

Petrographic, Mineralogic, and X-Ray Fluorescence Analysis of Lunar Igneous-Type Rocks and Spherules

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as small ($<20 \mu\text{m}$) droplets in glass spherules and glass fragments or as small grains in the fine-grained breccia matrix. Nickel contents range from 0.5 to 19.8 percent; Co ranges from 0.35 to 0.94 percent.

Troilite occurs as an intergrowth with native iron or as a separate phase. Minor amounts of Mn (0.4 percent) and Cr (0.03 percent) are common.

Chlorapatite was identified with the electron microprobe; however, the grain size is too small ($<10 \mu\text{m}$) to allow accurate quantitative microprobe analysis.

Glass spherules and fragments are similar in composition for any given color (Table 2). The amounts of SiO_2 , Al_2O_3 , and CaO decrease as the color of the spherules darkens, whereas the amounts of Cr_2O_3 , TiO_2 , FeO , and MgO increase; other oxides show no definite trends.

Igneous glass occurs in minute patches $<30 \mu\text{m}$ in diameter of silica-rich glass which range in SiO_2 from about 72 to 84 percent. A typical analysis is: SiO_2 , 78.1 percent; TiO_2 , 1.11 percent; Al_2O_3 , 10.6 percent; FeO , 0.96 percent; MnO , 0.04 percent; MgO , 0.07 percent; CaO , 5.1 percent; Na_2O , 1.24 percent; K_2O , 3.4 percent; P_2O_5 , 0.19 percent; Cr_2O_3 , 0.05 percent; ZrO_2 , 0.04 percent; total, 100.90 percent.

The following tentative conclusions may be drawn from the data presented herein: (i) There are no indications of chemical weathering or the presence of hydrous minerals. (ii) The presence of troilite, native iron, and the less oxidized end members ulvöspinel (Fe_2TiO_4), rather than magnetite (Fe_3O_4), in the magnetite-ulvöspinel series; ilmenite (FeTiO_3), rather than hematite (Fe_2O_3), in the hematite-ilmenite series; "ferro-pseudobrookite" (FeTi_2O_5), rather than pseudobrookite (Fe_2TiO_5), in the "ferro-pseudobrookite"-pseudobrookite series indicates that the oxygen fugacities of the lunar rocks are low relative to those of terrestrial rocks. (iii) Contributions (by weight) of meteoritic material to lunar surface rocks appear to be small. (iv) The texture of sample 10045-29 and many lithic fragments is typical of rapidly cooled rocks and is analogous to terrestrial volcanic or hypabyssal rocks. (v) The ilmenite content of all samples is higher (~ 15 to 20 percent by weight) than that of most terrestrial rocks and is similar in bulk composition to that of meteoritic ilmenite. (vi) Shock features indicate that at least some of the loose surface material and breccias are impact-produced. (vii) Metallic nickel-iron

present in glass spherules and glass fragments is interpreted as being of meteoritic origin.

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4. We made electron microprobe analyses at the University of New Mexico and at the NASA Ames Research Center, using techniques described elsewhere [K. Keil, *Fortschr. Mineral.* 44, 4 (1967)]. We thank G. Conrad, J. Erlichman, R. Geitgey, F. Busche, and J. Rasho for assistance in the electron microprobe work, and R. Taylor and Mrs. R. Taylor, Mrs. J. Etheridge, and Miss M. Busch for assistance in the data reduction. Supported in part by NASA contract NAS9-9365.

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Abstract. Three lunar rocks show almost identical mineralogy but grain sizes that vary from basaltic to gabbroic. Clinopyroxene is zoned from augite to subcalcic ferroaugite compositions and is accompanied by decrease in Cr, Al, and Ti. Plagioclase is zoned from 93 to 78 percent anorthite. Olivine (68 percent forsterite) is present in one rock and apatite is rare. Cristobalite, ilmenite with Ti-rich lamellae, ulvöspinel (often Cr-rich), troilite, and kamacite are low in trace elements. Glassy spherules are of basaltic or feldspathic (92 percent anorthite) composition but contain abundant iron spheres of taenite composition (13 percent Ni). Four rock analyses by x-ray fluorescence show affinity with terrestrial basalts but with anomalous amounts of Ti, Na, Cr, Zr, Y, Rb, Nb, Ni, Cu, and Zn.

Three polished thin-rock sections (17/50, 45/35, 58/23) were provided for nondestructive optical and electron microprobe analysis, and three 2-g samples of rock powders (44/39, 45/24, 60/25) for nondestructive x-ray fluorescence analysis of minor elements. A 5-g sample of 1-mm to 1-cm heterogeneous fragments (85/3) yielded different rock types, which were prepared for microprobe analysis, and 2 g of 1-

to 3-mm size was powdered and analyzed for major and minor elements by x-ray fluorescence.

The three main rock types are very similar in mineralogy and have no terrestrial or meteoritic analogs. They are closest to terrestrial tholeiitic basalt and meteoritic eucrite, but the high titanium and reduced state of each lunar rock make such comparisons superficial. The textures and mineral assemblage

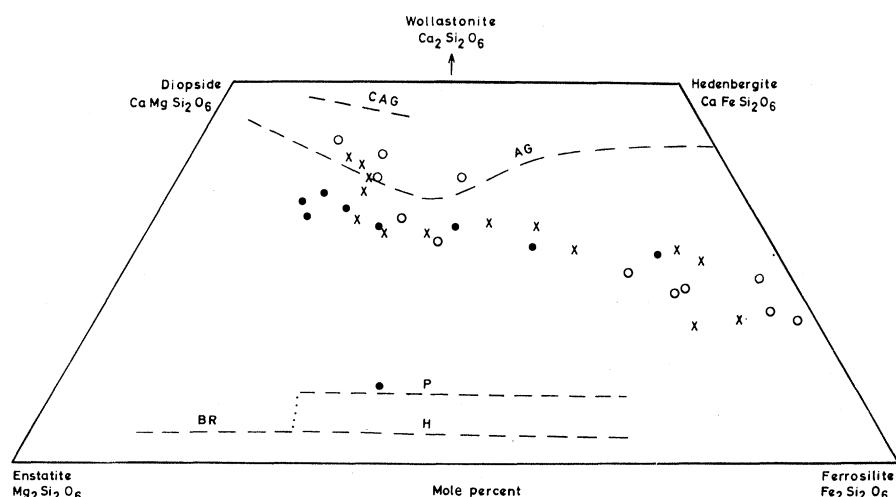


Fig. 1. Pyroxene compositions in relation to the trends (2) for terrestrial igneous pyroxenes (broken lines: CAG, calcic augite; AG, augite; BR, bronzite; H, hypersthene; P, pigeonite series). Symbols refer to the three igneous-type rocks (Table 1): closed circles, A; crosses, B; open circles, C. The pale yellow phase (crystallographically a pyroxenoid according to S. O. Agrell *et al.*, this issue) is present as the most iron-rich compositions in B and C. Only one pigeonite composition was obtained, but more measurements are needed.

favor crystallization from a silicate-rich melt, without crystal sorting, and from a lava mass near the surface. The grain size varies from basaltic, with pyroxene in excess of plagioclase nuclei (17/50), to diabasic (45/35) and gabbroic (58/23), with ophitic texture in which nuclei proportions are reversed. The coarser rocks could be blocks derived either from shallow subsurface plutons or from the centers of thick lava masses. Preferred flow or sedimentation orientation of grains was not observed. Range values are given because grain sizes and proportions vary too much for a dependable statistical analysis on a limited volume.

Clinopyroxene, plagioclase feldspar, ilmenite, cristobalite, troilite, ulvöspinel, and kamacite, in decreasing order of abundance, are ubiquitous. Olivine and chrome spinel are only in section 45/35, and apatite in section 58/23. For the three rocks we find clinopyroxene (47 to 59.4 percent, 0.1 to 2 mm); plagioclase (25.1 to 37.2 percent, 0.04 to 1 mm); ilmenite (10.5 to 14.5 percent, 0.1 to 3 mm); olivine (0 to 4.6 percent, 0.6 mm); cristobalite (0.2 to 5.1 percent, 0.1 to 1 mm); troilite (0.3 to 1.9 percent, maximum of 130 μm); kamacite (0.05 to 0.4 percent,

maximum of 50 μm); trace of apatite (150 by 10 μm needles). Ulvöspinel (50 to 200 μm) and exsolution lamellae in ilmenite (maximum width 5 μm) were not counted before coating.

A Cambridge Instruments Company Geoscan Mk2 electron microprobe was used for all mineral composition analyses (Table 1). Standards of natural and synthetic minerals were used, and correction procedures followed Boyd (1). At a beam size of 2 μm (15 kv), grains below 5 μm gave poor resolution.

Pale brown clinopyroxene is strongly zoned from augite to subcalcic ferro-augite. Pale yellow rims and interstitial patches are chemically, but not necessarily crystallographically, subcalcic ferro-augite. The 35 plotted points (Fig. 1) show a distinctive band trend, and the full range is spanned by some crystals. The one-clinopyroxene trend may be indicative of much higher crystallization pressures than the cristobalite stability would suggest, although pyroxene metastability should be recognizable from x-ray diffraction, cryptoperthitic intergrowth patterns. Minor elements are fractionated, as between terrestrial Ca-rich and Ca-poor phases (2, 3). The amount of Ti is fairly low,

and Al is comparable with the amount in low-pressure tholeiitic pyroxenes. Broad (?strain) lamellae, short 5- μm -thick lamellae of another translucent phase (too oblique for analysis), and hourglass zoning require further analysis.

Plagioclase is unusually calcic (93 percent anorthite) for a water-poor basalt (2) but the more sodic rims (to 78 percent anorthite) complement the pyroxene rims as indicators of crystallization from a cooling liquid. Olivine is very low in nickel. Although magnesian (65 to 70 percent forsterite), it is apparently compatible with cristobalite since only augite forms rare, probable reaction rims. The mosaic of fractures in cristobalite is attributed to inversion to the twinned low form already recorded (4). A similar shock mosaic in quartz (Lac Couture, Quebec) is discounted here in view of the sparseness of shock lamellae in the plagioclase. Al is the only important trace element, and an upper pressure limit of 5 kb is likely. Areas in the gabbroic rock suggest alteration associated with the cristobalite and low-temperature plagioclase and pyroxenic rims.

Ilmenite is far more abundant than in basaltic or achondritic analogs. Melanocratic Skaergaard ferrodiorites (5) are more ilmenitic but are distinctly cumulative and are rich in alkalis. The grains vary much in Mg, and exsolution lamellae are enriched in FeTi_2O_5 (7 percent) relative to the host. Ulvöspinel as discrete, often vermicular and cruciform crystallites is not intimately associated with ilmenite. Cr is clearly concentrated in the spinel phase, and one crystal contains 22 percent Cr_2O_3 ($\text{Cr} : \text{Ti} = 1 : 1$).

Troilite generally seems to be a late phase and appears either as irregular patches or spheres. Minor elements found in meteoritic troilites (6) are traces here. Kamacite (0.5 percent Ni) invariably occurs as spheres within the troilite. The low nickel is reflected in the rock analyses and contrasts with the dust and microbreccia nickel (Table 2). The iron : troilite ratio (approximately 1 : 6) is slightly higher than for the Fe-FeS eutectic at low pressure (7) but either this proportion is raised by Ni (8) or O (9), or there is 2-liquid equilibrium.

The tiny apatite needles were only confirmed qualitatively for P.

A pure plagioclase rock fragment (3 mm^3) contains about 3000 crystals and could not therefore be from a gabbroic specimen. It is strong evidence

Table 1. Mineral compositions (percentages by weight) by electron microprobe analysis. Minor phase data are given in text. Samples are (A) basalt type 17/12, (B) diabase type 45/35, (C) gabbro type 58/23, and (D) large-spherule rims from fines 85/3. The number of preferable quality analyses is given in parentheses in the sample column. Compositions were averaged over points and crystals. Three dots in a column indicate that an element was sought but, if present, was below 0.05 percent.

Sample	Si	Al	Fe	Mg	Ca	Na	Mn	Ti	S	Ni	Co	Cr
<i>Clinopyroxene cores</i>												
A(5)	23.5	1.4	9.5	9.5	11.1	...	0.2	1.4				0.4
B(5)	22.6	2.4	9.6	8.6	12.2	...	0.2	1.9				0.5
C(6)	22.0	1.0	11.6	7.6	12.0	...	0.3	1.1				0.2
<i>Clinopyroxene rims</i>												
A(3)	22.8	0.8	22.5	5.3	9.8	...	0.3	0.7				0.2
B(5)	20.7	0.9	26.9	2.5	6.8	...	0.3	0.7				0.1
C(5)	21.1	0.4	28.0	2.0	6.9	...	0.4	0.6				0.1
<i>Plagioclase cores</i>												
A(4)	22.9	17.0	0.4		11.5	1.5		0.1				
B(5)	21.4	17.9	0.3		12.9	0.6		0.1				
C(3)	21.7	18.8	0.3		12.7	1.0		0.1				
D(5)	21.3	18.4			13.2	0.3		0.1				
<i>Olivine</i>												
B(13)	18.2	...	21.0	19.8	0.2		0.3	0.1	...			0.1
<i>Cristobalite</i>												
A(1)	45.8	0.8	0.1		0.2	0.1		0.3				
C(2)	45.6	0.4	0.1		0.1	0.1		0.2				
<i>Ilmenite</i>												
A(2)	35.5	0.7	...		0.4	32.7				0.5
B(1)	0.1	...	35.3	0.7	0.1		0.4	33.4	0.4
<i>Chrome spinel</i>												
B(1)	0.2		37.4	2.9	0.1		0.4	13.3	15.0
C(1)	0.1	0.8	49.3	...	0.1		0.2	22.9	0.1
<i>Troilite</i>												
A(1)	0.1		60.2		0.1	0.1	36.6	0.1
C(1)	...	0.1	59.2		0.1	...	39.2
<i>Iron</i>												
A(1)	0.6	...	96.4	...	0.2		0.1	0.1	1.0	0.5	0.5	0.3
C(1)	0.1	...	98.5		0.1	0.1	0.8	0.1
D(1)	0.2		84.1		0.1	0.1	0.1	13.4	0.5	...

Table 2. Minor elements (in ppm) by x-ray fluorescence analysis of rock and fines samples. Samples: (A) dust-size fines, 85/3; (B) gabbro-type, 44/39; (C) diabase-type, 45/24; (D) microbreccia type, 60/25. Mineralogy and petrology of 44/39 by J. Zussman and of 60/25 by S. O. Agrell, and major element chemistry (including Cr) of 44/39, 45/24, and 60/25 by J. Scoon, this issue. The following elements were also determined but were close to or below the detection limit (5 ppm): U, Th, Bi, Pb, Sb, Sn, Cd, Ag, and Mo. Only sample 45/24 contained detectable Sn (15 ppm). Standard deviations for sample A are given in parentheses in column 2.

Element	Samples			
	A*	B†	C†	D†
Ni	117 (3.1)	4	4	162
Cu	16 (2.5)	4	6	6
Zn	19 (0.9)	3	3	30
Rb	3 (1.0)	1	1	5
Sr	159 (1.8)	206	145	164
Y	124 (1.6)	147	85	127
Zr	351 (3.1)	366	219	393
Nb	15 (1.1)	21	12	16
Ba	257 (15.7)	82	44	162

* Thirty-two determinations. † Two determinations.

for crystal fractionation near the lunar surface, with magnetic sinking or floating of 92 percent anorthite.

A polished slice (with a diameter of 2 mm) from across the largest spherule in the fines sample shows almost complete quenching to plagioclase laths (92 percent anorthite), the glass trace being of the same composition. Minor taenite (Table 1) and troilite rims are the only other phases; thus the dry liquidus temperature would have been about 1500°C. Metallic fragments (1 to 5 μm) concentrated in the hollow spherical core during sawing are rich in Cu, Ni, and Co, but their original location could not be determined. Seven 1-mm spherules are of vesicular glass, which varies from calc-feldspathic to

Ti-rich basaltic and includes subangular ilmenite, and abundant small spheres (1 to 13 μm) of taenite (13 percent Ni) sometimes rimmed by a thin sheath of troilite. Absence of detectable exsolution suggests taenite freezing above 650°C. The high Ni content of the spherules' iron phase and the high iron:troilite ratio are in contrast to the phase-assemblage of the volcanic rocks and indicate meteoritic origins for part of each spherule. The calcic normative feldspar and high Ti in the rest of each spherule indicates melting of the lunar surface volcanic debris.

A Philips-1212 automatic x-ray fluorescence spectrometer was used for four rock analyses. Major and trace elements were obtained from a prepared briquette (10) for the fines sample (Tables 2 and 3) but the other three rocks were loaned to us by another investigator (Table 2) before his analysis for major elements; it was therefore necessary to present them to the x-ray beam as powders mounted on 6-μm Mylar film in sealed chambers. The trace element data (Table 2) could not, therefore, be based on so many determinations and could not be subjected to statistical analysis. For trace elements, calibration curves were drawn from special glasses (14) synthesized relative to preliminary data (4) for matrix and spiked accurately with the trace elements being sought. Interelement interference precluded analysis for Sc, V, and Co. For major elements, reliance was placed on a glass standard (14) with high Ti, in conjunction with international rock standards (10).

The fines analysis could represent a mean either of fragments of larger Apollo 11 rocks or of the regolith at Tranquillity Base. The regolith mean is favored because of the marked chemical correlation (Table 2) between fines and microbreccia and because of chemical distinction from the two volcanic rocks (see Ni, Zn, Rb, Ba). Nickel, in particular, illustrates the contribution of metallic meteoritic material to the fines (about 0.1 percent) and suggests that the microbreccia is of indurated regolith fragments. The volcanic rocks show low Ni, Zn, Cu, Rb, and high Y, Nb, Zr compared with most terrestrial basalts, but Zr is lower and Nb higher than reported earlier (4). Major and other minor elements (Table 3) of the heterogeneous sample illustrate features common to other Apollo 11 rocks in comparing with terrestrial basalts except for low SiO₂ and Na₂O and extremely high TiO₂, fairly high Cr₂O₃,

and a combination of high AR and FR ratios (see Table 3, footnote).

The most remarkable aspect of the lunar rock chemistry is the high titanium content. Eucritic meteorites (11), like terrestrial basalts (12), do not have this feature. Most Apollo 11 rocks examined are believed to be volcanic, with textures and mineral zoning indicative of crystallization from a slowly cooled liquid. Troilite and kamacite crystallized at low oxygen fugacities which, assuming a quartz-fayalite-iron type buffer (13), would be about 10⁻¹³ bar at 1200°C and low total pressures. Low Ni (even by basaltic standards) and the pyroxene assemblage have no meteoritic analogs. The igneous rocks could be fractionated basalt equivalents if alkalis had been lost during the extensive vesiculation and if Ti had increased through crystal fractionation, but the pyroxene evidence does not support Mg-Fe fractionation between separated crystals and liquid. The contribution from meteoritic material is confined to the spherules, and then only to the nickeliferous iron parts.

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Table 3. Major oxides and norm of dust-size fines sample analyzed by x-ray fluorescence. Total iron was calculated as FeO except for the trace of Fe₂O₃ estimated from wet chemical data on comparable rocks by Scoon (this issue). The metallic Fe value is not known.

Oxide	* Mean (%)	S.D.	Mean norm	
			CIPW	%
SiO ₂	42.13	0.123	Qz	1.7
Al ₂ O ₃	13.64	0.071	Or	1.0
FeO ₃	0.06		Ab	4.6
FeO	15.29	0.063	An	34.7
MnO	0.21	0.002	Wo	8.9
MgO	7.38	0.076	En	18.6
CaO	11.32	0.041	Fs	14.1
Na ₂ O	0.54	0.065	Mt	0.1
K ₂ O	0.16	0.003	IIm	14.7
TiO ₂	7.69	0.038	Ap	0.3
P ₂ O ₅	0.10	0.005	Tr	0.9
Cr ₂ O ₃	0.33	0.001	Chr	0.5
S	0.31	0.004	FR†	0.67
Total	99.16		AR‡	0.86

* Thirty-two determinations. † FR, iron ratio (FeO/MgO + FeO). ‡ AR, anorthite ratio by weight (An/An + Ab + Or).