Far infrared and Raman spectroscopic investigations of lunar materials from Apollo 11, 12, 14, and 15

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Abstract—We have studied the elastic and inelastic light scattering of twelve lunar surface rocks and eleven lunar soil samples from Apollo 11, 12, 14, and 15, over the range 20–2000 cm^{-1}. The phonons occurring in this frequency region have been associated with the different chemical constituents and are used to determine the mineralogical abundances by comparison with the spectra of a wide variety of terrestrial minerals and rocks. Kramers-Kronig analyses of the infrared reflectance spectra provided the dielectric dispersion (ε' and ε'') and the optical constants (n and k). The dielectric constants at $\sim 10^{11}$ Hz have been obtained for each sample and are compared with the values reported in the 10^2–10^6 Hz range. The emissivity peak at the Christianson frequencies for all the lunar samples lie within the range 1195–1250 cm^{-1}; such values are characteristic of terrestrial basalts. The Raman light scattering spectra provided investigation of small individual grains or inclusions and gave unambiguous interpretation of some of the characteristic mineralogical components.

INTRODUCTION

WE HAVE STUDIED the interaction of electromagnetic radiation with lunar materials using elastic and inelastic light scattering techniques. These investigations have many important applications as they identify the vibrational modes associated with the different chemical constituents and can be used to determine mineralogical abundances and give structural information. The data can be used for compositional mapping of the lunar surface and the uniqueness of the method suggests the possibility of performing remote infrared petrology using spectral matching techniques (Lyon, 1963; Aronson *et al.*, 1967; Perry and Lowndes, 1970). The establishment of the relative chemical constituents and their relation to the different rock and soil types on the lunar surface is made by comparison with spectra of a wide variety of terrestrial minerals and rocks.

The infrared studies were accomplished from measurements (mainly conducted at 300°K) of the specular component of the reflectivity over the thermal frequency range 20–2000 cm^{-1} (500–5 μ wavelength). The data were subjected to a Kramers-Kronig analysis as described previously (Perry *et al.*, 1971) and the dispersion of the real and imaginary parts of the dielectric function (ε', ε''), the refractive index n, and the absorption coefficient α were obtained. These fundamental optical constants are independent of the method of measurement and can be used directly to simulate emittance spectra of lunar materials for comparison with future remote sensed infrared spectra and radiometric measurements of the lunar surface (Mendell and Low, 1971).

The far-infrared data yield values of the dielectric constant and loss tangent at $\sim 10^{11}$ Hz. It is of interest to extrapolate these values of the dielectric function to

lower frequencies to provide useful information for electrical prospecting of subsurface layers in the 10^6–10^9 Hz range (Simmons *et al.*, 1971; Gold *et al.*, 1972; Howard and Tyler, 1972). Comparison can then be made with the values obtained in the 10^2–10^6 Hz range using standard capacitance techniques provided that these measurements have been made on dry material (Collett and Katsuba, 1971; Chung *et al.*, 1971; Chung, 1971; Chung and Westphal, 1972; Lowndes *et al.*, 1972).

The inelastic (Raman) light scattering techniques for determining the frequency, structural, and chemical properties of the constituents of lunar samples offers a complementary tool. In contrast to the infrared measurements which provide macroscopic information over large areas, this technique, by virtue of the small size ($<50\ \mu$ diameter) of the focused laser beam, allows the investigation of small individual grains or inclusions and has provided unambiguous interpretation of some of the characteristic mineralogical components (Perry *et al.*, 1971; White *et al.*, 1971; Estep *et al.*, 1972; Fabel *et al.*, 1972).

EXPERIMENTAL

Infrared measurements

We have obtained the infrared specular reflectance spectra of the following bulk samples which were in the form of polished butt ends: 10058,56, 12002,186, 12008,23, 12009,48, 12065,115, 12073,42, 14301,20, 14307,18, 14310,184, 14313,51, 14321,98, and 15426,2. The samples were polished to obtain one smooth flat face having an area of at least 0.25 cm^2.

Pressed disks ~ 0.1 cm thick of the fines samples were examined in a similar manner. The samples were prepared in a standard 0.5 cm diameter die with pressures of about 5×10^9 dynes/cm^2 being applied for approximately 5 minutes. The densities of all the samples ranged from 2.4–2.6 g/cm^3. The following fines samples were examined: 14141,37, 14161,36, 14163,31, 14230,95, 14259,38, 15021,159, 15071,60, 15091,65, 15221,71, 15471,68, and 15531,63.

Dry nitrogen flushed grating spectrometers (PE-301, PE-180, and PE-521) with specular reflectance attachments (angle of incidence 10°–15°) were used for the studies over the frequency range 200–4000 cm^{-1} (2.5–50 μ). From 20–250 cm^{-1} a Fourier transform Michelson type interferometer with a liquid-helium-cooled germanium detector was used (Perry *et al.*, 1966).

Raman measurements

Identifiable Raman spectra of a wide variety of individual grains and glassy inclusions were obtained on a number of lunar samples. Various excitation radiations were used, namely Ar$^+$ 4880 and 5145 Å and He/Ne 6328 Å, and some resonance effects were noted. The Raman scattered light was analyzed using a Spex 1401 double spectrometer and detected using photon counting techniques. Both oblique incidence and back-scattering sample geometries were employed. The power absorbed by the samples often represented a restriction on the Raman technique as the opaque regions showed a definite tendency to decompose under the influence of the focused laser beam ($<50\ \mu$ diameter with a power density of 5×10^4 W/cm^2). Both Stokes and anti-Stokes components of the spectrum were examined at room temperature.

Generally, the Raman spectra were of lesser complexity than their infrared counterparts and comparison with terrestrial mineral spectra provided unambiguous interpretation. The effects due to the lowering of site symmetry in the $(SiO_n)^{x-}$ group (Griffith, 1969), variation of Fs content in the pyroxenes, and Fa content in the olivines were demonstrated by frequency shifts in the spectra (Perry *et al.*, 1971; Estep *et al.*, 1971; 1972).

Dielectric studies

The low-frequency dielectric constants were determined through three terminal capacitance measurements in the frequency range 10^2–10^5 Hz. The capacitance measurements were recorded on a

General Radio 1615A transformer ratio arm bridge used in conjunction with a General Radio 1232A tuned amplifier and null detector. The capacitances were determined to an accuracy of ±0.1% at the lower frequencies and ±0.4% at 10^5 Hz. The variable temperature cell used to measure the dielectric constants has been described previously (Lowndes and Martin, 1969).

RESULTS AND DISCUSSION

The infrared reflectance spectra from 10–1700 cm^{-1} of some representative lunar rock samples from Apollo 11, 12, and 14 are shown in Fig. 1. From these spectra the real and imaginary parts of the dielectric constant were calculated and are plotted in Fig. 2. In Fig. 3 the infrared reflectance spectra of three Fra Mauro breccias 14301,20; 14307,18 and 14313,51, and a typical Apollo 14 soil 14161,36 (bulk sample) are displayed. The spectra of these breccias can be compared with those of an Apollo 12 mare breccia (12073,42) and an Apollo 15 breccia (15426,2) from the Apennine Front
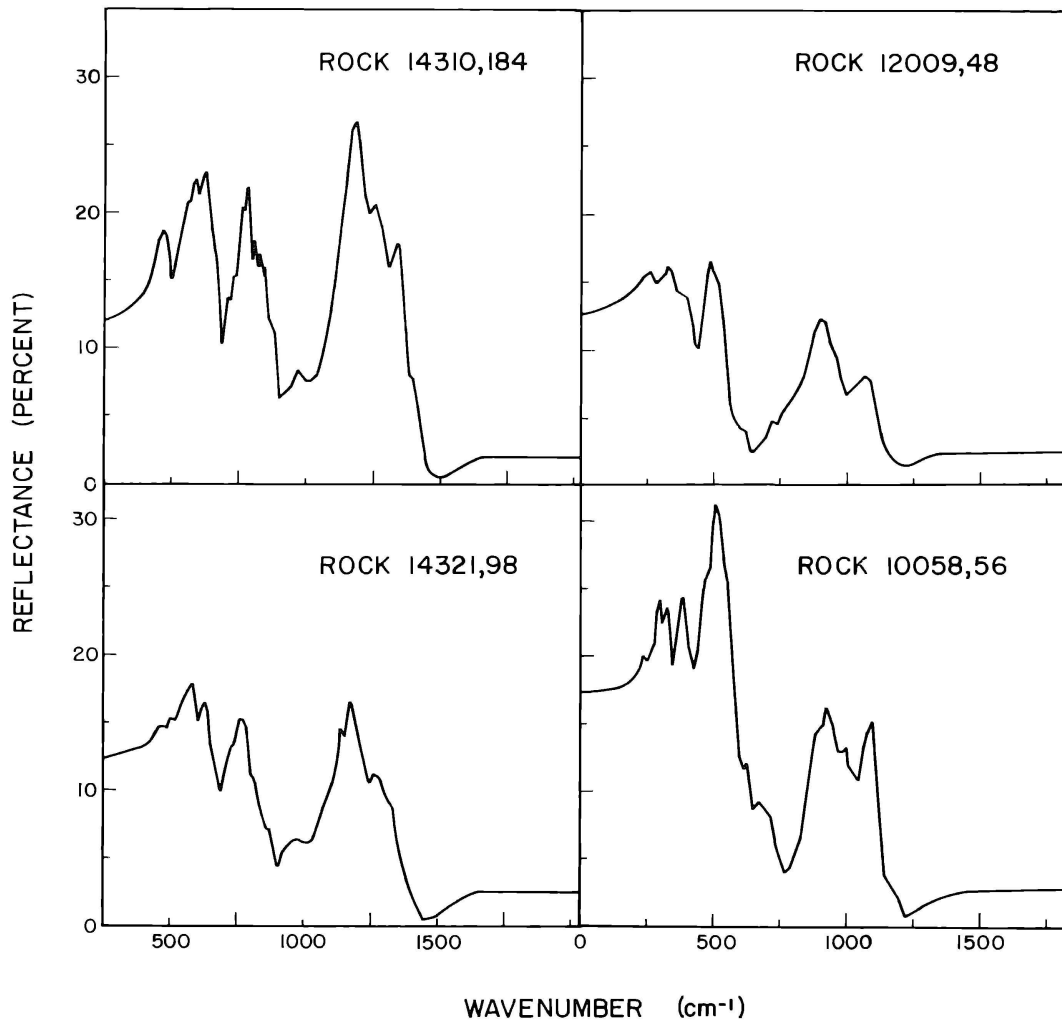

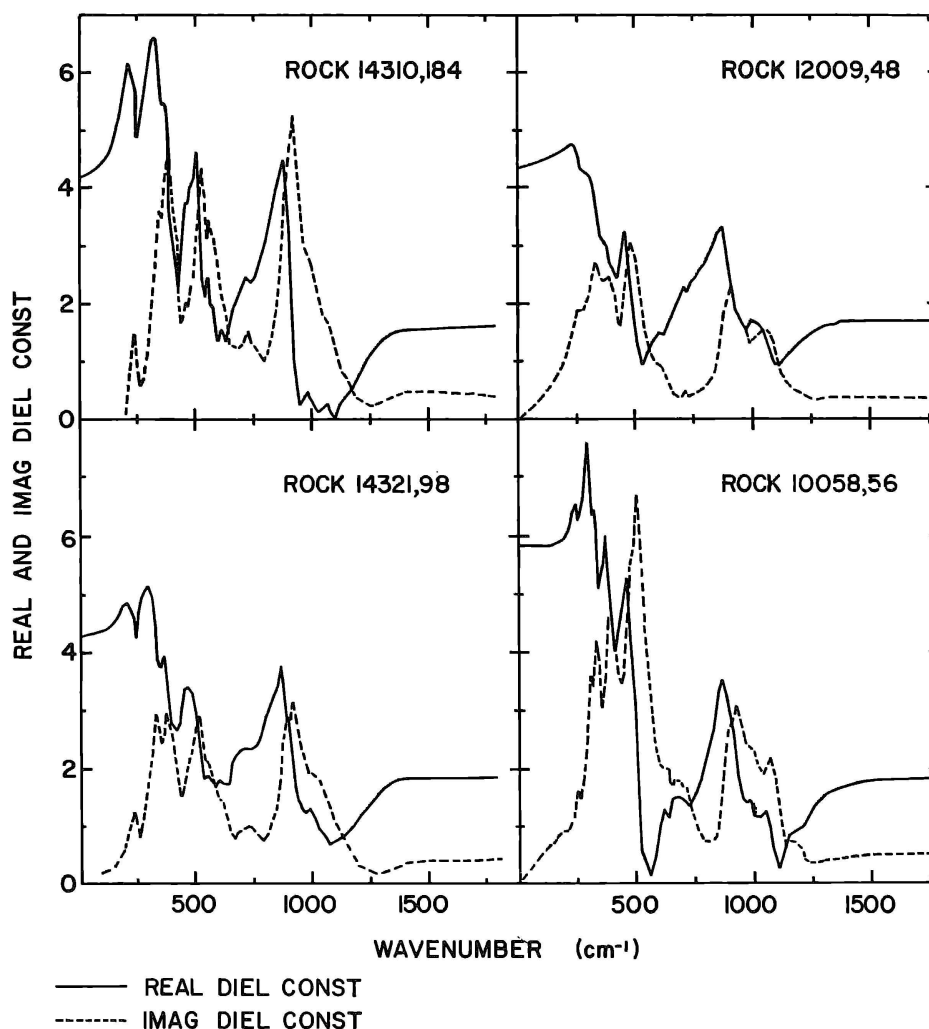Fig. 1. The infrared reflectance spectra of rock 14310,184, 12009,48, 14321,98, and 10058,56, from 0 to 1700 cm^{-1}.

Fig. 2. The real and imaginary parts of the dielectric constant for rock 14310,184, 12009,48, 14321,98, and 10058,56, from 0 to 1700 cm^{-1}.

shown in Fig. 4. Figure 5 comprises the spectra of five Apollo 14 fines (14163,31; 14161,36; 14259,38; 14230,95 (core sample); and 14141,37 (Cone Crater)) and one powdered rock sample 14321,263 (Cone Crater). The reflectance spectra of six Apollo 15 fines are shown in Fig. 6. The samples investigated were 15091,65 and 15221,71 from Station 2 at the foot of the Apennine Front, 15071,60 from Station 1 (Elbow Crater ejecta); 15021,159 from the LM area, 15471,68 from Dune Crater (Station 4), and 15531,63 from Station 9a at the rim of Hadley Rille.

The spectra shown in the first six figures represent the bulk mineralogical and chemical properties of the materials averaged over the area of the sample examined (25–100 mm^2). They form a basis for the comparison of these samples with each other and with known terrestrial materials. In Figs. 7 and 8 are shown some examples of the results of the Raman investigations. Because of differing selection rules in the scattering process, this technique is complementary to that of infrared spectroscopy in the sense that it provides information unobtainable by the latter. Furthermore, be-
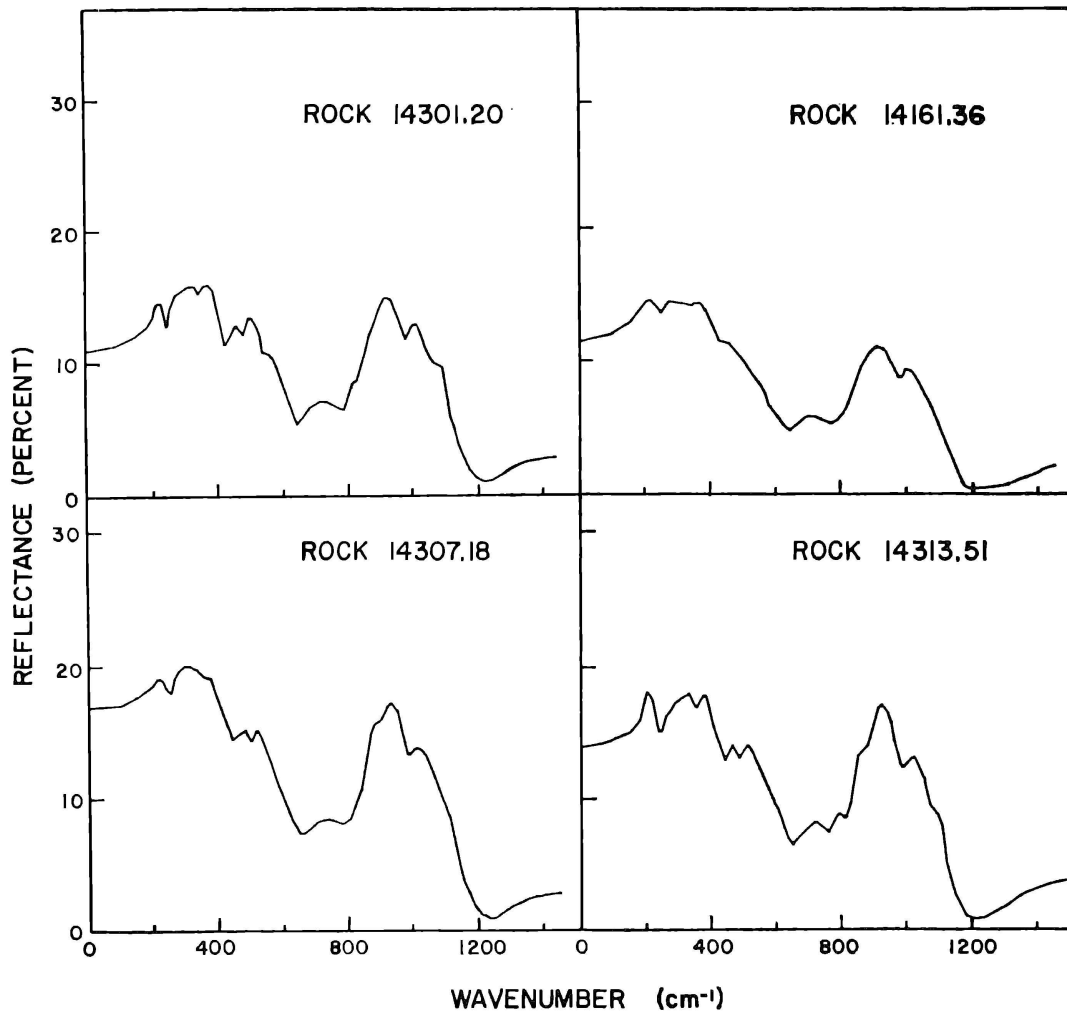
Fig. 3. The infrared reflectance spectra from 0 to 1400 cm^{-1} of three Fra Mauro breccias 14301,20, 14307,18, and 14313,51, and a typical Apollo 14 soil 14161,36 (bulk sample).

cause of the small size of the sample area investigated ($\sim 2 \times 10^{-5}$ cm^2), individual grains and inclusions may be studied, and the resulting spectra are usually simpler and the mineralogical identification is more straightforward. In Fig. 7, for example, the Raman spectra show some of the variations of lunar pyroxenes in samples 10058,56, 12002,186, 12065,115, and 14310,76 (Perry *et al.*, 1971, and as discussed by Estep *et al.*, 1972). The systematic frequency shift of the stretching vibration at ~ 1015 cm^{-1} (e.g., Estep *et al.*, 1972) and the bending vibration at ~ 650 cm^{-1} in these samples can be correlated with the ferrosilite content. In 14310,76 (with Fs$_{25}$–Fs$_{30}$) the latter band is almost a resolved doublet indicating the presence of both ortho- and clino-pyroxene. Sample 10058,56 contains mostly clinopyroxene ranging from pigeonite to augite (Fs$_{20}$–Fs$_{40}$). Samples 12002,186 and 12065,115 show broader, weaker spectra and the evaluation is less well defined but both again probably contain clino- and ortho-pyroxene. The Raman spectrum of a typical green glass sphere in sample 15426,2
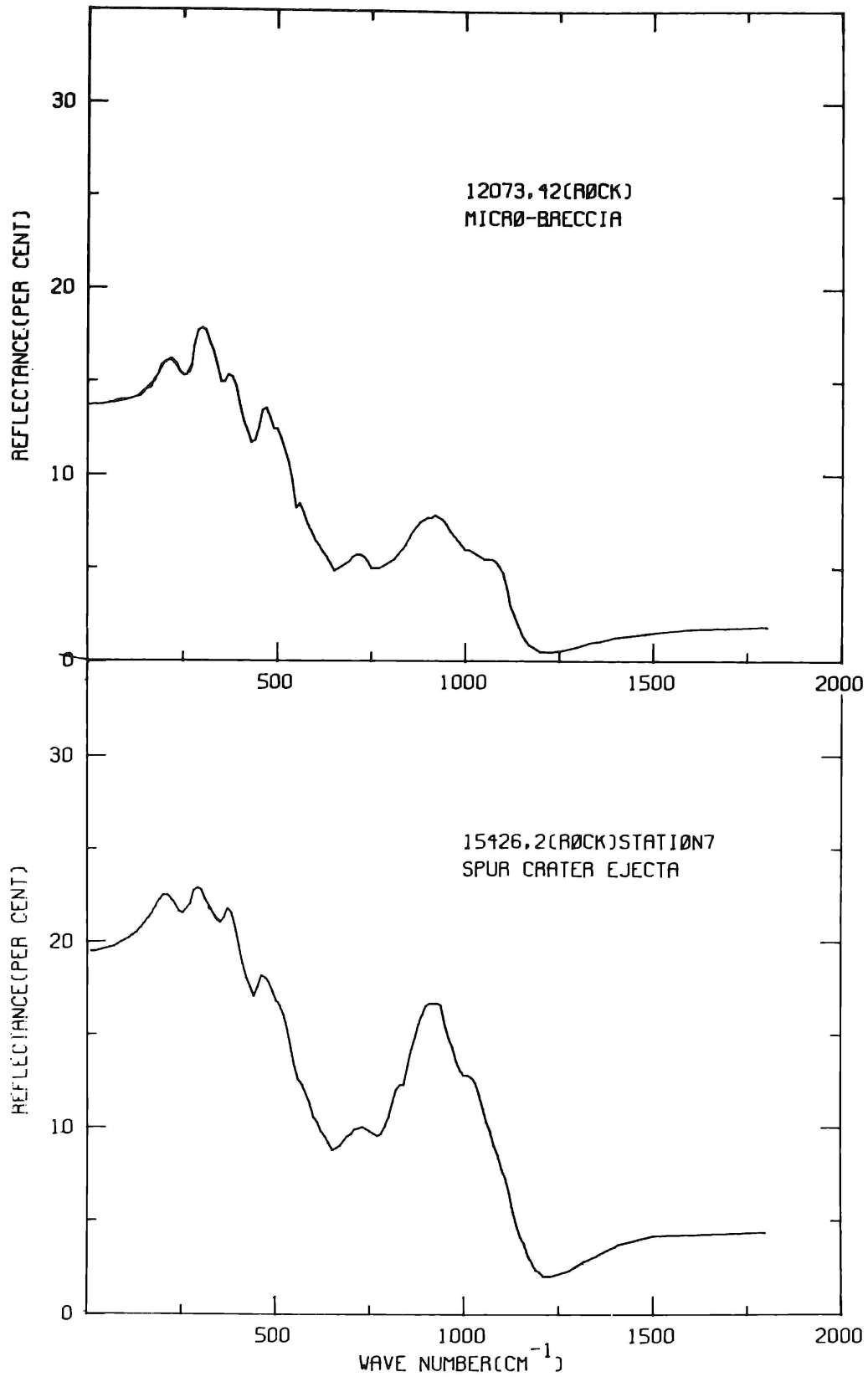
Fig. 4. The infrared reflectance spectra of an Apollo 12 mare breccia 12073,42 and an
Apollo 15 breccia 15426,2 from the Apennine Front.
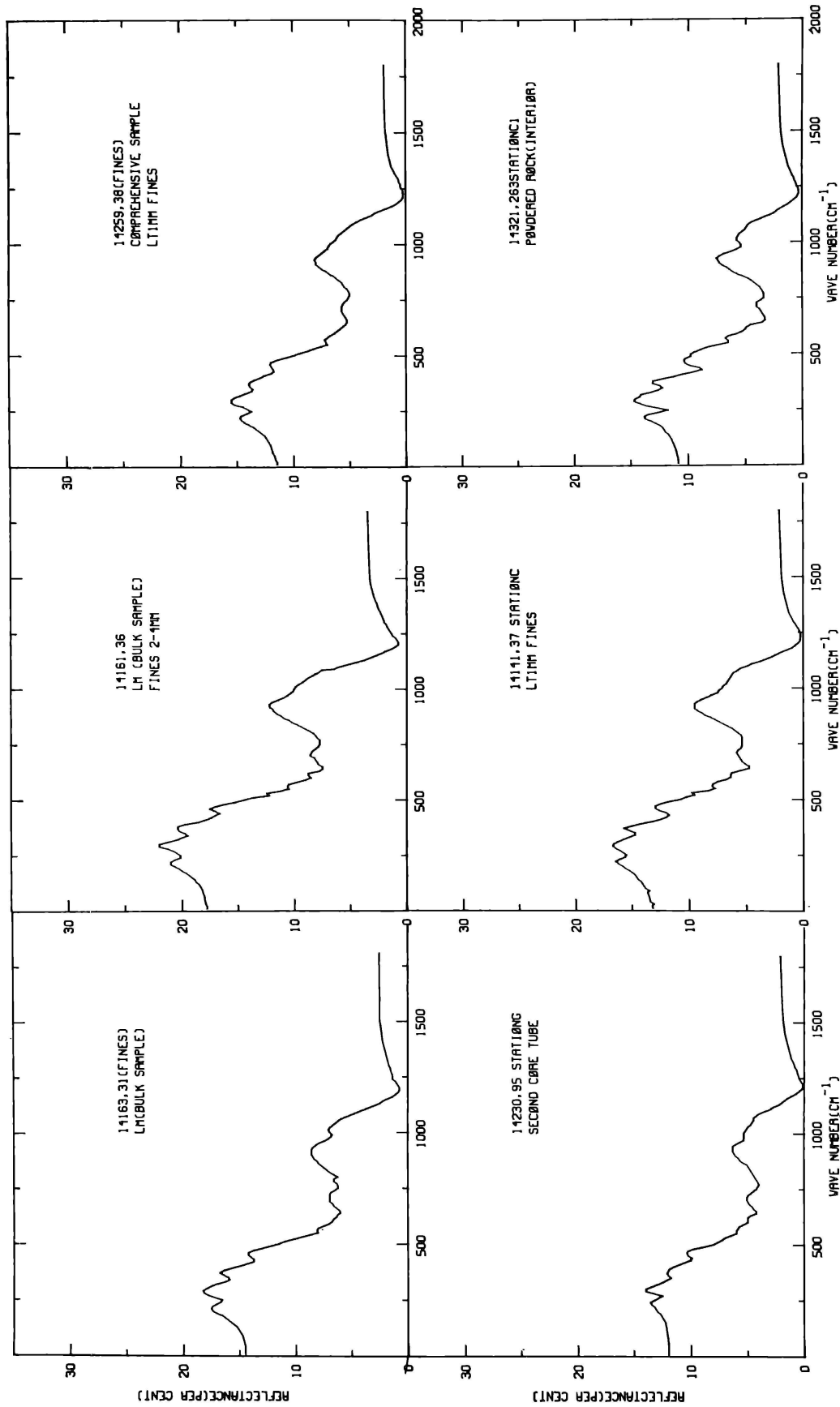
Fig. 5. The infrared reflectance spectra of five Apollo 14 fines (14163,31, 14161,36, 14259,38, 14230,95 (core sample), and 14141,37 (Cone Crater) and one powdered rock sample 14321,263 (Cone Crater) from 0 to 1700 cm^{-1}.
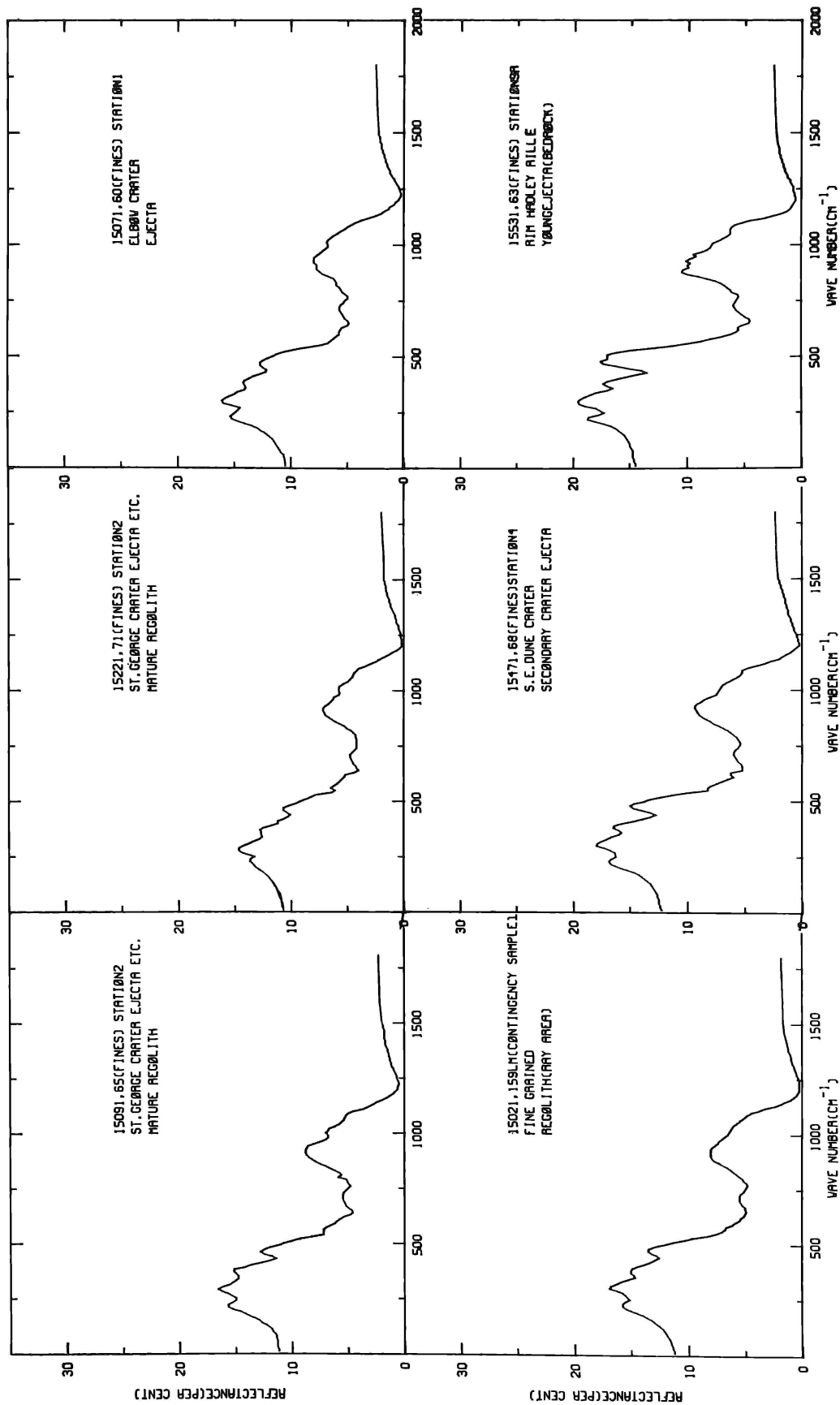
Fig. 6. The infrared reflectance spectra of six Apollo 15 fines (15091,65, 15221,71, 15071,60, 15021,159, 15471,68, and 15531,63) from 0 to 1700 cm⁻¹.
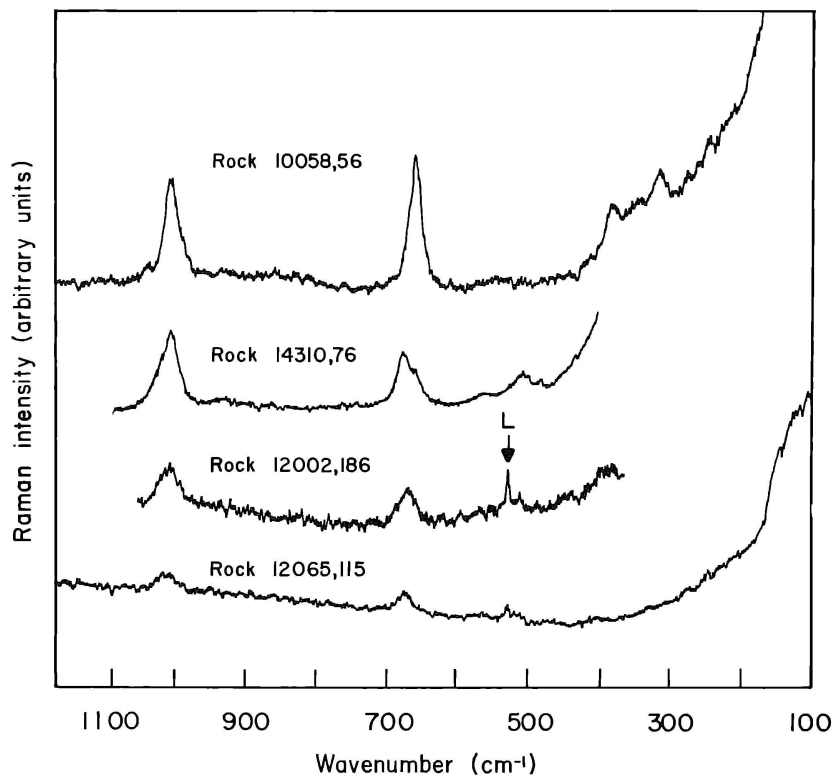
Fig. 7. The Raman spectra of lunar pyroxene inclusions in samples 10058,56, 14310,76, 12002,186, and 12065,115 showing the variation in the frequencies of bands that can be related with the ferrosilite content. The L refers to an extraneous laser line.
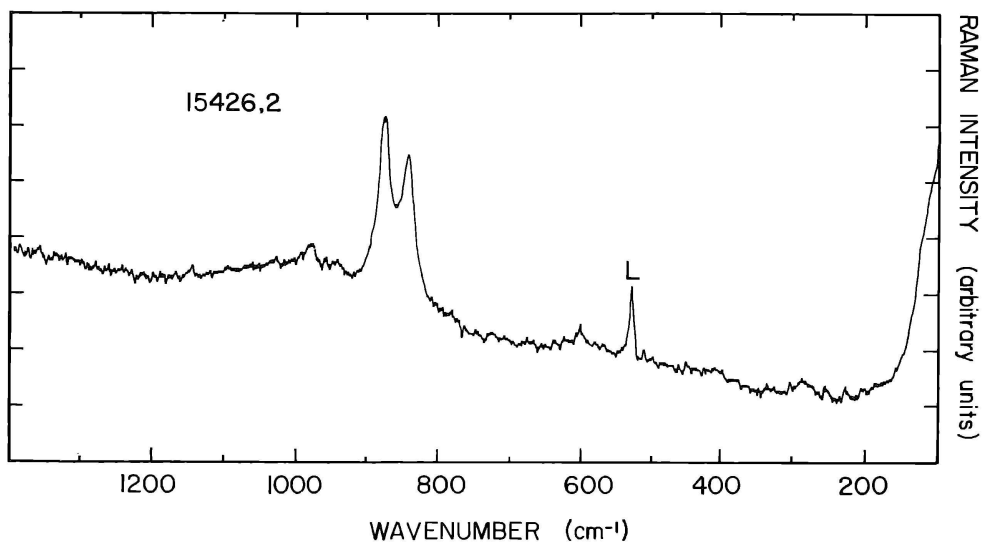
Fig. 8. The Raman spectrum of a typical green glass sphere in sample 15426,2. The strong doublet in the region of 850 cm^{-1} shows the presence of a particle that has undergone partial devitrification to olivine. The L refers to an extraneous laser line.

Table 1. A summary of the lunar rock samples investigated from the Apollo 11, 12, 14, and 15 missions. ω_c is the Christianson frequency corresponding to the emissivity peak and ε_0 is the dielectric constant at far infrared frequencies ($\sim 10^{11}$ Hz). The major chemical abundances are taken from the references cited.

Sample Number	Rock Classification	Lattice Modes / M-O-M cation-bend oxygen vibs. / M-O stretch / Combinations	ω_c (cm^{-1})	ε_0 at 10^{11} Hz	SiO$_2$	Al$_2$O$_3$	MgO	FeO	CaO	TiO$_2$	
14310,184	Basaltic cryst. rock		1250	5.2	50	20	8	8	11	1	§
14321,98	Breccia (cone crater)		1205	4.3	49	16	12	11	8	1	
12002,186	Basalt		1220	3.9							
14301,20	Coherent Breccia		1230	4.0	48	16	10	12	10	2	*
14307,18	Coherent Breccia		1230	5.5	47	16.5	10	12	11	2	**
14313,51	Coherent Breccia		1215	4.8							
15426,2	Breccia		1220	6.5							
12073,42	Microbreccia		1240	2.7	41	15	11	17	11.5	3	†
12008,23	Cumulate		1200	6.7	Major phase, ilmenite						
12009,48	Prophyritic Basalt		1240	4.3	41	11	12.5	20	10	3	†
10058,56	Ophitic Basalt		1220	5.8	41	11	6	17	12	11	×
12065,115	Variolitic Basalt		1200	3.8	39	12	9	22	12	4	†

WAVE NUMBERS (cm^{-1})

x Charles et al. (1971).   † LSPET (1970).   § LSPET (1972).   * Hubbard and Gast (1972).   ** Agrell et al. (1972).

is shown in Fig. 8. The strong doublet in the region of 850 cm^{-1} indicates devitrification to olivine (with Fa_{20}–Fa_{40}) of a contaminating particle either on or imbedded in the sphere. Raman spectra of lunar glasses have also been reported by White et al. (1971) and Fabel et al. (1972). However, Fabel et al. (1972) report a large number of closely spaced bands at low frequencies in some of their samples. We have observed similar bands in some of our samples but substitution of different laser excitation radiation revealed them to be grating ghosts.

Tables 1, 2, and 3 summarize all the lunar rock and soil samples that we have investigated from the Apollo 11, 12, 14, and 15 missions. A pictorial comparison is shown in Table 1 between the frequencies and oscillator strengths of the stretching, bending, and lattice modes for each sample. For more detailed information reference should be made to Perry et al. (1971, Figs. 3 and 4), and Tables 2 and 3.

Several researchers (Conel, 1969; Salisbury et al., 1970) have suggested that the frequency of the peak in the emissivity can be used as a diagnostic feature for determining the silica abundance in fine-powder emissivity spectra. This peak is directly related through the dielectric function ($\varepsilon' = n^2 - k^2$ and $\varepsilon'' = 2nk$, where n is the real part of the refractive index and k is the extinction coefficient) to the high-frequency minimum in the reflectivity and in fact our reflectance spectra are simply inverted emission spectra referenced to blackbody emissivity. For powder spectra both curves are complicated by particle size and packing fraction because of additional diffuse scattering mechanisms (Aronson, 1972). This frequency (known as the Christianson frequency and referred to as ω_c in Table 1) occurs in the region where $n \approx 1$ and $k \approx 0$. Perry et al. (1971) have shown that for lunar materials ω_c varies over the narrow range from about 1195 cm^{-1} ($\sim 40\%$ SiO_2) to about 1260 cm^{-1} ($\sim 50\%$ SiO_2). These results for terrestrial materials correspond to the intermediate to ultrabasic range as reported by Conel (1969) and Salisbury et al. (1970). The emissivity peak for 14259 soil by Logan et al. (1972) at 1220 cm^{-1} is in good agreement with the ω_c value

Table 2. Comparison of infrared transverse optical phonon frequencies for lunar rock samples from Apollo 14 and 15.

Suggested assignment Combination	14310,184 1065(w)	14321,198	14301,20	14307,18	14313,51	15426,2 1040(w)
M–O stretch					1015(m)	
ν_3''	990(m)	1010(w) 980(w)	1010(w)	1005(m)		
ν_3'	920(s)	920(m)	940(m)	930(s)	925(s)	
ν_3		890(m)				850(m)
ν_1'						810(w)
Cation-oxygen vibrations	725(w)		745(w)	745(w)	730(w)	710(w)
		620(w)				640(w)
	580(w)		570(w)			610(w)
	560(w)					570(w)
M–O–M bend	530(m)		530(m)			
ν_4'		520(m)		525(m)	520(m)	
ν_4''	470(m)		475(m)	485(m)	470(s)	450(w)
ν', ν_4'''	390(m)	390(m)	390(m)	380(m)	380(m)	370(w)
ν_2''	345(m)	335(m)	345(w)		345(m)	340(w)
Lattice modes	240(w)	240(w)	240(w)		225(w)	280(s)

Table 3. Comparison of the infrared optical phonon frequencies, ω_c (Christianson frequency) and ε_0 (dielectric constant for sample densities 2.4–2.6 g/cm^3) for Apollo 14 and 15 lunar fines.

	Fines (LM)	2-4mm Fines (LM)	Comp. <1 mm fines	Core sample	Station C <1 mm fines	Station C1 Powdered rock
Suggested assignment Combinations	14163,31	14161,36	14259,38	14230,95 1060	14141,37 1050	14321,263
M–O stretch	1020	1020	1010	1010		1020
		930	930	900	900	920
	860		870			
		810				
Cation-oxygen lattice vibrations	780			780		800
	690	690	700			690
		610		660	660	
				610	600	610
	560	560	570	560	550	560
		540	540		530	
M–O–M bend					510	490
	450	450	440	460	430	450
	370	360	370	370	360	360
						330
Lattice modes	290	290	300	280	260	270
		230	200	230	220	220
ω_c (cm^{-1})	1195	1210	1225	1215	1230	1225
ε_0	4.9	5.9	4.0	4.2	4.5	3.8

	Station 2 St. George Crater ejecta		Station 1 Elbow Crater ejecta	Ray area (LM)	Station 4 Dune Crater	Station 9a Hadley Rille
Suggested assignment Combinations	15091,65 1090	15221,71 1100	15071,60	15021,159 1040	15471,68 1100	15531,63 1070
M–O stretch	1000	1000	1000		1000	
					950	960
						930
			920	890		910
	880	890	870		860	870
			820			
Cation-oxygen lattice vibrations	790	790	780		770	790
	670	670	670	660	680	700
	600	610	610		620	630
	550	550	580		560	
M–O–M bend						510
	440	440	460	470	450	450
	360	370	370	370	370	380
Lattice modes	280	280	290	300	280	280
	220	230	230	210	230	220
ω_c (cm^{-1})	1220	1220	1225	1220	1210	1205
ε_0	4.0	4.2	3.8	4.0	4.2	4.9

(1225 cm^{-1}) obtained from our reflectance measurements as given in Table 3. Birkebak and Dawson (1972) obtained a value of 1210 cm^{-1} for 14163 soil having a density of 1.6 g/cm^3 which is within experimental error of our values of 1205 cm^{-1} for 14163,31 (LM sample) with a density of $\sim$2.5 g/cm^3. It is interesting to note that the infrared emissivity measurement of surface features in various lunar regions from balloon observations by Salisbury et al. (1970) and Murcray et al. (1970) vary from 1195 to 1235 cm^{-1} again within this narrow region. The 14310,184 sample, which we estimate to have a high anorthite content, compares with noritic gabbros and anorthitic basalts in terms of the Christianson frequency ($\omega_c \approx 1250$ cm^{-1}), but there are marked anomalies in the series, as can be seen in Table 1, where ω_c is compared with the major chemical abundances. However, portions of the specimens used to obtain the elemental analyses are not the same as the ones used to measure the ω_c values, and variations can be expected within the same parent sample. Consequently, correlation of the ω_c values with SiO_2 wt.% may be better than the data presented in Table 1, although particle size and packing of the material also effect the scattering components and can cause variations in the measured Christianson frequency.

In Tables 1 and 3 we have also shown the values of the far-infrared dielectric constant at $\sim 10^{11}$ Hz which were calculated from the Kramers-Kronig analysis. Our values for the lunar rocks appear to be in general agreement with Ade et al. (1971) far-infrared measurements at 337 μ where a cyanogen laser was used. For sample 12063,96 (type A basalt) and for 10065,30 (breccia) they obtain values of 6.25 and 3.7, respectively. Based on the results of Perry et al. (1971) one may estimate that both these samples contain 25–30 mole percent of titani-ferrous oxide. Sample 10017,64, another Apollo 11 type A basalt, has a high dielectric constant value of 7 which compares with our measured value of 6.7 for 12008,23, and consequently it probably has a comparable or slightly higher ilmenite content (i.e., 30–35%). Comparison can be made with the dielectric response determined by capacitance measurements at low frequencies (10^2–10^6 Hz) by Chung et al. (1971), Collett and Katsuba (1971), Chung and Westphal (1972), and Lowndes et al. (1972), and at 430 MHz by Gold et al. (1972). The disagreement with previous values of Chung et al. (1971) appears to be due to their samples not being dry (Chung et al., 1972). Our value for a 14310 sample of 5.2 (10^{11} Hz) and 5.99 (10^2–10^6 Hz) compares favorably with Chung and Westphal's (1972) value of 6–9 and the Gold et al. (1972) value of 6.6. However, there are still striking differences in sample 12002 where we obtained a dielectric constant (at 10^{11} Hz) of 4 which is to be compared with Chung et al.'s (1971) result of 8–10 and Collett and Katsuba's (1971) value of 9 at low frequencies. Similar differences were observed in our own measurements in 12008,23 where the dielectric constant varies between 6.7 at 10^{11} Hz and 33 at 10^6–10^2 Hz. As both these samples contain free iron and other high-conductivity materials, they may give rise to additional relaxation mechanisms or free carrier absorption which could account for this strong dispersion of the dielectric constant.

In an earlier report, Perry et al. (1971) have found that sample 12008,23 has a strong vibration at $\sim$890 cm^{-1}. The high value of the measured static dielectric constant of this sample indicates that it has a very high ($>30\%$) FeO content and it has also been reported that the major phase of the parent rock may be ilmenite (Warner,

1970). Sample 12009,48 has a lower FeO content ($\sim 20\%$) and the stretching vibration is now situated at ~ 920 cm^{-1}. With the increase in plagioclase content, as for example in 12002,186 ($\sim 30\%$ plagioclase), there is a continued shift of this band to higher frequencies (~ 930 cm^{-1}), and in 12065,115 (breccia), with about 50-50 plagioclase-pyroxene content, the trend is further indicated (~ 960 cm^{-1}).

In Fig. 1 we show some of the greatest variations that we have observed in the reflection spectra of lunar samples. The 14310,184 spectrum has features that clearly demonstrate that it is a high calcium oxide, alumina, and silica basalt and it has the highest ω_c frequency compared with the other lunar samples examined. It has high stretching vibrations at ~ 990 cm^{-1} and ~ 920 cm^{-1} and bending vibrations at ~ 470 cm^{-1} and 530 cm^{-1}. The lattice band at 240 cm^{-1} is characteristic of a high plagioclase material and is indicative of its high anorthite (An$_{90}$–An$_{100}$) content. For comparison the Cone Crater sample (14321,98) from Station C1 (which has comparable silica, alumina, and calcium oxide content) shows a lowering of the frequency of the band at ~ 500 cm^{-1}. This band appears to be related to the slightly higher orthopyroxene content. The spectrum of 12009,48 with its reduced silica and alumina content shows a further lowering of the bending vibration to ~ 490 cm^{-1} which appears associated with the increase in FeO content (see Table 1). Generally, as the dominance of the framework silicates change gradually to the more open chain silicates of the pyroxenes, a lowering of the internal frequencies may be expected and is apparently observed. Finally in Fig. 1, the new features in the spectrum of sample 10058,56, which has FeO, SiO$_2$, Al$_2$O$_3$, and CaO contents comparable with those of 12009,48, indicate that they can be directly associated with the increasing TiO$_2$ present and the subsequent reduction in MgO.

The three Apollo 14 breccias (or fragmental rocks) examined, namely, 14307,18, 14313,51, and 14301,20, show unmistakable spectral similarities, as seen in Fig. 3. All are typical of the Fra Mauro feldspar-rich breccias and their spectra, although slightly enhanced in intensity, possess features that correspond closely with those observed in the Apollo 14 fines sample of which the bulk sample 14161,36 from the LM vicinity is a typical example.

From Table 1 it is seen that these Fra Mauro breccias have lower silica and alumina contents than sample 14310 which is more likely of highland origin since it is rich in plagioclase (anorthosites). However, they are intermediate between the highland material and the mare material of Apollo 11 and 12 and these findings have been confirmed in the x-ray fluorescence experiment by Adler *et al.* (1972). These breccias are presumably representative of the ejecta blanket deposited by the impact that formed the Imbrium Basin and contain materials from the upper levels of the crust. The Apollo 14 soils also show considerable homogeneity in the spectra (see Fig. 5) and this is confirmed in the analyses (Compston *et al.*, 1972), where the average soil content is 48% SiO$_2$, 17% Al$_2$O$_3$, 9% MgO, 10% FeO, 11% CaO, and 2% TiO$_2$. These major chemical abundances are very similar to those found in the Apollo 14 breccias (see Table 1) and the spectral similarities between Fig. 3 and Fig. 5 indicate that the Fra Mauro soils were mainly produced by local impacts and consist of particulate debris from the rocks with a small admixture of other material (see, for example, Adams and McCord, 1972). From the infrared and Raman frequencies it

would appear that these samples contain plagioclase An_{70}–An_{90}, olivine Fa_{20}–Fa_{35}, and pyroxene Fs_{25}–Fs_{35}, and are in general agreement with the report on 14313 (Floran *et al.*, 1972).

The Cone Crater breccia sample from Station C, 14321,98, has spectral similarities that lie between 14310 and the other three Apollo 14 rock samples. It has the highest magnesium content and lowest calcium content and although the silica abundance is similar to 14310 its alumina and FeO contents are more like the Fra Mauro breccias. It may in fact be part of an earlier regolith that suffered from the Imbrian ejecta and was later ejected during the Cone Crater event. The increase in iron content in 14321 over the 14310 samples is exhibited in a shifting to lower frequencies of the band ~ 500 cm^{-1}. Its lower Christianson frequency probably results from its high MgO content. This reverse behavior of ω_c is apparent in 12009,48 which again has a comparable abundance of MgO even though the SiO_2 content is less and the FeO content is increased.

In Figs. 5 and 6 we can see a direct comparison between the Apollo 14 and 15 soil samples. Samples 14259,38, which is representative of the regolith, and 14163,31, which is from a depth of a few centimeters, both gave very similar spectra. Sample 14161,36, which consists of 2–4 mm fines, showed some slight sharpening of the reflectivity peaks. The sample 14230,95 from the second core tube again showed general overall spectral similarities and it was concluded that this sample was also representative of the soil in the area and confirmed its homogeneity. Some small spectral differences were observed with the <1 mm fines sample from Station C (14141,37) in the vicinity of Cone Crater. The most noticeable feature was the slight strengthening of the band about 450 cm^{-1} which showed that the Fra Mauro soil in this area was contaminated with the more pyroxene-rich Cone Crater soil ejecta. Some rock fragments from the interior of 14321 (associated with piece 14321,263) again showed some spectral enhancement of the features but they were not as pronounced as 14321,98 which was a polished butt end (presumably from the exterior). Again it would appear in fact that the interior pieces of this rock investigated more closely resembled the surrounding soil. In Fig. 6 the Apollo 15 soils show a larger variety of spectral differences that can be associated with their geographic locations and the corresponding mineralogical compositions. The two samples from the Apennine Front at Station 2 (15091,65 and 15221,71) comprise St. George Crater ejecta and other ejecta materials. The two showed some very slight spectral variations but in fact more closely resembled the Apollo 14 soils. Consequently, it would appear that the soils in the vicinity of the St. George Crater rim are substantially intermixed. To some extent this was also true of 15071,60 from Station 1 which might be expected to be more representative of Elbow Crater ejecta. Evidently, this is not the case and again here the soil is well intermixed. In the vicinity of the LM on the mare surface of Palus Putredinis are the faint rays from either of the craters Aristillus and Autolycus. The spectrum of the contingency sample 15021,159 is presumably representative of the fine-grain regolith and although the spectral features were not significantly different there was a lowering of some frequencies which is usually indicative of an increasing iron content and a corresponding slight decrease in the silica and alumina content. The surface layer here may be more representative of Imbrium or other ejecta from deeper crust levels

that would not have traveled as far to the Apollo 15 site compared to the Apollo 14 site. The spectrum of the Dune Crater sample 15471,68 from Station 4 shows further enhancement of the spectral feature at ~ 450 cm^{-1} which can be associated with a slight increase in the pyroxene content and this trend is further enhanced, as seen in Fig. 6, in 15531,63 from the rim of Hadley Rille. The spectra are more similar to some of the Apollo 12 rocks such as 12002,186 or 12009,48 which have high pyroxene contents. It may be expected that these young ejecta materials are more representative of bedrock whereas the material from the Apennine Front contains largely gardened mixtures.

The 15426,2 breccia from Station 7 at Spur Crater does not resemble the Fra Mauro breccias as it is obviously richer in pyroxene but it also does not show the same spectroscopic features as the Apollo 12 samples. In Fig. 4 it can be compared with the microbreccia 12073,42 and it also bears some resemblance to the Cone Crater sample 14321,263 in Fig. 5. However, we have not observed any exact spectroscopic analog from any of the soil samples.

SUMMARY

In this paper we have shown that the infrared and Raman spectra provide all the vibrational frequencies of the materials. These comprise the internal stretching and bending modes associated with the $(SiO_n)^{x-}$ groups, the weak cation-oxygen coupling between adjacent groups and the low-frequency vibrations that can be associated with translational and librational lattice modes. These groups may be isolated, as for example in the olivines, in chains or framework structures which are associated with the pyroxene and plagioclase classes, respectively. Generally as the structure changes from one that is more open to one that has considerable cross coupling, the frequencies of the vibrational modes increase.

The infrared measurements have the advantage that they provide information on the macroscopic properties that may be expected to be more representative of large areas. In consequence, the spectra are more difficult to interpret uniquely but they do indicate spectral differences. The complementary Raman techniques offer a non-destructive tool for determining mineralogical compositions of grains and inclusions and usually provide positively identifiable results.

The Christianson frequencies can be obtained concurrently with the infrared vibrational frequencies from a single infrared reflectivity measurement and a Kramers-Kronig analysis of the spectrum. This frequency, corresponding to the peak in the emittance spectrum, has been shown by others and on a restricted basis by ourselves to be a useful feature for diagnostic applications.

However, we believe that it is necessary to obtain the complete infrared spectrum from 100–2000 cm^{-1} in order to correlate the molecular vibrational frequencies and the Christianson frequency with the chemical constituents and to then deduce the major mineral abundances (Perry and Lowndes, 1970). This is of course done by comparison with terrestrial counterparts and an excellent background for this work has been provided by Estep *et al.* (1971 and 1972). Their comprehensive measurements on a large number of terrestrial materials are an important part of the program as the

uniqueness of the vibrational frequencies applied to mineralogical studies has been relatively unexploited by the geologist.

It is apparent from our data that differences in the chemical and mineralogical compositions of the lunar samples can be spectroscopically distinguished. A spectral difference can also be observed between the samples gathered from the different geographical locations, e.g., the spectra of lunar highland material indicate that they are less basic than the Fra Mauro breccias. These materials in turn are less basic than some of the crater ejecta, the Hadley Rille samples, and some of the mare materials from Apollo 11 and 12. These results in consequence have a direct bearing on the origin of the samples and comparison of spectra from various locations (either obtained from the Apollo missions or using remote sensing techniques) will be directly applicable as a petrological tool and will contribute to unraveling the history of the lunar surface.

The reflectance data provide the infrared dielectric dispersion (ε', ε'') and the optical constants, n, the refractive index and α, the absorption coefficient, over the range 10–5000 cm^{-1}. These properties do not depend on the type of measurement and they provide fundamental parameters for synthesizing spectra (e.g., emission spectra) for spectral matching models. Another product of the Kramers-Kronig analysis are values of the far-infrared dielectric constant at $\sim 10^{11}$ Hz. These results are less sensitive to sample dryness compared with the low-frequency dielectric constant obtained from capacitance techniques. The temperature dependence and pressure (density) dependence of the dielectric constants extrapolated to lower frequencies have important applications in radar studies of the depth and composition of the various surface layers. Our far-infrared and dielectric studies on lunar basalts are in agreement, but the difference in the results for the samples containing high abundances of iron and titanium indicate other relaxation processes are present at lower frequencies.

REFERENCES

Adams J. B. and McCord T. B. (1972) Optical evidence for regional cross-contamination of highland and mare soils (abstract). In *Lunar Science—III* (editor C. Watkins), pp. 1–3, Lunar Science Institute Contr. No. 88.

Ade P. A., Bastin J. A., Marston A. C., Pandya S. J., and Puplett E. (1971) Far infrared properties of lunar rock. *Proc. Second Lunar Sci. Conf., Geochim. Cosmochim. Acta* Suppl. 2, Vol. 3, pp. 2203–2211. MIT Press.

Adler I., Trombka J., Gerard J., Lowman P., Yin L., Blodgett H., Gorenstein P., and Bjorkholm P. (1972) Preliminary results from the S-161 x-ray fluorescence experiment (abstract). In *Lunar Science—III* (editor C. Watkins), pp. 4–6, Lunar Science Institute Contr. No. 88.

Agrell S. O., Scoon J. H., Long J. V. P., and Coles J. N. (1972) The occurrence of goethite in a microbreccia from the Fra Mauro formation (abstract). In *Lunar Science—III* (editor C. Watkins), pp. 7–9, Lunar Science Institute Contr. No. 88.

Aronson J. R. (1972) The prospects for remote infrared petrology (abstract). Proceedings of Conference on Lunar Geophysics, *The Moon* (in press).

Aronson J. R., Emslie A. G., Allen R. V., and McLinden H. G. (1967) Studies of the middle and far infrared spectra of mineral surfaces for application in remote compositional mapping of the moon and planets. *J. Geophys. Res.* **72**, 687.

Birkebak R. C. and Dawson J. P. (1972) Thermal radiation properties of Apollo 14 fines (abstract). In *Lunar Science—III* (editor C. Watkins), pp. 83–85, Lunar Science Institute Contr. No. 88.

Charles R. W., Hewitt D. A., and Wones D. R. (1971) H_2O in lunar processes: Stability of hydrous phases in lunar samples 10058 and 12013. *Proc. Second Lunar Sci. Conf., Geochim. Cosmochim. Acta* Suppl. 2, Vol. 1, pp. 645–664. MIT Press.

Chung D. H. (1971) Laboratory studies on seismic and electrical properties of the moon (abstract). Proceedings of Conference on Lunar Geophysics, *The Moon* (in press).

Chung D. H., Westphal W. B., and Simmons G. (1971) Dielectric behavior of lunar samples. *Proc. Second Lunar Sci. Conf., Geochim. Cosmochim. Acta* Suppl. 2, Vol. 3, pp. 2381–2390. MIT Press.

Chung D. H. and Westphal W. B. (1972) Dielectric properties of Apollo 14 lunar samples (abstract). In *Lunar Science—III* (editor C. Watkins), pp. 139–140, Lunar Science Institute Contr. No. 88.

Collett L. S. and Katsuba T. J. (1971) Electrical properties of Apollo 11 and Apollo 12 lunar samples. *Proc. Second Lunar Sci. Conf., Geochim. Cosmochim. Acta* Suppl. 2, Vol. 3, pp. 2367–2379. MIT Press.

Compston W., Vernon M. J., Berry H., Rudowski R., Gray C. M., Ware N., Chappell B. W., and Kaye M. (1972) Age and petrogenesis of Apollo 14 basalts (abstract). In *Lunar Science—III* (editor C. Watkins), pp. 151–153, Lunar Science Institute Contr. No. 88.

Conel J. E. (1969) Infrared emissivities of silicates: Experimental results and a cloudy atmosphere model of spectral emission from condensed particulate mediums. *J. Geophys. Res.* **74**, 1614.

Estep P. A., Kovach J. J., and Karr C. Jr. (1971) Infrared vibrational spectroscopic studies of minerals from Apollo 11 and Apollo 12 lunar samples. *Proc. Second Lunar Sci. Conf., Geochim. Cosmochim. Acta* Suppl. 2, Vol. 3, pp. 2137–2151. MIT Press.

Estep P. A., Kovach J. J., Waldstein P., and Karr C. Jr. (1972) Infrared and Raman spectroscopic studies of structural variations in minerals from Apollo 11, 12, and 14 samples (abstract). In *Lunar Science—III* (editor C. Watkins), pp. 244–246, Lunar Science Institute Contr. No. 88.

Fabel G. W., White W. B., White E. W., and Roy R. (1972) Structure of lunar glasses by Raman and soft x-ray spectroscopy (abstract). In *Lunar Science—III* (editor C. Watkins), pp. 250–251, Lunar Science Institute Contr. No. 88.

Floran R. J., Cameron K., Bence A. E., and Papike J. J. (1972) The 14313 consortium: A mineralogic and petrologic report (abstract). In *Lunar Science—III* (editor C. Watkins), pp. 268–269, Lunar Science Institute Contr. No. 88.

Gold T., Bilson E., and Yerbury M. (1972) Grain size analysis, optical reflectivity measurements and determination of high frequency electrical properties for Apollo 14 lunar samples (abstract). In *Lunar Science—III* (editor C. Watkins), pp. 318–320, Lunar Science Institute Contr. No. 88.

Griffith W. P. (1969) Raman studies on rock-forming minerals. Part I. Orthosilicates and cyclosilicates. *J. Chem. Soc.*, Ser. A, 1372.

Howard H. T. and Tyler G. L. (1972) Bistatic-radar observations of the lunar surface with Apollos 14 and 15 (abstract). In *Lunar Science—III* (editor C. Watkins), p. 398, Lunar Science Institute Contr. No. 88.

Hubbard N. J. and Gast P. W. (1972) Chemical composition of Apollo 14 materials and evidence for alkali volatilization (abstract). In *Lunar Science—III* (editor C. Watkins), pp. 407–409, Lunar Science Institute Contr. No. 88.

Logan L. M., Hunt G. R., Balsamo S. R., and Salisbury J. W. (1972) Mid infrared emission spectrum of Apollo 14 soil: Significance for compositional remote sensing (abstract). In *Lunar Science—III* (editor C. Watkins), pp. 490–492, Lunar Science Institute Contr. No. 88.

Lowndes R. P. and Martin D. H. (1969) Dielectric dispersion and the structure of ionic lattices. *Proc. Roy. Soc.*, Ser. A, **308**, 473.

Lowndes R. P., Rastogi A., and Perry C. H. (1972) Dielectric properties of some lunar samples. To appear.

LSPET (Lunar Sample Preliminary Examination Team) (1970) Preliminary examination of the lunar samples for Apollo 12. *Science* **167**, 1334.

LSPET (Lunar Sample Preliminary Examination Team) (1971) Preliminary examination of lunar samples from Apollo 14. *Science* **173**, 688.

Lyon R. J. P. (1963) Evaluation of infrared spectrophotometry for compositional analysis of lunar and planetary solids. Stanford Res. Inst. Final Report under contract NASr-49(04), NASA Tech. Note, TND-1871.

Mendell W. W. and Low F. J. (1971) Differential flux scans of the moon at $\lambda = 22$ μ (abstract). Proceedings of Conference on Lunar Geophysics, *The Moon* (in press).

Murcray F. H., Murcray D. G., and Williams W. J. (1970) Infrared emissivity of lunar surface features, I. Balloon-borne observations. *J. Geophys. Res.* **75**, 2662.

Perry C. H., Geick R., and Young E. F. (1966) Solid state studies by means of Fourier transform spectroscopy. *Applied Optics* **5**, 1171.

Perry C. H. and Lowndes R. P. (1970) The study of the reflectivity of inorganic materials for remote sensing applications. Final Report AFCRL-70-0512.

Perry C. H., Agrawal D. K., Anastassakis E., Lowndes R. P., Rastogi A., and Tornberg N. E. (1971) Infrared and Raman spectra of lunar samples from Apollo 11, 12, and 14 (abstract). Proceedings of Conference on Lunar Geophysics, *The Moon* (in press).

Salisbury J. W., Vincent R. K., Logan L. M., and Hunt G. R. (1970) Infrared emissivity of lunar surface features, II. Interpretation. *J. Geophys. Res.* **75**, 2671.

Simmons G., Strangway D., Bannister L., Cubley D., La Torraca G., Rossiter J., Watts R., and Annan A. (1971) Surface electrical properties experiment (abstract). Proceedings of Conference on Lunar Geophysics, *The Moon* (in press).

Warner J. (1970) Apollo 12 lunar-sample information. *NASA Technical Report R-353*, p. 75.

White W. B., White E. W., Görz H., Henisch H. K., Fabel G. W., and Roy R. (1971) Examination of lunar glass by optical, Raman and x-ray emission spectroscopy and by electrical measurements. *Proc. Second Lunar Sci. Conf., Geochim. Cosmochim. Acta* Suppl. 2, Vol. 3, pp. 2213–2221. MIT Press.