

## Opaque oxide mineral crystallization in lunar high-titanium mare basalts

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### Abstract

Lunar high-Ti ( $\text{TiO}_2$ , 8–14 weight percent) mare basalts include low-K ( $\text{K}_2\text{O} < 0.1$  weight percent) Apollo 11 and 17 and high-K ( $\text{K}_2\text{O} \sim 0.3$  weight percent) Apollo 11 varieties. Subdivision of low-K Apollo 11 and 17 basalts is made, primarily on the basis of trace-element data. Magmatic crystallization of opaque oxide minerals commences early, with the following characteristic assemblages:

Low-K	[	Apollo 17	Cr-ulvöspinel <sup>1</sup> + armalcolite + ilmenite
		Apollo 11	Cr-ulvöspinel + ilmenite
High-K		Apollo 11	Armalcolite + ilmenite (Cr-ulvöspinel rare or absent)

Compositions of the above minerals vary according to their textural setting. Late-stage, nearly pure ulvöspinel is also often present, especially in coarse-grained basalts. Subsolidus assemblages (1) Cr-ulvöspinel (host) + ilmenite  $\pm$  native Fe and (2) ilmenite (host) + rutile + aluminian chromite  $\pm$  native Fe and/or troilite are common in high-Ti mare basalts, particularly Apollo 17. Systematic lamellar orientation of the subsolidus oxide minerals suggests, for the most part, an origin by exsolution rather than by reduction. Compositional data indicate that host minerals undergo only minor changes in MgO and  $\text{Fe}/(\text{Fe}+\text{Mg})$  as a result of subsolidus crystallization.

Composition of the magma, its cooling rate, and oxygen fugacity affect the stability, abundance, and order of crystallization of opaque oxides in high-Ti mare basalts. Cr-ulvöspinel is restricted to basalts with  $>0.3$  weight percent  $\text{Cr}_2\text{O}_3$ . Armalcolite crystallizes from melts with  $\geq 10$  weight percent  $\text{TiO}_2$  and ceases to crystallize when  $\text{Fe}/(\text{Fe}+\text{Mg})$  of armalcolite reaches  $\sim 0.70$  and a reaction relation occurs. Slower cooling enhances reaction of armalcolite with the melt and results in decreased modal abundance. The modal abundance of Cr-ulvöspinel also decreases with slower cooling, probably because of increased Cr substitution in pyroxene and earlier nucleation of plagioclase. Ilmenite modal abundance is directly related to  $\text{TiO}_2$  content of the magma and is independent of cooling rate. However, slower cooling tends to produce ilmenite grains of more magnesian composition through increased resorption of early olivine crystals. Absence of armalcolite in Apollo 11 low-K basalts and rarity of Cr-ulvöspinel in Apollo 11 high-K basalts may be due to crystallization at oxygen fugacities, respectively, above  $\sim 10^{-13}$  or below  $\sim 10^{-14}$ .

Cr-ulvöspinel, armalcolite, and ilmenite are enriched in  $\text{TiO}_2$  and  $\text{Cr}_2\text{O}_3$  relative to high-Ti mare basalt magmas. Gravitational crystal settling of one, two, or all three of these minerals

<sup>1</sup> Cr-ulvöspinel is used throughout this paper as an abbreviation for chromian ulvöspinel.

will produce derivative liquids increasingly poorer in  $\text{TiO}_2$  and  $\text{Cr}_2\text{O}_3$ . Simultaneous fractionation of olivine depletes the derivative liquids in  $\text{MgO}$ . Compositional variations observed in high-Ti mare basalts can be accounted for by moderate (Apollo 17) to small (Apollo 11) amounts of fractionation involving early-crystallizing opaque oxide minerals and olivine.

### Introduction

Mare basalts returned by the Apollo 11 and 17 lunar missions are unusually rich in  $\text{TiO}_2$  (8–14 weight percent) and hence are referred to as high-titanium (high-Ti) mare basalts. The high Ti content clearly distinguishes these basalts from terrestrial basaltic rocks and from other lunar mare basalts poorer in  $\text{TiO}_2$ . Lunar high-Ti mare basalts also contain 0.2–0.6 weight percent  $\text{Cr}_2\text{O}_3$ , which is somewhat less  $\text{Cr}_2\text{O}_3$  than in low-Ti mare basalts but an order of magnitude greater than in terrestrial basalts. Due to this unusual composition, crystallization of one or more opaque oxide minerals commences at or near the liquidus of the rocks and continues in abundance throughout the entire crystallization sequence. Possibilities thus exist for fractionation of early-crystallizing opaque oxide minerals. This has important implications for the differentiation of high-Ti mare basalt magmas.

In order to assess the role of early opaque oxide mineral crystallization in the differentiation of lunar high-Ti mare basalt magmas, we have undertaken a detailed study of the opaque oxide mineralogy of Apollo 11 and 17 high-Ti mare basalts. Within this suite there are fairly major variations in composition and texture. As a result, we can evaluate effects of magma composition (including oxygen fugacity) and cooling rate upon the stability, order of appearance, abundance, and composition of opaque oxide minerals. Subsolidus crystallization of these minerals has occurred in many high-Ti mare basalts. In order to ascertain to what extent this may modify original magmatic compositions, we have attempted to characterize the compositional changes associated with subsolidus crystallization.

### Methods of study

Polished thin sections of 62 Apollo 17 and 17 Apollo 11 samples were studied optically in reflected and transmitted light to determine textural relations of the opaque oxide minerals and to select representative grains for analysis with an ARL EMX-SM electron microprobe. Mineral analyses were corrected for instrumental effects following the procedure of Keil (1967) and for differential matrix effects using the method of Bence and Albee (1968) and Albee and

Ray (1970). Details as to analytical techniques and electron microprobe standards employed are presented in Warner *et al.* (1976a) and Nehru *et al.* (1976). Modes of Apollo 17 basalts were determined in reflected light and are reported in Warner *et al.* (1978).

### Classification of high-Ti mare basalts

High-Ti mare basalts may be divided on the basis of  $\text{K}_2\text{O}$  into low-K ( $\text{K}_2\text{O} < 0.1$  weight percent) and high-K ( $\text{K}_2\text{O} \sim 0.3$  weight percent) varieties. All the Apollo 17 and about half of the Apollo 11 high-Ti mare basalts belong to the low-K group. The remaining Apollo 11 basalts all are of the high-K variety.

Rhodes *et al.* (1976) subdivided the Apollo 17 high-Ti mare basalts into three types (A, B, and C) on the basis of trace-element (particularly REE) abundances and certain distinctive trace-element ratios (e.g., Ba/Rb; La/Sm). These types were defined on the basis of compositional data obtained on fine-grained basalts. While some coarse-grained basalts clearly may be assigned to one or another of these three types, many of them have trace-element abundances that fall outside the ranges defined by the fine-grained samples. Such basalts were assigned by Rhodes *et al.* to a fourth type (type U). Although these rocks possibly constitute a separate magma type, they more probably belong to one of the three above types and owe their chemical divergence to sampling problems associated with their coarse-grained nature. In this paper we follow the Rhodes *et al.* classification of the Apollo 17 high-Ti mare basalts, but with the proviso that we do not at this time recognize their type U category as forming a distinct basalt type.

Beaty and Albee (1978) subdivided the Apollo 11 low-K basalts into four groups ( $B_1$ ,  $B_2$ ,  $B_3$ , and  $B_4$ ) on the basis of mineralogy, texture, and age. Trace-element data support their grouping: group  $B_1$  basalts have high, groups  $B_2$  and  $B_4$  intermediate, and group  $B_3$  low REE abundances. REE abundances in group  $B_3$  basalts are comparable to those in type A Apollo 17 basalts. For the purposes of this paper we shall follow the Beaty and Albee classification of the Apollo 11 low-K basalts. However, we note that the very limited sampling at the Apollo 11 site makes

subdivision here statistically much less valid than for the Apollo 17 high-Ti basalts.

The Apollo 11 high-K basalts exhibit a much narrower range in composition than the Apollo 11 and 17 low-K basalts and appear to have been derived from a single lava flow. Consequently, they are not subdivided.

Table 1 shows the average and range in major element composition for the high-Ti mare basalt types enumerated above, based on a compilation of all analyses reported in the literature. Differences in major element composition among the Apollo 17 basalt types, particularly between A and B, are minor. Type C basalts (represented only by three samples collected from the same locality) contain the highest amounts of MgO and Cr<sub>2</sub>O<sub>3</sub>. Compared to the Apollo 17 basalts, Apollo 11 low-K basalts are, on the average, lower in TiO<sub>2</sub>, MgO, and Cr<sub>2</sub>O<sub>3</sub>. Individual samples overlap much of the Apollo 17 range, however. The group B<sub>1</sub> Apollo 11 low-K basalts have the lowest abundances of these oxides. The Apollo 11 high-K basalts are distinguished by significantly higher K<sub>2</sub>O (average 0.31 weight percent). They have similar average TiO<sub>2</sub> and slightly lower average MgO and Cr<sub>2</sub>O<sub>3</sub> than the Apollo 17 high-Ti mare basalts. Compared to the Apollo 11 low-K basalts, the Apollo 11 high-K basalts are, on the average, richer in TiO<sub>2</sub>, MgO, and Cr<sub>2</sub>O<sub>3</sub>.

Table 2 lists all the studied samples according to the classification presented above. Fine- and coarse-grained varieties within each type are distinguished. Note that: (1) all Apollo 17 type A and C basalts studied are fine-grained, although coarse-grained members have been reported by Rhodes *et al.* (1976); (2) all group B<sub>1</sub> Apollo 11 low-K basalts are coarse-grained and all group B<sub>3</sub> basalts fine-grained; (3) no group B<sub>2</sub> Apollo 11 low-K basalts were studied; (4) group B<sub>4</sub> consists of only one sample (10050—see Beatty and Albee, 1978); and (5) all Apollo 11 high-K basalts are fine-grained (James and Jackson, 1970). We have included two mare basalt lithic fragments from soil sample 10085 (10085,125 and 10085,666) with group B<sub>3</sub> on the basis of similarity in texture and mineralogy. Likewise, we have grouped mare basalt lithic fragments 10085,122 and 10085,251 with the Apollo 11 high-K basalts. In addition, we have included with the latter a clast in breccia sample 10060,71 that James and Jackson (1970) previously classed separately as a vitrophyric basalt. We have done so as the result of a defocused beam analysis (Prinz *et al.*, 1971) of the clast which showed it to be of high-K composition (weight percent: SiO<sub>2</sub>, 41.5;

TiO<sub>2</sub>, 11.3; Al<sub>2</sub>O<sub>3</sub>, 8.9; Cr<sub>2</sub>O<sub>3</sub>, 0.37; FeO, 18.7; MnO, 0.17; MgO, 7.3; CaO, 10.8; Na<sub>2</sub>O, 0.58; K<sub>2</sub>O, 0.31).

### Opaque oxide mineralogy

#### General

Early-crystallizing opaque oxide minerals in high-Ti mare basalts include ilmenite, armalcolite, and Cr-ulvöspinel. Armalcolite, previously unknown before its discovery in Apollo 11 samples, is essentially intermediate in composition between FeTi<sub>2</sub>O<sub>6</sub> and MgTi<sub>2</sub>O<sub>6</sub> (Anderson *et al.*, 1970), and also contains minor amounts of (Cr,Al,Ti<sup>3+</sup>)<sub>2</sub>TiO<sub>6</sub> (Kesson and Lindsley, 1975; Wechsler *et al.*, 1976). Cr-ulvöspinel is intermediate in composition between Fe<sub>2</sub>TiO<sub>4</sub> (ulvöspinel) and FeCr<sub>2</sub>O<sub>4</sub> (chromite), with substantial substitution of Mg for Fe and Cr for Al (Agrell *et al.*, 1970). Also present in high-Ti mare basalts are late-stage minerals such as nearly pure ulvöspinel, tranquillityite, zirconolite, and baddeleyite. These occur in cristobalite-rich or glassy matrix areas, particularly in coarse-grained basalts.

The Apollo 17, Apollo 11 low-K, and Apollo-11 high-K basalts are each characterized by a different assemblage, as shown below:

Low-K	[ Apollo 17	Cr-ulvöspinel/ulvöspinel + armalcolite + ilmenite
	[ Apollo 11	Cr-ulvöspinel/ulvöspinel + ilmenite
High-K	Apollo 11	Armalcolite + ilmenite (Cr-ulvöspinel/ulvöspinel rare or absent)

Modal abundance, compositional variation, and textural setting of the opaque oxides from the different basalt types are summarized in Table 3 and the following sections. Compositional data are from Warner *et al.* (1976a) and Nehru *et al.* (1976), supplemented by additional unpublished data. Note that the classification for Apollo 17 basalts used by Warner *et al.* (1976a) is based solely on textural criteria, and thus differs somewhat from that adopted here.

#### Cr-ulvöspinel and ulvöspinel

Cr-ulvöspinel is most common in low-K basalts (especially Apollo 17) and more abundant in fine- than in coarse-grained varieties. It is absent in low-K basalts that contain <0.3 weight percent Cr<sub>2</sub>O<sub>3</sub> (that is, group B<sub>1</sub> Apollo 11 low-K basalts and a few com-

Table 1. Average and range in composition of high-Ti mare basalts

	Apollo 17			
	Type A (29)	Type B (37)	Type C (3)	'U' (20)
SiO <sub>2</sub>	39.6 (38.4-41.9)	38.7 (37.8-40.3)	38.5 (38.2-38.6)	38.4 (37.8-40.2)
TiO <sub>2</sub>	11.8 (8.6-13.2)	12.1 (9.8-13.7)	12.3 (11.9-12.5)	11.9 (7.8-14.5)
Al <sub>2</sub> O <sub>3</sub>	9.0 (8.4-10.0)	9.1 (7.8-10.6)	8.7 (8.6-8.7)	9.1 (7.3-11.7)
Cr <sub>2</sub> O <sub>3</sub>	0.39(0.17-0.53)	0.39(0.26-0.61)	0.58(0.53-0.61)	0.45(0.23-0.65)
FeO	19.4 (18.0-20.9)	19.5 (17.0-20.8)	18.2 (18.1-18.3)	18.9 (16.1-20.6)
MnO	0.25(0.22-0.28)	0.25(0.22-0.29)	0.26(0.25-0.28)	0.25(0.22-0.28)
MgO	8.1 (5.2-10.0)	7.9 (6.8-9.4)	10.5 (10.4-10.6)	8.7 (6.3-10.3)
CaO	10.7 (9.3-12.4)	10.7 (9.3-13.3)	10.4 (10.3-10.5)	10.7 (9.5-13.6)
Na <sub>2</sub> O	0.41(0.37-0.48)	0.38(0.33-0.46)	0.36(0.35-0.37)	0.40(0.31-0.50)
K <sub>2</sub> O	0.07(0.06-0.08)	0.05(0.03-0.07)	0.08(0.07-0.09)	0.06(0.05-0.09)
TiO <sub>2</sub> /MgO	1.46	1.53	1.17	1.37
Fe/(Fe+Mg)	0.57	0.58	0.49	0.55

'U' = coarse-grained Apollo 17 basalts of uncertain affinity (see text)  
Number of basalts averaged in each type or group indicated in ( )

positionally-evolved Apollo 17 basalts, designated in Table 2 by asterisks). It is extremely rare in Apollo 11 high-K basalts.

The compositional variation exhibited by Cr-ulvöspinel is summarized in Table 3. In most basalts, the greatest variation from grain-to-grain is in Fe/(Fe+Mg) (FFM). Within the ranges indicated, variation in FFM is continuous. Concomitant variations of other major oxides are small, with Ti showing a tendency to increase and Cr and Al to decrease with increasing FFM. Individual grains are for the most part homogeneous. A few grains are zoned; these increase in Ti and Fe and decrease in Cr and Al from core to rim. Two additional observations are important. First, the range in FFM of Cr-ulvöspinel in Apollo 11 low-K basalts is less than that in Apollo 17 basalts, the difference being that Fe-rich grains (FFM < 0.91) are lacking in the Apollo 11 low-K basalts. Second, in some half-dozen type B Apollo 17 basalts with <0.37 weight percent Cr<sub>2</sub>O<sub>3</sub>, the Mg-rich grains (FFM < 0.85) are absent.

Compositions of individual grains vary according to their textural setting. The most Mg-rich grains generally occur as inclusions in olivine, or in titanite in the case of olivine-poor coarse-grained basalts. The inclusions in olivine are usually small (only a few tens of microns) idiomorphic crystals, and sometimes occur in clusters. The FFM of the

inclusions shows a positive correlation with the Fa content of the host olivines. Cr-ulvöspinel grains near the margins of olivine grains and elsewhere in the basalts are generally more Fe-rich. The latter tend to be larger than the inclusions in olivine, ranging in size to upwards of 100 μm (microphenocrystic in finest-grained Apollo 17 basalts—Fig. 1A).

Ulvöspinel is most abundant in coarse-grained low-K basalts and is found primarily in late-stage mesostasis. It occurs both as discrete grains or intergrown with ilmenite (Fig. 1B); metal and troilite are sometimes also present. It is nearly pure Fe<sub>2</sub>TiO<sub>4</sub>, with a narrow range in FFM (0.96-1.0). In fine-grained low-K basalts, ulvöspinel contains <1 weight percent Cr<sub>2</sub>O<sub>3</sub>, and a gap thus exists in Cr<sub>2</sub>O<sub>3</sub> between ulvöspinel and the most Fe-rich Cr-ulvöspinel grains. In coarse-grained low-K basalts, the amount of Cr<sub>2</sub>O<sub>3</sub> contained by ulvöspinel is much more variable, and the above-mentioned gap is smaller, and even bridged in a few Apollo 17 basalts.

#### Armalcolite

Armalcolite is present in most Apollo 11 high-K and Apollo 17 basalts, but is not found in Apollo 11 low-K or in the most compositionally-evolved (*i.e.*, TiO<sub>2</sub> < 10 weight percent) Apollo 17 basalts. It is more abundant in fine- than in coarse-grained ba-

Table 1. (continued)

Apollo 11 Low-K				Apollo 11 High-K
Group B <sub>1</sub> (3)	Group B <sub>2</sub> (2)	Group B <sub>3</sub> (4)	Group B <sub>4</sub> (1)	(8)
41.9 (41.0-42.5)	38.3 (37.9-38.6)	39.0 (38.1-39.9)	41.1	40.5 (39.6-41.0)
9.9 (9.1-10.7)	11.8 (11.4-12.2)	11.3 (10.5-12.7)	12.1	11.8 (11.3-12.5)
10.8 (10.2-11.3)	10.4 (10.3-10.5)	10.2 (9.5-11.3)	10.0	8.6 (7.9-9.5)
0.22(0.19-0.24)	0.25(0.23-0.27)	0.36(0.24-0.44)	0.33	0.36(0.32-0.37)
18.5 (17.9-19.2)	20.2 (19.8-20.5)	19.0 (18.4-19.4)	18.1	19.3 (18.7-19.6)
0.27(0.25-0.29)	0.25(0.23-0.27)	0.26(0.23-0.27)	0.27	0.23(0.21-0.25)
6.1 (5.9-6.3)	7.4 (7.3-7.5)	7.9 (7.1-8.9)	8.6	7.5 (7.0-7.8)
12.1 (11.7-12.3)	10.9 (10.5-11.2)	11.6 (11.3-12.2)	11.3	10.6 (10.1-11.0)
0.44(0.41-0.47)	0.39(0.38-0.39)	0.37(0.33-0.42)	0.38	0.50(0.48-0.53)
0.11(0.10-0.12)	0.04(0.03-0.05)	0.05(0.02-0.07)	0.05	0.31(0.28-0.33)
1.62	1.59	1.43	1.41	1.57
0.63	0.60	0.57	0.54	0.59

Table 2. Classification of samples studied in this investigation

Apollo 17					Apollo 11 Low-K			Apollo 11 High-K
Type A Fine	Type B Fine	Type B Coarse	Type C Fine	'U' Coarse	Group B <sub>1</sub> Coarse <sub>1</sub>	Group B <sub>3</sub> Fine <sub>3</sub>	Group B <sub>4</sub> Coarse <sub>4</sub>	Fine
71508	71507	71557	74245	71509	10044	10020	10050	10022
71527	71525	71566	74275	71536*	10047	10045		10024
71528	71526	71597		71549	10058	10062		10057
71529	71535	78575		71556		10085,125#		10071
71538	71537	78576		71559*		10085,666#		10072
71539*	71545			71565				10085,122#
71546	71547			71567				10085,251#
71548	71558			71568*				10060,71#
71555	71576			77535				(clast)
71569	71579			77536				
71575	71585			78505				
71577	71586			78578				
71578	71587							
78569	71588							
78579	71589							
78588	71595							
78595	71596							
78596	73219							
78598*	77516							
78599	78586							
	78587							
	78589							
	78597							

'U' = coarse-grained Apollo 17 basalts of uncertain affinity

\*Apollo 17 basalts with textural and mineralogical affinities to Apollo low-K basalts (see text)

#Samples renumbered from James and Jackson (1970, Table 1) as follows:

- 10060,71 = 10060,21-1
- 10085,122= 10085,32-2
- 10085,125= 10085,12-4
- 10085,251= 10085,32-11
- 10085,666= 10085,12-2

Table 3. Modal abundance and compositional range of opaque oxide minerals in high-Ti mare basalts

	Apollo 17					Apollo 11 Low-K			Apollo 11 High-K
	Type A Fine	Type B Fine	Type B Coarse	Type C Fine	'U' Coarse	Group B <sub>1</sub> Coarse <sup>1</sup>	Group B <sub>3</sub> Fine	Group B <sub>4</sub> Coarse <sup>4</sup>	Fine
<b>Cr-ulvöspinel</b>									
Modal abundance	0.2	0.2	<0.1	0.5	Tr	---	(0-0.5)	Tr	Tr
Fe/(Fe+Mg)	0.73-0.97	0.74-0.99	0.72-0.95	0.72-0.93	0.72-0.99	---	0.72-0.91	0.76-0.80	0.75, 0.89
Cr/(Cr+Al)	0.59-0.80	0.61-0.79	0.56-0.84	0.69-0.71	0.63-0.83	---	0.61-0.79	0.66-0.68	0.74, 0.76
2Ti/(Cr+Al+2Ti)	0.39-0.73	0.40-0.69	0.27-0.65	0.42-0.55	0.25-0.71	---	0.45-0.64	0.41-0.56	0.56, 0.58
<b>Armalcolite</b>									
Modal abundance	0.1	0.2	<0.1	1.3	<0.1	---	---	---	(0-0.5)
Fe/(Fe+Mg)	0.51-0.74	0.47-0.70	0.50-0.69	0.46-0.63	0.49-0.68	---	---	---	0.48-0.67
Cr <sub>2</sub> O <sub>3</sub> (%)	1.0-2.5	1.1-2.6	1.0-2.0	1.4-2.4	1.1-2.3	---	---	---	1.2-2.2
<b>Ilmenite</b>									
Modal abundance	16	16	16	15	16	10	14	14	(13-17)
Fe/(Fe+Mg)	0.70-0.99	0.70-1.00	0.69-0.98	0.81-0.98	0.68-1.00	0.95-0.99	0.74-0.99	0.86-0.95	0.79-0.99
Cr <sub>2</sub> O <sub>3</sub> (%)	0.1-1.7	0.1-1.3	0.4-1.0	0.3-1.2	0-1.0	0-0.6	0.2-1.7	0.5-0.7	0.1-1.0

Modal abundances for Apollo 17 basalts are averages of data reported in Warner *et al.* (1978); those for Apollo 11 basalts are from James and Jackson (1970, Table 2).

Compositional ranges for Apollo 17 basalts are from analyses given in Warner *et al.* (1976a) supplemented by additional unpublished data; those for Apollo 11 basalts are from analyses given in Nehru *et al.* (1976).

salts, and is most abundant in type C Apollo 17 basalts.

Armalcolite occurs as discrete single grains and with rims of ilmenite (Fig. 1D). The latter have originated from reaction of armalcolite with the surrounding melt (*cf.* Anderson *et al.*, 1970; James and Jackson, 1970). Preservation of discrete grains or of euhedral faces on grains that are only partly mantled by ilmenite (Fig. 1C) is the result of those faces being armored against reaction, usually by contact with early-formed olivine or titanite (Papike *et al.*, 1974).

Discrete armalcolite grains are usually homogeneous in composition. In contrast, ilmenite-mantled grains, particularly if they occur as microphenocrysts, are often zoned. In zoned grains Fe increases and Mg and Cr decrease from core to rim. Most of the zoning occurs in the outer few microns adjacent to ilmenite. A large part of the compositional range exhibited by armalcolite in a given rock may be present in a single zoned microphenocryst.

The overall range in FFM and Cr<sub>2</sub>O<sub>3</sub> displayed by armalcolite is similar in Apollo 11 high-K and Apollo 17 basalts (Table 3). Within the Apollo 17 suite there is a small but real compositional difference between the most Mg-rich grains present in B (lower FFM) as opposed to type A basalts (Fig. 2). The observed differences may be correlated with the habit and occurrence of the grains. In type B basalts armalcolite typically occurs as microphenocrysts completely mantled by ilmenite (Fig. 1D). Grains with FFM < 0.5 are, without exception, of this habit. Armalcolite

also occurs as tiny lathlike or needle-shaped inclusions in olivine; these grains have FFM > 0.5 and thus crystallized later. In type A basalts, grains with FFM < 0.5 are absent, and the most Mg-rich grains are inclusions in olivine. Tabular grains only partly mantled by ilmenite (Fig. 1C) are common in type A basalts and have higher FFM.

It has been suggested by El Goresy *et al.* (1974) that a compositional bimodality exists between armalcolites from fine-grained and coarse-grained Apollo 17 basalts, and that, consequently, there are two different varieties of armalcolite, as proposed by Haggerty (1973). Our data (Fig. 3) show no evidence for such bimodality. We thus concur with Smyth (1974), Williams and Taylor (1974), and Papike *et al.* (1974) that there is no compositional basis for distinguishing two varieties of armalcolite.

#### Ilmenite

Ilmenite is by far the most abundant opaque oxide in all high-Ti mare basalts (Table 3). The amount correlates directly with bulk-rock TiO<sub>2</sub> (Table 1). The average modal abundance is greatest in Apollo 17 basalts, whereas group B<sub>1</sub> Apollo 11 low-K basalts and Apollo 17 basalts with <10 weight percent TiO<sub>2</sub> have the lowest modal abundances.

Modal abundance is independent of average grain size of the basalts. However, there are significant differences in ilmenite morphology between fine- and coarse-grained rocks. In the former, ilmenite typically occurs as lathlike or acicular grains, often with skeletal sawtooth-bladed margins (Fig. 1E). Acicular

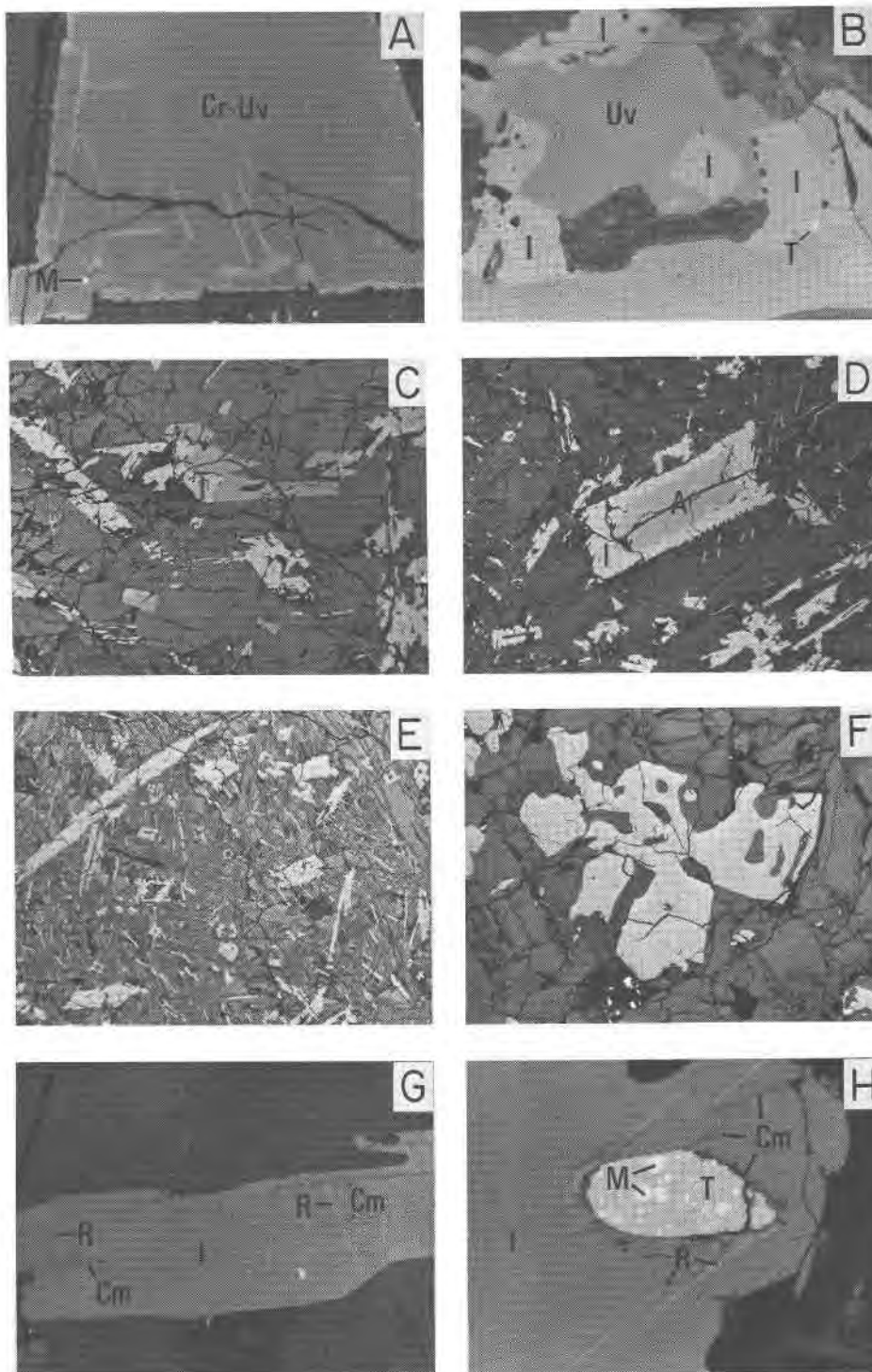


Fig. 1. Reflected light photomicrographs of opaque oxide minerals in lunar high-Ti mare basalts. (A) Cr-Ulvöspinel (Cr-Uv) microphenocryst in fine-grained Apollo 17 basalt 78587. Note presence of octahedrally-oriented ilmenite (I) lamellae and small grain of native Fe (M). Horizontal dimension  $\sim 200 \mu\text{m}$ . (B) Ulvöspinel (Uv)-ilmenite intergrowth in late-stage mesostasis in coarse-grained Apollo 11 low-K basalt 10047. T = troilite. Horizontal dimension  $\sim 200 \mu\text{m}$ . (C) and (D) Armalcolite (A)-ilmenite relationships in fine-grained types A (78596) and B (71595) Apollo 17 basalts, respectively. Horizontal dimensions  $\sim 1\text{mm}$ . (E) and (F) Representative ilmenite crystal habits in fine-grained (71596) and coarse-grained (78576) Apollo 17 basalts, respectively. Horizontal dimension  $\sim 2\text{mm}$ . (G) Intersecting rutile (R) and aluminian chromite (Cm) lamellae in ilmenite in coarse-grained Apollo 17 basalt 78576. Horizontal dimension  $\sim 200 \mu\text{m}$ . (H) Assemblage aluminian chromite + rutile at contact between ilmenite and composite metal-troilite grain in coarse-grained Apollo 17 basalt 77536. Horizontal dimension  $\sim 200 \mu\text{m}$ .

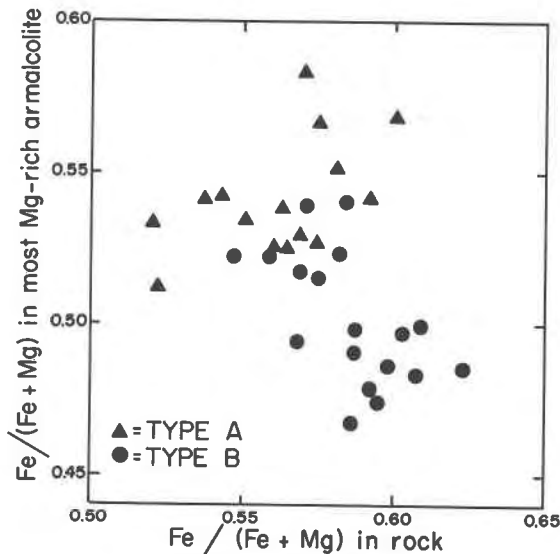


Fig. 2.  $\text{Fe}/(\text{Fe}+\text{Mg})$  in most Mg-rich armalcolite vs.  $\text{Fe}/(\text{Fe}+\text{Mg})$  in rock in fine-grained types A and B Apollo 17 basalts.

skeletal microphenocrysts up to 2–5 mm long are common in Apollo 17 basalts (particularly type B). In coarse-grained basalts, grains tend to be more equant and are characterized by “amoeboidal” (Papike *et*

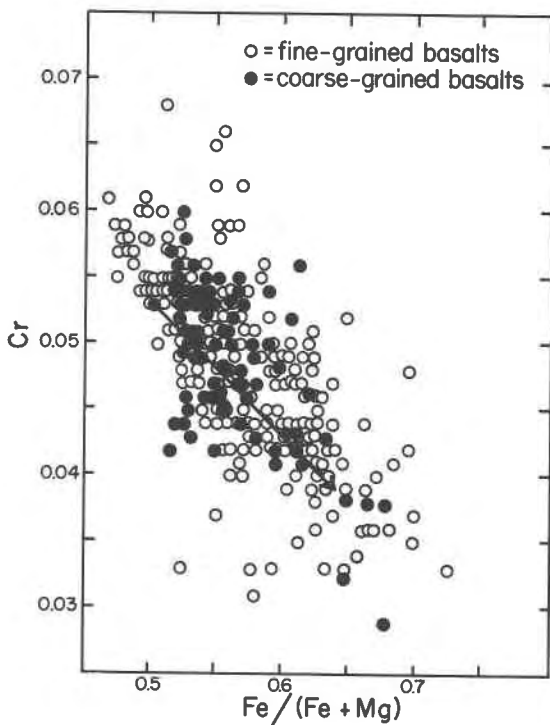


Fig. 3. Cr (cation proportion on basis of 5 oxygens) vs.  $\text{Fe}/(\text{Fe}+\text{Mg})$  in armalcolites in fine-grained and coarse-grained Apollo 17 basalts. Solid line indicates core-to-rim variation present in single zoned microphenocryst.

*al.*, 1974) morphology, with numerous holes or marginal embayments (Fig. 1F).

Individual grains of ilmenite are compositionally homogeneous in all samples. The overall range in FFM is approximately 0.7–1.0 in low-K basalts and 0.8–1.0 in Apollo 11 high-K basalts (Table 3). In group B, Apollo 11 low-K basalts and compositionally-similar Apollo 17 basalts the range is narrower (~0.9–1.0). An interesting feature of the Apollo 17 suite is that Mg-rich ilmenite grains (*i.e.*, those with  $\text{FFM} < 0.8$ ) are much more common in coarse- than in fine-grained basalts, despite the fact that the fine- and coarse-grained varieties are essentially isochemical.

In general, the composition of ilmenite is dictated by textural setting, irrespective of grain size. The most Mg-rich ilmenites occur within olivine (either as discrete crystals or associated with melt inclusions) or, in olivine-poor coarse-grained Apollo 17 basalts, within sector-zoned titanaugites. Ilmenite mantling armalcolite also tends to be Mg-rich. Microphenocrysts, matrix laths, *etc.*, are more Fe-rich, and the most Fe-rich grains are those associated with late-stage minerals such as cristobalite, pyroxferroite, ulvöspinel, and tranquillityite.

The  $\text{Cr}_2\text{O}_3$  content of ilmenite ranges from 0 to 1.7 weight percent and is more or less similar in all basalt types (Table 3). Usselman (1975) reported that ilmenites from Apollo 11 low-K and high-K basalts exhibit different trends on a  $\text{MgO}-\text{Cr}_2\text{O}_3$  variation diagram. Our ilmenite data indicate that the fields for Apollo 11 high-K and low-K basalts virtually overlap (Fig. 4), and do not support the separate trends shown by Usselman (1975, Fig. 2). However,  $\text{MgO}$  vs.  $\text{Cr}_2\text{O}_3$  variation in ilmenites from Apollo 17 basalts contrasts with that from Apollo 11 basalts. Here,  $\text{Cr}_2\text{O}_3$  is relatively insensitive to the amount of  $\text{MgO}$  in ilmenite (Fig. 4C). A possible explanation is discussed later in the paper.

#### *Fe-Mg partitioning between coexisting minerals*

Our data on the compositions of coexisting minerals in high-Ti mare basalts may be used to calculate  $K_D$  values for various mineral pairs. Using the parameter  $\text{Fe}/(\text{Fe}+\text{Mg})$ , or FFM, we have computed Fe-Mg partition coefficients between coexisting opaque oxide minerals and/or olivine (Table 4). In general, the calculated  $K_D$ 's are the same for Apollo 11 and 17 basalts. An exception is the pair armalcolite-ilmenite, where Apollo 11 high-K basalts yield a lower value (0.646) than Apollo 17 basalts (0.764). Part or all of this discrepancy may be due to analytical difficulties



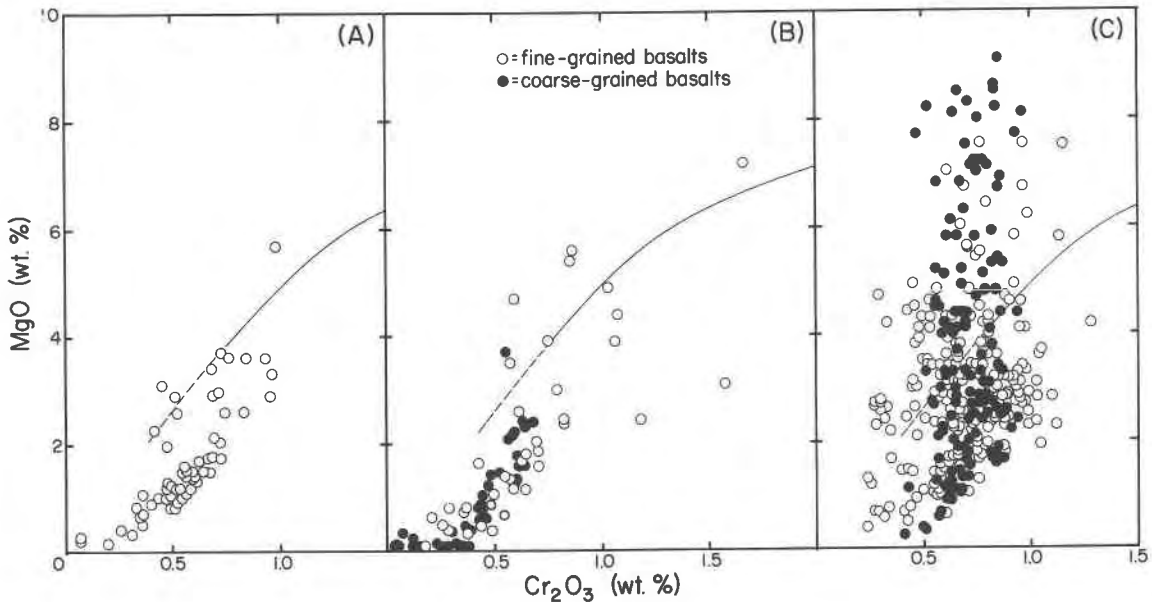


Fig. 4. Variation of MgO vs. Cr<sub>2</sub>O<sub>3</sub> in ilmenites in (A) Apollo 11 high-K, (B) Apollo 11 low-K and (C) Apollo 17 basalts. Solid-dashed line represents MgO vs. Cr<sub>2</sub>O<sub>3</sub> variation in ilmenite in equilibrium with synthetic high-Ti basaltic liquid (from Usselman, 1975).

in determining compositions of the margins of zoned armalcolite grains. The computed  $K_D$ 's show that FFM is lower in armalcolite than in coexisting Cr-ulvöspinel or mantling ilmenite, is approximately the same in ilmenite coexisting with Cr-ulvöspinel or ulvöspinel, and is much higher in opaque oxide minerals than in olivine.

### Subsolidus crystallization of opaque oxide minerals

#### Assemblages

Subsolidus crystallization is a common feature of opaque oxide minerals in high-Ti mare basalts (Haggerty, 1973; El Goresy and Ramdohr, 1975). The resulting assemblages are as follows:

- (1) Cr-ulvöspinel (host) + ilmenite ± native Fe
- (2) Ilmenite (host) + rutile + aluminian chromite ± native Fe and/or troilite.

These assemblages are very common in Apollo 17 basalts, less so in Apollo 11 high-K and group B<sub>3</sub> Apollo 11 low-K basalts, and rare or absent in group B<sub>1</sub> Apollo 11 low-K and compositionally-similar Apollo 17 basalts.

Assemblage (1) is characterized by octahedrally-oriented (Haggerty, 1971) lamellae of ilmenite within Cr-ulvöspinel (Fig. 1A). The ilmenite lamellae are usually  $\leq 1 \mu\text{m}$  thick and generally occur near the borders of the host crystal. They often contain sub-micron-sized specks of native Fe (uncertain identifi-

cation). In some Apollo 17 basalts larger, positively identifiable grains of metal are present.

Assemblage (2) is characterized by intergrown blebs and lamellae of rutile and aluminian chromite in ilmenite (Fig. 1G). The relative proportions of rutile and aluminian chromite are more or less sub-equal, except in the case of ilmenite rims on armalcolite. Here rutile is significantly more abundant, often amounting to 5 percent or more by volume of the ilmenite. The intergrowths consist of basally-oriented aluminian chromite intersected by rhombohedrally-oriented rutile (Cameron, 1970). The lamellae usually are well-defined, 1–3  $\mu\text{m}$  thick, and taper or pinch out at places of intersection. Occasionally, ilmenite grains contain irregular intergrowths of rutile and aluminian chromite in blebs up to 20–30  $\mu\text{m}$  thick. Native

Table 4.  $K_D$  values of coexisting minerals in high-Ti mare basalts

Mineral pair	$K_D^{\text{FFM}}$	$\sigma$	N
Armalcolite/ilmenite*	0.646	0.059	8
	0.764	0.038	43
Armalcolite/Cr-ulvöspinel	0.716	0.029	12
Ilmenite/Cr-ulvöspinel or ulvöspinel	0.973	0.014	27
Armalcolite/olivine	1.935	0.121	22
Cr-ulvöspinel/olivine	2.748	0.218	65

$\sigma$  = standard deviation

N = number of mineral pairs used in calculating  $K_D^{\text{FFM}}$

\* Upper and lower values denote data for Apollo 11 high-K and Apollo 17 basalts, respectively.

Fe is sometimes associated with this type of intergrowth in Apollo 17 basalts, but such occurrences are rare except in a few coarse-grained rocks.

A closely-related assemblage is that of troilite+ilmenite+aluminian chromite+rutile, which is quite common in coarse-grained Apollo 17 basalts. This assemblage occurs where troilite and ilmenite are in contact (El Goresy and Ramdohr, 1975) and consists of a band of aluminian chromite which is within the original grain boundary of ilmenite but follows the contours of the neighboring troilite (Fig. 1H). Rutile is usually associated with the aluminian chromite, and the ratio of the two varies widely. Both phases often connect with lamellae inside the ilmenite. The same assemblage is also found at contacts of ilmenite with native Fe or composite metal-troilite grains.

### Origin

Two principal mechanisms have been proposed for the origin of the subsolidus assemblages in high-Ti mare basalts. Haggerty (1971, 1973) and El Goresy and Ramdohr (1975) argue that these are the result of subsolidus reduction, while Haselton and Nash (1975) and Kesson and Lindsley (1975), among others, suggest that they originated *via* isochemical reactions leading to exsolution. Our observations lead us to prefer, in general, an exsolution mechanism. The ubiquitous octahedral orientation of ilmenite lamellae in Cr-ulvöspinel and the systematic lamellar orientation of rutile and aluminian chromite in ilmenite strongly suggest the operation of an internally-driven process (*i.e.*, exsolution) rather than an externally-imposed process (*i.e.*, reduction). Furthermore, we note that often native Fe is not even present, particularly in the rutile-aluminian chromite-host ilmenite assemblage. Even where it does occur, native Fe does not constitute *a priori* evidence in favor of subsolidus reduction, because oxygen fugacities at the time of magmatic crystallization were sufficiently low to permit precipitation of metal directly from the melt. Rather, as suggested by Haselton and Nash (1975) and Kesson and Lindsley (1975), native Fe in subsolidus assemblages may simply be due to an isochemical breakdown reaction between ferrous iron and exsolved trivalent titanium (the existence of trivalent titanium in lunar minerals has been confirmed by Sung *et al.*, 1974). In ilmenite grains susceptible to exsolution, contact with troilite and/or native Fe (Fig. 1H) apparently promotes exsolution of aluminian chromite and rutile, however (see Haggerty *et al.*, 1970). Nevertheless, in some high-Ti mare basalts subsolidus reduction may have

played a major role. The best candidates for this are a few coarse-grained Apollo 17 basalts in which ilmenite commonly contains bleblike intergrowths of rutile and aluminian chromite together with native Fe.

### Compositional considerations

An important aspect of subsolidus crystallization is the extent (if any) to which the original magmatic compositions of the opaque oxides are modified. This is difficult to ascertain for Cr-ulvöspinel grains, because the ilmenite lamellae are much too narrow for quantitative analysis except in a few instances. These show that MgO partitions in favor of the ilmenite lamellae, but that FFM of the host Cr-ulvöspinel is only slightly different (Table 5, cols. 1 and 3). Thus, exsolution of ilmenite has a very small effect on altering FFM in Cr-ulvöspinel. Within the host Cr-ulvöspinel there is commonly an enrichment in Cr<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> in a narrow zone adjacent to the ilmenite (Table 5, col. 2). However, away from the lamellae there is probably little compositional change, since we find no discernible difference in the composition of Cr-ulvöspinel between samples in which abundant exsolutions occur and those with little or none.

For the most part, aluminian chromite and rutile lamellae in ilmenite are also too small for quantitative analysis, except in some coarse-grained Apollo 17 basalts. Here, analyses show that rutile is nearly pure TiO<sub>2</sub> with 0.5–1 weight percent FeO and <0.2 weight percent MgO, and that aluminian chromites contain 40–50 weight percent Cr<sub>2</sub>O<sub>3</sub> and 10–20 weight percent Al<sub>2</sub>O<sub>3</sub> (*e.g.*, Table 5, cols. 4 and 5). MgO and FeO are lower in aluminian chromite than in the host ilmenite (Table 5) but FFM is only slightly lower. In fact,  $K_D^{FFM}$  (ilmenite/aluminian chromite) is near unity (analyses of 14 coexisting pairs yield a  $K_D$  of 1.036 with  $\sigma$  of 0.039). The net effect of exsolution is thus a marked decrease in Cr<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> and a slight increase in MgO and FeO in the host ilmenite, with FFM remaining essentially unchanged. TiO<sub>2</sub> in the host ilmenite decreases only when the amount of exsolved rutile is significantly greater than that of aluminian chromite, as is the case, for example, in TiO<sub>2</sub>-enriched ilmenites formed as reaction rims around armalcolite (*cf.* El Goresy *et al.*, 1974; Papike *et al.*, 1974).

El Goresy and Ramdohr (1975) and Usselman (1975) have cautioned that analyzed ilmenites from high-Ti mare basalts may not be representative of magmatic ilmenite compositions. From our compositional data we concur that this is valid as regards Cr<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>, but not necessarily for MgO and

certainly not for FFM. The MgO vs. Cr<sub>2</sub>O<sub>3</sub> variation of ilmenite in equilibrium with high-Ti basaltic liquid, as experimentally determined by Usselman (1975), is shown in Figure 4. The trend indicates a positive correlation between MgO and Cr<sub>2</sub>O<sub>3</sub>. Ilmenites from Apollo 11 low-K and high-K basalts generally have undergone rather limited subsolidus reequilibration, and tend to follow the experimentally-derived trend. Our ilmenite data do not support the separate trends shown by Usselman (1975, Fig. 2), and, therefore, his proposal that ilmenites from Apollo 11 low-K and high-K basalts have undergone substantially different post-magmatic reequilibration histories is unwarranted. Ilmenites from Apollo 17 basalts, especially those from coarse-grained rocks, deviate significantly from the trend, however. The deviation is one of Cr<sub>2</sub>O<sub>3</sub> deficiency, and increases in magnitude with increasing MgO; this in turn correlates with the abundance of exsolved aluminian chromite (cf. El Goresy and Ramdohr, 1975). Therefore, prior to exsolution, these ilmenite compositions probably followed the experimental trend. Assuming this to be the case, simple calculations show that exsolution should change MgO in the host ilmenite by at most a few tenths weight percent. For example, an ilmenite that originally contained 7 weight percent MgO should have ~2 weight percent Cr<sub>2</sub>O<sub>3</sub> according to Usselman (1975, Fig. 2). If this ilmenite exsolved 1.5 weight percent Cr<sub>2</sub>O<sub>3</sub> in the form of aluminian chromite lamellae, and an approximately equal amount of rutile was exsolved, MgO in the ilmenite would change only to ~7.3 weight percent. For a significantly greater change in MgO to occur would require the original ilmenite to have contained an implausibly high amount of Cr<sub>2</sub>O<sub>3</sub>. Thus, even in ilmenites that have undergone extensive exsolution, their MgO should depart from the original magmatic values by at most a few tenths weight percent, and FFM should be unchanged. We thus disagree with the conclusion of El Goresy and Ramdohr (1975, p. 737) that "high-MgO content cannot be used as an *a priori* evidence for early crystallization (of ilmenite)."

The operation of an internally-driven mechanism, triggered by Cr<sub>2</sub>O<sub>3</sub> supersaturation of the original ilmenites (and/or TiO<sub>2</sub> supersaturation in the case of ilmenite reaction rims on armalcolite), provides a simple explanation for the relative amounts of subsolidus crystallization products found in ilmenite on a grain-to-grain as well as a rock-to-rock basis. As shown by Usselman (1975), high Cr<sub>2</sub>O<sub>3</sub> correlates with high MgO. High-MgO ilmenites would thus be expected to preferentially exsolve aluminian chro-

Table 5. Representative electron microprobe analyses (weight percent) of minerals in subsolidus assemblages

	1	2	3	4	5	6
TiO <sub>2</sub>	53.8	17.4	22.4	97.1	6.4	54.5
Al <sub>2</sub> O <sub>3</sub>	.07	9.2	7.0	.04	11.9	.06
Cr <sub>2</sub> O <sub>3</sub>	1.71	29.2	23.2	.22	47.0	.76
FeO	35.3	36.3	39.4	.57	27.8	37.2
MnO	.42	.40	.41	*	.34	.41
MgO	8.0	7.1	6.7	.18	6.0	7.2
Total	99.3	99.6	99.1	98.1	99.4	100.1
Fe/(Fe+Mg)	0.71	0.74	0.77	0.64	0.72	0.74

Column (1): Analysis of ilmenite lamella in Cr-ulvöspinel (Apollo 17 basalt 71588). (2): Analysis of spinel immediately adjacent to ilmenite lamella. (3): Analysis of host Cr-ulvöspinel. (4): Analysis of rutile bleb in ilmenite (Apollo 17 basalt 77536). (5): Analysis of aluminian chromite associated with rutile. (6): Analysis of host ilmenite.  
\* = less than 0.01 wt.%

mite. As reported by El Goresy and Ramdohr (1975), and supported by our observations, a direct correlation exists in Apollo 17 basalts between MgO content of the host ilmenite and the amount of aluminian chromite and rutile visibly present. Furthermore, we note that Apollo 17 basalts (especially the coarse-grained samples) contain the most Mg-rich ilmenite grains (Table 3), and also show the greatest amounts of subsolidus crystallization in ilmenite. The group B<sub>1</sub> Apollo 11 low-K basalts (and a few compositionally-similar Apollo 17 basalts) contain the least Mg-rich ilmenite grains, and ilmenites in these rocks are virtually free of subsolidus reaction. Such a correlation would be fortuitous if the primary mechanism for subsolidus crystallization were an externally-imposed reduction process, as suggested by El Goresy and Ramdohr.

#### Factors affecting magmatic crystallization of opaque oxide minerals

##### *Magma composition and oxygen fugacity*

Overall compositional variation in high-Ti mare basalts is fairly significant, except in the Apollo 11 high-K suite. This affords an opportunity to examine effects of magma composition (and oxygen fugacity) on which opaque oxide minerals may crystallize, their abundance, order of appearance, etc.

Cr-ulvöspinel is present only in high-Ti mare basalts with >0.3 weight percent Cr<sub>2</sub>O<sub>3</sub>, indicating that this value is more or less critical for magmatic crystal-

lization of that phase. Neglecting variations caused by differences in rate of cooling (see following section), modal abundance of Cr-ulvöspinel correlates positively with bulk-rock  $\text{Cr}_2\text{O}_3$ . Thus, type C Apollo 17 basalts are the most  $\text{Cr}_2\text{O}_3$ -rich (Table 1), and in these Cr-ulvöspinel is most abundant (Table 3). Another critical factor that may control magmatic crystallization of Cr-ulvöspinel is oxygen fugacity. Experiments reported by O'Hara *et al.* (1975) indicate that Cr-ulvöspinel crystallization is constrained to oxygen fugacities above  $\sim 10^{-13.7}$ , and that at oxygen fugacities  $< 10^{-13.7}$  it is not stable. This probably accounts for difficulties that some laboratories have encountered in reproducing Cr-ulvöspinel crystallization of the natural lunar samples (*e.g.*, Longhi *et al.*, 1974), and it may also account for the scarcity of Cr-ulvöspinel in Apollo 11 high-K basalts, which average 0.36 weight percent  $\text{Cr}_2\text{O}_3$ .

Armalcolite is present only in high-Ti mare basalts with  $\geq 10$  weight percent  $\text{TiO}_2$ , suggesting that it crystallized only when  $\text{TiO}_2$  exceeded that amount in the melt. Lindsley *et al.* (1974) show that increasing FeO content decreases the stability of armalcolite with

falling temperature, and thus magmatic crystallization of armalcolite is further constrained in that FFM of the melt must be below a certain value. Papike *et al.* (1974) have suggested that armalcolite ceases to crystallize in high-Ti mare basalts when its FFM reaches 0.66 (our data suggest a value  $\sim 0.70$ ). As with Cr-ulvöspinel, oxygen fugacity is an additional important variable affecting armalcolite stability. A number of experimental studies (*e.g.*, O'Hara *et al.*, 1975; Usselman *et al.*, 1975; Friel *et al.*, 1977) show that armalcolite crystallization is oxygen-fugacity-dependent. Usselman *et al.* found that for a synthetic basalt containing 10.6 weight percent  $\text{TiO}_2$  armalcolite crystallized only at oxygen fugacities below  $\sim 10^{-13}$ . Similarly, O'Hara *et al.* reported armalcolite present in an experiment at an oxygen fugacity of  $10^{-13.7}$  but absent at higher oxygen fugacity. The absence of armalcolite in Apollo 11 low-K basalts (specifically those with  $> 10$  weight percent  $\text{TiO}_2$ ) and in a few Apollo 17 basalts that also contain  $> 10$  weight percent  $\text{TiO}_2$  may therefore be the result of crystallization at oxygen fugacities above  $\sim 10^{-13}$ .

The principal effect of magma composition on ilmenite crystallization is one of direct proportionality between amount of  $\text{TiO}_2$  in the melt and modal abundance of ilmenite. Thus, on the average, ilmenite is most abundant in Apollo 17 basalts (which have highest average  $\text{TiO}_2$ ) and least abundant in Apollo 11 low-K basalts (Tables 1 and 3).

High-Ti mare basalt magmas contain one or more opaque oxide minerals plus olivine as liquidus or near-liquidus phases (Longhi *et al.*, 1974; Walker *et al.*, 1975). Consequently, small changes in magma composition may alter the order of mineral crystallization. For example, although compositional differences between types A, B, and C Apollo 17 basalts are small (Table 1), they are sufficient to cause different paragenetic sequences. Figure 5 shows the crystallization sequences for the three types based on textural relationships in the samples. Crystallization sequences determined through experiments with samples 70215 (type B) and 74275 (type C) by Green *et al.* (1975, Fig. 1) are in excellent agreement with our deduced sequences for these rock types. In type C basalts, characterized by high MgO and  $\text{Cr}_2\text{O}_3$  and low  $\text{TiO}_2/\text{MgO}$  (Table 1), olivine crystallizes first and Cr-ulvöspinel precedes armalcolite. Type B basalts have higher  $\text{TiO}_2/\text{MgO}$  (Table 1), and the order of appearance of armalcolite and olivine is reversed. The position of Cr-ulvöspinel in the crystallization sequence is variable depending on the  $\text{Cr}_2\text{O}_3$  content of the rock, such that Cr-ulvöspinel precedes olivine

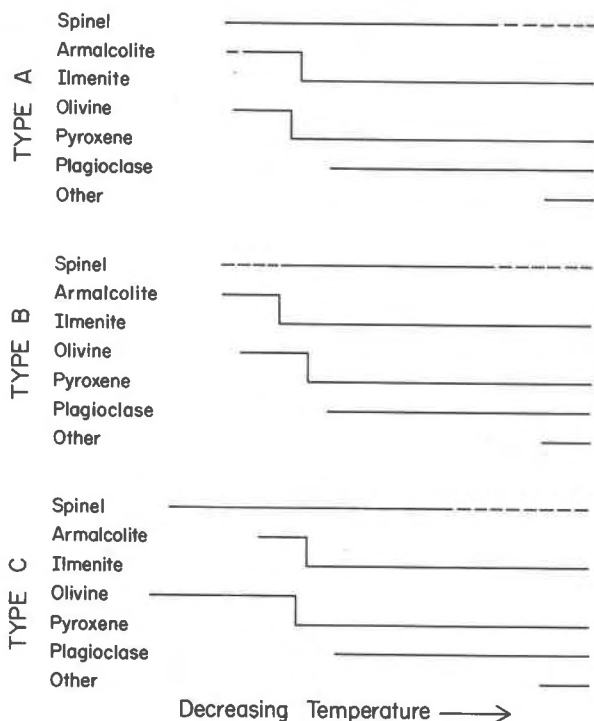


Fig. 5. Inferred crystallization sequences in types A, B, and C Apollo 17 basalts. Vertical connecting lines indicate reaction relationships. Dashed lines denote variations and uncertainties in appearance or disappearance of minerals. Shift of lines for type C basalts corresponds to higher liquidus temperatures.

when  $\text{Cr}_2\text{O}_3 > 0.37$  weight percent but follows olivine when  $< 0.37$ . In type B basalts ilmenite starts to crystallize before pyroxene, in contrast to type C basalts where pyroxene precedes ilmenite. In type A basalts, which have  $\text{TiO}_2/\text{MgO}$  values intermediate between types B and C (Table 1), Cr-ulvöspinel crystallizes first, with nearly simultaneous crystallization of armalcolite and olivine. From the foregoing discussion it is clear that no one single crystallization sequence is applicable to the Apollo 17 basalts. The crystallization sequence postulated by El Goresy *et al.* (1974) is valid only for a few Apollo 17 samples and should not be taken as being representative for all basalts. Similarly, Figure 5 updates the sequence given by Warner *et al.* (1975a).

The sequence of mineral crystallization in Apollo 11 basalts is similar to that in Apollo 17 basalts, except that armalcolite is absent in the low-K basalts and Cr-ulvöspinel is mostly absent in the high-K basalts. Cr-ulvöspinel apparently ceased crystallizing earlier in Apollo 11 low-K than in Apollo 17 basalts, because the most Fe-rich grains have FFM of 0.91 in Apollo 11 *vs.* 0.99 in Apollo 17 basalts. The relative order of appearance of armalcolite and olivine in Apollo 11 high-K basalts is ambiguous, as there are no instances in which either mineral is included in the other. We find no *a priori* textural evidence to indicate that armalcolite began to crystallize before olivine, as suggested by James and Jackson (1970, Fig. 7).

#### Cooling rate

In the Apollo 17 basalts there is an order of magnitude decrease in the average modal abundances of armalcolite and Cr-ulvöspinel between fine-grained (faster cooled) and coarse-grained (slower cooled) varieties. For armalcolite, this is because slower cooling rates afford greater opportunity for resorption of early-formed crystals, and armalcolite is therefore present in slowly cooled rocks only where it has been armored from reaction by olivine or pyroxene (occasionally plagioclase) grains. Unlike armalcolite, Cr-ulvöspinel continues to precipitate until late in the crystallization sequence (Fig. 5), and its relative depletion in the slower cooled basalts must be due to other causes. There are two effects connected with slower cooling rates that probably contribute to this depletion: (1) with decreasing cooling rate, the amount of Cr incorporated in the pyroxene structure increases (Warner *et al.*, 1975a, Fig. 9), and (2) the nucleation of plagioclase, which incorporates Al that would otherwise substitute for Cr in the spinel struc-

ture, is earlier in slower cooled basalts than in faster cooled ones (Warner *et al.*, 1975a; Papike *et al.*, 1974). As the above effects will not become operative until crystallization of pyroxene and plagioclase has commenced, it follows that it should be the intermediate- to late-crystallizing Cr-ulvöspinel grains that are most severely depleted in the coarse-grained rocks. Compositional data for Cr-ulvöspinel in Apollo 17 basalts reveal that this is indeed the case: ~60 percent of all grains analyzed from fine-grained basalts have FFM  $> 0.86$ , compared to  $< 30$  percent in the case of coarse-grained basalts.

In the Apollo 11 low-K basalts there is also a difference in modal abundance of Cr-ulvöspinel between faster cooled and slower cooled varieties. This difference is attributable primarily to a bulk compositional effect, since the coarse-grained (group B<sub>1</sub>) basalts contain considerably less  $\text{Cr}_2\text{O}_3$  than the fine-grained basalts (group B<sub>3</sub>, Table 1). However, coarse-grained sample 10050 (group B<sub>4</sub>) has  $\text{Cr}_2\text{O}_3$  comparable to that of the fine-grained Apollo 11 low-K basalts, yet contains noticeably less Cr-ulvöspinel. This occurrence is consistent with the cooling rate effect deduced for the Apollo 17 suite.

Differences in cooling rate do not affect ilmenite modal abundance but do affect ilmenite morphology (Figs. 1E,F). The  $K_D^{\text{FM}}$  (armalcolite/ilmenite) is such (Table 5) that ilmenite reaction rims have significantly higher FFM than associated armalcolite. Therefore, a gap in FFM is to be expected between the two minerals in a given rock or basalt type. Such a gap is observed in the Apollo 11 high-K basalts, in which the most Fe-rich armalcolite analyzed has FFM of 0.67, whereas the most Mg-rich ilmenite has FFM of 0.79 (Table 3). With the exception of ilmenites that crystallized from olivine melt inclusions and thus were isolated from the melt at a very early stage, there is a similar gap in fine-grained Apollo 17 basalts. However, in coarse-grained Apollo 17 basalts this gap is absent, because the most Fe-rich armalcolites and the most Mg-rich ilmenites have identical FFM (0.68). Since fine- and coarse-grained Apollo 17 basalts are essentially isochemical (Papike *et al.*, 1974), the presence or absence of this gap is apparently related to a cooling rate effect. There is an order of magnitude decrease in olivine modal abundances between fine- and coarse-grained Apollo 17 basalts (Warner *et al.*, 1975a; 1978), due to the fact that slower cooling provides greater opportunity for resorption of olivine crystals. Resorption of olivine should cause the melt to be locally enriched in MgO. Ilmenite and/or other minerals crystallizing in the

vicinity of reacting olivine grains should reflect this enrichment by being more Mg-rich than would normally be expected on the basis of the bulk rock composition. This would result in a greater population of Mg-rich ilmenite grains in the more slowly cooled coarse-grained basalts (as observed), and consequently also in a narrowing of the gap in FFM between armalcolite and ilmenite in the rock. A similar effect should hold for pyroxene as well, that is, pyroxene grains in coarse-grained Apollo 17 basalts should be more Mg-rich than in fine-grained rocks. Compositional data of Warner *et al.* (1975a, 1976b) indicate that this is the case, lending further support to the above interpretation.

Analyses of ilmenites in Apollo 11 low-K basalts show an opposite relation to that observed in the Apollo 17 basalts. Here, ilmenite grains in the coarse-grained group B<sub>1</sub> rocks tend to be more Fe-rich than those in the more rapidly cooled group B<sub>3</sub> basalts (Table 3). In this case the two groups are not isochemical, and it appears that the differences in bulk composition are the controlling variables. The group B<sub>1</sub> basalts have lower TiO<sub>2</sub> and higher FFM, and ilmenite is correspondingly both later crystallizing and more Fe-rich. We note also that the group B<sub>1</sub> basalts do not contain olivine, and so an olivine resorption effect was not possible. The most evolved Apollo 17 basalts are compositionally similar to the group B<sub>1</sub> Apollo 11 low-K basalts and they also contain no olivine and only Fe-rich ilmenites (Warner *et al.*, 1976a).

In summary, slower cooling enhances chances of armalcolite reaction with the melt, and therefore results in a decreased modal abundance of armalcolite. The modal abundance of Cr-ulvöspinel also decreases with slower cooling because of increased Cr substitution in pyroxene and because of earlier plagioclase nucleation (depleting the melt in Al that otherwise might go into Cr-ulvöspinel). Cooling rate greatly affects ilmenite morphology but not its abundance. Ilmenite compositions are cooling-rate-dependent only insofar as the relative cooling rate affects the degree of olivine resorption.

#### **Effect of early opaque oxide mineral crystallization on the differentiation of high-Ti mare basaltic magmas**

Crystallization of Cr-ulvöspinel from a high-Ti mare basaltic magma depletes the melt in Cr<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>, because the amounts of Cr<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> incorporated by Cr-ulvöspinel are enriched relative to the melt by factors of ~50 for Cr<sub>2</sub>O<sub>3</sub> and ~2 for TiO<sub>2</sub>. Magmatic crystallization of armalcolite also depletes

the melt in these components, since both TiO<sub>2</sub> and Cr<sub>2</sub>O<sub>3</sub> are enriched in armalcolite relative to high-Ti basaltic liquids by factors >5. Similarly, TiO<sub>2</sub> and Cr<sub>2</sub>O<sub>3</sub> partition strongly in favor of ilmenite as opposed to high-Ti mare basaltic magmas. Clearly, then, the net effect of early crystallization of one, two, or all three of the above opaque oxide minerals is to rapidly deplete the melt in TiO<sub>2</sub> and Cr<sub>2</sub>O<sub>3</sub>.

Partitioning of MgO between Cr-ulvöspinel, armalcolite, or ilmenite and high-Ti basaltic liquids is near unity in each case, so that the amount of MgO in the melt is largely unaffected by their crystallization. FFM of armalcolite is slightly lower than that of the coexisting melt, whereas FFM of Cr-ulvöspinel and ilmenite is much higher than in the melt. Consequently, early opaque oxide mineral crystallization has a tendency to slightly lower FFM in high-Ti basaltic liquids. However, MgO is continuously being depleted in the melt and FFM raised, because of simultaneous crystallization of first olivine and later pyroxene. It is this effect which causes the opaque oxide minerals to become increasingly more Fe-rich as crystallization proceeds.

Gravitational crystal settling of early-formed opaque oxides should produce derivative liquids that become poorer in TiO<sub>2</sub> and Cr<sub>2</sub>O<sub>3</sub>. Simultaneous olivine fractionation will also result in the derivative liquids becoming increasingly MgO-poor. An example of the general differentiation trend to be expected is given by the equilibrium liquid-line-of-descent determined for an Apollo 17 basalt (70215) by Kesson (1975). The original composition contained (in weight percent) TiO<sub>2</sub>, 13.2; Cr<sub>2</sub>O<sub>3</sub>, 0.46; MgO, 8.7; FeO, 19.9 (FFM = 0.56). At 1135°C, the liquid composition changed to (in weight percent) TiO<sub>2</sub>, 10.1; Cr<sub>2</sub>O<sub>3</sub>, 0.18; MgO, 6.4; FeO, 19.5 (FFM = 0.64).

The compositional variations observed in Apollo 17 basalts reasonably match this experimentally determined liquid-line-of-descent. For types A and B basalts, mixing calculations (Wright and Doherty, 1970) indicate that deriving the most fractionated members from the most primitive requires separation of ~12 percent armalcolite + ilmenite, ~1 percent Cr-ulvöspinel and ~12 percent olivine (Warner *et al.*, 1975b). If the most primitive compositions are the result of addition of the above minerals, even less fractionation may have been involved. Compositions of Apollo 11 low-K basalts fall along the equilibrium liquid-line-of-descent determined for Apollo 17 high-Ti basalt, thus suggesting that they may be differentiates of parental magmas similar to those parental to Apollo 17 basalts (Longhi *et al.*, 1974; Green *et al.*,

1975). To account for the compositional variations among the various types of Apollo 11 low-K basalt requires significantly lesser opaque oxide and olivine fractionation than is necessary for the Apollo 17 suite. The high  $K_2O$  content of the Apollo 11 high-K basalts makes it unlikely that they could be related to either the Apollo 17 or Apollo 11 low-K basalts by fractional crystallization (James and Jackson, 1970; Walker *et al.*, 1975). Within this suite, compositional variation is very limited (Table 1), suggesting that little or no fractionation has occurred.

The concurrence of observed compositional variations in high-Ti mare basalts with those predicted from gravitational crystal settling of early opaque oxide minerals (and olivine) strongly suggests that modest fractionation of this type has occurred. However, aside from one olivine-enriched Apollo 17 basalt described by Warner *et al.* (1977), evidence for the existence of corresponding cumulate-enriched samples is lacking. Possibly such rocks exist and simply were not sampled. Alternatively, if fractionation took place during emplacement of the flows, early-settling opaque oxides may have been frozen into place before they could form an obvious cumulate layer and, instead, the "cumulates" are represented by clusters of early crystals dispersed throughout the interior of the flows. Such partial cumulates could be difficult to identify and may be represented among the returned samples by the more  $TiO_2$ -,  $Cr_2O_3$ -, and MgO-rich basalts.

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