

## Spinel-Group Minerals and Ilmenite in Apollo 15 Rake Samples

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### Abstract

Spinel-group minerals and ilmenite in 28 mare basalts (pyroxene-phyric basalts, olivine-phyric basalts, olivine microgabbros, feldspathic microgabbros, and feldspathic peridotites), 3 rocks of high-alumina basalt and 2 of ANT composition from the Apollo 15 rake samples were analyzed with an electron microprobe. In mare basalts chromite is usually early, euhedral, and often included within olivine. Later chromite often has irregular outlines (resorption), and is often mantled by ulvöspinel, which also occurs as a groundmass mineral. Ilmenite crystallizes relatively late. The compositional gap between chromite and ulvöspinel and the change in compositional trend is most pronounced in pyroxene-phyric basalts, smaller in olivine-phyric basalts and olivine microgabbros, and absent in feldspathic peridotites; feldspathic microgabbro has only ulvöspinel. Ilmenite is least magnesian in pyroxene-phyric basalts, intermediate in olivine-phyric basalts and olivine microgabbros, and most magnesian in feldspathic peridotites, with the feldspathic microgabbro being variable. Three rocks of high-alumina basalt composition have either spinel, chromite, or ulvöspinel. Ilmenite is high in MgO in spinel- and chromite-bearing rocks, but low in the ulvöspinel-bearing rock. Rocks of ANT composition have chromite, some with high Fe/(Fe + Mg). Cr<sub>2</sub>O<sub>3</sub> in these chromites increases with increasing Fe/(Fe + Mg), in contrast to mare basalts, probably as the result of simultaneous crystallization with early plagioclase, rather than with early olivine alone, as in mare basalts. The spinel-group mineral relationships in mare basalts are more satisfactorily explained by the pyroxene peritectic hypothesis than by the miscibility gap hypothesis; comparison of pyroxene zoning trends with spinel compositions in pyroxene-phyric rocks indicates the existence of a time gap between crystallization of chromite and ulvöspinel. Compositionally, spinel-group minerals and ilmenite can be correlated to the bulk composition of the melts from which they crystallized; high MgO content of ilmenite is not the result of crystallization at high pressures.

### Introduction

Mineralogy, petrology, and chemistry of 33 rake samples of igneous origin from Apollo 15 were studied to gain a clearer understanding of their petrogenesis. One aspect of this study was concerned with textural and chemical relationships of spinel-group minerals and ilmenite within and between rocks. Availability of other mineralogical and petrological data on these rocks (Dowty, Prinz, and Keil, 1973b; Dowty, Keil, and Prinz, 1974b) allows further insight into the significance of the spinel-group minerals and ilmenite data. Rocks studied are 28 mare basalts (6 pyroxene-phyric basalts, 7 olivine-

phyric basalts, 12 olivine microgabbros, 2 feldspathic peridotites, 1 feldspathic microgabbro), 3 rocks of high-alumina basalt (KREEP) and 2 of ANT composition.

The purposes of this study are: (1) to recognize the textural and compositional characteristics of spinel-group minerals and ilmenite in these rocks; (2) to relate these characteristics to the petrologic histories of the rocks; and (3) to compare these results with other studies.

### Methods of Study

Polished thin sections were studied optically in transmitted and reflected light to determine textural characteristics such as zoning, mantling of one spinel over another, paragenesis, *etc.* Minerals were analyzed with an ARL EMX-SM electron microprobe using mineral and synthetic standards. Nine elements (Si, Ti, Al, Cr, V, Fe, Mn, Mg, Ca) were

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determined, and instrumental (Keil, 1967) and differential matrix effect corrections (Bence and Albee, 1968; Albee and Ray, 1970), were made. Only a few representative analyses are presented here; for complete analyses see Nehru *et al* (1973), and Dowty *et al* (1973a). Because of the correction uncertainties, vanadium is reported uncorrected for the effect of overlap of the  $TiK\beta$  with the  $VK\alpha$  peak (Snetsinger, Bunch, and Keil, 1968). We estimate that the  $V_2O_3$  contents in ilmenite and ulvöspinel are too high by approximately 0.3 and 0.15 percent, respectively.

### Presentation of Data

The Apollo 15 rake samples are from three locations, namely Station 2, about 1 km NE of the St. George crater rim and about 1/2 km SW of the Elbow crater rim (15100 series); Spur crater at Station 7 (15300 series); and Station 9a, just East of Hadley Rille rim (15600 series).

The mare basalts were classified by Dowty *et al* (1973b) as pyroxene-phyric basalts (15116, 15118,

15125, 15666, 15682, 15684), olivine-phyric basalts (15105, 15607, 15647, 15665, 15669, 15676, 15678), olivine microgabbros (15610, 15613, 15615, 15617, 15620, 15623, 15633, 15641, 15643, 15651, 15663, 15672), feldspathic peridotites (15385, 15387), feldspathic microgabbro (15388). Rocks 15356, 15359, 15382 are of high-alumina basalt (Prinz *et al*, 1973b) or KREEP composition (Meyer *et al*, 1971) and are described by Dowty *et al* (1972a) and Hlava *et al* (1973). Two samples studied belong to the ANT suite (Prinz *et al*, 1973b), namely anorthositic norite 15308 (Dowty *et al*, 1972a; Hlava *et al*, 1973) and anorthosite 15362 (Dowty, Keil, and Prinz, 1972b).

Spinel group mineral data are plotted on an atomic percent basis as cations per 32 oxygens against the  $Fe/(Fe+Mg)$  ratio (Figs. 1-7). There, spinel plots to the extreme left, chromite to the left, and ulvöspinel to the right. Compositions are expressed as five end members, or molecules: chromite,  $FeCr_2O_4$  (Cm); picrochromite,  $MgCr_2O_4$  (Pc); spinel,  $MgAl_2O_4$  (Sp); hercynite,  $FeAl_2O_4$

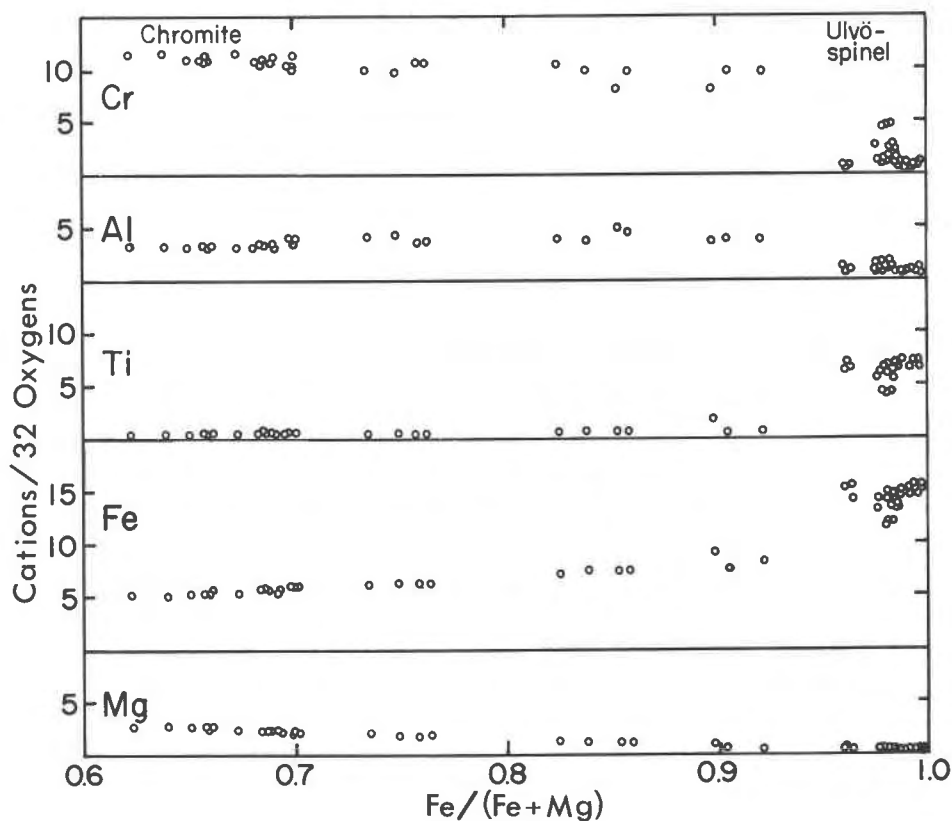


FIG. 1. Plot of  $Fe/(Fe + Mg)$  against cations/32 oxygens for Cr, Al, Ti, Fe, Mg (atomic percent) for spinel-group minerals of Apollo 15 pyroxene-phyric mare basalt rake samples.

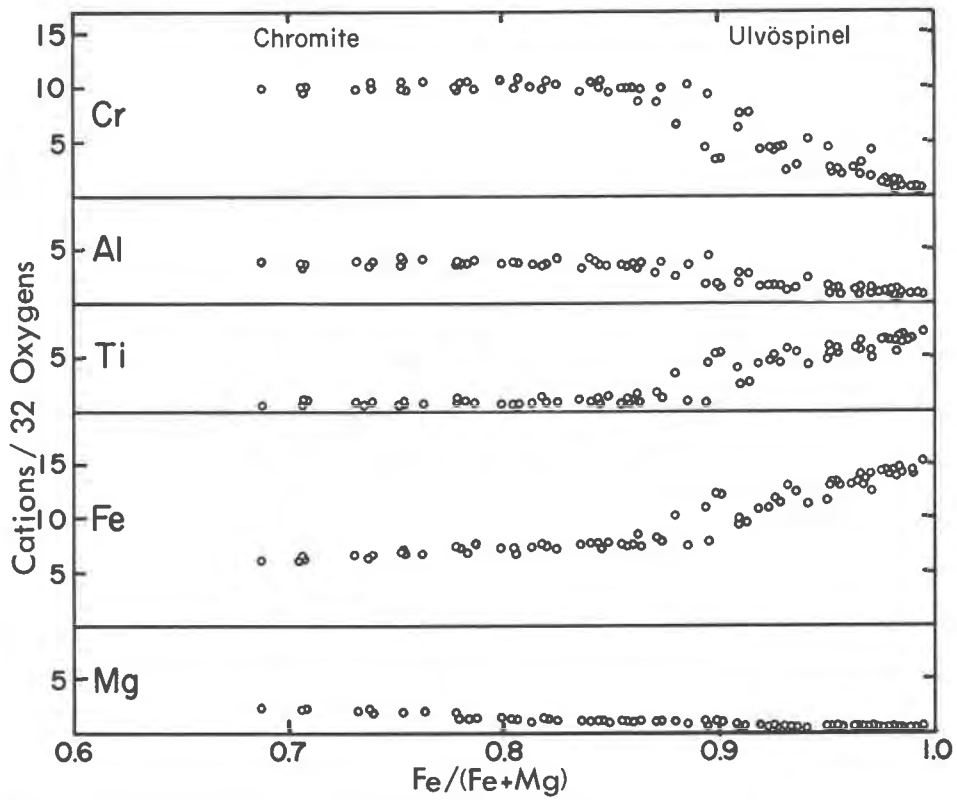


FIG. 2. Plot of  $Fe/(Fe + Mg)$  against cations/32 oxygens for Cr, Al, Ti, Fe, Mg (atomic percent) for spinel-group minerals of Apollo 15 olivine-phyric mare basalt rake samples.

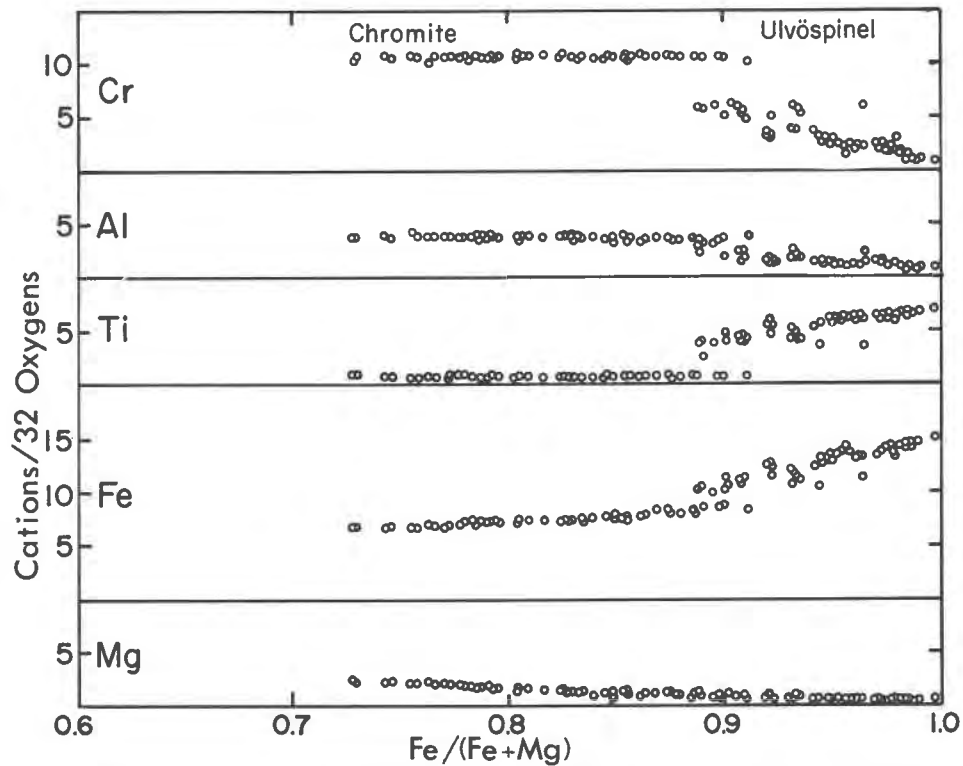


FIG. 3. Plot of  $Fe/(Fe + Mg)$  against cations/32 oxygens for Cr, Al, Ti, Fe, Mg (atomic percent) for spinel-group minerals of Apollo 15 olivine microgabbro mare basalt rake samples.

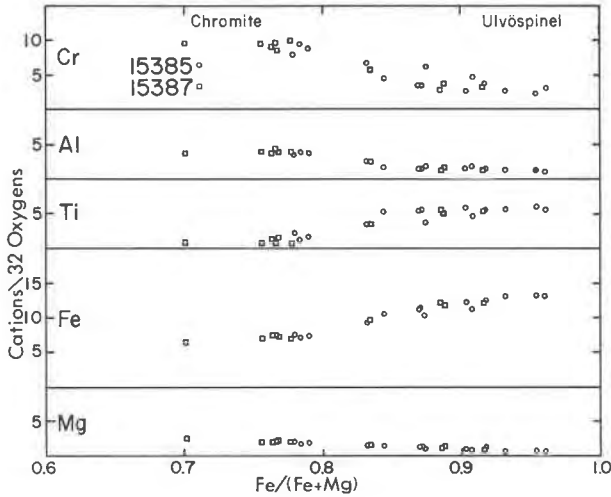


FIG. 4. Plot of Fe/(Fe + Mg) against cations/32 oxygens for Cr, Al, Ti, Fe, Mg (atomic percent) for spinel-group minerals of Apollo 15 feldspathic peridotite mare basalt rake samples.

(Hc); and ulvöspinel,  $Fe_2TiO_4$  (Uv). Terminology is as follows: chromite is used for the spinel-group mineral rich in Cm; ulvöspinel for those rich in Uv; and spinel for those rich in Sp. One end member is always dominant in lunar spinel-group minerals, but all contain other end members, and if the secondary component is stressed in the description it is used as a modifier (*e.g.*, Cm-rich ulvöspinel).

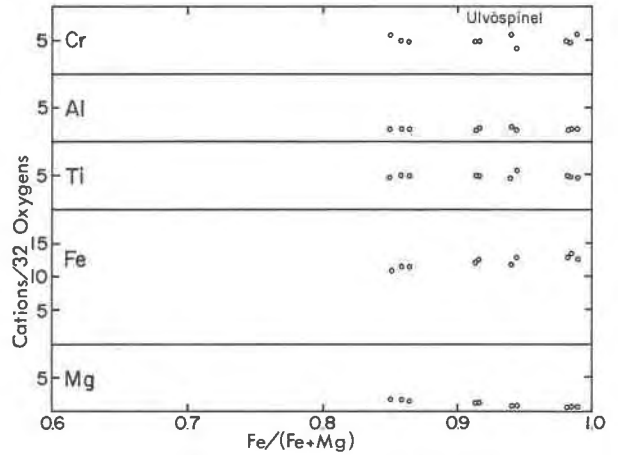


FIG. 5. Plot of Fe/(Fe + Mg) against cations/32 oxygens for Cr, Al, Ti, Fe, Mg (atomic percent) for spinel-group minerals in Apollo 15 feldspathic microgabbro mare basalt rake sample.

**Textural Relationships**

In mare basalts, chromite grains are usually small (a few microns), although some are as large as 300 microns. Uv-rich chromite grains are generally larger in size than the Cm-rich ones. Smaller chromite grains included within early minerals, commonly olivine, are usually euhedral but larger, more Uv-rich chromite, which is generally found in the

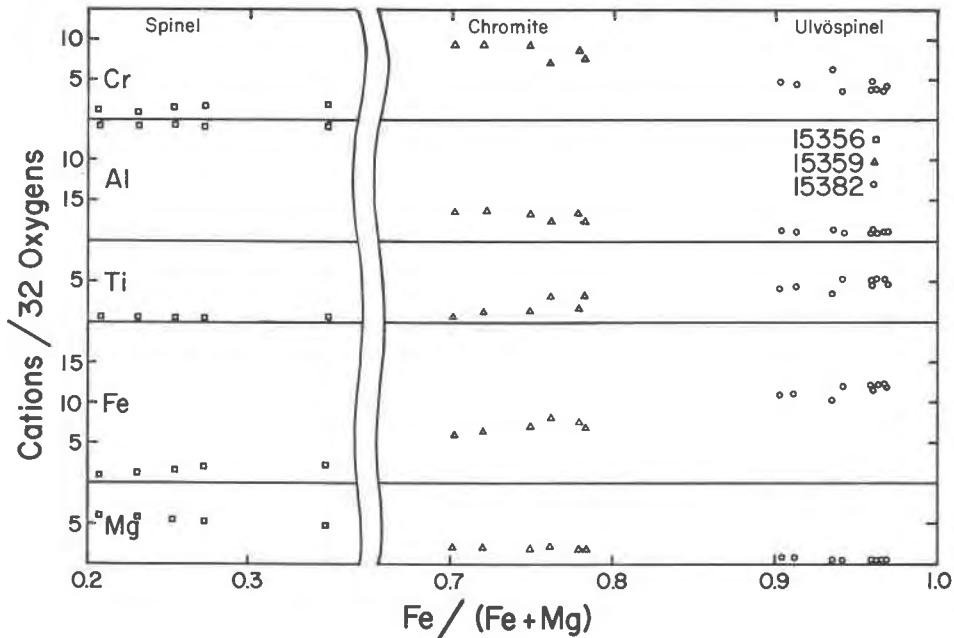


FIG. 6. Plot of Fe/(Fe + Mg) against cations/32 oxygens for Cr, Al, Ti, Fe, Mg (atomic percent) for spinel-group minerals of high-alumina basalt Apollo 15 rake samples.

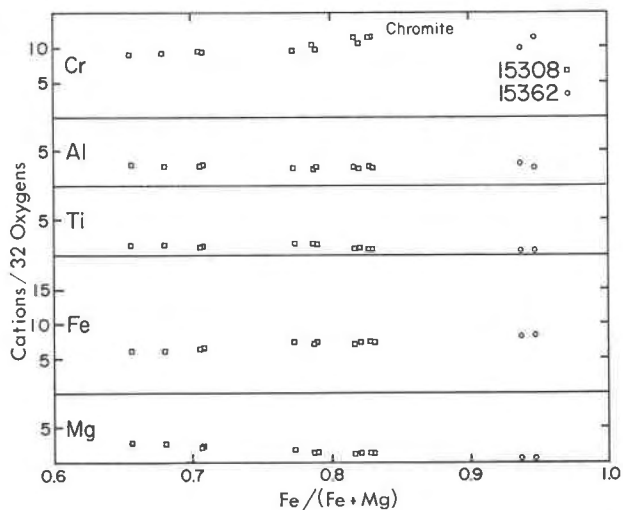


FIG. 7. Plot of  $\text{Fe}/(\text{Fe} + \text{Mg})$  against cations/32 oxygens for Cr, Al, Ti, Fe, Mg (atomic percent) for spinel-group minerals of ANT rock Apollo 15 rake samples.

groundmass, may have irregular or rounded outlines. Cm-rich euhedral chromite is compositionally homogeneous, whereas Uv-rich chromite is commonly zoned to more Uv-rich borders.

Chromite is often mantled by ulvöspinel of varying Cm content. The boundary between the chromite core and ulvöspinel mantle may be sharp (*e.g.*, 15116, 15623, 15633, 15665) or gradational (*e.g.*, 15607, 15647). Sometimes both types of boundary relationships are found within the same rock (*e.g.*, 15617, 15641, 15643). Mantles are often zoned outwards toward Uv-rich compositions, but mantles with gradational boundaries are generally inhomogeneous due to irregularities on the outer surface of the chromite.

Ulvöspinel is late in the order of crystallization and, when not mantling chromite, occurs as anhedral ground mass grains and along grain boundaries of major minerals. It is often intergrown with ilmenite and, sometimes, contains lamellae of ilmenite. Metallic Ni-Fe and troilite are often associated with ilmenite and ulvöspinel.

Textural relationships indicate that in mare basalts, chromite is the earliest spinel-group mineral to form, followed by olivine or pyroxene. Large irregular or skeletal ilmenite and ulvöspinel grains form relatively late, either as mantles on earlier chromite or as individual crystals. Much of the ilmenite and ulvöspinel forms very late in residual melt areas. Ulvöspinel may break down into lamellar ilmenite and metallic Ni-Fe. Ilmenite also forms

as plates in silicate-melt inclusions trapped in olivine crystals. The rather distinct occurrences of chromite and ulvöspinel and the fact that chromite not included in relatively early phases (olivine, Mg-rich pyroxene) is often resorbed, even when mantled by ulvöspinel, suggests a possible time gap between the formation of the two minerals.

Of the three rocks of high-alumina basalt composition, only 15382 has igneous texture. The others are brecciated, but the restricted range of mineral compositions indicates that they may have been largely derived from single rocks. Ulvöspinel and ilmenite in 15382 generally occur in residual areas, and chromite is absent. Rock 15356 has only spinel, and 15359 contains chromite and Cm-rich ulvöspinel, with ilmenite in both. These phases are present as small grains in the brecciated texture.

The two ANT rocks are shock metamorphosed. In cataclastic anorthosite 15362, only two small grains of chromite were found, each in contact with pyroxene. Small grains of ilmenite occur along grain boundaries of plagioclase. Anorthositic norite 15308 has small grains of chromite and ilmenite, but recognition of any igneous textures is impossible because the rock appears to have been partly melted by shock. On large ilmenite grain is intergrown with Zr-armalcolite, armalcolite, and chromite.

### Compositional Relationships of Spinel Group Minerals

#### Pyroxene-Phyric Basalts

Pyroxene-phyric basalts, in order of decreasing cooling rate, are 15125, 15666, 15682, 15118, 15684, and 15116 (Dowty *et al.*, 1974b). Chromite compositions appear to change systematically in this sequence, although there is some overlap:  $\text{Fe}/(\text{Fe} + \text{Mg})$ , Al, and Ti increase and Cr decreases (Dowty *et al.*, 1973a).

Chromite has very high Cm and Pc but low Uv contents (Fig. 1). Within the rock sequence, chromite increases in Hc, and decreases in Sp. The restricted range of  $\text{Fe}/(\text{Fe} + \text{Mg})$  of chromite in 15125 and 15666, combined with significant increase in  $\text{Al}_2\text{O}_3$ , differs from chromite reported in most other mare basalts. Weigand and Hollister (1973) reported similar chromite in a pyroxene-phyric rock (15597).  $\text{Al}_2\text{O}_3$  is exceptionally high in chromite of 15118 (17.6, 19.0 percent). This is, to our knowledge, the most aluminous lunar chromite reported to date in a mare basalt (Table 1).

Ulvöspinel is found in all pyroxene-phyric basalts, but in 15125 the grains are too small for analysis. Ulvöspinel is generally Uv-rich and, combined with the Cm-rich nature of the chromite, the compositional gap (Fig. 1) is larger for this mare basalt group than the others: 15116 has the narrowest, and 15666 the widest compositional gap (Dowty *et al*, 1973a). Thus, there is some suggestion that the gap is narrower in the more slowly-cooled rocks.

#### Olivine-Phyric Basalts

Chromite generally has higher Fe/(Fe+Mg) than in the pyroxene-phyric basalt group (Fig. 2, Table 2) and is similar to that of Apollo 12 mare basalts (*e.g.*, Busche *et al*, 1972). Ulvöspinel is also similar to those found in Apollo 12 mare basalts. Mantling of chromite by ulvöspinel is common. Often the chromite core is homogeneous, and the ulvöspinel mantle is zoned outward toward Uv-rich compositions, with a sharp core-mantle boundary. Resorbed and rounded chromite grains without mantles have been observed in 15669.

#### Olivine Microgabbros

Chromite and ulvöspinel are compositionally similar to those in olivine basalts (Fig. 3, Table 2). Chromite is generally euhedral, small, and often

TABLE 1. Representative Electron Microprobe Analyses of Chromite and Ulvöspinel in Pyroxene-Phyric Basalt Apollo 15 Rake Samples (in weight percentages)

Sample No. Grain No.	15116,1-4 1G	15116,1-4 1K	15118,1-1 17	15125,1-2 5	15682,2-2 11
SiO <sub>2</sub>	1.00	0.84	0.65	n.d.	0.65
TiO <sub>2</sub>	3.7	20.8	4.1	2.49	3.7
Al <sub>2</sub> O <sub>3</sub>	12.0	5.0	19.0	10.4	13.5
Cr <sub>2</sub> O <sub>3</sub>	44.3	20.6	37.1	52.5	45.8
V <sub>2</sub> O <sub>3</sub>	1.03	0.62	0.51	0.99	0.76
FeO	34.2	51.1	34.7	24.4	29.5
MnO	0.31	0.39	0.19	0.32	0.32
MgO	2.01	1.16	3.3	8.2	5.9
CaO	0.51	0.40	0.29	0.11	0.38
Total	99.06	100.91	99.34	99.41	100.51
	Molecular End Members				
Cm	64.6	31.1	51.0	58.5	63.1
Pc	--	--	--	14.1	--
Hc	21.4	10.9	27.1	--	4.5
Sp	4.0	--	11.3	21.0	22.8
Uv	10.0	58.0	10.7	6.4	9.6

n.d. = not determined

Complete analyses for spinel-group minerals in pyroxene-phyric basalts in Nehru *et al* (1973).

occurs as homogeneous cores within zoned or homogeneous ulvöspinel. Rarely, small chromite grains are rounded and appear to be resorbed. Ulvöspinel sometimes has ilmenite lamellae or inclusions.

#### Feldspathic Peridotites

The two feldspathic peridotites appear to be cumulates enriched in early olivine crystals (Dowty

TABLE 2. Representative Electron Microprobe Analyses of Chromite and Ulvöspinel in Some Olivine-Phyric Basalt, Olivine Microgabbro, Feldspathic Peridotite and Feldspathic Microgabbro Apollo 15 Rake Samples (in weight percentages)

Sample No. Grain No.	Olivine-phyric Basalt and Olivine Microgabbro					Feldspathic Peridotite			Feldspathic Microgabbro	
	15610,5 20A	15669,2-2 10	15607,6 19B	15672,2-1 13B	15623,2-2 11	15385,1-1 5	15387,1-2 15	15385,1-1 9	15388,10 15	15388,10 16
SiO <sub>2</sub>	0.52	0.41	0.46	0.36	0.11	n.d.	n.d.	n.d.	0.85	1.01
TiO <sub>2</sub>	3.6	3.9	11.9	24.1	32.6	4.2	21.5	27.8	19.0	25.1
Al <sub>2</sub> O <sub>3</sub>	10.7	12.1	8.4	4.2	2.58	11.8	5.1	3.9	5.8	3.5
Cr <sub>2</sub> O <sub>3</sub>	47.1	46.8	34.2	16.3	1.28	45.6	21.9	10.8	22.9	13.9
V <sub>2</sub> O <sub>3</sub>	0.87	1.13	0.79	0.47	<0.01	0.96	0.59	0.38	n.d.	n.d.
FeO	32.8	27.6	40.8	53.4	62.7	31.6	47.1	52.5	48.1	53.3
MnO	0.35	0.36	0.36	0.32	0.31	0.38	<0.01	<0.01	0.40	0.48
MgO	2.94	7.0	2.27	1.16	0.52	5.1	2.74	3.2	1.75	1.85
CaO	0.34	0.27	0.17	0.34	0.26	0.37	0.22	0.30	0.48	0.55
Total	99.22	99.57	99.35	100.65	100.36	100.01	99.15	98.88	99.28	99.69
	Molecular End Members									
Cm	67.8	61.2	50.0	24.3	1.9	64.5	26.5	8.7	33.8	20.8
Pc	--	4.1	--	--	--	--	5.8	7.3	--	--
Hc	13.4	--	10.7	8.7	5.7	8.4	--	--	12.8	7.8
Sp	9.1	24.5	7.2	0.4	--	15.9	9.0	8.3	--	--
Uv	9.6	10.2	33.2	66.6	92.4	11.0	58.7	75.7	53.4	71.4

n.d. = not determined

Complete analyses for spinel-group minerals in all rocks in these groups in Nehru *et al* (1973).

*et al.*, 1973b). Rock 15385 has abundant small, usually euhedral chromite grains. They often form clusters and are commonly present in early olivine, but also in the groundmass. Ulvöspinel is subhedral to anhedral and is present in some of the later-formed major minerals, but mainly in the groundmass. Some ulvöspinel-ilmenite intergrowths were observed. Rock 15387 is similar to 15385 but has less chromite and more ulvöspinel.

In both rocks chromite seems to grade compositionally into ulvöspinel, and the compositional gap of the pyroxene-phyric and olivine-phyric basalts and olivine microgabbros is not apparent (Fig. 4). Some grains are intermediate in composition between chromite and ulvöspinel (Table 2). During crystallization,  $\text{Cr}_2\text{O}_3$  and MgO decrease markedly, whereas  $\text{TiO}_2$  and FeO increase sharply (Fig. 4). Chromite has a relatively low Cm percentage and ulvöspinel a relatively low Uv percentage such that titanian chromite grades into chromian ulvöspinel.

#### *Feldspathic Microgabbro*

Feldspathic microgabbro 15388 is medium coarse-grained, with subparallel pyroxene and plagioclase laths. It is unique among our Apollo 15 rake samples in that plagioclase is zoned ( $\text{An}_{94-89}$ ), and bulk FeO is low (17.2%) and  $\text{Al}_2\text{O}_3$  high (10.9%). It is low in KREEP and has a positive Eu anomaly (Laul and Schmitt, 1972). Because of the small size of the sample available for study, some of the data may not be representative of the rock.

Ulvöspinel is present in minor amounts (Fig. 5) and occurs as inclusions in ilmenite; sometimes lamellae of ilmenite are present in ulvöspinel. Textural evidence indicates that ulvöspinel crystallized later than clinopyroxene. Ulvöspinel is relatively  $\text{Cr}_2\text{O}_3$ -rich and has a wide range of MgO values (Table 2);  $\text{Fe}/(\text{Fe}+\text{Mg})$  ranges from about 0.85 to near 1.0, but the major oxides show little or no variation within this range.

#### *High-Alumina Basalts*

Rock 15382 has subophitic texture and many petrologic similarities to 14310 (Dowty *et al.*, 1972a; Hlava *et al.*, 1973). Rocks 15356 and 15359 are brecciated, but have very restricted mineral compositions, indicating that each may have been derived mainly from a single rock. They are tentatively described as monomict breccias.

Although all three rocks are of high-alumina basalt (KREEP) composition, each has distinct

spinel group minerals. Rock 15356 has only small homogeneous pink spinel grains (Fig. 6, Table 3), generally similar to those in Apollo 14 microbreccias (Roedder and Weiblen, 1972; Steele, 1972), but MgO is generally higher and FeO lower. It is also similar to spinel found in spinel troctolites from Apollo 16 (Prinz *et al.*, 1973a) and Luna 20 (Prinz *et al.*, 1973b; Brett *et al.*, 1973), although most Apollo 16 and Luna 20 spinels are richer in MgO and  $\text{Al}_2\text{O}_3$  (Sp molecule).

Rock 15359 has chromite (Table 3) with a limited range of  $\text{Fe}/(\text{Fe}+\text{Mg})$ , about 0.7-0.8 (Fig. 6). The compositional trends differ from those of chromite of most mare basalts but are similar to those of chromite and ulvöspinel from feldspathic peridotites (Fig. 4).

Ulvöspinel in rock 15382 (Table 3) is relatively high in  $\text{Cr}_2\text{O}_3$  and low in  $\text{Al}_2\text{O}_3$ . A few chromite cores within ulvöspinel were found but are too small for quantitative analysis. The core-mantle boundaries are gradational and the mantles are inhomogeneous.

#### *ANT Suite Rocks*

Chromite in ANT rocks appears to have some noteworthy compositional characteristics that distinguish it from chromite in mare basalts (Fig. 7, Table 4). In chromite from 15308,  $\text{Cr}_2\text{O}_3$  increases and  $\text{TiO}_2$  decreases as  $\text{Fe}/(\text{Fe}+\text{Mg})$  increases from about 0.65-0.85 percent (Fig. 7, Table 4). This is in marked contrast to chromite in mare basalts with similar  $\text{Fe}/(\text{Fe}+\text{Mg})$ , where  $\text{Cr}_2\text{O}_3$  either remains near-constant or decreases, and  $\text{TiO}_2$  either remains near-constant or increases (Figs. 1-4). Chromite is very low in  $\text{Al}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$  and high in  $\text{TiO}_2$  and MgO.

Cataclastic anorthosite 15362 has two chromite grains (Table 4) of very low MgO and  $\text{Al}_2\text{O}_3$  and high FeO (very high Cm, 70.0-73.2%, and very low Sp, 0.0-3.2%). The  $\text{Fe}/(\text{Fe}+\text{Mg})$ , about 0.95, is unusually high for a chromite (Fig. 7).

#### *Some Elemental Variations in Spinel Group Minerals*

Cr occupies the octahedral site and Al substitutes for it during crystallization of spinel and chromite. In spinel there is an apparent trend of increasing Al with decreasing Cr, and a suggestion of a similar trend in chromite (Fig. 8), although for chromite it is more obvious when individual rocks are considered. These phases crystallize before plagioclase and during early crystallization of olivine; hence, concentration of Al would increase in the melt (and

Cr might decrease), thus explaining the observed relationships. Ulvöspinel has a positive correlation of Cr with Al. It crystallizes later, when Ti is abundant in the melt. Ti replaces Cr and Al in the octahedral site as ulvöspinel approaches the end member composition. Plagioclase is crystallizing then, and Al may have been somewhat depleted. Cr was depleted earlier by crystallization of chromite and pyroxene and, hence, Cr and Al decrease from chromite to ulvöspinel.

A plot of Cr + Al + V vs Ti + Si shows an excellent fit to a 2:1 ratio line (Fig. 9), indicating that the total number of octahedral cations is close to the expected number throughout the series. Haggerty (1972b), when plotting Ti vs Cr + Al, found that his data consistently plotted below the 2:1 ratio line and concluded that "the B site is either deficient, or if it is indeed satisfied (16 cations/32 O<sup>2-</sup>), then at least part of the divalent cations must also exhibit octahedral coordination." Although

TABLE 3. Electron Microprobe Analyses of Spinel, Chromite, and Ulvöspinel from Three High-Alumina Basalt Apollo 15 Rake Samples (in weight percentages)

Grain No.	15356,1					15359,2					
	13	10	99	12	11	12	7 <sup>*</sup>	10A	1	11	4
SiO <sub>2</sub>	0.76	0.80	0.81	0.74	0.76	0.31	0.50	0.45	0.53	0.48	0.45
TiO <sub>2</sub>	<0.01	0.01	0.07	0.07	0.15	3.2	5.6	7.2	8.8	15.4	15.5
Al <sub>2</sub> O <sub>3</sub>	61.2	58.3	60.0	56.0	61.2	12.0	11.2	11.0	10.2	7.4	7.4
Cr <sub>2</sub> O <sub>3</sub>	6.9	10.2	8.6	10.7	6.2	47.8	47.7	43.9	39.1	33.2	32.6
V <sub>2</sub> O <sub>3</sub>	<0.01	<0.01	<0.01	<0.01	<0.01	0.65	0.58	0.60	0.54	0.54	0.47
FeO	9.8	12.3	11.7	15.3	11.0	27.5	29.0	31.5	33.7	37.9	37.6
MnO	0.01	0.03	<0.01	0.06	<0.01	0.41	0.37	0.40	0.44	0.47	0.43
MgO	20.8	18.5	19.2	16.1	20.3	6.6	6.3	5.9	5.4	5.9	6.4
CaO	0.45	0.47	0.47	0.50	0.48	0.67	0.24	0.39	0.49	0.39	0.34
Total	99.92	100.61	100.85	99.47	100.09	99.14	101.49	101.68	99.20	101.68	101.19
Molecular End Members											
Cm	7.0	10.5	8.8	11.3	6.3	66.9	54.9	54.5	55.4	31.9	30.4
Pc	--	--	--	--	--	--	9.0	5.1	--	13.6	14.5
Hc	--	--	0.1	0.1	0.3	0.1	--	--	0.6	--	--
Sp	15.4	17.6	17.5	24.3	18.2	24.5	22.1	22.0	20.6	14.9	15.0
Uv	77.6	71.8	73.6	64.3	75.1	8.5	14.0	18.4	23.4	39.6	40.1
15382,7											
Grain No.	13	11	8	9	12	14	6	16	10		
SiO <sub>2</sub>	0.85	0.91	1.08	0.99	1.02	0.88	0.95	0.93	0.84		
TiO <sub>2</sub>	18.0	21.2	21.8	22.2	22.3	23.6	23.8	24.3	24.7		
Al <sub>2</sub> O <sub>3</sub>	4.6	4.2	4.1	4.6	3.9	3.3	3.5	3.4	3.4		
Cr <sub>2</sub> O <sub>3</sub>	28.0	21.6	22.0	19.5	21.1	17.2	17.5	16.2	16.8		
V <sub>2</sub> O <sub>3</sub>	0.41	0.33	0.43	0.27	0.34	0.23	0.25	0.34	0.30		
FeO	45.4	49.3	46.7	51.0	48.3	51.9	51.9	53.1	51.0		
MnO	0.41	0.47	0.50	0.44	0.44	0.43	0.41	0.49	0.44		
MgO	1.78	1.17	2.85	0.99	2.64	1.24	1.11	1.04	1.78		
CaO	0.42	0.43	0.38	0.45	0.45	0.58	0.46	1.24	0.48		
Total	99.87	99.61	99.84	100.44	100.49	99.36	99.88	101.04	99.74		
Molecular End Members											
Cm	40.8	32.1	25.8	28.7	27.8	26.0	26.0	24.4	23.6		
Pc	--	--	6.4	--	3.0	--	--	--	1.2		
Hc	49.4	58.9	59.2	61.4	60.9	66.8	66.4	68.1	67.9		
Sp	8.4	3.4	8.7	1.3	8.3	--	2.6	--	7.3		
Uv	1.4	5.7	--	8.7	--	7.3	5.0	7.5	--		



TABLE 4. Electron Microprobe Analyses of Chromite from Anorthositic Norite (15308) and Anorthosite (15362) in Apollo 15 Rake Samples (in weight percentages)

Grain No.	15308,1											15362,1	
	2-3	2-2	1-2	1	7	5	9	8-1	8-3	6	2-4	1	2
SiO <sub>2</sub>	0.09	0.20	0.25	1.01	0.24	0.57	0.15	0.68	0.48	0.14	0.17	0.27	0.43
TiO <sub>2</sub>	3.7	4.0	4.0	5.4	6.4	6.5	7.6	7.8	7.9	8.4	9.0	3.2	3.3
Al <sub>2</sub> O <sub>3</sub>	8.4	8.5	8.7	8.7	9.7	9.8	9.2	9.3	9.6	9.1	7.3	8.2	10.0
Cr <sub>2</sub> O <sub>3</sub>	51.8	48.6	50.1	47.3	45.7	44.8	46.3	43.0	43.6	44.1	47.7	49.0	48.6
V <sub>2</sub> O <sub>3</sub>	0.43	0.41	0.37	0.38	0.54	0.56	0.49	0.49	0.51	0.55	0.44	0.90	0.83
FeO	30.2	31.3	31.1	31.9	30.2	29.3	32.9	29.3	29.0	33.5	31.2	35.4	34.9
MnO	0.36	0.34	0.35	0.33	0.30	0.35	0.32	0.26	0.26	0.35	0.36	0.43	0.39
MgO	3.8	3.6	3.6	3.9	7.0	6.8	4.9	7.7	8.5	5.5	4.7	1.13	1.31
CaO	0.12	0.12	0.10	0.14	0.22	0.36	0.32	0.23	0.23	0.24	0.12	n.d.	n.d.
Total	98.90	97.07	98.57	99.11	100.30	99.04	102.18	98.76	100.08	101.88	100.99	98.53	99.76
Molecular End Members													
Cm	70.9	70.7	71.0	67.2	56.0	53.9	56.3	46.4	44.4	54.3	48.5	73.2	70.0
Pc	1.8	--	--	--	7.5	8.8	6.1	13.9	15.8	5.9	22.6	--	--
Hc	--	4.4	1.6	0.6	--	--	--	--	--	--	--	17.9	17.9
Sp	17.5	13.9	16.7	17.7	19.8	20.2	18.3	19.2	19.5	18.3	3.6	--	3.2
Uv	9.8	11.0	10.7	14.5	16.7	17.1	19.3	22.5	20.5	21.5	25.3	8.9	8.9

n.d. = not determined

Haggerty (1972b) states that "no other elements were detected in the proportions necessary to fit the data coincidentally to the octahedral line," it is clear from our data (Fig. 9) that the observed departure from this line in his data is apparently due to his neglecting to include Si (with Ti) and V (with Cr + Al). Hence, there is no evidence that spinel group minerals are B-site deficient or that divalent cations are in octahedral coordination.

### Compositional Relationships in Ilmenite

MgO and Cr<sub>2</sub>O<sub>3</sub> are low in ilmenite of pyroxene-

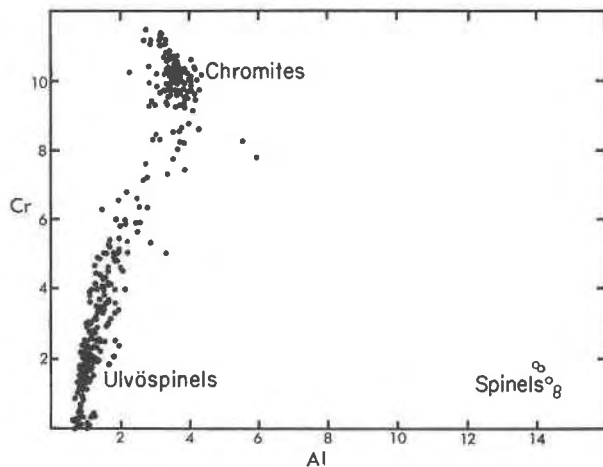


FIG. 8. Plot of Cr against Al (atomic percent) for spinel-group minerals of Apollo 15 rake samples. Spinel is shown by open circles, chromite and ulvöspinel by filled circles.

phyric basalts (Figs. 10, 11); 15125 has no measurable ilmenite. These oxides are somewhat higher in ilmenite from olivine-phyric basalts and olivine microgabbros and appreciably higher in ilmenite from feldspathic peridotites, possibly indicating crystallization of ilmenite in a more magnesian melt, portion of a melt, or early crystallization when Mg/Fe was highest. Since feldspathic peridotites have relatively low bulk TiO<sub>2</sub>, ilmenite is not likely to crystallize early and, hence, the former hypothesis is preferred. Ilmenite in feldspathic microgabbro 15388 has the widest variation of MgO and Cr<sub>2</sub>O<sub>3</sub> of any of the mare basalt rocks (Figs. 10, 11).

Ilmenite in rocks of high-alumina basalt composition 15356 and 15359 is uniformly high in MgO

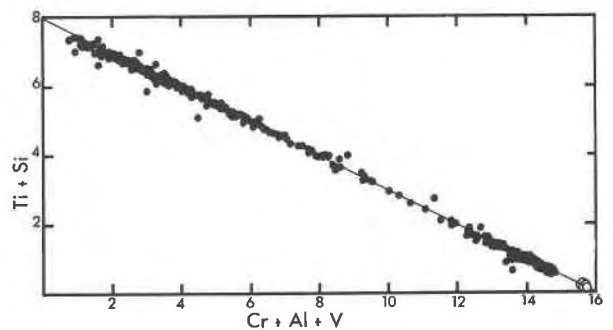


FIG. 9. Plot of Ti + Si against Cr + Al + V (atomic percent) for spinel-group minerals of Apollo 15 rake samples. Spinel is shown by open circles, chromite and ulvöspinel by filled circles.

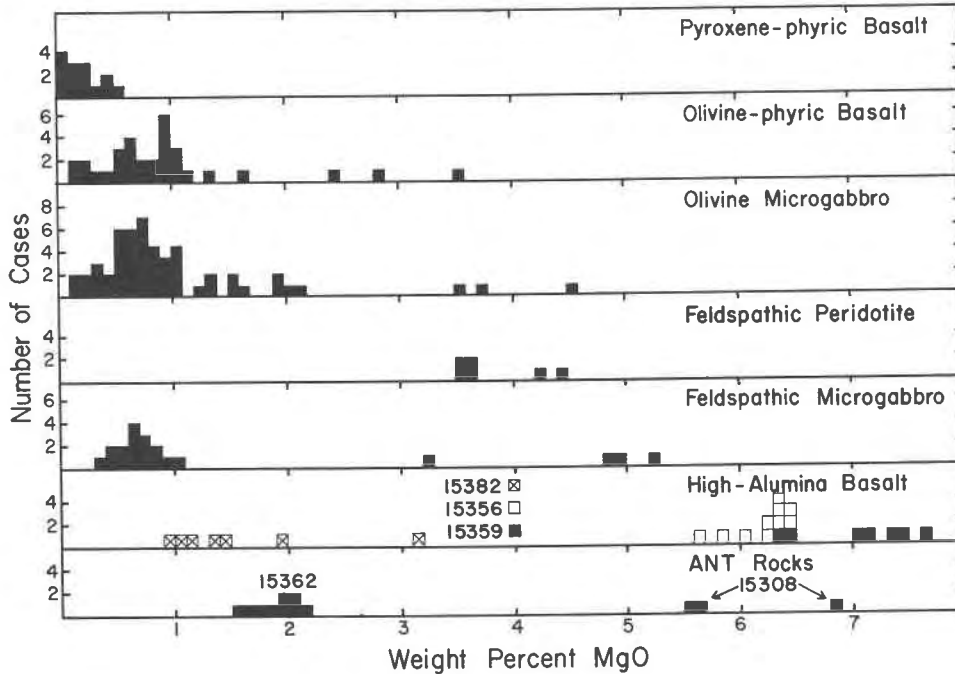


FIG. 10. Histograms of wt percent MgO in ilmenite for all groups of Apollo 15 rake samples.

(Figs. 10, 11).  $Cr_2O_3$  is within the range of mare basalts, despite the high MgO contents; these two rocks are MgO-rich (15356, 13.7%; 15359, 11.0%). Rock 15382 has ilmenite similar in MgO and  $Cr_2O_3$  to that of mare basalts (Fig. 11). The rock also has relatively low bulk MgO (7.1%) similar to mare basalt. All three rocks of high-alumina basalt composition have moderately low bulk  $Cr_2O_3$ , in spite of the high bulk MgO contents of two of them. Thus, MgO and  $Cr_2O_3$  contents of ilmenite appear to be related to the bulk compositions of the host rocks.

Ilmenite in anorthositic norite 15308 has high MgO and relatively low  $Cr_2O_3$  (Figs. 10, 11). Rock 15308 has 6.7 percent bulk MgO but, since it is

probably a cumulate, it is possible that the melt from which the ilmenite crystallized was MgO-rich. Anorthosite 15362 has ilmenite with relatively low MgO; it may have crystallized from the same type of parent melt as 15308, but at a later stage. Alternatively, the composition of the ilmenite may represent metamorphic equilibrium. The very low  $Cr_2O_3$  content of ilmenite in 15362 suggests the same alternatives.

In general, average MgO in ilmenite tends to increase with increasing  $Mg/(Mg + Fe)$  in the bulk-rock (Fig. 12). Hence, bulk-rock MgO content appears to determine the MgO content of ilmenite, rather than crystallization from ultrabasic liquids at high pressures, as suggested by Haggerty (1973).

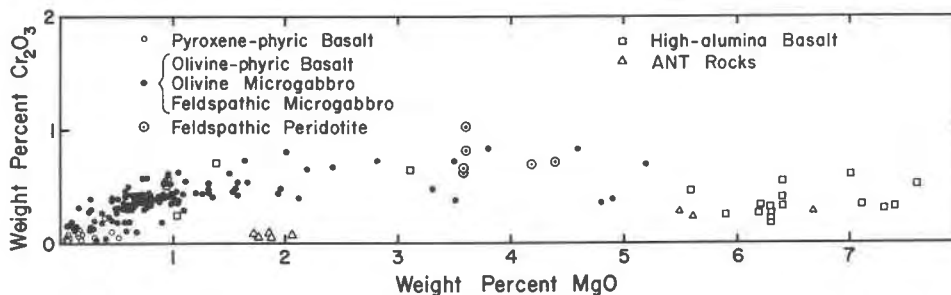


FIG. 11. Plot of wt percent MgO against wt percent  $Cr_2O_3$  in ilmenite of all groups of Apollo 15 rake samples.

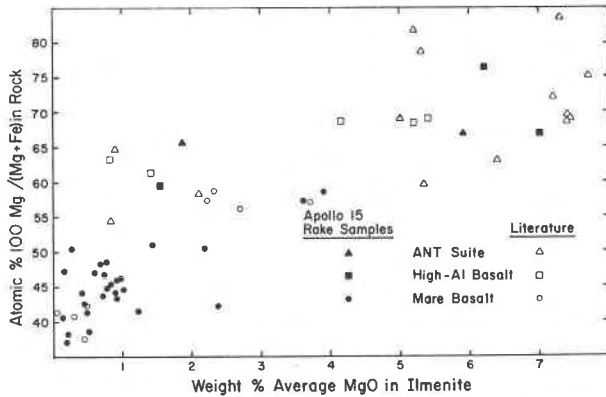


FIG. 12. Plot of average wt percent MgO in ilmenite against atomic percent 100 Mg/(Mg + Fe) in host rock for all Apollo 15 rake samples studied, and similar data selected from the literature.

Note that similar relationships have been observed by Lovering and Widdowson (1968) for terrestrial magnesian ilmenite. A number of factors may be responsible for some of the scatter in the data of Fig. 12: (1) There is sometimes a wide range in MgO content of ilmenite within single samples. (2) Some of the rocks are cumulates and, hence, mineral compositions are not necessarily related in the same way to bulk rock composition. (3) There may have been poor sampling of the small rake samples, or data from different laboratories may be difficult to compare. (4) Ilmenite crystallizes at different times and temperatures in rocks with differing TiO<sub>2</sub> contents.

### Discussion

#### *Rocks of High-Alumina Basalt and ANT Composition*

Relatively little is known of spinel-group minerals in rocks of high-alumina basalt and ANT compositions. Since none of these rocks studied here can be unambiguously interpreted as primary igneous rocks, with the possible exception of 15382, it is not clear whether the spinel-group minerals reflect igneous or metamorphic processes and/or possibly mixing of different rock compositions. Rock 15382 has igneous texture, but as in the case of 14310, it is not clear whether this is primary or reflects crystallization from a shock melt.

Compositions of chromite and ulvöspinel in 15359 and 15382 are within the range of these minerals in mare basalts. Hence, conditions of formation may have been similar to those of mare

basalts. Spinel in 15356 is compositionally similar to that from rocks of high-alumina basalt composition in Luna 20 and Apollo 14 microbreccias, its composition being as expected for this bulk rock composition (Walker, Longhi, and Hays, 1972; Prinz *et al.*, 1973b).

The wide range of compositions (spinel, chromite, and ulvöspinel) in three rocks of high-alumina basalt composition is difficult to explain without experimental data and/or further data on spinel populations in a wide variety of such rocks. Some of this variation may be due to mixing rocks of alkalic, high-alumina basalt composition with ANT rocks (Dowty *et al.*, 1972a). However, there is a good correlation of bulk-rock and spinel composition. A comparison of bulk-rock Mg/(Mg + Fe) ratio to spinel-group mineral compositions shows the following: 15356 has a ratio of 76.5 and contains spinel; 15359 has a ratio of 67.1 and has chromite; and 15382 has a ratio of 59.5 and has ulvöspinel. Melts with higher Mg/(Mg + Fe) ratios are probably more primitive in a fractionation sequence and would be expected to contain spinel. With fractionation toward melts which crystallize larger amounts of pyroxene, chromite may be the liquidus spinel. More highly fractionated melts may have relatively little chromite which may have settled out or totally reacted with the melt.

ANT group rocks contain chromite, apparently having a trend of increasing Cr<sub>2</sub>O<sub>3</sub> (and decreasing TiO<sub>2</sub>) as Fe/(Fe + Mg) increases, a reverse trend to chromite in mare basalts. Similar trends are shown by chromite in Apollo 16 ANT rocks (unpublished data). One of the principal factors for the differences in compositional trends for chromite from ANT rocks and mare basalts may be that mare basalts did not crystallize plagioclase until relatively late, and thus Al and Al/Cr probably increased considerably during early crystallization of olivine and chromite. Trends in the feldspar-rich ANT rocks would be different, especially in rocks which preserve some of their cumulate history as compared to impact melt rocks which crystallize from a much more feldspathic melt.

#### *The Chromite-Ulvöspinel Compositional Gap*

The reason for the distinct compositional gap between Cm-rich and Uv-rich members of the spinel-group mineral series of some lunar rocks (particularly well-seen in Cr vs Ti plots), and the concomitant change in compositional trend in relations of

these and other elements, remains controversial, despite much discussion on the subject. Of several hypotheses proposed to explain this gap (reviewed previously by Busche *et al.*, 1972), two are considered here. The first involves a solvus<sup>3</sup> in the spinel group (chromite-ulvöspinel) series itself, where a continuous solid-liquid loop in the chromite-ulvöspinel system is required, descending from chromite to ulvöspinel, with a solvus whose crest is below the solidus. In some rocks (*e.g.*, most Apollo 12 and 15 mare basalts), actual crystallization temperature would be reduced sufficiently by the addition of other components so that the solvus would be intersected, producing a compositional gap; in other rocks of different bulk compositions, crystallization temperature would be sufficiently high that the solvus would not be intersected, and spinel compositions could lie within the compositional gap (*e.g.*, most Apollo 11 rocks), or vary almost continuously from chromite to ulvöspinel (*e.g.*, 12051; Busche *et al.*, 1972). The critical factor in this hypothesis is not whether the solvus exists (it evidently does; see below) but whether or not it exists at a sufficiently high temperature that it can be intersected during the crystallization of these rocks. The relationship in this hypothesis involves, at equilibrium, a peritectic reaction of chromite with liquid to form ulvöspinel. Once a spinel-group mineral had begun to crystallize, it would continue to do so; the compositional gap between chromite and ulvöspinel would occur instantaneously, and if crystallization was sufficiently rapid that there was no actual reaction, ulvöspinel could simply begin to form rims on chromite crystals.

The second hypothesis involves a reaction (under equilibrium conditions) of chromite, and probably olivine as well, to form a chromian pyroxene (reviewed in Busche *et al.*, 1972). After this reaction, the liquid would crystallize chromian pyroxene without spinel for a time, and would then recommence spinel-group mineral crystallization, this time ulvöspinel, because Cr would have been depleted in the melt by pyroxene crystallization, and Ti in the melt would have continually increased. The behavior of spinel-group minerals according to this hypothesis is an example of recurrent crystallization, and it might be illuminating to consider a system in which recurrent crystallization is known to be a

possibility, and which could therefore be analogous. The system forsterite-fayalite-silica (Bowen and Schairer, 1935) fulfills the requirements for analogy, and also must be important in its own right in elucidating the major-phase behavior of the same rocks. In the more Mg-rich parts of this system, the relationship between olivine and pyroxene is peritectic, but this changes to cotectic at higher iron contents and lower temperatures. Bowen and Schairer (1935) give several examples of liquid compositions which, under either equilibrium or fractionation conditions, begin to crystallize olivine alone, then crystallize pyroxene alone, then crystallize both together. We suggest that the behavior of spinel-group minerals could be, in a sense, analogous to that of olivine in this system; the early spinel-group mineral, crystallizing alone (actually, with olivine), would be chromite, and the one crystallizing later (with pyroxene) would be ulvöspinel. The relation between the spinel-group mineral system and the olivine-silica system would, in fact, be even closer than an analogy; the proposed chromite-pyroxene reaction would probably occur simultaneously with the olivine-pyroxene reaction (the chromian pyroxene molecule could not, of course, exist by itself), and perhaps the later ulvöspinel would also reappear simultaneously with the later olivine, although this latter relation is more conjectural.

The critical distinction between the two hypotheses discussed here lies in the fact that there is necessarily continuous crystallization of spinel-group minerals in the chromite-ulvöspinel peritectic (solvus) hypothesis, whereas there is a time-gap between crystallization of chromite and ulvöspinel in the chromite-pyroxene peritectic hypothesis; during this time-gap, pyroxene would be crystallizing in the absence of a spinel-group mineral phase. The question of a time-gap has been discussed previously (*e.g.*, Cameron, 1971; Busche *et al.*, 1972), and some textural evidence for its existence has been cited. Our study of the textures of the Apollo 15 mare basalts suggests that there is a time gap; however, such textural considerations are rather subjective and may not be considered conclusive. More concrete evidence is obtained from compositional trends in pyroxene of certain rocks. The finest-grained and, presumably, most rapidly cooled pyroxene-phyric basalt, 15125 (Dowty *et al.*, 1974b) contains early chromite crystals and pyroxene phenocrysts in a very fine, almost glassy groundmass.

<sup>3</sup> We use the term "solvus" rather than "miscibility gap" in order to avoid confusion with the distinct concept of a compositional gap.

Many chromite grains are included in the pigeonite cores of the pyroxene phenocrysts, indicating that chromite began to crystallize before very much pyroxene had formed. Grains of ulvöspinel large enough to analyze quantitatively were not found, although some very fine ulvöspinel is optically discernible in the groundmass; apparently, ulvöspinel crystallized during the groundmass stage after the phenocrysts had been essentially completely formed.

The composition of the liquid—at least with respect to Cr, Al, and Ti—is reflected in these rocks by the zoning in the pyroxene phenocrysts (Bence and Papike, 1972; Hollister, 1972). The zoning trends of the pyroxene phenocrysts in 15125 (Fig. 13, see also Dowty *et al.*, 1974b) show that from the beginning of pyroxene crystallization to the point at which groundmass crystallization began, as represented by the edges of the phenocrysts and the ends of the trends in Figure 13, there were very drastic changes in the concentrations of Cr, Al, and Ti in the liquid. During this time, Cr decreased and Ti and Al increased, each by factors of 3 to 20, judging by the concentrations in the pyroxene. There is no reason to believe that changes in the partition coefficients of these elements between pyroxene and melt are responsible for any significant parts of these trends, especially in the augite part of the pyroxene wherein Ca content is approximately constant. The Fe/(Fe + Mg) ratio in the liquid also changed a great deal in this interval.

On the other hand, composition of chromite in this rock is essentially constant with respect to

Cr, Al, Ti, and Fe/(Fe + Mg) ratio (Fig. 13). It is quite unreasonable to believe that the changes in liquid composition shown by the pyroxene phenocrysts would not also be reflected in the chromite, and the conclusion is inescapable that chromite crystallized only for a relatively short time in this rock, probably before a significant amount of pyroxene had formed. The interval between chromite crystallization and the onset of groundmass crystallization, before which no ulvöspinel crystallized, represents a time-gap in the crystallization of spinel-group minerals. This time gap must correspond roughly to the formation of the pyroxene phenocrysts, and is therefore a substantial part of the crystallization history of the rock, because the phenocrysts amount to almost 50 percent by volume (Dowty *et al.*, 1974b). The existence of a time gap is not consistent with hypotheses involving a solvus in the spinel system itself.

A further strong objection to the chromite-ulvöspinel peritectic (solvus) hypothesis is provided by the results of synthesis experiments in the spinel system (Muan, Hauck, and Löfall 1972). These experiments establish the existence of a chromite-ulvöspinel solvus, but it appears that its crest at the Cr/Al and Fe/Mg compositions of the lunar spinel-group minerals could not be above about 800°C. Phase equilibrium studies on Apollo 12 and 15 rock compositions suggest that crystallization occurred in the approximate interval 1200-1050°C (Green *et al.*, 1971; Biggar *et al.*, 1971). The lower value from these equilibrium experiments is probably

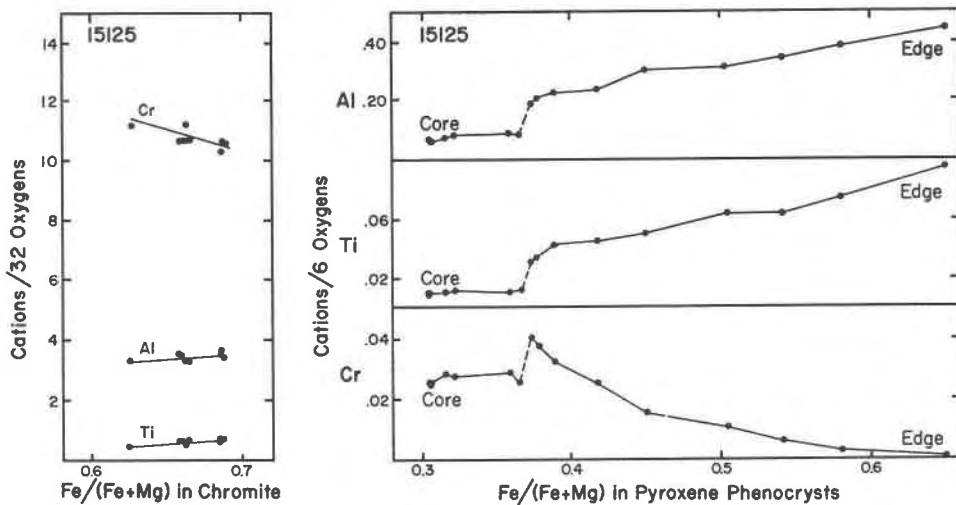


FIG. 13. Plots of Fe/(Fe + Mg) in chromite and pyroxene against cations/32 oxygens for Al, Ti, Cr (atomic percent) for pyroxene-phyric Apollo 15 mare basalt rake sample 15125.

a bit high, because homogenization experiments on rock 12021 (Ross, Huebner, and Dowty, 1973) showed that some iron-rich pyroxene crystallized at temperatures as low as 950°. However, if we consider that in order to produce a compositional gap in the spinel-group mineral systems, the solvus must have been intersected at a fairly early stage in crystallization (in 15125, spinel-group minerals would have to stop crystallizing at about the same temperature that early pigeonite formed, at about 1175°C), it seems that there is still a discrepancy of several hundred degrees. It has been suggested that supercooling may have caused the solvus to be intersected (Haggerty, 1972a), but the required degree of supercooling seems unreasonably high.

The above considerations seem to rule out the solvus hypothesis, and although they do not provide direct refutations of some other hypotheses, we consider that the chromite-pyroxene peritectic hypothesis has distinct advantages over any of the latter as an explanation for the chromite-ulvöspinel compositional gap. Changes in the liquidus slopes, as suggested by Weill *et al* (1971) might also produce compositional trends such as those in 15125, but such changes would have to be very extreme, and this hypothesis seems intrinsically rather unlikely. The texture of the pyroxene-phyric rocks might suggest a two-stage cooling history which also, as proposed by Weill *et al* (1971), could be a possible explanation for the compositional gap. The texture, however, may be misleading, and these rocks probably originated in a single-stage cooling process (Dowty *et al*, 1974b). One of the reasons, in fact, is the correlation of the trend in chromite compositions with the coarseness of the groundmass crystals, as noted above, which suggests a continuous cooling process in each rock.

Haggerty (1972b) suggested that the difference between the normal spinel structure in chromite and the inverse structure in ulvöspinel might be an explanation for the gap. First, the distinction between normal and inverse in this instance is purely formal; the *A* site occupancy is essentially the same in both chromite and ulvöspinel (Fe with some Mg), and the disorder of Fe and Ti in the *B* site is no more likely to cause instability in the intermediate members of the solid solution series than it is in pure ulvöspinel. Second, such crystal-chemical factors must be reflected in the phase relations, and do not constitute an independent explanation for the compositional gap. There would be disorder of Cr *vs*

Ti + Fe in intermediate members of the chromite-ulvöspinel series, but such disorder is present in the intermediate members of any solid-solution series, and it is precisely such factors which lead to the appearance of a solvus.

Petrologic studies on terrestrial spinel-group minerals are also consistent with a chromite-pyroxene peritectic hypothesis. Evans and Moore (1968), Gunn *et al* (1970), and Thompson (1973) have found the complete chromite-titanomagnetite series in volcanic rocks, and Cameron (1973) found a similar series in pegmatites of the eastern Bushveld complex. Although oxygen fugacities of terrestrial systems differ significantly from those in lunar systems, resulting in titanomagnetite rather than ulvöspinel, it does indicate that there is no evidence for a miscibility gap or metastable crystallization in terrestrial systems. Furthermore, Cameron (1973) points out that spinel-group minerals intermediate between chromite and titanomagnetite are absent from the normal layered part of the Bushveld complex. Irvine (1967) and Cameron (1973) review evidence that the onset of pyroxene crystallization terminated the crystallization of chromite in the main series. This is further supported by Dickey, Yoder, and Schairer (1971), who found that chromian diopside melts incongruently to chromian spinel + liquid at 1 atm.

#### Acknowledgments

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#### References

- ALBEE, A. L., AND L. RAY (1970) Correction factors for electron probe microanalysis of silicates, oxides, phosphates, and sulfates. *Anal. Chem.* **42**, 1408-1414.
- BENCE, A. E., AND A. L. ALBEE (1968) Empirical correction factors for the electron microanalysis of silicates and oxides. *J. Geol.* **76**, 382-403.
- , AND J. J. PAPIKE (1972) Pyroxenes as recorders of lunar basalt petrogenesis: chemical trends due to crystal-liquid interaction. *Proc. Third Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. 3*, **1**, 431-468.
- BIGGAR, G. M., M. J. O'HARA, A. PECKETT, AND D. J. HUMPHRIES (1971) Lunar lavas and the achondrites; petrogenesis of protohypersthene basalts in the maria lava lakes. *Proc. Second Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. 2*, **1**, 617-643.
- BOWEN, N. L., AND J. F. SCHAIRER (1935) The system MgO-FeO-SiO<sub>2</sub>. *Am. J. Sci.* **29**, 151-217.
- BRETT, R., R. C. GOOLEY, E. DOWTY, M. PRINZ, AND K. KEIL (1973) Oxide minerals in lithic fragments from Luna 20 fines. *Geochim. Cosmochim. Acta*, **37**, 761-773.
- BUSCHE, F. D., M. PRINZ, K. KEIL, AND T. E. BUNCH (1972)

- Spinel and the petrogenesis of some Apollo 12 igneous rocks. *Am. Mineral.* **57**, 1729-1747.
- CAMERON, E. N. (1971) Opaque minerals in certain lunar rocks from Apollo 12. *Proc. Second Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. 2*, **1**, 193-206.
- (1973) Unusual titanian-chromian spinels from the eastern Bushveld Complex. *Am. Mineral.* **58**, 172-188.
- DICKEY, J. S., H. S. YODER, AND J. F. SCHAIRER (1971) Chromium in silicate-oxide systems. *Carnegie Inst. Wash. Year Book*, **70**, 118-122.
- DOWTY, E., M. PRINZ, K. KEIL, AND T. E. BUNCH (1972a) Non-mare rock types in Apollo 15 rake samples (abstr.). *Abstr. Programs, Geol. Soc. Am.* **4**, 491-492.
- , K. KEIL, AND M. PRINZ (1972b) Anorthosite in the Apollo 15 rake sample from Spur Crater. *The Apollo 15 Lunar Samples*, Ed. J. W. Chamberlain and C. Watkins, Lunar Science Institute, Houston, Texas, p. 62-66.
- , G. H. CONRAD, J. A. GREEN, P. F. HLAVA, K. KEIL, R. B. MOORE, C. E. NEHRU, AND M. PRINZ (1973a) Catalogue of Apollo 15 rake samples from Stations 2 (St. George), 7 (Spur Crater), and 9a (Hadley Rille). *Spec. Publ. No. 8*, Institute of Meteoritics, Univ. of New Mexico, 75 p.
- , M. PRINZ, AND K. KEIL (1973b) Composition, mineralogy, and petrology of 28 mare basalts from Apollo 15 rake samples. *Proc. Fourth Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. No. 4*, **1**, 423-444.
- , K. KEIL, AND M. PRINZ (1974a) Igneous rocks from Apollo 16 rake samples (abstr.). *Lunar Science V*, Lunar Science Institute, Houston, Texas.
- , ———, AND ——— (1974b) Lunar pyroxene-phyric basalts: Crystallization under supercooled conditions. *J. Petrol.* (in press).
- EVANS, B. W., AND J. G. MOORE (1968) Mineralogy as a function of depth in the prehistoric Makaopuhi tholeiitic lava lake, Hawaii. *Contrib. Mineral. Petrol.* **17**, 85-115.
- GREEN, D. H., A. E. RINGWOOD, N. G. WARE, W. O. HIBBERSON, A. MAJOR, AND E. KISS (1971) Experimental petrology and petrogenesis of Apollo 12 basalts. *Proc. Second Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. 2*, **1**, 601-615.
- GUNN, B. M., R. COY-YLL, N. D. WATKINS, C. E. ABRAMSON, AND J. NOUGIER (1970) Geochemistry of an oceanite-ankaramite-basalt suite from East Island, Crozet Archipelago. *Contrib. Mineral. Petrol.* **28**, 319-339.
- HAGGERTY, S. E. (1972a) Solid solution characteristics of lunar spinels. *Carnegie Inst. Wash. Year Book*, **71**, 474-480.
- (1972b) Solid solution, subsolidus reduction, and compositional characteristics of spinels in some Apollo 15 basalts. *Meteoritics*, **7**, 353-370.
- (1973) Luna 20: mineral chemistry of spinel, pleonaste, chromite, ulvöspinel, and rutile. *Geochim. Cosmochim. Acta*, **37**, 857-867.
- HLAVA, P. F., J. A. GREEN, M. PRINZ, C. E. NEHRU, K. KEIL, E. DOWTY, AND T. E. BUNCH (1973) Apollo 15 rake sample microbreccia and non-mare rocks: Bulk rock, mineral, and glass, electron microprobe analyses. *Spec. Publ. No. 11*, Institute of Meteoritics, Univ. of New Mexico, 78 p.
- HOLLISTER, L. S. (1972) Implications of the relative concentrations of Al, Ti, and Cr in lunar pyroxenes. In *Lunar Science III*, Ed. C. Watkins, p. 344-346. The Lunar Science Institute, Houston, Texas.
- IRVINE, T. N. (1967) Chromian spinel as a petrogenetic indicator. Part II. Petrologic applications. *Can. J. Earth Sci.* **4**, 71-103.
- KEIL, K. (1967) The electron microprobe X-ray analyzer and its application in mineralogy. *Fortschr. Mineral.* **44**, 4-66.
- LAUL, J. C., AND R. A. SCHMITT (1972) Bulk and REE abundances in three Apollo 15 igneous rocks and six basaltic rake samples. *The Apollo 15 Lunar Samples*, Ed., J. W. Chamberlain and C. Watkins, Lunar Science Institute, Houston, Texas, p. 225-228.
- LOVERING, J. F., AND J. R. WIDDOWSON (1968) The petrological environment of magnesium ilmenites. *Earth Planet. Sci. Lett.* **4**, 310-314.
- MEYER, C., R. BRETT, N. J. HUBBARD, D. A. MORRISON, D. S. MCKAY, F. K. AITKEN, H. TAKEDA (1971) Mineralogy, chemistry, and origin of the KREEP component in soil samples from the Ocean of Storms. *Proc. Second Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. 2*, **1**, 393-411.
- MUAN, A., J. HAUCK, AND T. LÖFALL (1972) Equilibrium studies with a bearing on lunar rocks. *Proc. Third Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. 3*, **1**, 185-196.
- NEHRU, C. E., M. PRINZ, E. DOWTY, AND K. KEIL (1973) Electron microprobe analyses of spinel group minerals and ilmenite in Apollo 15 rake samples of igneous origin. *Spec. Publ. No. 10*, Institute of Meteoritics, Univ. of New Mexico, Albuquerque, New Mexico, 91 p.
- PRINZ, M., E. DOWTY, K. KEIL, AND T. E. BUNCH (1973a) Spinel troctolite and anorthosite in Apollo 16 samples. *Science*, **179**, 74-76.
- , ———, ———, AND ——— (1973b) Mineralogy, petrology, and chemistry of lithic fragments from Luna 20 fines: Origin of the cumulate ANT suite and its relationship to high-alumina and mare basalts. *Geochim. Cosmochim. Acta*, **37**, 979-1006.
- ROEDDER, E., AND P. W. WEIBLEN (1972) Occurrence of chromian, hercynitic spinel ("pleonaste") in Apollo 14 samples and its petrologic implications. *Earth Planet. Sci. Lett.* **15**, 376-402.
- ROSS, M., J. S. HUEBNER, AND E. DOWTY (1973) Delineation of the one-atmosphere augite-pigeonite solvus. *Am. Mineral.* **58**, 619-635.
- SNETSINGER, K., T. E. BUNCH, AND K. KEIL (1968) Electron microprobe analysis of vanadium in the presence of titanium. *Am. Mineral.* **53**, 1770-1773.
- STEELE, I. M. (1972) Chromian spinels from Apollo 14 rocks. *Earth Planet. Sci. Lett.* **14**, 190-194.
- THOMPSON, R. N. (1973) Titanian chromite and chromian titanomagnetite from a Snake River Plain basalt, a terrestrial analogue to lunar spinels. *Am. Mineral.* **58**, 826-830.
- WALKER, D., J. LONGHI, AND J. F. HAYS (1972) Experimental petrology and origin of Fra Mauro rocks and soil. *Proc. Third Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. 3*, **1**, 797-817.
- WEIGAND, P. W., AND L. S. HOLLISTER (1973) Basaltic

vitrophyre 15597: An undifferentiated melt sample. *Earth Planet. Sci. Lett.* **19**, 61-74.

WEILL, D. F., R. A. GRIEVE, I. S. MCCALLUM, AND Y. BOTTINGA (1971) Mineralogy-petrology of lunar samples. Microprobe studies of samples of 12021 and 12022; viscosities of melts of selected lunar compositions. *Proc.*

*Second Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. 2*, **1**, 413-430.

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