sured with MoKα radiation by 2θ scan to a limit of $(\sin \theta)/\lambda = 1.25$, encompassing 1135 independent reflections. Of these, 600 gave values more than twice the standard error based on counting statistics, and these were used for the structure analysis. The low proportion of observed reflections is characteristic of the systematic intensity weighting of a superstructure lattice of this type. The data were processed in the usual way for Lorentz and polarization corrections, but no account was taken of absorption or extinction. Although absorption is moderate (linear coefficient = 135.2 cm^{-1}), it is ignored in this study because the crystal is small (~0.15 mm). The structure parameter overdetermination is quite large (600 intensities/6 parameters), and the final standard error for these parameters is satisfactorily low.

The refinement was carried out by least squares analysis (*4*). The mode is anisotropic, and the program automatically controls the parameter dependencies imposed by the symmetry. A scale factor, 6 structure parameters, and 14 thermal parameters were allowed to vary. The data were treated as F values with unit weights. The starting parameters were those of Bertaut (*5*), which gave $R = 0.29$; convergence was complete after four cycles. Anomalous dispersion effects were included, but, without absorption corrections, they did not significantly affect the final result. The final unweighted conventional reliability factor was $R = 0.084$. The structure factors are listed in a table not included here (*6*).

Bertaut (*5*) previously solved the problem of the nature of the distortion of the ideal NiAs structure inherent in troilite. Using visually estimated Weissenberg data obtained with CoKα radiation from a synthetic crystal, he determined the space group and a structure consistent with the intensities of the superstructure reflections. Without considering the thermal motions, he derived his parameters by least squares analysis of 31 of these data, obtaining $R = 0.195$. The present analysis of lunar troilite wholly confirms Bertaut's structure proposal and now measures the bond lengths with a standard error of the order of 0.004 Å. The final parameters are listed in Table 1.

The structure is characterized, as Bertaut (*5*) found, by a moderate drawing together of the Fe atoms into triangular groups normal to the c axis (Fig. 1). The hexagonal close-packed sulfur framework remains essentially undistorted, except for a small displacement of S_2 (0.14 Å) parallel to the c axis away from the center of the Fe triangles. The Fe-Fe distances are apparently longer than they are in pyrrhotite, where they may range down to 2.84 Å. In fact, atomic displacements may be present in pyrrhotite also (as well as ordered vacancies), so that this estimate of Fe-Fe distance may be too low, and the distances may actually be comparable to those in troilite. The shortest Fe-Fe distance in troilite is in the horizontal triangular groups (2.920 Å), where the octahedra are edge-shared (3.43 Å in pyrrhotite), rather than in the c direction as might be expected, through the shared octahedral face (2.947 to 2.985 Å). The FeS_6 octahedron is rather severely distorted, with six different Fe-S bond lengths ranging from 2.359 to 2.721 Å. The dimensions of the thermal ellipsoids of the atoms are given in Table 2. The ellipsoid for Fe is nearly isotropic and for the S atoms is slightly elongated along the c direction. Absorption corrections may be needed to improve the reliability of the latter result.

Finally, the neutron powder diffraction study of troilite by Andresen (*7*) should be mentioned. In order to account for his neutron diffraction intensities, he found it necessary to adjust Bertaut's structure parameters for Fe to $x = 0.383 \pm 0.005$ and $y = 0.050 \pm 0.005$. These values are within one standard deviation unit of the ones in this study. Andresen further found that the magnetic moments of the Fe atoms are oriented parallel to the c axis in an antiparallel arrangement, with all moments in one horizontal layer pointed in one direction, opposite to those in the next layer. At the transition temperature of 140°C, where the superstructure disappears, the magnetic structure also changes, with the moments now directed normal to the c axis. The magnetic ordering then decreases with temperature increase to the Néel temperature of 327°C.

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Opaque Minerals in Lunar Samples

Abstract. *Microscope study and electron microprobe analysis of lunar rocks and soil show that ilmenite, troilite, and native iron are accompanied by trace amounts of ulvöspinel, titanochromite (new mineral name), an unidentified Ti-Fe oxide, and a complex Zr-Y silicate. The assemblage requires a strongly reducing environment. Textures and modal proportions show that the rocks present are not a differentiation series. The restricted nature of the opaque mineral assemblage suggests a narrow range of composition for the materials from which the parent liquids of the rocks were generated. Textural variety must reflect differences in cooling rates, probably related to depths of formation.*

Opaque minerals in four samples of lunar igneous rocks (10022, 10044, 10049, and 10058), in one fragmental rock (10060), and in rock fragments separated from a sample of the less than 1 mm fraction of the lunar soil (10084) were studied by microscope and electron microprobe. Principal attention was given to the crystalline materials, but opaque minerals in glass fragments and spheres were examined briefly.

In all four igneous rocks and in all holocrystalline rock fragments in the other samples, the dominant opaque mineral is ilmenite, 10 to 17 percent by volume in various rocks. Troilite containing globules of iron is the next most abundant mineral, ranging from 0.3 to 1.3 percent by volume. The troilite-iron ratio in 10044, as indicated by results of image analysis, is roughly 35 to 1. Though minor in amount, troilite and native iron are present in all holocrystalline rocks and rock fragments and are almost uniformly disseminated.

Other minerals thus far found, all in trace amounts, are the following: (i) An aluminous ulvöspinel, disseminated in 10044 and 10058 and found

Table 1. Chemical compositions of minerals in lunar samples. The samples are: 1. 10022, ilmenite. 2. 10049, ilmenite. 3. 10044, ilmenite. 4. 10058, coarse ilmenite. 5. 10058, ilmenite intergrown with ulvöspinel. 6 to 8, Ilmenites in various rock fragments from lunar soil. 9 to 11, From single rock fragment in lunar soil—homogenous ilmenite (9); titanium-iron oxide (11), rimmed by ilmenite (10). 12. Ulvöspinel. 13. Titanochromite 2. 14. Titanochromite 1.

Sample	Oxides							
	TiO_2	Al_2O_3	Cr_2O_3	FeO*	MnO	MgO	CaO	Total
1	53.6	0.11	0.63	45.0	0.34	2.0	0.08	101.8
2	53.0	0.32	0.45	43.8	0.34	0.82	n.d.	98.7
3	52.9	0.14	0.27	45.8	0.37	0.93	n.d.	100.4
4	52.9	0.06	0.33	47.7	0.40	0.22	0.13	101.7
5	52.1	0.17	0.04	47.2	0.33	0.15	0.0	100.0
6	51.1	1.7	2.0	44.5	0.03	0.88	0.23	100.4
7	51.8	0.14	0.7	44.0	0.32	1.4	0.48	98.8
8	52.9	0.2	1.0	42.4	0.31	2.5	0.14	99.5
9	53.5	1.6	1.2	41.1	0.33	3.5	0.11	101.3
10	55.6	0.07	0.87	38.9	0.33	4.1	0.18	100.5
11	72.3	2.0	1.4	17.0	0.02	6.0	0.13	98.8
12	33.2	2.21	0.47	64.4	0.30	0.16	0.02	100.8
13	20.6	5.2	20.9	49.8	0.36	1.1	n.d.	98.0
14	17.4	10.1	26.6	39.5	0.30	5.0	n.d.	98.9

* Total iron as FeO.

also in a single rock fragment from lunar soil; (ii) titanochromite 1, a Ti-rich chromite found in one rock fragment from lunar soil; (iii) titanochromite 2, a second Ti-rich chromite found in a single rock fragment from the soil; (iv) an unidentified titanium-iron oxide, found in 8 fragments from lunar soil; and (v) a Fe-Ti-Zr-Y silicate disseminated in two lunar rocks (10044, 10058).

Compositions of oxide minerals were determined by microprobe analysis (Table 1). The analytical procedure of Bence and Albee (*1*) was used. Reflectivities of oxide minerals are given in Table 2. Accuracy of the procedure for major elements is considered to be 1 to 5 percent of the amounts present (*2*), but summations and calculations of atomic proportions for minerals reported here suggest an accuracy closer to the lower figure.

Ilmenite exhibits a variety of crystal habits, and much additional analytical work is needed to determine its range in composition. Data thus far obtained suggest that ilmenite in each of the four igneous rocks (samples 1 to 5, Table 1) is uniform in composition and that individual crystals are homogeneous. Compositions, except that of 10022, are those of common ilmenites; that is, elements other than Ti and Fe are present only in trace amounts. Some ilmenites from rock fragments in lunar soil, however, show Al_2O_3, Cr_2O_3, or MgO in excess of 1 percent (samples 6 to 10, Table 1). Analyses 9 and 10 are for ilmenite in a rock fragment in which the mineral occurs both as homogeneous crystals (sample 9, Table 1) and as rims on the unidentified Ti-Fe oxide (sample 11, Table 1). Both differ from normal ilmenite in MgO or Cr_2O_3, or both.

Ulvöspinel is known in earth rocks only from fine-scale intergrowths with titanomagnetite; hence its reflectivity (Table 2) has not previously been reported. In 10044 and 10058, it is always intergrown with ilmenite, but homogeneous areas as large as 120 by 50 μm appear in the sections. Its genetic relations to ilmenite are unclear. Textures can be interpreted to indicate either simultaneous crystallization with ilmenite or replacement of ulvöspinel by ilmenite. The indicated formula for ulvöspinel in 10058 (sample 12, Table 1) is $(Fe_{1.98}Mn_{.01}Mg_{.01})(Ti_{.90}Al_{.09}Cr_{.01})O_4$, remarkably close to pure Fe_2TiO_4.

The two other spinels reported above, like ulvöspinel, occur in relatively coarse-grained rocks, in crystals 220 μm or less in diameter. They differ in composition but are both essentially Ti-rich chromites. A preliminary search of the literature indicates that no comparable terrestrial spinel is known. The name titanochromite is accordingly proposed for members of the spinel group, such as those described above, that are rich in Ti, Fe, and Cr. Reflectivities, crystal habits, and hardness are within the range characteristic of members of the spinel group. Both titanochromites show incipient alteration to ilmenite along octahedral planes or grain margins. The indicated formulas are: Titanochromite 1 $(Fe_{1.15}Mn_{.01}Mg_{.26}Ti_{.45}Al_{.41}Cr_{.72})O_4$; titanochromite 2 $(Fe_{1.53}Mn_{.01}Mg_{.06}Ti_{.57}Al_{.22}Cr_{.61})O_4$.

Accessory mineral (iv), essentially a titanium-iron oxide, has been found only in rocks that appear to contain two generations of ilmenite, an earlier generation composed of relatively large, well-formed crystals, and a later one composed of thinly platy to skeletal crystals. In each of eight rock fragments, one or more grains (120 μm or less in diameter) consist of crystals of the oxide marginally replaced and therefore rimmed by ilmenite. The unknown thus appears to be an early-formed phase that reacted with the parent liquid to form ilmenite. Both the ilmenite of the rims (sample 9, Table 1) and that of the homogeneous crystals (sample 10, Table 1) are of abnormal composition. The unknown mineral is bluish gray and distinctly anisotropic (Table 2), with A_r equal to 1.0° in air and 1.9° in oil ($n = 1.515$). The reflectivity is in the range exhibited by terrestrial spinels, not that of the TiO_2 group of minerals, but the anisotropism suggests nonisometric symmetry, and calculation to a spinel formula shows a 20 percent cation deficiency. Structural

Table 2. Reflectivities (in percent; accuracy ± 0.2 percent) of ilmenite and spinels in lunar samples.

Wave-length (nm)	Ilmenite (10049)		Ulvö-spinel	Titano-chromite 1	Titano-chromite 2	Ti-Fe oxide	
	R_ω	R_ε				R_1	R_2
450	18.9	15.8	15.1	14.0	14.8	14.1	15.2
470	18.6	15.6	14.7	13.8	14.8	14.0	15.0
500	18.5	15.4	14.6	13.6	14.8	13.8	14.7
520	18.5	15.4	14.8	13.4	14.8	13.7	14.5
546	18.7	15.7	15.1	13.6	15.0	13.4	14.4
589	18.9	16.1	15.6	13.7	15.1	13.3	14.3
620	19.2	16.6	16.1	13.9	15.2	13.2	14.2
640	19.5	17.0	16.4	14.0	n.d.	13.0	14.1

work is clearly needed if larger crystals can be found.

Accessory mineral (v) is found in blades and clusters of blades sparsely disseminated in 10044 and 10058. The largest crystal is 120 μm in length. The mineral is gray in reflected light, isotropic, and semiopaque. It has a reflectivity of 12.9 ± 0.2 percent at 546 nm. Dispersion of the reflectivity is negligible. The approximate composition indicated by microprobe analysis is (in percent) SiO_2 14, TiO_2 20, ZrO_2 16, Y_2O_3 5, Al_2O_3 1, FeO 43, and CaO 1.

Troilite has not been analyzed. In 10044, ten metallic globules in troilite gave 0.6 to 0.9 percent Co, averaging 0.7 percent. In 10058, ten globules gave 0.7 to 1.3 percent O, averaging 0.8 percent. No Ni was detected.

The total opaque mineral assemblage in the lunar samples examined has features in common with both terrestrial rocks and meteorites. It differs, however, from assemblages in terrestrial rocks in the association of ilmenite with troilite and native iron and in the presence of the other Ti-rich oxides here described. It differs from assemblages in meteorites in the high content of ilmenite, in the apparent absence of Ni in iron, and the presence of Ti oxides other than ilmenite.

The various holocrystalline rocks and rock fragments show a wide range of average grain size and a variety of textural fabrics. Average grain size of ilmenite ranges from 5 to 300 μm in various rocks. Fabrics range from subophitic to microgranular to combinations of tabular and skeletal ilmenite. Four features of this display appear significant. (i) Ilmenite and troilite plus iron are constantly associated in all holocrystalline rocks, regardless of grain size or fabric. (ii) No correlation between modal proportions of these minerals and grain size or fabric is apparent. (iii) Textural features that are characteristic of cumulates, such as igneous lamination, are absent. (iv) Textural relations of ilmenite suggest that it has formed in the early to middle stages of crystallization of the host rocks. Taken together, these features set narrow limits on the interpretation of the high Ti content of the samples. Specifically, there is no evidence of a differentiation series leading to concentration of ilmenite in special rock types. The appearance of the unknown Ti-Fe oxide as an early and transitory phase is too minor a feature to be of much significance, although it indicates local fractional crystallization involving the Ti-Fe content of the parent liquid. It is thus necessary to conclude that the crystalline rocks closely reflect the bulk compositions of the parent liquids and that these liquids had a limited compositional range. The striking variety of textural fabrics must be assigned to differences in rates of cooling probably related to depths of formation.

In terrestrial igneous rocks, comparable or higher concentrations of titanium minerals are found in both intrusive and extrusive rocks. Intrusive rocks are those of the Precambrian gabbroanorthosite complexes and those of the layered or zoned mafic intrusives. Concentrations in these rocks are variously ascribed to separation of immiscible liquids, to fractional crystallization and gravitative settling of early-formed Ti-Fe minerals, or to concentration of Ti and Fe in late residual liquids. The textural features and modal proportions of the lunar rocks are contrary to the operation of any of these mechanisms. The high concentration of titanium in the lunar rocks must therefore go back to the stage at which the parent liquids were generated, by melting of preexisting materials. Either these materials were already rich in Ti, or the process of melting was selective, and the resulting liquid or liquids became enriched in the process.

Lavas relatively rich in TiO_2 have been reported from certain basalts from Iceland (*3*), Hawaii (*4*), and north-central Oregon (*5*); all basalts reported to be of oceanic origin. There is a genetic resemblance between these and lunar rocks, in that high Ti content appears to reflect bulk compositions of parent liquids. The Ti-rich rocks of Hawaii are regarded as special differentiates of tholeiitic magmas, whereas there is no suggestion of such parental magmas in Apollo 11 rocks. The alkalic basalts of central Oregon are reported (*5*) to contain up to 11.5 percent opaques, mostly ilmenite, and Robinson regards these as derived from primary alkali basalt magma. Both the Hawaiian and Oregon basalts are alkali-rich, whereas Apollo 11 rocks are reported (see *6*) to be notably deficient in alkalis.

An appraisal of the chemical system in which the Apollo 11 rocks crystallized must rest on consideration of both opaque and transparent minerals, but some conclusions can be drawn from the opaque mineral assemblage alone. The constant association of ilmenite, troilite, and native iron suggests that these minerals are an equilibrium assemblage, one that must have formed in a strongly reducing environment with low oxygen fugacity. The absence of magnetite is consistent with this conclusion.

The reported absence (see *6*) of hydroxyl-bearing minerals and the presence of cristobalite instead of quartz suggests an anhydrous system crystallizing at high temperatures. Taken in sum, the chemical parameters seem significantly different from those that characterize igneous systems on earth.

Rock fragments from the lunar soil include numerous glass spheres and fragments, glass-welded fragmental material, and holocrystalline rock fragments with fusion crusts. Metallic globules are present in many glass fragments and spheres. The total mineralogy of these is very complex and has been given only preliminary investigation. The globules, however, are of special interest because, unlike the globules in the holocrystalline rocks, some of these contain, in addition to iron or iron plus troilite, phosphorus and nickel in significant amounts. The possible derivation of some of these fragments from meteoritic materials similar to those found on earth obviously requires investigation (*7*).

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