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The Luna 24 sample from Mare Crisium: New structural features in lunar glasses deduced from a study of crystal-field spectra

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Abstract—The Luna 24 samples contain colored glass fragments that range in composition from basalt to anorthite. The crystal-field spectra of green glasses in the sample correlate with composition and oxygen fugacity. The green glasses have oxidation states approximately equivalent to those of the same composition synthesized experimentally at 1400°C, $-\log P_{O_2} = 9.1$. The brown glasses have spectra unlike those previously measured for lunar glass. Their spectra have sharp and distinct bands, closely similar to the spectra of augitic pyroxene. Therefore, the high degree of short-range order of these glasses that must exist suggests that they have a structural state intermediate between those of glass and crystal but unlike known glass states or devitrification products. The brown glass spectra do not correlate with composition, oxygen fugacity, or any other experimentally determined properties of glasses. Contributions of brown glass spectra to telescope spectra of Mare Crisium should be taken into account if these glasses are abundant in the Mare Crisium regolith.

INTRODUCTION

Silicate glasses sampled from the moon's surface possess a wealth of information. They have been used to identify rock types from which they are thought to be quenched melt portions. Their compositions have been used to model liquid lines of descent from "parental" or "derivative" igneous liquids. The lunar glasses are generally not igneous in origin, however, in the sense that most, if not all, reported samples of lunar glass were produced by shock processes that accompanied meteorite impacts on the moon's surface. The impact processes have, in many instances, introduced complexities of chemical fractionation, elemental sputtering, and other less well understood "shock" effects; thus the lunar glasses may be inadequate for deducing the liquid descent of lunar igneous rocks, but the glasses are suited for interpretation of surface processes that occur in the lunar regolith.

Some of lunar glasses are true "quench products" of impact melting that preserve information on oxidation/reduction conditions in the regolith at the instant of quench. Furthermore, the glasses preserve various structural stages of crystallization to rock textures (such as those of rock 14310) by progressive stages of impact (thermal) metamorphism. In this study absorption spectroscopy is used to assess both oxidation state and degree of order of glasses; some glass

types are observed for the first time in Luna 24 glass fragments. The spectral data serve an additional purpose in the interpretation of telescope and remote sensing surveys of the moon's surface, because the absorption bands in lunar glasses contribute significantly to the composite soil or regolith absorption (reflectance) spectra. The new data may have critical bearing on the interpretation of telescope data of Mare Crisium.

THE LUNA 24 SAMPLES

Multiple-grain mounts (several hundred polished grains per mount) were kindly loaned to us by Dr. Larry A. Taylor from his allocation for this study. The data reported in this paper can be considered representative of glasses in the Luna 24 samples listed in Tables 1 and 2.

Glass color and composition

The lunar glasses in general, and the Luna 24 glasses specifically, have been classed by petrographers in a system by color and bulk chemical composition (e.g., Norman *et al.*, 1977; Grove and Vaniman, 1977). In the present study it has been determined that there is always a direct relationship between color and spectral properties, but correlation of color alone with chemical composition is often invalid. Clearly there are causes of color changes and "darkening" other than changes in composition. For example, the brown glasses, "tea-colored" (green-brown) glasses, and green glasses, variously referred to as "ferrobasalt," nondescript, and the Luna 24 green glass or "low-titanium basalt" have essentially the same composition. There is more compositional variation (especially for Mg) within the green glasses than between green and brown glasses. Various other glasses, ranging from light green to colorless (spectrally very light green to ultra light green), have been named "Fra Mauro basalt" and "Highlands basalt," on the basis of chemical composition.

The relation between color and composition of several Luna 24 glasses can be seen in Tables 1 and 2. The brown glasses are relatively uniform in composition, whereas the green glasses have variable magnesium content (Table 1). The light green and colorless glasses have relatively low iron content. The former are relatively high in titanium and aluminum; the latter, very low in titanium, high in calcium, and very high in aluminum. Some glasses appear colored apparently owing to shock or radiation, which is a "darkening" effect not related to chemical composition.

CRYSTAL-FIELD SPECTRA

The crystal-field spectra of lunar glasses have been correlated in detail with experimental data on synthetic glasses relating composition and oxygen fugacity by Bell *et al.* (1976). In Luna 24 glasses, two additional effects that influence the spectra, but are not as yet correlated experimentally, were found. They are

Table 1. Electron microprobe analysis and optical absorption spectral features of glass fragments in multiple grain mount 24077,45.

	Brown glass			Tea-colored glass			Green glass			Light green		Colorless glass	
	d	g	b	e	j	a	h	c	f	i			
SiO ₂	46.60	46.46	44.71	44.60	45.72	46.67	47.44	50.19	45.26	45.30			
TiO ₂	1.02	1.00	0.99	1.49	1.00	1.08	0.95	1.96	0.30	0.19			
Al ₂ O ₃	12.08	12.16	13.48	10.73	12.29	11.62	11.12	15.98	25.14	27.43			
Cr ₂ O ₃	0.29	0.30	0.52	0.47	0.45	0.32	0.30	0.04	0.14	0.14			
FeO	20.80	20.82	18.86	19.08	18.82	21.13	19.75	11.87	5.53	5.66			
MgO	6.85	6.86	9.61	12.37	10.90	7.65	7.58	6.49	9.92	6.08			
CaO	12.38	12.28	11.90	10.22	11.25	11.79	11.50	11.64	14.56	15.85			
MnO	0.32	0.33	0.29	0.31	0.45	0.33	0.32	0.16	0.07	0.08			
Total	100.33	100.20	100.36	99.27	100.73	100.59	98.96	98.32	100.93	100.73			
Slope*	18.7	20.8	18.2	16.0	8.3	14.7	10.0	11.1	—	—			
λ_{\min} , nm	800	820	660	590	590	590	590	625	—	—			
λ_{\max} , nm	985	985	1040	1080	1080	1080	1090	1100	1080	1080			
σ_{\max} , cm ⁻¹	192	272	170	205	158	178	148	108	37	33			

*Slope of absorption edge at 20,000 cm⁻¹, in units of cm⁻¹ per 1000 cm⁻¹ wave number.

Table 2. Electron microprobe analysis and optical absorption features of glass fragments in multiple grain mounts 24210,48; 24182,48; 24149,49; and 24174,51.

	24210,48			24182,48		24149,49		24174,51	
	Dark brown	a	Brown glass	b	Colorless	d	c	Brown glass	Green glass
	c							a	b
SiO ₂	46.36	46.69	46.84	44.98	43.88	44.98	47.16	46.11	46.94
TiO ₂	0.95	0.96	0.96	0.21	0.00	0.21	0.99	0.15	0.95
Al ₂ O ₃	11.89	11.96	11.84	27.44	34.55	27.44	12.00	29.23	11.83
Cr ₂ O ₃	0.25	0.22	0.25	0.09	0.00	0.09	0.28	0.04	0.21
FeO	19.34	19.46	19.04	3.80	0.46	3.80	20.55	3.21	19.50
MgO	6.69	6.85	6.93	5.67	0.16	5.67	7.04	3.21	6.70
CaO	12.15	12.19	12.32	15.74	19.11	15.74	12.81	16.37	12.08
MnO	0.35	0.33	0.29	0.10	0.01	0.10	0.32	0.09	0.32
Na ₂ O	0.28	0.28	0.28	0.17	0.48	0.17	—	0.66	0.24
Total	98.26	98.95	98.74	98.20	98.65	98.20	101.15	99.07	98.77
Slope*	>100	11.5	15.6	0	1.5	0	1.98	9.4	12.0
λ_{\min} , nm	840	800	850	—	—	—	830	—	590
λ_{\max} , nm	970	980	970	—	—	—	970	—	1040
α_{\max} , cm ⁻¹	141	87	67	—	—	—	181	—	150

*Slope of absorption edge at 20,000 cm⁻¹, in units of cm⁻¹ per 1000 cm⁻¹ wave number.

structure (development of short-range order) and degree of devitrification. The four basic effects can be recognized unambiguously from the spectra, and thus this discussion will be subdivided into effects on the spectra caused by composition and oxygen fugacity, short-range order, and devitrification.

The absorption spectra were measured with microparticle techniques developed by Mao and Bell (1973). An important parameter in calculation of the absorption coefficient (α, cm^{-1}) is the grain thickness. The section laboratory at the Johnson Spacecraft Center was unable to state the thickness more accurately than approximately $30 \mu\text{m}$ because of the irregularities of the present grain mounts (Mr. John Annexstad, pers. comm., 1978). The grain thickness could not be accurately measured by micrometer or by other mechanical device. Therefore, a thickness uncertainty of $\pm 5 \mu\text{m}$ and an absorption coefficient uncertainty of $\pm 15\%$ should be applied to all the spectral data in this study.

SPECTRAL CORRELATION WITH OXYGEN FUGACITY AND CHEMICAL COMPOSITION

The green Luna 24 glasses have normal glass spectra, that is, broad, intense absorption bands caused by octahedrally coordinated Fe^{2+} and a steep apparent absorption edge caused by $\text{Ti}^{3+}-\text{Ti}^{4+}-\text{Fe}^{2+}$ charge-transfer effects (Bell *et al.*, 1976). Representative compositions are given in Tables 1 and 2. Figure 1 shows the spectra of a series of four green glasses from sample 24077,45. These glasses have a range of iron concentration (Table 1) that correlates with experimentally observed wavelengths and intensities of the peak maximum of the octahedral Fe^{2+} crystal-field absorption band centered near $1 \mu\text{m}$ (Fig. 2). The slope at 20,000 wave numbers also correlates with composition when compared with experimental data on the compositional product, $\text{FeO} \times \text{TiO}_2$ (in weight percent) plotted in Fig. 3. Reference to the plot of TiO_2 (weight percent) vs. absorption minimum in Fig. 4 and to the results of Bell *et al.* (1976), who obtained experimental data on spectra and oxygen fugacity of synthetic glasses, indicates that the Luna 24 green glasses are the same as, or slightly more oxidized than, synthetic glasses of the same composition quenched at 1400°C , $-\log P_{\text{O}_2} = 9.1$.

The correlations of spectral features of the Luna 24 green glasses with experimental data are much the same as those obtained with other lunar glasses. Apparently the configurations of iron and titanium sites in Luna 24 green glass are similar to those in all other green and orange (often referred to as "red") lunar glasses studied.

SPECTRAL CORRELATION WITH SHORT-RANGE ORDER IN GLASS

Previously unrecognized in lunar glasses (and in glasses in general) is the development of a highly ordered state, as observed in many of the Luna 24 glasses. These glasses are usually deep brown or have a brown tone, but their spectral patterns have not been reported previously. Figure 5 shows spectra of a brown glass, an intermediate brown-green ("tea-colored") glass, and a normal

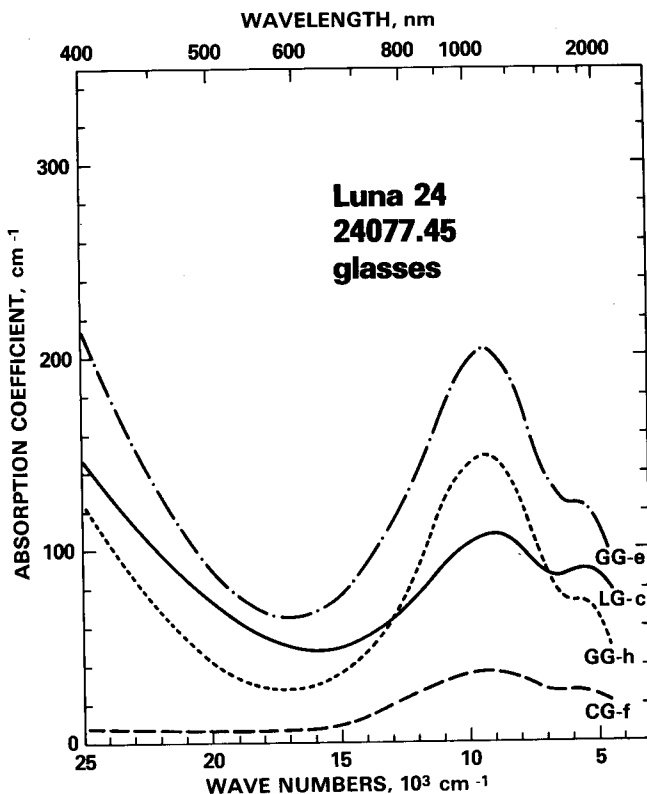


Fig. 1. Optical absorption spectra of glass fragments from Luna 24077,24. GG, green glass; LG, light green glass; CG, colorless glass. The spectra of the green to colorless series correlate with the compositions given in Table 1.

green glass from section 24077,45. The absorption spectra of the brown glass are sharp and are essentially the same as would be obtained with a polycrystalline sample of iron-bearing pyroxene (Bell *et al.*, 1976). These sharp spectral features are unlike the broad absorption bands of green and orange (red) glasses studied in other lunar samples. For example, the band at approximately $1.08 \mu\text{m}$ in normal glasses is shifted to $0.98 \mu\text{m}$ in brown glasses, and the broad, low-energy shoulder is observed as a distinct band at approximately $2 \mu\text{m}$ in the brown glasses. The brown glasses absorb more intensely along the near ultraviolet edge, and in some cases a small peak is observed at 500 nm . The brown glass spectra correlate with the spectra of lunar pyroxene of augite composition.

Figure 6 is a photomicrograph of a common Luna 24 brown glass fragment. These glasses are not devitrified on a microscopic scale (to $\times 40,000$, SEM magnification), but typically they contain a few inclusions of plagioclase crystals (nearly pure anorthite, on the basis of scanning electron microscope nondispersive analysis). The inclusions could have been in the original liquid or could be

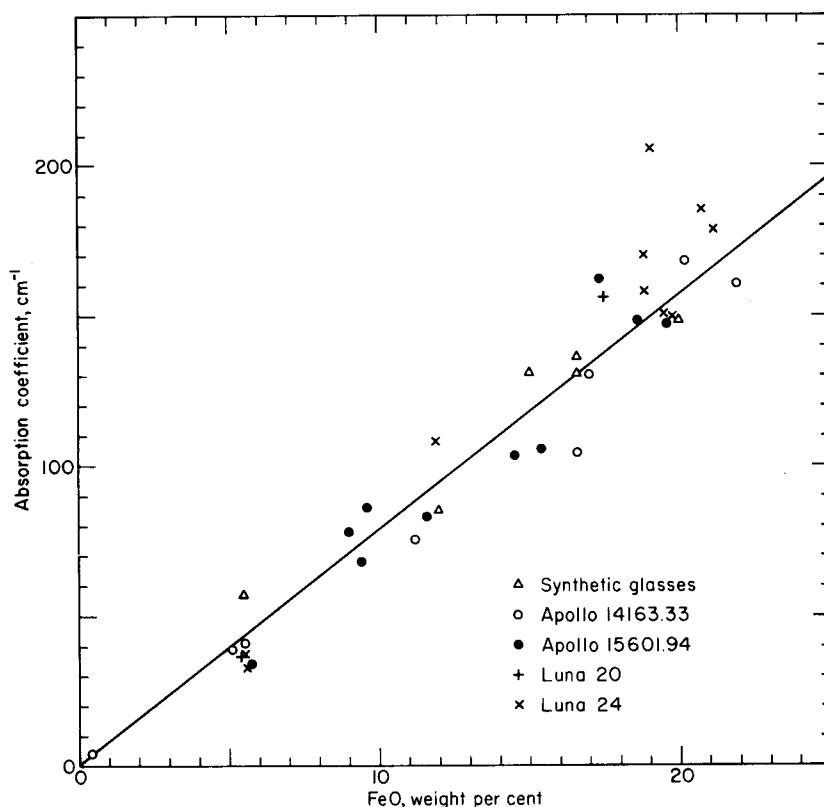


Fig. 2. Intensity of $1\ \mu\text{m}$ crystal field observation band of glasses vs. FeO content (total Fe expressed as FeO). The symbol x represents the present Luna 24 glasses (brown glasses excluded). All other data are from Bell *et al.* (1976).

devitrification products. The grain shown in Fig. 6 shows bleached-appearing zones around the inclusions, but microprobe analysis indicates no compositional gradients. The glass portions of the brown glasses are uniform in composition.

Where extensive submicroscopic devitrification is observed, the intensity of absorption diminishes owing to light diffraction effects. The bulk spectra are significantly different from that of the glass portion. (The devitrification products are pyroxene, olivine, plagioclase, and opaque minerals.) The short-range order of the brown glass is an intermediate, distinct stage that apparently occurred before devitrification.

Figure 7 shows a photomicrograph of a brown glass fragment of uniform composition, most of which contains microcrystalline devitrification products. Only the glassy portions (i.e., left edge of the grain) give a sharp pyroxene-like absorption spectrum (Fig. 8, 24210,48a). The devitrified zones (Fig. 8, 24210,48b) give only weak bands and a strong absorption slope into the near

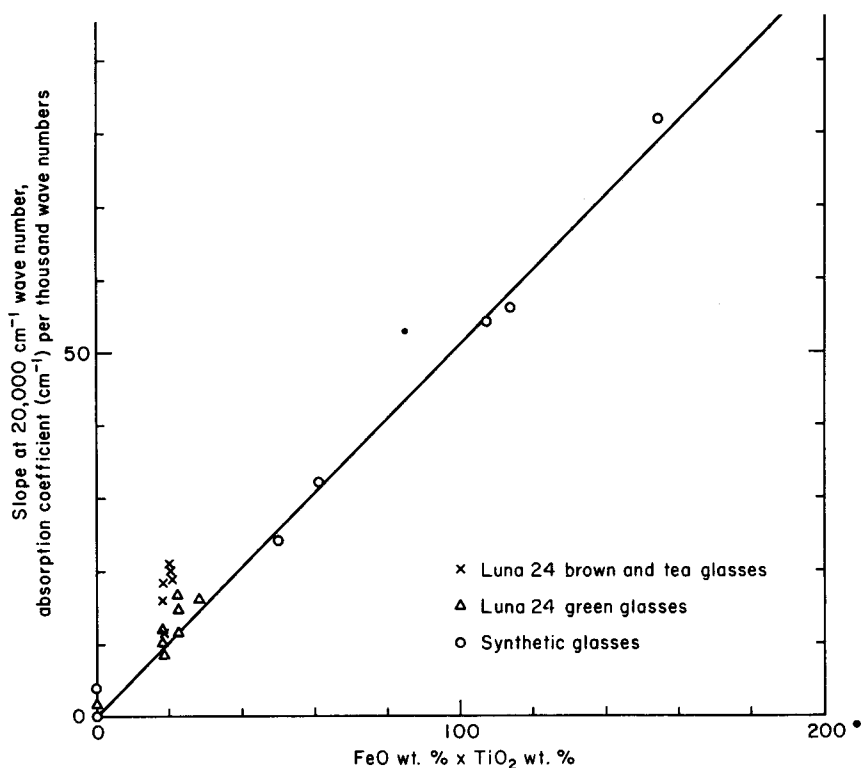
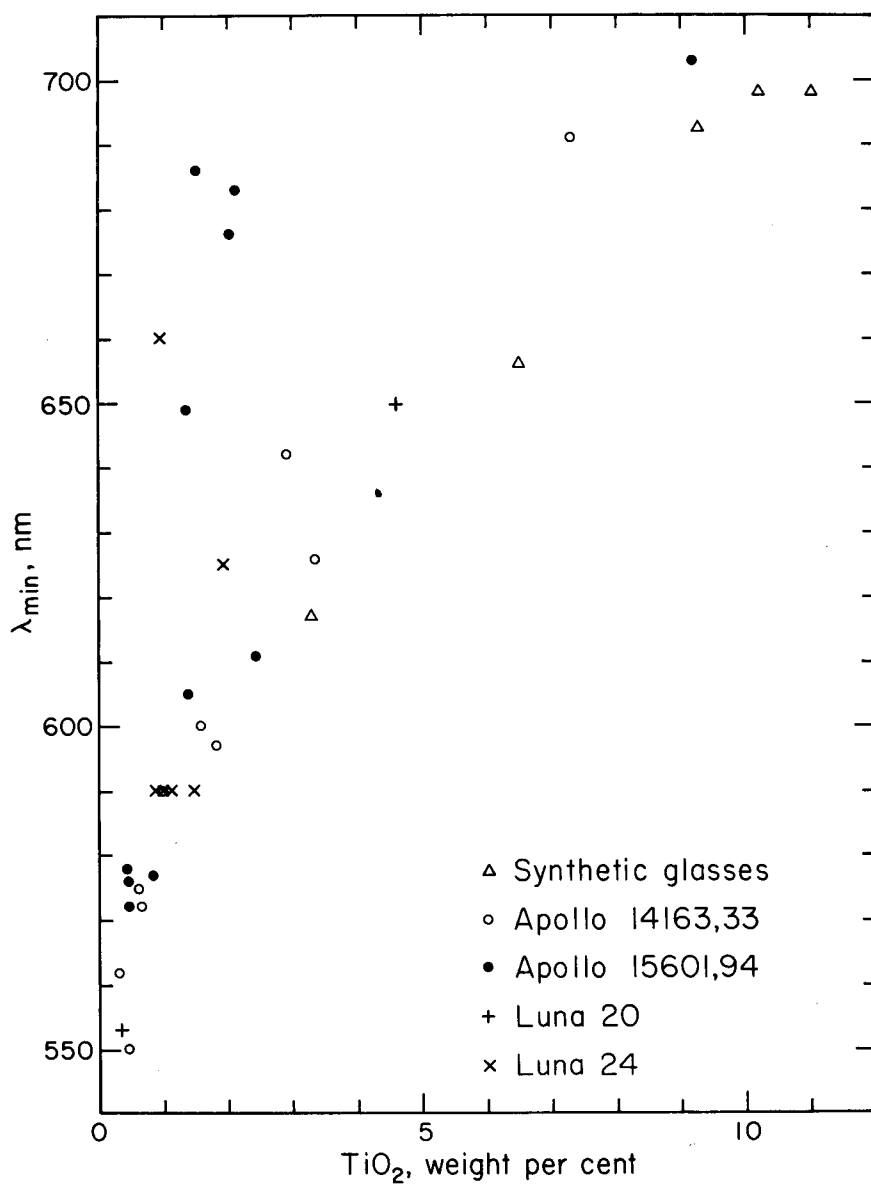


Fig. 3. Slope of absorption edge of glasses at $20,000\text{ cm}^{-1}$ (500 nm) vs. the product of total Fe and total Ti content (expressed as FeO and TiO_2). The data for synthetic glasses are from Bell *et al.* (1976).

ultraviolet region. The most intense and the sharpest absorption spectrum in Fig. 8 (24149,49c) was obtained from the glassy portions of another brown glass of the same composition that had extensive devitrified portions.

One can conclude from these results that spectra or color and composition of the brown glasses do not correlate. This lack of correlation can be seen in Fig. 3, where the brown and "tea-colored" (brownish-green) glasses plot off the composition line. (The Luna 24 glasses are exceptionally low in titanium, and their plot is crowded at one end of the diagram, but the brown glasses plot significantly distant from the composition line.)

Assignment of the absorption bands in the brown glasses is important because, on the basis of the observed spectral features, these glasses have structural states that were unknown previously. Those grains, which have sharp pyroxene-like spectra, represent a structural state observed for the first time in lunar glass. The grains are otherwise indistinguishable from normal lunar glass. The sharp spectral features, however, indicate that most Fe^{2+} cations are in an M2



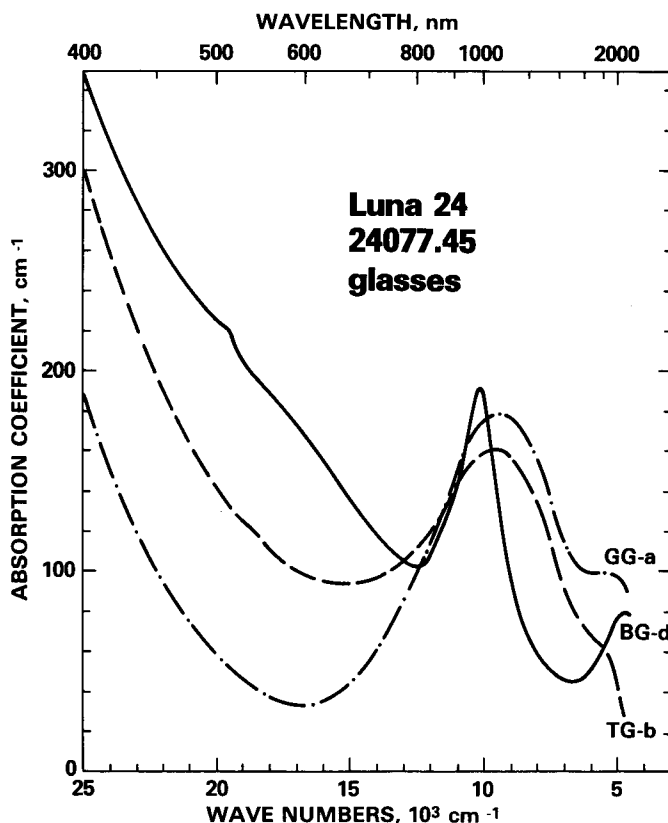


Fig. 5. Optical absorption spectra of glass fragments from Luna 24077.24. GG, green glass; TG, tea-colored (brownish-green) glass; BG, brown glass. The green to brown series have almost identical compositions, yet different spectra.

pyroxene-like site, implying that small regions of pyroxene-like chains exist within the glass. These "M2 brown glasses," therefore, possess aspects of both the glass and the single crystalline state. Radial distribution X-ray studies are needed to elucidate structural details of this unusual lunar glass. When and if sufficient material becomes available, index of refraction measurements would be useful in interpreting possible high-pressure shock effects in the glasses. Structural states in glass that are related to the "glass point" (critical Tamann viscosity), devitrification, shocked glass states ("expanded lattice" crystals), and smectic states can be ruled out in this instance. In effect, the brown glasses, approximately of basalt composition, exhibit some of the properties of a single crystal. Development of M2-like sites suggests that glasses have a high degree of short-range order. When the glasses crystallize or devitrify into a polyphase assemblage, this short-range ordering is altered as the single glass structure is

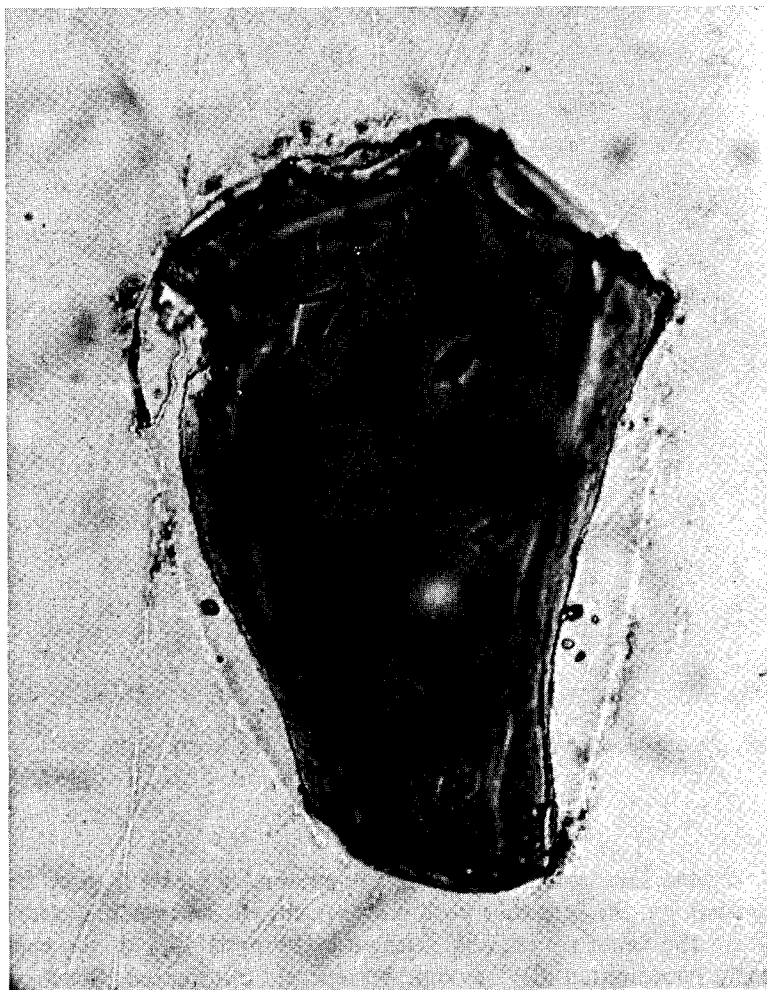


Fig. 6. Photomicrograph of brown glass 24077,45d. The length of the grain is 0.2 mm.

destroyed to reform as olivine, plagioclase, pyroxene, and opaque mineral structures.

The proposed assignment of the absorption bands is much the same as those of pyroxenes (Burns and Vaughan, 1975). The energy-level diagram for d^6 ions (Fe^{2+} , i.e., the Tanabe-Sugano diagrams by Berkes, 1968) indicates that the fundamental $T_{2g} \rightarrow E_g$ electronic transition is multiply degenerate, and both the ground and excited states undergo crystal-field splitting when the d^6 ion is in a pyroxene-like M2 site (Bancroft and Burns, 1967). The sharp absorption bands at wavelengths near 1 and 2 μm correspond to the transitions ${}^5A_1 - {}^5A_1$ and

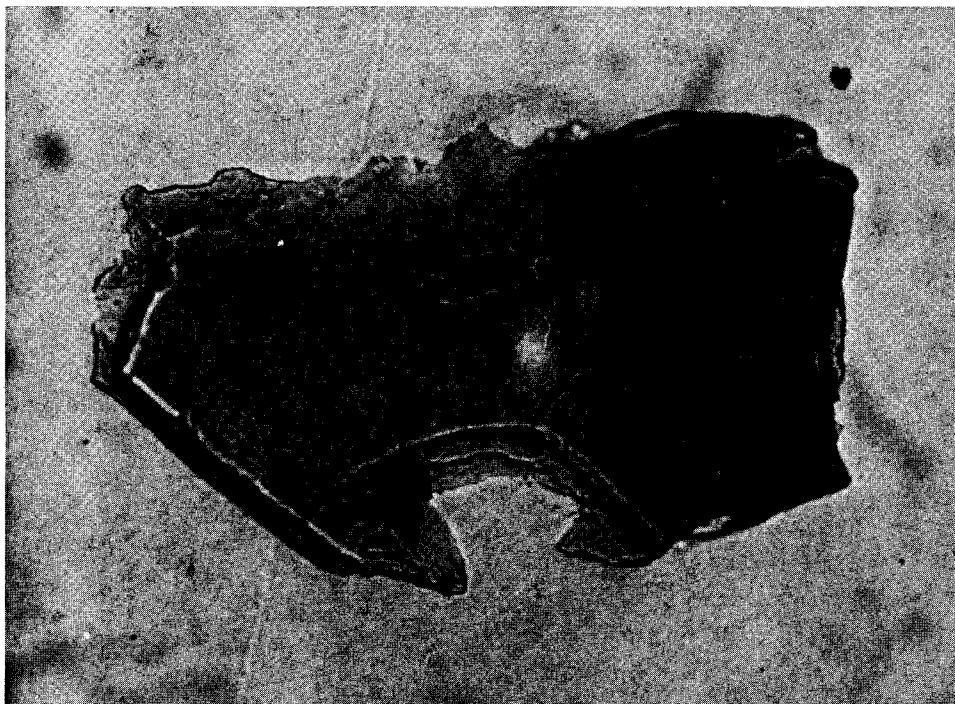


Fig. 7. Photomicrograph of brown glass 24210,48b. The length of the grain is 0.2 mm.

${}^5A_1 - {}^5B_1$ for the selection rules of M2 site symmetry (see Fig. 6 of Bell *et al.*, 1975). By analogy, the fact that both bands occur in the brown glasses suggests that they are the same transitions. Although the possibility of the existence of tetrahedrally coordinated Fe^{2+} cannot be entirely eliminated, there is little, if any, evidence in the spectra that could be used to support arguments for its existence.

Figure 8 also shows a relatively sharp but weak absorption feature near 500 nm. This feature corresponds with the weak, sharp band observed in lunar pyroxenes (see, for example, Appollo 14 pigeonite spectra of Bell and Mao in Burns and Vaughan, 1975). These bands are assigned as spin-forbidden bands (change of spin multiplicity) of Fe^{2+} in pyroxenes, and are additional confirmation of the existence of octahedrally coordinated Fe^{2+} ions in the brown glasses.

ANORTHITE GLASS SPECTRA

Glasses of nearly pure anorthite composition comprise a separate set of glasses spectrally. Some of these glasses appear partially or completely brown (Fig. 9), and they should not be confused with the brown glasses already described. The

coloring is not due to the presence of iron or other transition elements, but appears to be due to submicroscopic devitrification or perhaps to shock effects or radiation damage. The spectrum of the damaged areas appears as a nearly continuous, sloping absorption background in Fig. 10. Also shown in Fig. 10 is the spectrum of a glass fragment of slightly impure anorthite composition (see Table 2). There is a small feature near $1\text{ }\mu\text{m}$ that could be caused by Fe^{2+} , but otherwise there is simply a sloping absorption continuum. In both types of anorthite glass, the undamaged or clear zones do not show this absorption background. Previous to these observations, the only reported absorption effects of this kind in lunar materials were thought to be caused by metallic coatings on glass or crystals (Bell and Mao, 1977).

CONCLUSIONS

The crystal-field spectra of Luna 24 glasses have revealed several effects:

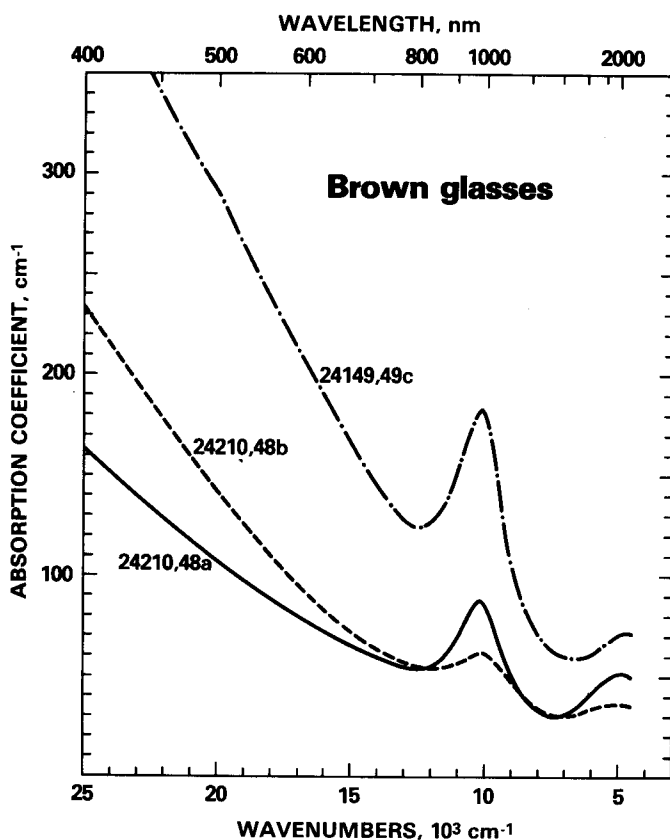


Fig. 8. Optical absorption spectra of three brown glasses with identical chemical compositions.

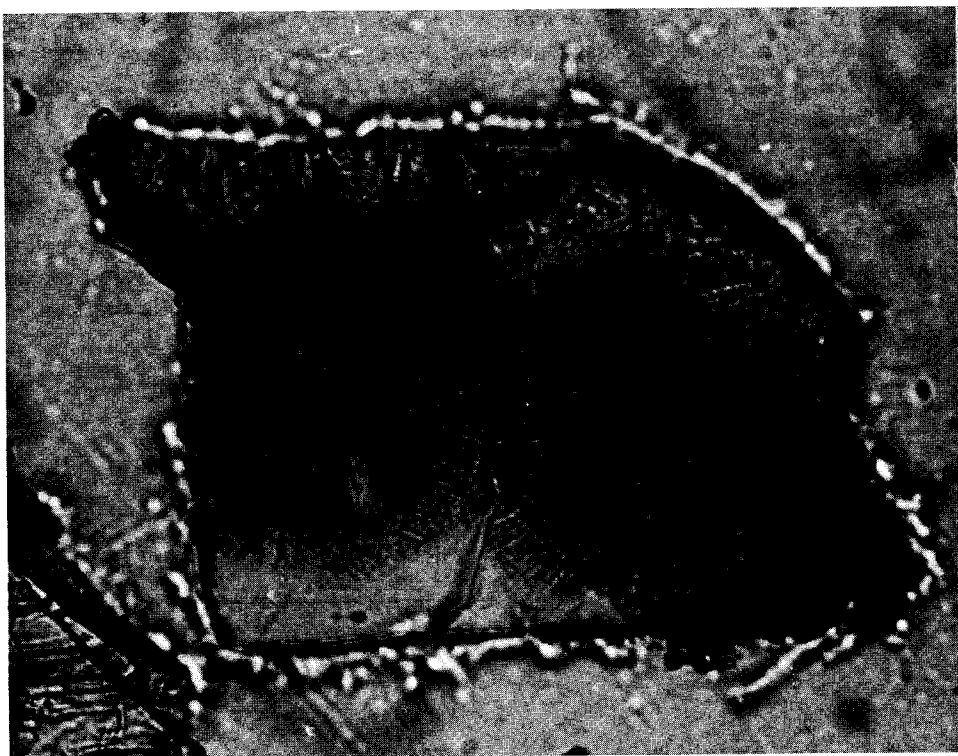


Fig. 9. Photomicrograph of the partially devitrified anorthite glass 24174,51a. The length of the grain is 0.2 mm.

composition, oxygen fugacity, structural state, degree of devitrification. The last two are described for the first time in this report.

In summary, spectra of the green glasses are very much like those of other lunar glasses and thus are normal. The iron and titanium concentrations can be deduced directly from experimental data. The Ti^{3+} – Ti^{4+} ratios were compared with those of other lunar glasses and with those of synthetic glasses. The oxygen fugacities of the green glasses vary slightly but cluster about the equivalent value $-\log P_{\text{O}_2} = 9.1 (\pm 0.05)$ for synthetic glasses of the same composition quenched at 1400°C . The spectral features are typical of iron-titanium bearing lunar glasses, and thus their spectral contribution to the soil spectra causes no errors in the interpretation of telescope spectra of the Mare Crisium.

The brown glasses are different. These spectra appear like those of iron-titanium bearing pyroxenes, and yet it has been demonstrated in this study that this is not a true devitrification effect because the glass spectra are essentially those of a single crystal. Where devitrification is observed, the product is a polycrystalline basalt. These spectral features vary considerably with the apparent development of order in the glasses, and they do not correlate well with

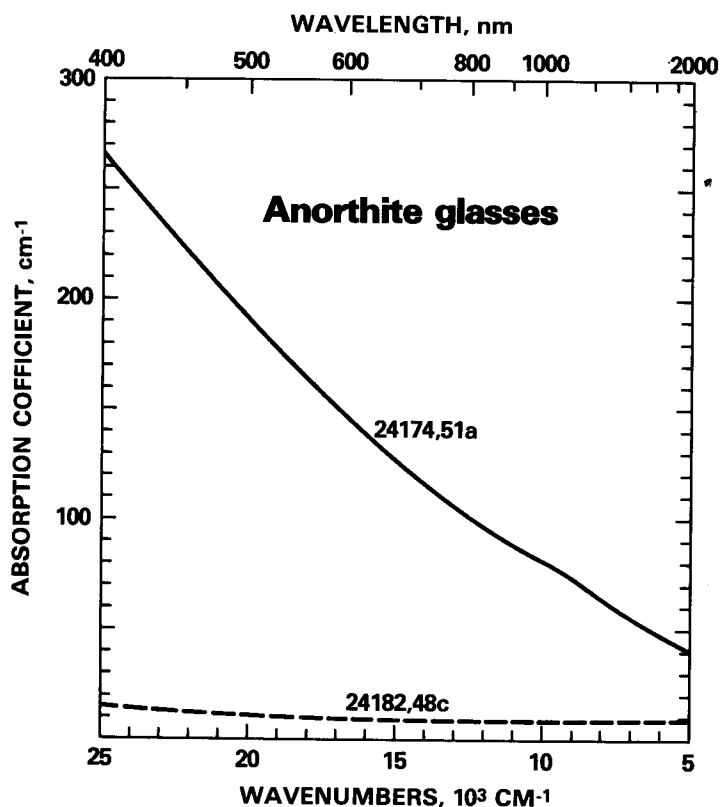


Fig. 10. Optical absorption spectra of the clear anorthite glass 24182,48c and the devitrified anorthite glass 24174,51a.

composition or oxygen fugacity. Fortunately, the spectral features of the brown glasses can be recognized from the present data and should not pose problems of interpretation. Preliminary studies of natural shocked glasses have not revealed these spectral features, but it would now be desirable to examine a range of terrestrial impact basalt glasses.

The brown glasses have a degree of order not previously reported in lunar samples. They are not brown because of composition alone, and thus it would be incorrect to assume that they are a given "basalt" type on the basis of visual observation. It will be important to reassess telescope spectra of Mare Crisium, but the distinct spectral features of the brown glasses should make reassessment possible.

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