are often undetectable. When a small target area is illuminated, transmission and scattering of light hinders detection of the body component of reflected light, although the O-H stretch near 3 μm can be discerned (Figure 8).

[31] At longer wavelengths, where the extinction coefficient (k) is high, reflectance spectra exhibit a strong signal and distinctive absorption features. Absorption band positions measured using the Continuum microscope are similar to those measured using macroscopic diffuse reflectance and emittance spectroscopy. However, the strengths of absorptions vary significantly from grain to grain on both particulate and cut surfaces. Much of this variation is due to natural variations in grain orientation with respect to the geometry of measurements.

[32] Slight variations in band strengths may also be introduced by specular reflectance on cut surfaces, though these effects are minimal for 400-grit (or more diffuse) slabs. Anomalous specular reflectance is commonly noticeable for highly polished surfaces. Reststrahlen band positions are nevertheless still consistent with other macroscopic and microscopic methods (Figure 12).

[33] A Christiansen feature is observed for a given mineral as n changes rapidly and approaches the refractive index of the medium around the sample [Salisbury, 1993]. Since n and k do not vary with mineral form, the reflectance minimum (Christiansen feature) should be constant for each mineral. However, as discussed above, the Christiansen feature measured using microspectroscopy occurs at a slightly longer wavelength than when measured for each of the particulate minerals using macroscopic diffuse reflectance (Figure 12). These observed variations may be due to differences in scattering properties at different scales or to instrumental effects. Possible explanations include the following. Macroscopic diffuse reflectance of particulate samples include a significant component of volume scattered light in the near to mid-infrared at wavelengths shorter than the Reststrahlen bands [Salisbury, 1993]. In microscopic measurements where a single grain is illuminated, little to none of this body component returns to the detector. Differences in the amount of volume scattered light measured at wavelengths shorter than the Reststrahlen band result in an observed shift in the minimum reflectance (Christiansen feature). An alternative explanation could be that because the Christiansen feature is very sensitive to slight variations in n and k, small differences in instrument configuration may affect the effective optical constants of the system and alter the position of the reflectance minimum.

[34] The strong signal of reflectance microspectroscopic measurements in the mid-infrared makes microspectroscopy a viable tool for compositional analysis of submillimeter-sized grains at these wavelengths. For example, the 12-μm band used to characterize iron-magnesium ratios in olivine [Duke and Stephens, 1964; Burns and Huggins, 1972] is prominent and well-defined in microscopic measurements of both particulate and cut slab surfaces. Using the band position of the 12-μm band from any of the microscopic olivine reflectance spectra with equation (2) is shown to produce a magnesium number that is consistent with electron microprobe analyses to within half a percent.

6. Conclusions

[35] Optical constants of samples and instrument geometry place physical constraints on what can and cannot be measured using microspectroscopy. For near-infrared reflectance, where photons enter the body of a crystal and are multiply scattered by different grains, a smaller target means few photons will return to the detector from the target area. This precludes most reflectance measurements of small grains or samples in the near infrared.

[36] In contrast, transmission spectra produce strong, well-defined absorption features in the near infrared. Although transmission measurements only rely on the extinction coefficient (k) and not the refractive index (n), band positions can be directly compared to reflectance spectra. For samples to be measured by transmission, all supporting glass and glue must be removed. Highly polished thin sections allow the maximum amount of light to be transmitted through a thin section, and are necessary for the best results. Moderately polished (400-grit) or similarly textured cut surfaces allow sufficient transmission for qualitative analysis but produce artifacts (red slopes) and are not recommended.

[37] Microspectroscopic reflectance measurements in the mid-infrared detect well-defined absorption features for most samples (particulate minerals; polished and unpolished slabs). Cut surfaces, as might be available for in situ experiments, are suitable for reflectance measurements in the mid-infrared. Although the intensity of absorption features varies from grain to grain, band positions are consistent with macroscopic diffuse reflectance and emittance measurements of bulk samples, and can be used to extract general chemical information such as iron/magnesium ratios of olivines. Because microspectroscopy often examines single grains, differences in spectra due to crystal orientation are accentuated, however, and must be considered in analyses.

[38] Acknowledgments. We thank Jack Mustard for providing us with the Ronda peridotite sample. We are grateful to Bill Collins and Mike Kravecynski for their help in preparing thin sections, Zach Morgan for his help with electron microprobe analyses, and Gerard Marchand for instruction in handpicking mineral separates. Many thanks are owed to Anne Hofmeister and Andreas Morlok for their constructive reviews. This research was supported by NASA grants NNG04GG11G and 2090GEC562. RELAB is a multiuser facility supported by NASA grant NAG5-13609.
References


Burns, R. G. (1993a), 


Mustard, J. F., and J. E. Hays (1997), Effects of hyperfine particles on reflectance spectra from 0.3 to 25 um, Icarus, 125, 145–163.


R. L. Klima and C. M. Pieters, Department of Geological Sciences, Brown University, Box 1846, Providence, RI 02912, USA. (rachel_klima@brown.edu)