Reports

Lunar Soil: Iron and Titanium Bands in the Glass Fraction

Abstract. *A study of absorption bands in simulated lunar glasses resulted in the discovery of a Ti^{4+}-O^{2-} charge transfer band at 0.26 micrometer and two Fe^{2+}-Ti^{4+} bands at 0.34 and 0.42 micrometer. These results indicate that the properties of lunar soil are somewhat affected by the glass content but are controlled by other factors.*

With the end of manned lunar landings, remote-sensing techniques for studying the compositions of lunar and planetary surfaces have become increasingly important. McCord and his associates (*1, 2*) have demonstrated from Earth-based observations of lunar reflectivity that compositional information is present in the spectra and have made progress in interpretation, particularly in the use of the 1.0-μm Fe^{2+} band to determine the presence of iron silicate minerals. Charette *et al.* (*2*) reported a correlation between the TiO_2 content of lunar soils and the ratios of the reflectivities at 0.40 and 0.56 μm; they explained this relationship as due to possible charge transfer bands involving Ti^{3+}, Ti^{4+}, and Fe^{2+} in the glass fraction of the soil. The charge transfer bands of Fe and Ti have become interesting also because of recent advances in molecular orbital theory (*3, 4*), which have made it possible to predict the positions of both ligand-metal and metal-metal bands.

One of the major questions in the study of lunar soil is the extent to which glass contributes to the optical properties of the soil. One widely held view is that glass, probably associated with agglutinates, is the primary agent that transforms the pulverized rock, with its high albedo and well-defined absorption bands, into the lunar soil, with its low albedo and nearly featureless spectra (*5*). This view was based on experiments in which melted lunar rocks were reported to have low, almost featureless, spectral reflectivities, a result that was attributed to possible Fe-Ti charge transfer bands in the ultraviolet, visible, and infrared. An opposing view was based on measurements of vacuum-melted lunar rocks, actual lunar glasses, and simulated lunar glasses, which were found to have distinct bands and a high reflectivity "window" in the visible region (*6–8*). Since these glasses were made under conditions that more closely simulated lunar conditions, these investigators (*7, 8*) concluded that vitrification was not an important mechanism for soil darkening. Hapke *et al.* (*8*) suggested that the cause of the low reflectivity of the soil is abundant submicroscopic particles of metallic Fe created by vaporization as a result of meteorite impact with subsequent recondensation of soil material or by solar wind sputtering with subsequent recondensation. In order that remote-sensing observations of the lunar surface be adequately interpreted, the contribution of glass to the optical properties of the lunar soil must be determined. Thus, an understanding of Fe-Ti charge transfer bands in lunar glass is essential.

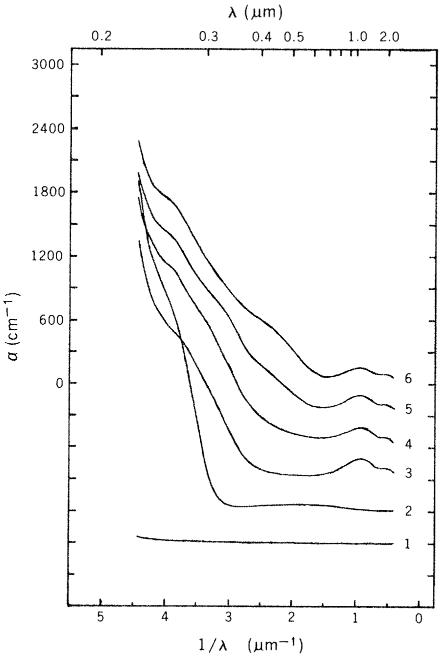

Fig. 1. Absorption spectra of glasses. The effective absorption coefficients (*a*) were calculated from reflectivity measurements as described in the text. Each curve has been set off vertically by 300 cm^{-1} to avoid confusion. All glasses were melted in vacuum. Curve 1, base glass; curve 2, 10 percent TiO_2; curve 3, 18 percent FeO; curve 4, 18 percent FeO + 1 percent TiO_2; curve 5, 18 percent FeO + 5 percent TiO_2; and curve 6, 16 percent FeO + 10 percent TiO_2.

We have made a series of glasses of approximate lunar composition and measured their bidirectional spectral reflectivities. The glasses were made from a base glass consisting of 57 percent SiO_2, 18 percent Al_2O_3, 11 percent MgO, and 14 percent CaO, a composition that approximates the proportions of the major nonabsorbing cations in Apollo 11 soil. Varying concentrations of oxides of the light-absorbing cations of Fe and Ti were added to this base glass. Meltings were carried out under both oxidizing and reducing conditions. We report here only on a few of the glasses made under moderate reducing conditions in vacuum. The vacuum meltings were carried out at 1400°C in a Ta resistance furnace at pressures below 10^{-5} torr (oxygen fugacity, 10^{-9} to 10^{-10} atm) in Pt crucibles. The glasses were examined under a petrographic microscope to ensure the absence of crystalline material and were pulverized to a particle size of < 37 μm in an agate mortar. Concentrations and valence states of Fe and Ti were determined by wet chemical, electron microprobe, electron spin resonance, and Mössbauer techniques. Mössbauer and electron spin resonance measurements indicated that less than 1 percent of the Fe could be present as Fe^{3+} and that the ratio of Ti^{3+} to Ti^{4+} varied from about 0.1 for Fe-free glasses to less than 0.01 for glasses with a high Fe content.

Because of the large number of glasses ($\sim$ 50) and the high absorptivities, the use of transmission techniques to measure absorption coefficients was impractical and we found it necessary to resort to reflection methods. We measured the spectral reflectivities (relative to a calibrated $BaSO_4$ standard) of the powdered samples, using a spectrophotometer (Cary 14R) with a bidirectional reflectance attachment of our own design, in which the incident and reflected beams made angles of 30° to the normal, with a phase angle of 60°. We converted the reflectivities to approximate spectral absorption coefficients $a(\lambda)$ by calculating the average single scattering albedo $\omega_0(\lambda)$ of a glass particle. We assumed that

$$\omega_0 = \frac{s}{a + s} \approx \frac{1}{1 + ad}$$

where $s \approx 1/d$ is the effective scattering coefficient and d is the particle diameter. This procedure and the underlying assumptions are analogous to the remission function $F(R)$ of hemispherical reflection spectroscopy (*9*). We verified the potential of the method by making measurements of the effective absorption coefficients of Co-doped glass and fused silica, using both reflection and transmission measurements. The $a(\lambda)$ values deduced in these two ways agreed to within 15 percent for 5 cm^{-1} < a < 1500 cm^{-1}.

Figure 1 shows the equivalent absorption spectra of our glasses. Curve 1 is the spectrum of the base glass, showing the lack of appreciable absorption. Curve 2 is the spectrum for a glass containing 10 percent TiO_2 but no FeO. The broad weak band near 0.5 μm is commonly found in solids and solutions containing Ti^{3+}, and is usually attributed to a *d-d* transition of Ti^{3+} (*10*). However, there have been identifications of Ti^{3+}-Ti^{4+} charge transfer bands in this spectral region in liquids and minerals, and Loeffler *et al.* predicted from molecular orbital theory a charge transfer band at 0.62 μm (*4*). If the 0.5-μm band were due to a *d-d* transition in Ti^{3+}, the molar extinction coefficient would be independent of Ti^{3+} and Ti^{4+} concentrations and of the order of 10 to 30 liter cm^{-1} per mole of Ti^{3+} (*11*). However, in our glasses the extinction coefficient increases rapidly with Ti^{3+} concentration, and for the glass with 15 percent TiO_2, the extinction coefficient is 190 liter mole^{-1} cm^{-1}. Therefore, we conclude that in our glasses the band is predominantly a Ti^{3+}-Ti^{4+} charge transfer band.

The only other band clearly seen in curve 2 (Fig. 1) is at 0.26 μm. The strength of the band and its position in the ultraviolet suggest a ligand-metal charge transfer band. Loeffler *et al.* (*3*) predicted Ti^{4+}-O^{2-} bands at 0.26 and 0.30 μm and Ti^{3+}-O^{2-} bands at 0.22 and 0.25 μm. We found that the ultraviolet absorptivity is somewhat higher in vacuum-melted glasses than in air-melted glasses; this finding implies that Ti^{3+} also contributes to this band, although the primary contributor must be Ti^{4+}. The predicted band of Ti^{4+} at 0.30 μm is not apparent in curve 2, but a weak band could be hidden in the wing of the stronger band. We have also observed a possible band at 0.21 μm in our Ti glasses, but the data are questionable below 0.25 μm because of the uncertain corrections for the $BaSO_4$ standard and the presence of scattered light in the spectrophotometer.

Curve 3 (Fig. 1) presents the results for a glass containing 18 percent FeO but no TiO_2. The band at 1.1 μm is the well-known *d-d* transition of Fe^{2+} in octahedral coordination, which is observed in the region from 0.9 to 1.2 μm in many minerals (*10*). The band at 1.9 μm is also well known but has been variously identified as a *d-d* transition in tetrahedral Fe^{2+} (*12*) or in Fe^{2+} in distorted octahedral coordination (*10, 13*). We believe that Fe^{2+} in a distorted octahedral site similar to the M2 site in pyroxene is the correct interpretation of this band for several reasons. (i) In glasses of this composition, the only tetrahedral site is the Si site (*14*), and we do not think that Fe^{2+} is likely to go into this site because of its large size and small charge. (ii) The Fe^{2+} in the distorted M2 sites in pyroxenes has two bands, near 0.95 and 1.9 μm (*10*), due to splitting of the energy levels by the distorted ligand fields. (iii) Mössbauer measurements show that isomer shifts and quadrupole splittings, which depend in part on the distortion of the site, have the same values (within errors of measurement) for our glasses and lunar glasses as for the M2 site in pyroxene (*6*). (iv) At low Fe concentrations, the 1.9-μm band is almost as strong as the 1.1-μm band; however, the strength of the 1.1-μm band increases more rapidly with increasing Fe concentrations. This result suggests that the Fe is predominantly in an M2-type site at low concentrations but is increasingly found in a different, less distorted site as concentrations increase, either because all available M2-type sites are filled or because of a decrease in the number of M2-type sites caused by a change in structure.

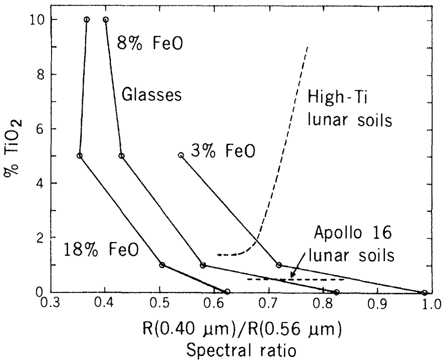

Fig. 2. The TiO_2 content of glasses and lunar soils versus the ratio of the reflectivity at 0.40 μm to the reflectivity at 0.56 μm. The solid lines connect the data for our glasses. The upper dashed curve is drawn through data points for mature soils from the Apollo 11, 12, 14, 15, and 17 and Luna 16 missions. The lower dashed curve corresponds to Apollo 16 and Luna 20 (highland) soils, some of which are immature. Curves for immature high-Ti soils fall to the right of the upper dashed curve.

The band at 0.27 μm in the Fe glass of curve 3 has been reported by Runciman *et al.* (*15*) and others, and is at the position predicted by Loeffler *et al.* (*3*) for Fe^{2+}-O^{2-} charge transfer. This band occurs at nearly the same wavelength as the Ti^{4+} band discussed above.

The results for three vacuum-melted glasses containing both FeO and TiO_2 are presented in curves 4, 5, and 6 (Fig. 1). The spectra of these glasses are similar to those of Mao *et al.* (*6*), who worked at wavelengths longer than 0.4 μm. Except in the region from 0.3 to 0.5 μm, the changes in the absorption coefficient with an increase of TiO_2 can be understood as the superposition of the Fe and Ti bands discussed above. Since the absorption at 0.3 to 0.5 μm occurs only when both Fe^{2+} and Ti^{4+} are present, it is highly probable that this absorption is due to metal-metal charge transfer between Fe^{2+} and Ti^{4+}. Close examination of the spectra reveals two bands at 0.34 and 0.42 μm. The 0.34-μm band is the stronger of the two at low concentrations of Fe and Ti, but the 0.42-μm band becomes the stronger for high concentrations. By contrast, Loeffler *et al.* (*4*) predicted that the Fe-Ti band will occur between 0.50 and 0.58 μm in crystalline materials.

We have also observed a band at 0.34 μm in an Apollo 11 rock and a 0.42-μm band in a glass made from the rock (*7, 8*). It is likely that the 0.34-μm band is due to Fe-Ti charge transfer in augite in the rock, on the basis of Cohen's report (*16*) of a band at this position in lunar augite. This observation is further evidence for the suggestion of the presence of sites in the glass similar to the M2 pyroxene sites, and suggests that the Fe involved in the 0.34-μm Fe^{2+}-Ti^{4+} charge transfer band is present in that site. We have no evidence to indicate whether Ti^{4+} is present in the same M2-type site or in another distorted site. According to the models of Loeffler *et al.* (*4*), band positions shift to longer wavelengths as the metal-metal distances decrease. Therefore, the appearance of the 0.42-μm band at high Fe and Ti concentrations can result from either Fe or Ti (or both) going into new sites that decrease the Fe-Ti distances. Our discussion of the 1.9-μm band of Fe suggests that Fe enters a new site as the concentration increases. We have not observed the 0.42-μm band in any crystalline materials; thus this band may be useful for remote-sensing as an indicator of glass.

Figure 2 is a plot of TiO_2 concentrations versus the ratio of the reflectivity R at 0.40 μm to that at 0.56 μm for our glasses (solid lines) and for lunar soils (dashed lines) as measured by Charette *et al.* (*2*). Charette *et al.* used the ratio of the reflectivity values taken from a linear least-squares fit to the observational data. They called this quantity a "slope," but we prefer the more descriptive term "spectral ratio." As the TiO_2 content increases, the spectral ratio decreases for glasses, because of the growth of the Fe^{2+}-Ti^{4+} bands; the opposite behavior is observed for mature lunar soils. Therefore, glass cannot alone be the cause of the observed correlation between spectral ratio and TiO_2 content in the mature lunar soils.

The data of Charette *et al.* (*2*) also show that immature soils with high Ti contents have spectral ratios that are too large for the mature soil curve. However, as a soil with a high Ti content matures, its spectral ratio decreases until it reaches the curve for mature soil. These relationships between TiO_2 content and spectral ratio can be accounted for by a mixture of glass with a high Ti content, with a band at 0.42 μm and thus a low spectral ratio, and ilmenite, with a band at 0.53 μm and thus a high spectral ratio (1.07). As a soil matures, some of the ilmenite is converted into glass and the spectral ratio diminishes, at constant TiO_2, until some sort of equilibrium between glass and crystalline phases is reached. Most highland soils have a separate curve because their TiO_2 contents are too low and their spectral ratios are determined mainly by the width of the 0.27-μm FeO band. In addition, the spectral ratios will also be influenced by other factors, especially the submicroscopic metallic Fe content of the soils.

Our glasses have no absorption bands in the range from 0.6 to 0.7 μm, where lunar rock powders also have low absorption but where lunar soils are strongly absorbing (*7, 8*). None of our Fe or Ti glasses have strong absorption bands between 0.5 and 0.9 μm, unless they are partly oxidized. Since lunar soils are reduced and not oxidized, simple vitrification cannot be the primary mechanism for lunar soil darkening. The most viable hypothesis for lunar darkening remains submicroscopic metallic Fe formed in impact events and solar wind sputtering; evidence for such Fe, its probable origin, and its effect on the spectra of lunar soils has been presented elsewhere (*8*).

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Sulfate Aerosol: Its Geographical Extent in the Midwestern and Southern United States

Abstract. *Sulfate particles (sulfuric acid and its neutralization products with ammonia) dominate the submicrometer-sized, light-scattering component of the aerosol in more than 90 percent of 2850 pairs of humidographic measurements made over a 3-month period at three rural midwestern and southern sites. The nearly continuous optical dominance by sulfate in the aerosol at these spatially varied locations, particularly in the Ozark Mountains, suggests that sulfate is a component of the submicrometer-sized aerosol that is distributed over a large geographical region and is not due to local sources.*

The autumn hazes and high turbidity that occur over sparsely populated, vegetated areas of the Southeast (*1*) have been described as naturally occurring aerosols produced by photochemical transformation of terpenes during leaf decay in deciduous forest (*2*). We present here data showing that these hazes are dominated not by natural organic compounds but by sulfate aerosol particles, probably from the oxidation of SO_2 emitted by regionally distributed sources.

In earlier papers (*3*) we described the use of humidity-controlled nephelometry (humidograph) for in situ optical sensing of the deliquescence of $(NH_4)_2SO_4$ aerosol particles either directly or after the addition of NH_3 to the aerosol. This scheme thereby detects, as different species, acid sulfates (NH_4HSO_4 or H_2SO_4, or both), the neutralized salt $[(NH_4)_2SO_4]$, and occasionally letovicite $[(NH_4)_3H(SO_4)_2]$. The particles in the optical size range from 0.1 to 1.0 μm in diameter are most sensitive to detection by this method (*4*). Direct comparison in rural Missouri of the humidographic technique with an infrared technique confirmed the utility of the humidograph for distinguishing periods in which acid or salt sulfate particles dominate the submicrometer-sized aerosol (*5*). In 1973, sulfate aerosol in the form of H_2SO_4 or its neutralization products with NH_3, or both, was shown to be the dominant submicrometer-sized aerosol species in all but one of 88 measurements in rural Missouri (*3*). We hypothesized (*3*) that the submicrometer-sized aerosol detected at this site resulted from regionally distributed sources and perhaps extended for distances comparable with SO_2 oxidation distances (about 1000 km). We report here results of experiments to test this hypothesis with respect to the geographical extent of the sulfate aerosol.

Humidographic measurements were made during the fall of 1975 at three spatially separated rural locations in the Midwest and South: an Ozark Mountain site in rural, northwestern Arkansas (*6*), a rural midwestern site in southeastern Michigan (*7*), and the same Missouri site (*8*) as used in 1973. Site locations were chosen for geographical representation of the hypothesized sulfate region and variable proximities to SO_2 sources (*6–8*). In this way effects of local source chemistry as well as the geographical extent of the sulfate haze might be observed. Systematic differences in the temporal variability of the molecular form of sulfate or in the percentage of time dominated by sulfate aerosol would be expected if local source chemistry were to dominate at any or all of the sites.

The experimental procedure duplicated that used in the 1973 measurements (*3*). Pairs of humidograms were used to detect the deliquescence of $(NH_4)_2SO_4$ automatically every half-hour with about 1 part per million of NH_3 add-