Iron-Titanium Oxides and Olivine from 10020 and 10071

Abstract. *A new mineral (approximately $Fe_{0.5}Mg_{0.5}Ti_2O_5$) related to the pseudobrookite series has been discovered in section 10071,28. Electron-probe analyses for this mineral, a coexisting ilmenite, and a chromian ulvöspinel-ilmenite assemblage in section 10020,40 indicate crystallization under highly reducing conditions. Analytical and optical absorption studies of the olivine in 10020 show it to contain unusually high Cr (1400 parts per million) probably as Cr^{2+}.*

Petrographic and electron-probe studies carried out primarily on rocks 10020 and 10071 have revealed a variety of opaque minerals whose compositions differ in considerable detail from terrestrial counterparts. Reflection microscopy indicates that ilmenite whose composition closely approaches $FeTiO_3$ is by far the most abundant primary opaque phase, forming 10 to 20 percent by volume of the crystalline rocks (Table 1). Magnesian ferropseudobrookite, chrome spinel, and chromian ulvöspinel have been found in accessory amounts. The magnesian ferropseudobrookite is sufficiently distinctive in chemical composition to merit consideration as a new mineral. Troilite, containing blebs and subhedral crystals of metallic iron, has been observed in all samples as a late-stage precipitate.

Three grains of magnesian ferropseudobrookite, all mantled by ilmenite, were discovered in section 10071,28. One of these grains (Fig. 1) was analyzed for 12 elements with the electron probe (Table 2) and found to be essentially $Fe_{0.5}Mg_{0.5}Ti_2O_5$ with minor amounts of Cr, Al, Mn, and Ca. The mineral is pale gray and shows medium to strong reflection anisotropy in oil. Its white-light reflectivity in air is in the range 15 to 18 percent, and it is softer than ilmenite. The three grains are rectangular in outline with longest dimensions from 100 to 300 μm, whereas their ilmenite overgrowths are 100 to 200 μm thick. These grains and their overgrowths appear to be primary.

The electron-probe analysis (Table 2) shows that the magnesian ferropseudobrookite is intermediate in composition between $Fe^{2+}Ti_2O_5$ (ferropseudobrookite) and $MgTi_2O_5$ (karrooite). Both $Fe^{2+}Ti_2O_5$ and $MgTi_2O_5$ have been synthesized, but a solid solution series between them has not been experimentally demonstrated.

The formula of pure pseudobrookite is $Fe^{3+}{}_2TiO_5$, and solid solution of $MgTi_2O_5$ or $Fe^{2+}Ti_2O_5$ with this phase is accomplished by the coupled substitution (Mg, Fe^{2+})-Ti for Fe^{3+}-Fe^{3+}. Both $Fe^{2+}Ti_2O_5$ and $MgTi_2O_5$ have been found as subordinate components in various pseudobrookite-like minerals in terrestrial occurrences (*1*). An example of such a mineral is kennedyite ($Fe^{3+}{}_2MgTi_3O_{10}$), a phase found in the Karroo basalts (*2*). Kennedyite is isostructural with pseudobrookite and contains 28.77 percent Fe_2O_3 and 60.33 percent TiO_2. The MgO content of kennedyite (6.45 percent) is similar to that of the lunar phase (7.70 percent), but the apparent absence of Fe_2O_3 and higher TiO_2 content in the lunar phase makes its occurrence distinctive.

A low content of Fe_2O_3 in the lunar magnesian ferropseudobrookite is obviously essential for its recognition as a new mineral. A technique for the analysis of Fe^{3+} with the electron probe is being developed (*3*), but its application to this group of minerals will require further work. There are several reasons, however, that lead to the strong presumption that the concentration of Fe^{3+} is very small in this lunar phase.

If the electron-probe analysis of the magnesian ferropseudobrookite is recalculated to an ionic formula where $O = 5$ (Table 2), Ti is found to equal 1.97, in comparison with the maximum possible value of 2.00. Inasmuch as half of any Fe^{3+} present must replace Ti, there is obviously not much possibility of significant Fe^{3+}. Moreover native Fe was observed as a phase in specimen 10071. As discussed below, the presence of native Fe and the compositions of other solid solutions indicate that these rocks crystallized under highly reducing conditions.

A spinel has been discovered in section 10020,40, whose composition is as unique as that of the magnesian ferropseudobrookite described above. Unlike the magnesian ferropseudobrookite, however, the spinel is a solid solution between two well-established minerals, ulvöspinel (Fe_2TiO_4) and chromite ($FeCr_2O_4$).

Grains of spinel in section 10020,40 are generally euhedral with dimensions from 100 to 200μm, and they form about 10 percent by volume of the Fe-Ti oxides. These spinels are opaque, opti-

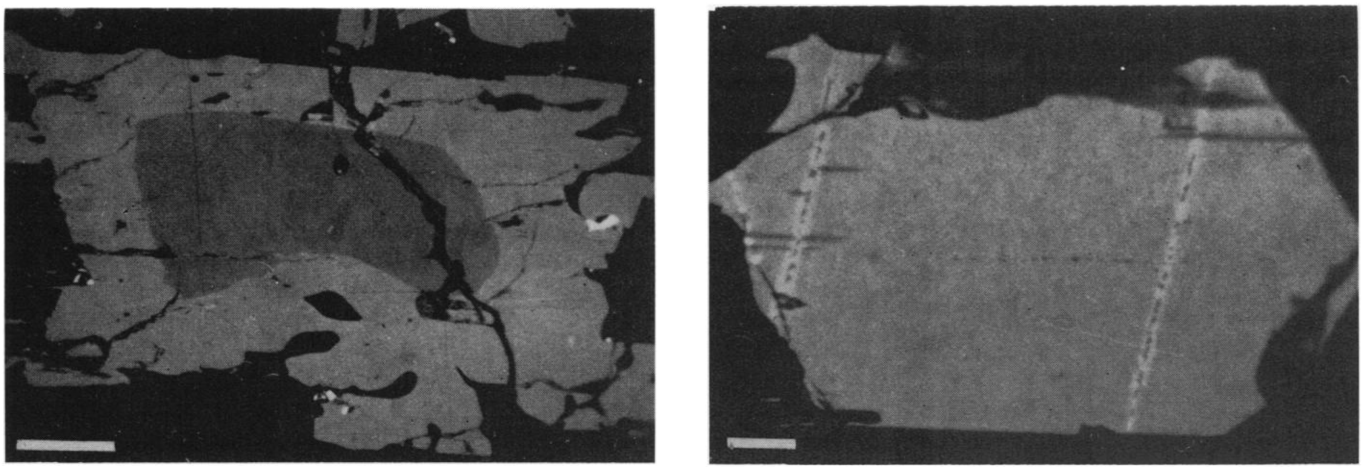

Fig. 1 (left). Magnesian ferropseudobrookite (dark gray) mantled by an overgrowth of ilmenite (pale gray). Note the fine lamellae of rutile (pale white) in the ilmenite and also the associated troilite (bright white) along the grain boundaries (scale 50 μm). Fig. 2 (right). An ilmenite crystal (medium gray) with two thick lamellae of exsolved rutile (pale white). Lensoidal rods of spinel (dark gray) occur in the ilmenite, whereas irregular blebs occur within the rutile. The crack is infilled with troilite (bright white) (scale 10 μm).

Table 1. Modal analyses measurements were made on areas of thin sections selected for minimum density of voids. The average area measured was 32 mm^2.

Section	Pyroxene	Opaque	Plagioclase	Olivine	Cristobalite	Other	Hole or vesicle
10003,37	51.7	18.2	29.0		0.3 (?)	0.2	0.5
10020,31	54.8	17.1	21.4	4.8	0.9 (?)		0.9
10020,40	52.9	13.5	28.5	2.9	1.7 (?)	<0.1	0.6
10057,35	50.9	15.7	19.2		<0.1	3.3	10.8
10071,28	58.3	14.7	21.7		0.8	2.7	2.0
10072,36	59.4	14.8	20.4		0.2 (?)	3.7	1.5

cally homogeneous, tan in color, and weakly anistropic with white-light reflectivity values from 18 to 20 percent. Many of them are mantled by ilmenite, in contrast to occurrences in terrestrial lavas, where all similar overgrowths are observed to be titanomagnetite. Spinel inclusions in olivine and pyroxene in 10020,40 are not mantled. In terrestrial rocks Cr-spinel is one of the earliest minerals to crystallize, whereas in meteorites it is always later than olivine and usually later than pyroxene (*4*). These spinels (Table 1) have compositions unlike any previously reported, and for purposes of comparison may be regarded either as Cr-rich titanomagnetites (23.5 percent Cr_2O_3) or Ti-rich chromites (20.9 percent TiO_2). Terrestrial titanomagnetites contain between 0.01 percent and 0.07 percent Cr_2O_3 (*5*). Chromites generally have rather small concentrations of TiO_2, although both rutile (*4*, *6*) and ilmenite (*4*, *7*) have been observed as exsolution intergrowths. Among terrestrial chromites those richest in TiO_2 are usually found in basaltic lavas and range between 1.3 and 2.5 percent TiO_2 (*8*). An unusual occurrence in the Bushveld, however, has a reported TiO_2 content of 12.8 percent (*9*). A meteoritic chromite analyzed by Buseck and Keil (*6*) contains 2.9 percent TiO_2. A complete solid solution exists between magnetite (Fe_3O_4) and chromite ($FeCr_2O_4$) and also between magnetite (Fe_3O_4) and ulvöspinel (Fe_2TiO_4). Although a solid solution series has not been experimentally demonstrated between Fe_2TiO_4 and $FeCr_2O_4$, our analysis of the chromiferous ulvöspinel in rock 10020 strongly suggests that such a series exists, confirming the suggestion of Legg (*7*). The absence of alteration or exsolution products in the spinel is indicative of relatively rapid cooling and low oxygen fugacity.

Ilmenite is generally euhedral, although coarse skeletal crystals with trapped pyroxene, metallic iron, and troilite are present in specimen 10047. Fine skeletal ilmenite in large concentration is also found in partly devitrified glass spheres and fragments in the breccias. Ilmenite is generally homogeneous, but some grains contain lamellae of rutile <10 μm thick oriented along $\{01\bar{1}2\}$ and lensoidal rods of spinel along $\{0001\}$. The secondary spinel and rutile invariably coexist within ilmenite, and they are often intimately associated (Fig. 2). Both spinel and a second generation of ilmenite have been observed within the rutile, suggesting that the rutile was iron-enriched when it crystallized. The textures of these intergrowths suggest that the phases are interrelated by a complex rather than a simple exsolution process with possibly one phase triggering nucleation and growth of the other. Glass or silicate inclusions and contacts with metallic iron or troilite appear to have promoted exsolution. Such intergrowths in ilmenite have not been reported in terrestrial rocks but have been observed in meteorites (*6*). Growth of rutile in ilmenite is generally the result of oxidation, but Ramdohr (*10*) has suggested that reduction could also cause the generation of rutile by the breakdown of ilmenite in environments of low oxygen fugacity. However, the reaction

$$2FeTiO_3 \rightarrow 2TiO_2 + 2Fe + O_2$$

liberates free iron, and this was not observed in the lunar ilmenite. The rutile intergrowths have a texture suggesting exsolution rather than alteration, inasmuch as they are oriented parallel to $\{01\bar{1}2\}$ and have well-defined contacts that pinch at the intersection of two or more lamellae.

Table 2. Electron-probe analyses of iron-titanium oxides and olivine.

Substance	Section 10020,40			Section 10071,28	
	Olivine	Chromian ulvöspinel	Ilmenite	Ilmenite	Magnesian ferropseudobrookite
			Percent by weight		
SiO_2	37.5				
TiO_2	0.09	20.9	53.9	52.8	73.4
Al_2O_3	0.05	8.61	0.11	0.15	1.62
Cr_2O_3	0.21	23.5	1.30	0.59	2.15
FeO*	25.5	42.1	41.9	44.2	15.3
MnO	0.30	0.25	0.47	0.32	0.08
MgO	36.5	4.23	2.59	2.06	7.70
CaO	0.33	0.03	0.07	0.01	0.01
V_2O_3	<0.01	0.4	<0.3	<0.3	<0.5
CoO	<0.03	<0.03	<0.03	<0.03	<0.02
NiO	<0.01	<0.01	<0.01	<0.01	<0.01
CuO	<0.01	<0.01	<0.01	<0.01	<0.01
ZnO	<0.01	<0.01	<0.01	<0.01	<0.01
ZrO_2	<0.10	<0.10	<0.10		
Total	100.5	100.0	100.3	100.1	100.3
			Atomic proportions		
	O = 4	O = 4	O = 3	O = 3	O = 5
Si	0.989				
Ti	0.002	0.541	0.995	0.987	1.969
Al	0.001	0.349	0.003	0.004	0.068
Cr	0.004	0.638	0.025	0.012	0.061
Fe	0.561	1.213	0.860	0.919	0.456
Mn	0.007	0.007	0.010	0.007	0.007
Mg	1.433	0.217	0.095	0.076	0.410
Ca	0.009	0.001	0.002		
V		0.011			
Totals	3.006	2.977	1.990	2.005	2.966

*Total Fe as FeO.

Electron-probe microanalyses of two optically homogeneous ilmenite grains (Table 2) in rocks 10020,40 and 10071,28 show the presence of considerable MgO and Cr_2O_3. Ilmenite from the Farmington chrondrite (*6*) in which 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 $Fo_{72}Fa_{28}$ (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 ferropseudobrookite and chromian ulvöspinel, and (iii) exceptionally high Cr in the olivine, believed to be present as Cr^{2+}.

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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 dysanalyte. Dysanalyte 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 μm especially the magnetic ones and those denser than 4.03 were thoroughly studied. Hence we