VISIBLE-REGION SPECTRA OF THE MOON: PROGRESS TOWARDS CHARACTERIZING THE CATIONS IN Fe-Ti-BEARING MINERALS.

Chemical and mineralogical mapping of the moon's surface by remote sensing spectral measurements during future automated lunar explorations depends on correct assignments being made of electronic transitions in lunar and related materials [1,2]. Iron and titanium, which are the most abundant transition elements on the moon, also dominate the spectra of lunar materials in the near ultraviolet (u.v.), visible, and near infrared (i.r.) regions [3], with the result that earth-based telescopic reflectance profiles are being used to locate Fe and Ti rich areas on the moon [4]. However, the origins of some of the diagnostic spectral features remain ambiguous: Whereas absorption bands in the near i.r. region (0.9-2.5 microns) attributable to crystal-field transitions in Fez+ in various silicate minerals and glasses are generally well understood [5], considerable uncertainty still exists over assignments of bands in the near u.v. and visible regions (0.3-0.7μ) attributed to Ti [1,2,4]. In this report, we indicate some of the problems concerning the resolution and assignment of spectral features in lunar minerals in the visible region, and outline recent experimental and computational data bearing on the transition energies of Fe-Ti-bearing minerals.

Because Fe and Ti each may occur in two different oxidation states in silicate and oxide minerals, several electronic transitions are possible within and between the various cations. They include:

(1) Crystal field, spin-allowed transitions in Fe2+, which in pyroxenes occur between 0.9-1.05μ and 1.8-2.3μ [5,6];
(2) Crystal field, spin-forbidden transitions in Fe2+, which give weak but sharp peaks in the visible region [5];
(3) Crystal field, spin-forbidden transitions in Fe3+, which contribute both sharp and broad, but weak, peaks in the visible region. Positions and relative intensities of these peaks differ slightly for octahedrally and tetrahedrally coordinated Fe3+ [5];
(4) Crystal field, spin-allowed transitions in Ti3+, which occur between 0.45 and 0.65μ [7];
(5) Fe2+-Fe3+ homonuclear charge transfer transitions, known energies of which fall in the range 0.55-0.80μ [3];
(6) Ti3+-Ti4+ homonuclear charge transfer transitions;
(7) Fe2+-Ti4+ heteronuclear charge transfer transitions; and
(8) Oxygen-metal charge transfer, the energies of which are calculated to lie in the near u.v. [1].

Ferric ions are virtually absent in lunar materials, particularly pyroxenes, so that transitions (3) and (5) do not apply on the moon. However, they need to be identified in certain ter-

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restrial minerals such as titanaugites, correlative data for which are discussed later. In lunar materials, uncertainty existed over transitions (4), (6), and (7) involving Ti. Recently, however, elegant measurements [8] of the titaniferous pyroxene from the Allende meteorite cleared the controversy [7,9] over spectral assignments for this Ti$^{3+}$-bearing mineral. Thus, generally accepted energies for transitions (1) through (6) are summarized in Table 1. The one outstanding problem is the transition energy for the Fe$^{2+}$→Ti$^{4+}$ charge transfer process which is considered to contribute to the spectra of lunar pyroxenes, ilmenites, ülvospinels, armalcolites, and certain glasses [2,4,6].

In order to obtain information on the Fe$^{2+}$→Ti$^{4+}$ charge transfer transition energy, we have measured the Mössbauer and electronic absorption spectra of a suite of terrestrial titanaugites with variable Fe$^{3+}$/Fe$^{2+}$ ratios and different site occupancies of Fe$^{3+}$ and Fe$^{2+}$ ions. Representative electronic spectra are illustrated elsewhere [3,11,12]. These ferric-bearing pyroxenes contain negligible Ti$^{3+}$ ions [13], so that transitions (4) and (6) assignable to trivalent titanium may be ignored. The spectra of titanaugites [13] show the broad Fe$^{2+}$→Fe$^{3+}$ charge transfer band around 0.7-0.8 μ, and prominent weak peaks at 0.45, 0.505, and 0.55 μ attributed to spin-forbidden transitions in Fe$^{3+}$ and Fe$^{2+}$ ions. Underlying these weak peaks is a broad region of absorption which appears to maximize around 0.45-0.50 μ. This broad intense band we assign to Fe$^{2+}$→Ti$^{4+}$ charge transfer. The Fe$^{2+}$→Ti$^{4+}$ charge transfer band thus overlaps one of the Ti$^{3+}$ crystal field bands, and both electronic transitions contribute to absorption around 0.5 μ in the published spectra of lunar pyroxenes [14].

The position of the Fe$^{2+}$→Ti$^{4+}$ charge transfer band deduced to occur around 0.5 μ in lunar pyroxenes contrasts with the band at 0.6 μ found in the diffuse reflectance spectra of ilmenite [6], which was previously assigned to Fe$^{2+}$→Ti$^{4+}$ (and/or Ti$^{3+}$→Ti$^{4+}$) charge transfer. The energy difference may be related to different orientations of the metal-metal vectors relative to the surrounding oxygen coordination polyhedra. Thus, in ilmenite the Fe-Ti interactions take place across face-shared octahedra, as opposed to edge-shared octahedra in the pyroxene structure. Energy level calculations currently underway on dimeric clusters are aimed at determining the dependence of charge transfer energies on metal-metal distances and on the symmetry and orientation of linked coordination polyhedra [15].

References:
Table 1: Energies for Electronic Transitions Involving Fe and Ti Cations in Pyroxenes

<table>
<thead>
<tr>
<th>Transition</th>
<th>Type</th>
<th>Energy (μ)</th>
<th>Assignment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>Fe²⁺</td>
<td>0.9-1.15 and/ or 1.8-2.3</td>
<td>components of &quot;5T₂g&quot;→&quot;5E_g&quot;</td>
<td>[5,6]</td>
</tr>
<tr>
<td>(2)</td>
<td>Fe²⁺</td>
<td>0.505, 0.55</td>
<td>components of &quot;5T₂g&quot;→3T₁g, 3T₂g</td>
<td>[5]</td>
</tr>
<tr>
<td>(3)</td>
<td>Fe³⁺</td>
<td>0.45, 0.50, 0.56</td>
<td>6A₁g→4A₁g, 4E₉; 4T₁g; and 4T₂g</td>
<td>[5]</td>
</tr>
<tr>
<td>(4)</td>
<td>Ti³⁺</td>
<td>0.47-0.61</td>
<td>components of &quot;2T₂g&quot;→&quot;2E_g&quot;</td>
<td>[7]</td>
</tr>
<tr>
<td>(5)</td>
<td>Fe²⁺→Fe³⁺</td>
<td>0.70-0.75</td>
<td>charge transfer</td>
<td>[3,5]</td>
</tr>
<tr>
<td>(6)</td>
<td>Ti³⁺→Ti⁴⁺</td>
<td>0.64-0.67</td>
<td>charge transfer</td>
<td>[8,9, 10]</td>
</tr>
<tr>
<td>(7)</td>
<td>Fe²⁺→Ti⁴⁺</td>
<td>approx. 0.5</td>
<td>charge transfer</td>
<td>this work.</td>
</tr>
</tbody>
</table>