the absence of iron and the presence of spinel in association with troilite in the large droplet described above indicate local variation in the oxygen and sulfur fugacities of the sulfide liquid. The oxygen and sulfur fugacities at 1050°C for magnetite, pyrrhotite and liquid are $10^{-10.04}$ and 1 bar respectively (*2*). The smaller of the sulfide liquid droplets are more likely to be buffered by the host silicate magma. The fine-grained iron/troilite droplets therefore probably indicate the very low fugacities of oxygen and sulfur for the silicate magma.

In sample 45.35.5 native copper occurs in association with troilite and iron as a small segregation in troilite at a troilite/ilmenite contact. This is further evidence of the low oxygen and sulfur fugacities since the native copper appears to have crystallized as a primary phase.

In sample 72.46 the ragged boundaries of the troilite/iron composite droplets enclosed within silicates contrast strongly with the smooth contacts against ilmenite. A fine-grained disseminated bright phase in silicates bordering troilite globules may represent an iron residuum from the breakdown of troilite. This sulfur loss may be related to the process responsible for natural cracks in the rock. In one case iron has migrated along a crack and cut a composite iron/troilite droplet enclosed within ilmenite. In another case possible troilite is present in a crack crosscutting ilmenite. These features may best be explained by a metamorphic event which resulted in loss of sulphur after the rock had solidified and which occurred while it was hot.

In the glasses of sample 85.4.14, grain 12, troilite and iron occur intergrown in spherical globules (*3*). The variety of textures observed may be accounted for by the phase relations in system Fe-S below 1600°C (*1*). Liquids range in composition from pure iron to troilite. This implies (*1*) temperatures over 1535°C at one atmosphere for the iron sulfide liquids in this sample. In general the smaller the globule the greater the probability that it consists entirely of iron. A diffusion of very fine globules showing a flow pattern occurs in glass in sizes down to the resolution limit of the microscope. Each iron/sulfide globule tends to act as a complete system not in equilibrium with adjoining globules from which it may differ radically in bulk composition. Iron globules give evidence of shearing in glass where iron forms infilling in a zone of dilation, thereby indicating that some glass suffered mechanical deformation shortly after solidifying. A strongly anisotropic phase is noted forming fine spots and bands within troilite in a troilite/iron globule in a chondrule-like body from sample 85.4.14, grain 7. This phase is tentatively identified as mackinawite.

Modal analyses for the principal opaque phases in rocks are given in Table 1. The primary igneous rocks (types A and B) have comparable amounts of ilmenite, troilite, and iron, whereas the breccia (type C) exhibits depletion of ilmenite and troilite relative to the primary igneous rocks. Iron modes for the breccia are comparable with those of primary igneous rocks. However, the presence of nickel in amounts ranging from 0.6 precent up to 10.3 percent in the iron in the breccia suggests that this iron has a diverse origin.

The low modal amounts of ilmenite and troilite in breccia relative to primary rock types suggest that ilmenite and troilite of the primary igneous rocks are destroyed in the glass-forming process. The presence of skeletal ilmenite crystals and composite iron/troilite globules in glass from coarse fines, sample 85.4, supports this conclusion. The glass-forming process may also involve some loss of sulfur. Ilmenite, troilite, and iron are unlikely to be preferentially preserved or destroyed in this process. However, material of iron or iron-nickel composition is enriched relative to ilmenite and troilite in the breccia by a factor of 4 as compared with the abundance of iron in the primary igneous rocks. It would appear, therefore, that approximately 75 percent of the iron or iron-nickel alloy in the breccia could have a meteoritic origin.

Reflectance measurements (*4*) in air and oil have been made on selected ilmenites to determine the reflectance, R, absorption coefficient, k, and refractive index, n, in the wavelength range 400 to 700 nm (Fig. 1). The shocked ilmenite described above in sample 85.4.16 exhibits simple absorption of the ordinary ray, whereas the unshocked ilmenite from sample 45.35,5 displays a curve with a maximum at about 590 nm, which may be indicative of more complex bonding.

The following phases were analyzed by electron probe: ilmenite, chrome-titanium spinel, ulvöspinel, native iron, native copper, iron-nickel alloys and troilite. All data are corrected by computer programs written by Aucott (*5*). The nickel content of iron in breccia varies between 0.6 and 10.3 percent, whereas nickel is low, or lacking, in iron in the igneous rocks. Cobalt is often present up to 0.65 percent in these cases. Table 2 presents analyses for some phases. Ilmenites in all rock types are unzoned and carry appreciable but variable amounts of Mg, Al, Si, Ca, Cr, and Mn.

Primary igneous rocks studied have a simple mineralogy as far as opaque minerals are concerned. The opaque mineral assemblages have crystallized under conditions of very low oxygen and sulfur fugacities. Similar opaque mineral assemblages are present in glasses, but in this case equilibrium has not been established. Optical data indicate that ilmenites in the fines are affected by shock metamorphism. The fines contain some metal of meteoritic origin.

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Lunar Troilite: Crystallography

Abstract. *Fine, euhedral crystals of troilite from lunar sample 10050 show a hexagonal habit consistent with the high-temperature NiAs-type structure. Complete three-dimensional counter intensity data have been measured and used to confirm and refine Bertaut's proposed low-temperature crystal structure.*

The rare mineral troilite is formed under strongly reducing conditions and has previously been found in nature only in serpentinized rocks and meteorites. Troilite was early recognized as a very minor but generally occurring constituent of the material returned by Apollo 11 from the Sea of Tranquillity.

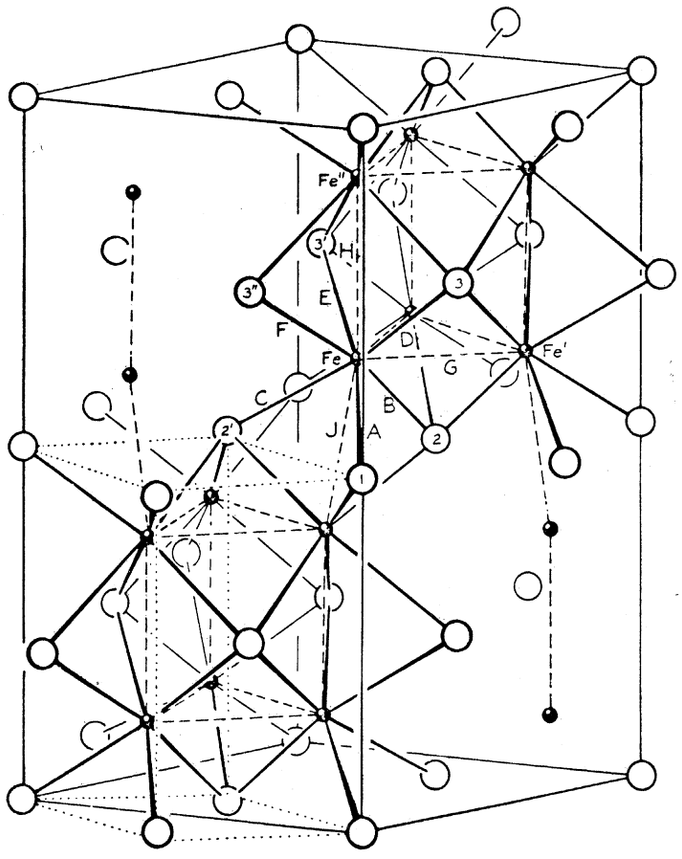

Fig. 1. Crystal structure of troilite. Dashed lines, shortest Fe-Fe distances; dotted lines at lower left, the NiAs-type subcell. Interatomic distance vectors are listed in Table 2.

Table 1. Structure and thermal parameters for lunar troilite. Standard errors are shown in parentheses in terms of the last significant digits.

Atom	Site	Structure parameters x	y	z
Fe	12(i)	0.3797(3)	0.0551(3)	0.1230(1)
S_1	2(a)	0	0	0
S_2	4(f)	⅓	⅔	0.0199(4)
S_3	6(h)	0.6652(9)	−0.0031(8)	¼

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{31}
			Thermal parameters			
Fe	0.0100(4)	0.0087(3)	0.00167(4)	0.00049(3)	−0.0001(2)	0.0000(2)
S_1	0.0051(11)	$=\beta_{11}$	0.0025(3)	$=\beta_{11}/2$	0	0
S_2	0.0064(6)	$=\beta_{11}$	0.0018(2)	$=\beta_{11}/2$	0	0
S_3	0.0060(8)	0.0051(8)	0.0019(1)	0.0027(7)	0	0

Table 2. Interatomic distances and thermal ellipsoids in lunar troilite. Standard errors are shown in parentheses in terms of the last significant digits.

To atom	Interatomic distances for Fe (vectors labeled in Fig. 1) Vector	Distance (Å)
S_1	A	2.565(2)
S_2	B	2.379(3)
S_2'	C	2.504(3)
S_3	D	2.359(4)
S_3'	E	2.416(4)
S_3''	F	2.721(4)
Fe'(2)	G	2.919(3)
Fe''	H	2.947(3)
Fe'''	J	2.984(3)
Fe		3.669(3)
Fe		3.796(3)

Atom	Thermal ellipsoids, rms axes (Å) u	v	w
Fe	0.104(3)	0.109(2)	0.116(2)
S_1	0.083(14)	$=u$	0.131(8) ($\|\|c$)
S_2	0.092(8)	$=u$	0.114(6) ($\|\|c$)
S_3	0.083(7)	0.091(7)	0.116(4) ($\|\|c$)

So far, troilite is the only sulfide positively identified in these lunar samples.

Troilite is found in the massive lunar material as thin stringers in ilmenite, or small blebs up to 0.3 mm in size, which are commonly finely polycrystalline. The masses of troilite often contain small particles of metallic iron. The mineral also sometimes appears on the walls of cavities, where it forms bright metallic yellow patches, rounded as though solidified from a molten droplet. In lunar sample 10050, two fine, euhedral single crystals were found implanted on pyroxene crystals that lined a vug. One of these crystals was removed for single crystal study, the results of which are reported below.

The crystals are well developed, with bright faces that give good optical signals. The crystal studied was the upper part of a somewhat barrel-shaped habit. The forms m, p, and s are those that would be expected for the simple NiAs-type crystal unit cell that prevails above 140°C. (Miller indices are $\{10\bar{1}0\}$, $\{10\bar{1}1\}$, and $\{10\bar{1}2\}$, respectively, for the high-temperature cell and $\{11\bar{2}0\}$, $\{11\bar{2}2\}$, and $\{11\bar{2}4\}$ for the low-temperature cell.) The crystal gave sharp, undistorted Buerger precession diffraction patterns and was very well suited to crystal structure study. Another euhedral crystal taken from lunar sample 10047 proved to be an aggregate of subparallel crystals ranging in orientation over 5°.

X-ray powder diffraction patterns (Debye-Sherrer) and single-crystal, x-ray goniostat measurement give d-spacing and unit cell data that are in close agreement with those of Haraldsen (*1*). The unit cell is hexagonal, space group $P\bar{6}2c$, with $a = 5.962 \pm 0.002$ Å, $c = 11.750 \pm 0.003$ Å, and a cell content of 12 FeS. This cell represents a superstructure of the simple NiAs-type structure, as originally found by Hägg and Sucksdorff (*2*), based on small displacements of the Fe and S atoms from their ideal positions. The chemistry is assumed to be very close to stoichiometric. Experimental work (*3*) has shown that, up to very high temperatures, for the phase $Fe_{1-x}S$, x does not take any measurable negative value. Other investigators have found that lunar troilite may contain up to a total of 1 percent Co, Ni, and Ti in solid solution, but the crystal studied here has not been analyzed. The density calculated for pure FeS is 4.841 g/cm³.

With a Picker automatic diffractometer, diffraction intensities were mea-

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