

rutile and chromite were observed as exsolution products has a similar composition but contains significantly lower Cr and higher Mg.

Sparse crystals of olivine in rock 10020 range up to 1.4 mm in their largest dimension and have the appearance of phenocrysts. Nevertheless, most olivine crystals in this rock grade down in grain size to 0.036 mm, which is equivalent to the coexisting pyroxene, feldspar, and opaque minerals. The olivine forms 3 to 5 percent by volume of the rock (Table 1). It has proved ideal for optical absorption and x-ray studies and for electron-probe analysis because of its coarse grain size and relative homogeneity and because lattice distortions due to shock are absent.

The 10020 olivine has been analyzed for 14 elements with the electron probe, and of these Mg, Fe, Si, Ca, Mn, Cr, Al, and Ti were found in significant concentration (Table 2). A dozen or more grains of the olivine in section 10020,40 were included in the analysis, and the average composition is $\text{Fo}_{72}\text{Fa}_{28}$ (mole percent) with a range in composition of approximately ± 3 mole percent Fo. The Cr_2O_3 content of the olivine (0.21 percent by weight) is higher by a factor of 2 than that of any known terrestrial olivines, and the NiO content (<0.01 percent by weight) is considerably lower than that of most terrestrial olivines of igneous origin. The latter usually contain 0.01 percent by weight or less Cr_2O_3 , with the exception of olivine crystals that form inclusions in natural diamond; these olivine inclusions have been found to have Cr_2O_3 contents ranging up to 0.1 percent by weight (11). A common factor in the crystallization of olivine in a lunar lava and in a terrestrial diamond is a reduced oxygen fugacity, suggesting that the chromium may be present as Cr^{2+} . More direct evidence in support of this suggestion is cited below.

Preliminary microscopic measurements of the crystal field absorption spectra were made on a single crystal picked from a chip of sample 10020 and on olivines in section 10020,40. The spectra exhibit broad bands in the near infrared, similar to those observed for terrestrial olivines close to this composition (12). Specifically, absorption bands were observed at approximately 9000 and 10,600 Å, corresponding to Fe^{2+} in octahedral coordination. When the crystal was rotated about the *a* axis, pleochroism was observed when the *b-c* plane was made parallel with the plane of polarization of the substage nicol.

Minimum absorption with maximum resolution occurred approximately parallel to *b*. These phenomena are well known in olivines (13), but differences were observed in that the weak band at 6300 Å usually attributed to Fe^{3+} in octahedral coordination is absent and a weak, poorly resolved band at about 10,400 Å is present. We believe this band is caused by a trace of Cr^{2+} . No near-infrared bands for Cr^{3+} were observed. Weak absorption was measured at both ends of the visible region. Maximum transmission occurred between 4000 and 5000 Å, characteristic of Cr^{2+} (14). The absence of Cr^{3+} was confirmed by the fact that no band occurred in that region. Divalent chromium [$d^4(t_{2g})^3(e_g)^1$] is peculiar in that it causes severe Jahn-Teller distortion of an octahedral site (15) and thereby is destabilized relative to Cr^{3+} . If chromium were incorporated as Cr^{2+} during crystallization, it would imply an extremely reducing environment.

The x-ray diffraction of an olivine crystal picked from 10020 is consistent with the accepted space group of *Pbnm* for terrestrial olivines. The unit cell parameters are $a = 4.76 \pm 0.01$, $b = 10.284 \pm 0.004$, $c = 6.018 \pm 0.003$ Å, consistent with the composition determined by electron probe.

A number of features observed in these samples that distinguish them from terrestrial rocks appear to result from highly reducing conditions during primary crystallization. Outstanding features are (i) the presence of metallic iron, (ii) unusual oxide phases rich in ferrous iron, including magnesian fer-

ropseudobrookite and chromian ulvöspinel, and (iii) exceptionally high Cr in the olivine, believed to be present as Cr^{2+} .

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References and Notes

1. D. G. W. Smith, *Amer. Mineral.* **50**, 1982 (1965).
2. O. von Knorring and K. G. Cox, *Mineral. Mag.* **32**, 676 (1961).
3. A. L. Albee and A. A. Chodos, Abstract of paper presented at Geological Society of America Meeting, Atlantic City, New Jersey, part 7, 1 (1969).
4. P. Ramdohr, *J. Geophys. Res.* **68**, 2011 (1963).
5. W. A. Deer, R. A. Howie, J. Zussman, *Rock-Forming Minerals* (Wiley, New York, 1962), vol. 5; I. S. E. Carmichael, *Contrib. Mineral. Petrol.* **14**, 36 (1967).
6. P. R. Buseck and K. Keil, *Amer. Mineral.* **51**, 1506 (1966).
7. C. Legg, *ibid.* **54**, 1347 (1969).
8. J. Babkine, F. Conqueré, J. Vilminot, K. D. Phan, *Bull. Soc. Franc. Mineral. Crist.* **88**, 447 (1965); S. E. Haggerty, thesis, University of London (1968).
9. J. J. Frankel, *South African J. Sci.* **38**, 152 (1942).
10. P. Ramdohr, *Carnegie Inst. Wash. Year Book* **63**, 217 (1964).
11. H. O. A. Meyer and F. R. Boyd, *ibid.* **68**, in press.
12. R. G. Burns, thesis, University of California, Berkeley (1965); W. B. White and K. L. Keester, *Amer. Mineral.* **51**, 774 (1966).
13. R. G. Burns, in preprint of *The Application of Modern Physics to the Earth and Planetary Interiors*, S. K. Runcorn, Ed. (Wiley, New York, 1969).
14. The visible and near-infrared spectra of a pure chromous olivine (Cr_2SiO_4) provided by G. Healy were measured as a comparison for us by W. White.
15. L. E. Orgel, *An Introduction to Transition-Metal Chemistry: Ligand Field Theory* (Wiley, New York, 1960).
16. We thank NASA for financial support with the contract NAS 9-9988.

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Opaque Minerals of the Lunar Rocks and Dust from Mare Tranquillitatis

Abstract. The opaque minerals in the lunar rocks 10047, 10050, 10057, 10059, 10068 and in the dust were studied. Rock 10047 contains ilmenite as a main component besides Al-bearing chromian ulvöspinel, a new Ti, Fe, Zr, Y, Ca silicate, troilite, cobaltian α Fe, minor hafnian baddeleyite and dysanallyte. Dysanallyte contains Ca, Ti, and Fe as major elements and shows concentrations (rare earth elements together ≈ 10 percent) of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Hf, Y, and Zr plus traces of Nb, Ba, and Na. The chemistry of ilmenite in the igneous rocks shows no appreciable variations. A new mineral of the solid solution series MgTi_2O_5 - FeTi_2O_5 has also been encountered in the polymict breccias. The microbreccias and the fines contain meteorite debris indicating an impact origin.

Three igneous rocks (10047, 10050, 10057), two polymict microbreccias (10059, 10068) and 5 grams of lunar dust were studied in reflected light and with the electron microprobe. The dust

was separated under acetone to six fractions. Of those fractions only some dozens of grains $> 200 \mu\text{m}$ especially the magnetic ones and those denser than 4.03 were thoroughly studied. Hence we

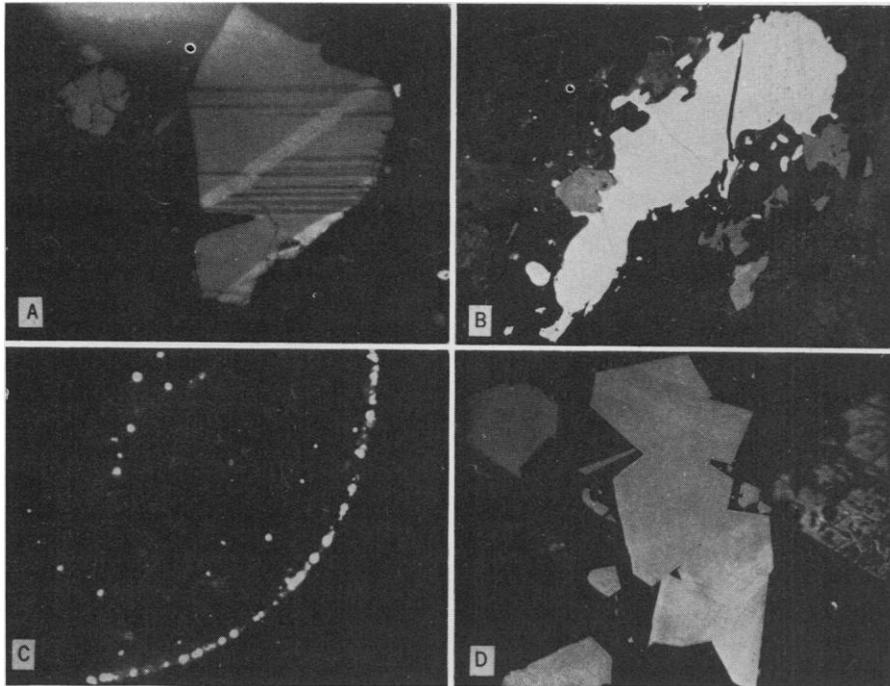


Fig. 1. (A) Ilmenite (in the breccia) containing lamellae of "anosovite" parallel to (0001) and two broad lamellae of rutile (with internal reflections) (oil immersion, $\times 300$). (B) Troilite overgrown by a baddeleyite crystal. The groundmass consists of pyroxene, fayalite, and K-rich glass (oil immersion, $\times 150$). (C) A globule of homogenized glass (some spherules of iron) with a rim of iron spherules migrated to the surface (oil immersion, $\times 125$). (D) A new spinel mineral similar to magnetite, idiomorphic and zoned (oil immersion, $\times 150$).

will be presenting data on breccias and dust which appeared to be important with respect to their mineralogy and observations which seemed to be peculiar. Electron microprobe analyses were carried out on many coexisting minerals with emphasis on the opaques and semiopaques. Observations on transparent components will also be discussed. Geologically, it is evident that the crystalline igneous rocks here represent the primary rock components of the original lunar surface. These rocks are fresh, and show no alterations except on their outermost surface due to numerous impacts of micrometeorites and to the effect of the solar wind. In contrast, the breccias and dust are of polygenic origin and contain products of many geological events, mainly meteorite impacts. All stages of impact metamorphism starting from stress twinning up to indications of complete melting of ilmenite, rutile, and the silicates were encountered in the breccias and the dust. It seems that the sum of influences of small meteorites is minute compared to those caused by bigger ones. Very large impacts create peak pressures and temperatures causing partial to complete melting and evaporation of huge amounts of the target rocks and tremendous shock effects in the surrounding rocks. The meteorite itself,

depending on its impacting mechanics, may be partially or completely evaporated.

The impacting bodies are mostly either stony or iron meteorites. Stony meteorites, being brittle and more fusible than iron meteorites hardly survive such impacting. Only once did we observe a globule comparable with a real chondrule. In the breccias some chromite grains—probably relicts of chondrites—were also encountered. On the other hand we observed relicts of iron meteorites in the form of molten or condensation globules and splinters of nickel-iron in the breccias and dust. Considering the very low content and the small quantity of iron in the igneous rocks, this iron cannot be mistaken for meteoritic iron. Only in the case of very small grains which could not be analyzed with the probe is the recognition between autochthonic and meteoritic iron impossible. In the case of troilite the situation is more complex.

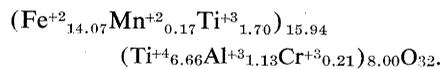
The crystalline igneous rocks and rock splinters in the breccias have been briefly described (1). With some restrictions regarding the high TiO_2 content, those rocks are comparable to doleritic feldspar basalt, high in SiO_2 and thus poor in olivine. In general, the high TiO_2 content is not exceptional for such rocks; some basalts with >4 percent

TiO_2 are known. The mineral assemblage is the same, consisting of clinopyroxene, calcic feldspar ($\text{An}_{75}\text{--An}_{98}$), ilmenite, cristobalite, tridymite, and small amounts of troilite and cobaltian iron. Troilite and iron form eutectic intergrowths. Small amounts of potassium-rich glass (in part, two immiscible phases) are common. Besides the main components we observed the following accessories which were not observed before: ulvöspinel, a new Fe, Ti, Zr, Y, Ca silicate, hafnian baddeleyite, dysanallyte with high concentrations of rare earths, a member of the $\text{MgTi}_2\text{O}_5\text{--FeTi}_2\text{O}_5$ solid solution series and an unknown fibrous mineral. Fayalite has been observed in myrmekitic intergrowths with clinopyroxene and K-rich glass. Hematite occurs as fine lamellae within a few ilmenite grains in the shocked breccias. The optical identification of hematite was confirmed by microprobe analyses. Rutile exsolution lamellae are quite rare. Only one small grain of native Cu was observed.

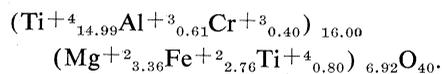
Ilmenite is always an early mineral like plagioclase. The crystals are identical to those in many basalts, gabbros and norites; the form being somewhat skeletal, due to preferential growth of the (0001) face. No exsolutions could be observed with highest magnification, as in most terrestrial basalts. In the crystalline rocks twin lamellae are present but quite rare. In similar rock splinters, in the breccias and dust, twinning of ilmenite is abundant but without magnetite at twin crossings. The composition does not vary considerably in the different rocks. Ilmenite in rock 10057 has the average composition (%): TiO_2 , 61.7; FeO , 36.6; MgO , 0.62; MnO , 0.52; Al_2O_3 , 0.26; Cr_2O_3 , 0.26. Coarser grains are slightly enriched in Cr_2O_3 . The formation of colorless rutile in broad to thin sharp lamellae parallel to (224 3) of ilmenite is mostly restricted to the splinters in the breccias and dust and is probably caused by shock.

Ulvöspinel was observed in every rock specimen examined and in the rock splinters of the breccias as well. It occurs mostly as tiny grains with or without ilmenite as inclusions in the pyroxene. The optical properties are typical but its recognition is rather difficult due to optical similarities to ilmenite. In part it replaces ilmenite. Loose skeletons appear to be young and may belong to the latest crystallization in the interstices. Quantitative electron microprobe analysis of numerous grains revealed ulvöspinel to be rich in Al, Cr, and Mn (57.8 percent FeO , 38.2 percent TiO_2 , 3.29

percent Al_2O_3 , 0.89 percent Cr_2O_3 , 0.67 percent MnO). Ulvöspinel in the crystalline rocks has the formula:



A dark blue grayish mineral with low reflectivity, very probably a new member of the MgTi_2O_5 - FeTi_2O_5 solid solution series was observed as thin sharp lamellae parallel to (0001) of ilmenite (Fig. 1A). This gray mineral is quite similar to some lamellae observed (2) in the mesosiderite Vaca Muerta. The same mineral occurs in the rock splinters in the breccias, mostly as coarse inclusions in ilmenite, and is partly replaced by the latter. Quantitative electron microprobe analysis revealed: 75.6 percent TiO_2 , 11.9 percent FeO, 8.12 percent MgO, 1.87 percent Al_2O_3 , and 1.81 percent Cr_2O_3 . Accordingly the formula is:



Baddeleyite, ZrO_2 : Regarding the exceptionally high ZrO_2 content of the rocks we looked for a Zr-bearing mineral (in vain) in rock 10057. In 10047,13 we found baddeleyite partly in crystalline grains (Fig. 1B). Zircon, with similar properties, was not observed. In the breccias and in a heavy concentrate from the dust, large clusters of baddeleyite were encountered. The U and Th contents of baddeleyite are quite low, which explains the high transparency and the lack of metamictization. Baddeleyite is quite rich in Hf (≈ 2 percent) and contains other minor elements, for example, rare earths. The mineral forms thick, tabular, untwinned grains, which is quite different from terrestrial occurrences.

A new mineral A was first mistaken for kennedyite (a mineral not rare in acid basalts) due to optical similarities. Electron microprobe analysis indicated, however, that the mineral is a Ti, Fe, Zr silicate with lower concentrations of Ca and Y and minor amounts of Mn, Gd, Nd, Dy, Hf, Ce, Al, and Na. The new mineral, very probably a basic silicate, occurs in clusters of presumably orthorhombic crystals. Its color is gray to dark gray without noticeable anisotropism. The mineral is opaque with a reflectivity similar to Ti_3O_5 or ludwigite.

Dysanlyte: This mineral, or at least a member of the perovskite group, was discovered in the coarse crystalline rock 10047,13 during the probe analysis of baddeleyite with which it is intimately intergrown. It forms round, in part perfectly crystallized, grains with distinct

purple internal reflections. Electron microprobe analysis revealed the major elements Ca, Ti, and Fe with high concentrations of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Hf, Y, and Zr besides traces of Nb, Ba, and Na. The mineral differs from members of the pyrochlore family due to the low Nb content and its high reflectivity. Another species, mineral B, rich in Ce and Ca (probably a member of the apatite group) was also observed. A mineral C, with a form similar to titanomagnetite but much lower in reflectivity was observed in the breccias. It is a two-phase unmixing product containing hexagonal, spindle-shaped lamellae in an isometric matrix.

In the dust we observed a mineral D occurring in idiomorphic grains intergrown with ilmenite, rutile, and baddeleyite. Mineral D is enormously hard (probably >9) and shows some internal reflections.

Native copper was observed only once in the coarse crystalline rock 10047,13. This is not unusual if we remember that native copper occurs in many basalts.

Troilite and iron are minor components in the igneous rocks and form mainly eutectic intergrowths. The troilite is stoichiometric in composition with traces of Ti (0.07 to 0.3 percent). The iron is nearly Ni free but contains up to 0.7 percent Co.

The breccias (10059,25 and 10068,25) consist essentially of five groups of components: (a) fragments of the above described rock; (b) foamy, pumice-like fragments sometimes more abundant than the former; (c) glassy globules of two types; c_1 not homogenized, full of schlieren; c_2 completely homogenized, but partly devitrified; (d) globules of metal or troilite or both; and (e) splinters of meteorites, mostly nickel-iron.

Group (a) differs from the igneous rocks described above only through indications of shock metamorphism (for example, formation of rutile and hematite and stress twinning in ilmenite). Group (b) consists of material of different origin, partly fused to glass but not evaporated. It represents prevalently lunar material as observed from the non-digested remnants—mainly ilmenite and anorthite. During fusion plentiful gas formed many gas bubbles, yielding pumice-like structures. Minute iron globules are quite abundant, more abundant than in the igneous rocks, and very probably originated from evaporated nickel-iron of an impacting meteorite. Globules of c_1 have variable refractive

indices, since they are full of schlieren. Globules of c_2 type may have variable refractive indices between 1.45 and 1.90. As mentioned above, c_2 globules are clear, without inclusions or bubbles. Such homogeneous glasses could only be formed in short times by condensation from vapor. Strong variation in reflectivity indicates remarkable variation in chemistry. The presence of evenly distributed fine iron dust supports the idea that globules are condensed from a silicate cloud evaporated following a meteorite impact.

The rose or blue colored pearls or globules (I) are composed of acidic glass with the lowest refractive index. Those colors are caused by colloidoptical effects (like colors of rose quartz or blue quartz) of finest devitrification products. Practically opaque basic glasses with high n show much stronger devitrification into different components below the resolution power of the microscope.

A peculiar single observation may be added here. A large type c_2 globule contains, besides a few tiny iron spherules in its center, thousands of iron spherules at the outermost layer of the glass globule (Fig. 1C). Dr. R. Bloch (Bersheba) (3) gave a possible explanation. The fact that iron spherules form a complete layer without touching each other may indicate that this phenomenon is probably a frozen flotation process. The lyophobic, equally loaded spherules of iron swim up quickly in the lyophilic silicate melt. The equal loading of the iron spherules prevents their coagulation.

Group (d) globules of iron or troilite or both are partly identical to the condensation spherules of Meteor Crater in Arizona (4). Often they contain (as in Meteor Crater) thin films of schreibersite. In any case they are products of large iron meteorite impacts. Obviously the relative quantities Fe : FeS : Fe_3P will vary. Sometimes Fe : FeS is nearly 1 : 1 or 1 : >1 , a ratio very rare in iron meteorites (except Soroti), but in stony meteorites such a ratio is common. Nearly always Ni : Fe is high, so that a genetic relationship to lunar iron is precluded.

Group (e), splinters of meteorite iron, disrupted by the impact explosion at any stage, are rare. We observed such splinters only three times in the breccias and often in a concentrate of heavy minerals from the dust. Sometimes they reach a size of 1 mm or more. After these explanations, the dust merits only a short discussion. Only the relative abundance of the groups (a) to (e) vary.

The magnetic and heavy fractions,

however, contain some constituents observed only in minute quantities in the breccias. First, the above-mentioned splinters of iron and globules of iron and troilite, and so on are different. Baddeleyite and dysanlyte are abundant in this fraction and may be studied in detail. Last we discovered well-developed octahedral crystals, distinctly zoned, in all properties (polishing, reflectivity, color, up to details of the natural faces) very similar to magnetite; very probably a new spinel (Fig. 1D).

The iron spherules in the dust also have their peculiarities. Some spherules contain a radiating structure of troilite

and silicate inclusions (in the form quite similar to enstatite chondrules). In others the ratio Fe : FeS and their intergrowth varies strongly. One splinter of schreibersite was observed with idiomorphic kamacite crystals.

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References

1. Lunar Sample Preliminary Examination Team, *Science* 165, 1211 (1969).
 2. P. Ramdohr, *Monatsber. Deut. Akad. Wiss. Berlin* 7, 12 (1965).
 3. R. Bloch, personal communication.
 4. P. Ramdohr, *Chem. Erde* 25, 3, 259 (1966).
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Search for Magnetite in Lunar Rocks and Fines

Abstract. Magnetite crystals larger than 2 micrometers are absent from rocks and fines. Smaller opaque spheres in the fines can tentatively be identified as magnetite. Their concentration is not higher than 1×10^{-6} particle per particle smaller than 1 millimeter. In the fines from the sampling site, the contribution of material similar to type 1 carbonaceous meteorites is insignificant, either because it never existed, or because it was evaporated or comminuted by impact or was diluted by indigenous material. Other magnetite habits typical of carbonaceous meteorites or possibly of cosmic dust or comets were also sought without success—such as rods, platelets, framboids, spherulites, and idiomorphic crystals.

The magnetite in Wiik's type 1 carbonaceous meteorites shows well defined crystal habits, some of which are exclusively found in these meteorites (1). These habits are easily recognizable under the reflecting microscope; their properties emerge sufficiently and thus the specific particles are quickly discernible, even when in small proportions in mixtures.

This mineral may thus be used as a path-finder for Orgueil-like materials, either indigenous or foreign. The discovery on the moon of materials belonging to this type is very important for the theories of the moon, planets, meteorites, comets, and cosmic dust (2). We thus undertook a search for the

typical magnetite crystals in lunar materials, with the fines representing a mixture of indigenous and foreign materials and the hard rocks providing a good basis of comparison with materials of lunar origin.

Our results do not prove any theory and must be considered as part of a series dealing with sampling sites with various histories.

We studied rocks 10060,40 and 10072,31 and fines 10084,96. The rocks were analyzed by photonic microscopy (transmitted and reflected light), electron microprobe, x-ray diffraction, and scanning electron microscopy. An original method of mounting and polishing small quantities of micron-sized par-

ticles was devised (3). Control of contamination was attained by mounting the fines in the glove box, filtering all fluids on Millipore, and running blanks concurrently with all the experiments.

The only oxide in sample 10072,31 that could superficially be confused with magnetite was ilmenite. It occurs as idiomorphic laths (sections of thin platelets) and as larger poikilitic monocrystals (0.1 to 1 mm) with an idiomorphic tendency. Optical properties are those which may be observed and measured on pure ferriferous members in terrestrial rocks. A decisive property for differentiating ilmenite from magnetite is the pleochroism in air and oil (4-6). Table 1 summarizes the data obtained for lunar and terrestrial ilmenites, as well as terrestrial magnetite. The ilmenite in this hard rock is never twinned. Two other oxides were found: rutile as fine exsolutions and rare chromite.

Rock 10060,40 is very friable, made up of a loose conglomerate of all the rock and mineral fragments found in the fines.

From fines sample 10084,96, transparent polished sections were prepared as follows: (i) The powder was sieved at less than 1 mm; (ii) the size fractions obtained by sieving under a CCl_4 -jet were 1 to 0.250 mm, 0.250 to 0.100 mm, 0.100 to 0.044 mm, and less than 0.044 mm; (iii) the heavy liquid centrifugates obtained from each size fraction had densities (g/cm^3) of $d < 2.8$, $2.8 < d < 3.3$, and $d > 3.3$. Magnetic separations were tried without noticeable success. The calculated concentration factor for the heaviest fraction of grain smaller than 0.044 mm is about 30.

Several free opaque or half-opaque minerals were found: ilmenite, sulfides, metallic iron, hematite, and goethite (?). Sulfides and iron are often altered into transparent, red, or brown low-reflecting oxides, which seem to be at least partially due to artifacts.

Ilmenite occurs in the fines as irregular fragments with conchoidal fractures. It is transparent under intense illumination (different from magnetite) and often twinned. Spheres of ilmenite have never been found, but opaque spheres of very low reflectivities are frequent (chromite and glass of various composition?). No one opaque mineral whose optical and morphological properties could fit in with those of magnetite has been found. Because the number of scanned heavy particles comes to at least 1×10^6 , the concentration of typical magnetite crystals does not exceed 1 in 3×10^7 particles smaller than 1 mm.

Table 1. Reflectivity of magnetite and ilmenite. Not determined, N.D.

Sample	Reflectivity at 546 nm (%) (with maximum absolute error)	
	In air	In oil ($n_{546} = 1.517$)
SiC standard	20.61 ± 0.01	7.51 ± 0.01
Magnetite from Bisperg, Sweden	19.2 ± 0.5	6.9 ± 0.4
Ilmenite from Ilmen Mts., U.S.S.R. (R_0)*	20.1 ± 0.7	7.5 ± 0.7
Three Mg-free ilmenites (R_0)		
Miask, U.S.S.R.†	19.9	N.D.
Ilmen Mts, U.S.S.R.†	20.1	N.D.
Bodenmais, Germany†	19.5	N.D.
Ilmenite from lunar sample 10072,31 (R_0)	19.3 ± 0.5	6.9 ± 0.2

* See (5). † See (6).