Ilmenite and Armalcolite in Apollo 17 Breccias

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Abstract

Recrystallized Apollo 17 breccias contain high-Mg ilmenite, "Zr-", and "Cr-Zr-armalcolites"; textural relations indicate growth during recrystallization. The Mg/Fe ratios of both armalcolite types correlate positively with the Mg/Fe ratio of coexisting silicates; the distribution coefficient $K_{D} = (Mg/Fe)_{Ti-oxide}/(Mg/Fe)_{silicate}$ differs for the two armalcolite types ($K_{D_{Zr-Arm}} \approx 0.29; K_{D_{Cr-Zr-Arm}} \approx 0.12$), suggesting different structural control. Ilmenite from breccia is consistently high in MgO (range 4.6–7.6, average 6.5 wt percent MgO) compared to ilmenite from ilmenite basalt (range 0.8–3.5, average 1.8 wt percent MgO) reflecting the higher Mg/Fe ratio of the breccia; $K_{D_{Hf}} = 0.125$ for recrystallized breccia. CaO in breccia ilmenite tends to be higher than in basaltic ilmenite.

Both armalcolite types coexist with high-Mg silicates [Mg/(Mg + Fe) > ~0.75] while ilmenite occurs with silicates of lower Mg content. This relationship and the armalcolite $\rightarrow$ ilmenite reaction in ilmenite basalts suggest that armalcolite is a stable Ti-oxide phase coexisting with high-Mg silicates. Such an assemblage should be considered in lunar partial melting models especially because armalcolite can carry appreciable light rare-earth elements.

Introduction

Ti-oxide phases are common in lunar rocks, and numerous studies have been made on their compositional variation (e.g., Haggerty, 1973a; El Goresy, Ramdohr, and Taylor, 1971; Brett et al., 1973; Taylor, McCallister, and Sardi, 1973). Few data exist regarding relationships between Ti-oxides and coexisting silicates. The most common observation is the positive correlation between the MgO content of ilmenite and the bulk rock Mg/Fe value (e.g., Powell and Weiblen, 1972; Drake et al., 1970). Anderson et al. (1972) used the distribution of Mg between ilmenite and low-Ca pyroxene to estimate temperature of breccia equilibrium, but calibration at low temperatures was poor. Akella and Boyd (1973) investigated experimentally the distribution of Ti and Al between coexisting silicates, oxides, and liquids. The basic problem in interpreting silicate–Ti-oxide data is whether equilibrium was attained, especially for igneous samples with zoning and incomplete reactions. From silicate compositions and textures of Apollo 14 samples, Warner (1972) showed that equilibrium is approached for fine-grained recrystallized breccia, a rock type common at the Apollo 16 and 17 sites (Cameron et al., 1973). Apollo 17 breccias were used in the present study because both textures and silicate compositions indicate equilibrium, and because Ti-oxides are especially common with textures suggesting growth during recrystallization. Special attention was given to Ti-oxide compositions and their relation to coexisting silicate compositions.

General Characteristics of Samples and Analytic Technique

The samples available for study comprised 1 to 2 mm fines 78462.2, 78442.2, 78482.5, 72502.19, 78422.2, and 73242.2. Thin sections were prepared and petrographic descriptions made for all fragments larger than ~ 0.5 mm. Fine-grained, holocrystalline breccia is common in all six, whether from the South Massif or Sculptured Hills stations. Calcium-rich plagioclase, low-Ca pyroxene, and high-Mg olivine dominate and minor opaque oxides are usually present. These breccias are always fine-grained (< 0.1 mm) although coarser clasts are sometimes present. Figures 1a–1d illustrate the textures of four fragments. Most typically, the Ti-oxides occur as grains much larger than the silicate grains which they enclose (Fig. 2a). This is interpreted as a result of late growth of the Ti-oxide phase. Less commonly, small Ti-oxide grains occur, but these
also tend to enclose silicate grains suggesting late growth (Fig. 2b).

Electron-microprobe analyses of Mg, Ca, and Fe were obtained for 10 to 25 silicate grains selected at random in each fragment. Silicon was determined by difference and Bence-Albee (1968) matrix corrections were applied. Nearly all fragments show very restricted ranges of silicate compositions dominated by low-Ca pyroxene but rarely by olivine (see Fig. 3). These restricted patterns indicate that equilibrium was attained during metamorphism (Warner, 1972), and enable assignment of a \( mg (= 100 \frac{Mg}{Mg + Fe}) \) value to each fragment (Table 1). In addition several ilmenite basalt fragments are listed without \( mg \) values because the small sample size precluded obtaining accurate \( mg \) ranges; however, analyses of other ilmenite basalts indicate \( mg \) values less than \( \sim 70 \). The one plagioclase basalt in Table 1 has \( mg \) values ranging from \( \sim 95 \) to 75, but these values probably do not represent olivines occurring with ilmenite in the mesostasis.

The fragments enumerated in Table 1 were chosen for detailed study because they had: (1) a narrow range of silicate compositions for any one fragment; (2) a wide range of silicate \( mg \) values for all fragments; (3) a texture suggesting late growth of Ti-oxides; and (4) reasonably large (>20 \( \mu m \)) Ti-oxide grains suitable for microprobe analysis. In addition five ilmenite basalt fragments were selected at random as well as one plagioclase basalt so as to evalu-

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Fig. 1. Photomicrographs illustrating textures of fragments studied. (a) 72502,19-3; (b) 73242,4-15; (c) 78422,2-15; (d) 78442,2-25. Scale: a,b,c—long dimension = 0.9 mm; d—0.45 mm. Transmitted plane-polarized light.
ate Ti-oxide compositions in relation to rock type.

Microprobe data were obtained for the Ti-oxide phases usually by analyzing two grains in each fragment. Standards were: Ti,Fe–A128 ilmenite; Ca,Si,Mg–diopside glass; Mn–Mn-hortonolite; Zr–baddeleyite; Al–anorthite glass; Cr–MB5 chromite. Backgrounds were collected for each mineral type, and all data were obtained without moving the sample with respect to the beam. Operating conditions were: 15 kV; 0.3 μA beam current; focused beam (∼ 2 μm). Standard corrections were applied for deadtime, drift, and background. Matrix corrections were taken from Albee and Ray (1970). Oxide sums for representative ilmenites (Table 2a) are quite acceptable (100 ± 1.5 wt percent), but armalcolite1 sums (Table 2b) were low (94–99 percent). Because rare earths have been observed in “Cr–Zr–armalcolite,” wavelength scans were made. Lanthanum and the light rare earths (Ce,Pr,Nd, and Sm) were detected as were traces of Hf,Nb, and Y; however, all were below 0.1 oxide wt percent except La₂O₃(=0.15 wt percent) and Ce₂O₃(=0.32 wt percent). No other elements were detected. Low sums for “Cr-Zr-armalcolite” were also obtained by Steele and Smith (1972) using the same standards. Peckett, Phillips, and Brown (1972) noted the difficulty in obtaining proper oxide totals from other Zr–Ti oxides and suggested the presence of light elements, especially Li; however, Haggerty (1972, 1973a), Albee, Gancarz, and Chodos (1973) and Peckett, Phillips, and Brown (1972) did obtain good oxide totals for “Cr–Zr–armalcolite.” Several ilmenite analyses were rejected because of high oxide values for Si, Ca, and Al which probably came from silicate overlap. Rather high values for Si, Ca, and Al (>0.5 oxide wt percent) recorded in the literature for ilmenites are questionable since overlap with a silicate is probable.

The name armalcolite is used only to signify a similarity in composition; a structural similarity is not implied. Quotes are used for the specific terms “Zr-” and “Cr-Zr-armalcolite” to emphasize this point (Brown et al., 1973).

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**Fig. 2.** Photomicrographs showing details of oxide-silicate intergrowth in two fragments illustrated in Figure 1. (a) 72502,19-3; (b) 78422,2-15. Scale: long dimension = 0.45 mm.

**Fig. 3.** Partial pyroxene quadrilateral showing ranges of pyroxene and olivine compositions for fragments illustrated in Figure 1. See text for details.
Table 1. 100 Mg/(Mg + Fe) (mole percent) in Olivine and Low-Ca Pyroxene Associated with Ti-Oxides

<table>
<thead>
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<th>olivine</th>
<th>pyroxene</th>
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Discussion

Ilmenite

Ilmenite from Apollo 17 breccias shows consistently high contents of Mg substituting for Fe from a minimum of 4.5 to a maximum of 7.6 wt percent MgO. Such high values correlate with the high Mg-contents of the coexisting silicates. Ilmenites from ilmenite basalts have lower Mg contents (Fig. 4) which probably reflect either the lower bulk mg value for this type of basalt or the late crystallization of ilmenite from a progressively more Fe-rich liquid, or both. Thus ilmenites crystallizing in the mesostasis should have the lowest MgO content, and examination of the two analyses (14a and 14b) of ilmenite in the mesostasis of feldspathic basalt given in Table 2a does show this effect (even the MgO value of 0.66 for point 14a of the feldspathic basalt may be too high; note the high SiO₂ and CaO values).

The generally higher values of CaO in ilmenite from breccias with respect to ilmenite basalts correlate with the higher CaO content of the breccias. A check of published data for lunar ilmenite does not show a consistent trend of higher MgO in ilmenite from breccias. 

Table 2a. Representative Apollo 17 Ilmenite Analyses

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<thead>
<tr>
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<td>74</td>
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not confirm this result, and the present observation may result from the limited types of fragments studied. Alternatively, secondary fluorescence of Ca-rich phases may produce the high Ca values, but because most analyzed ilmenite grains were at least 0.1 mm in size and high Si values were not observed (although the secondary fluorescence effect would be less), the high-Ca values probably do not result from secondary fluorescence. The MgO–CaO plot (Fig. 4) shows distinct ranges for ilmenites from the three rock types; unfortunately ilmenites from plagioclase basalts are poorly represented. Brett et al. (1973) did not find such distinct ranges for ilmenites from Luna 20 specimens; however, consistent differences were observed for ZrO$_2$ between ilmenites from “highland” rocks (low ZrO$_2$) and mare basalts (high ZrO$_2$). The present data for ZrO$_2$ are consistently low (<0.11 wt percent) and usually close to the detection limit (0.02). Values for ilmenites from Apollo 17 ilmenite basalts tend to be slightly higher than for breccia. Only the two ilmenites from the mesostasis of the plagioclase basalt show distinctly high values, but this is to be expected because of Zr enrichment in late liquids. Prinz et al. (1973) observed a weak correlation between MgO and Cr$_2$O$_3$ in ilmenites but no correlation was found here.

Of the minor elements in ilmenite, Mg seems to best reflect the crystallization conditions. The

![Fig. 4. CaO vs MgO in ilmenites from recrystallized breccia, ilmenite basalts, and plagioclase basalt.](image)
Mg/Fe distribution between oxide and the silicate may depend mostly on temperature, and be almost independent of bulk composition. Anderson et al. (1972) attempted to evaluate the temperature dependence of this distribution for coexisting pyroxene and ilmenite. For high temperatures (>900°C), \( K_D \) increases ~0.04 for a 100°C rise in temperature, and the Mg/Fe fractionation between olivine and low-Ca pyroxene is close to unity (Ramberg and DeVore, 1951). The ilmenite-olivine data for recrystallized breccias (Fig. 5) form a tight grouping with \( K_D \) near 0.125: this corresponds to an estimated temperature near 950°C. Different \( K_D \) values for other lunar breccias should indicate different temperatures of equilibration relative to the Apollo 17 breccia. Presumably one could estimate the Mg/Fe value of olivine in equilibrium with ilmenite in an ilmenite basalt; this in turn would imply the Mg/Fe value of the bulk liquid at the time of crystallization, assuming equilibrium crystallization of ilmenite and olivine.

The combination of different bulk-rock Mg values and equilibration temperatures could account for the distinct ranges of MgO (Brett et al., 1973; Fig. 4, this work) for ilmenites from mare-type basalts (low MgO in ilmenite, low bulk Mg) and plagioclase-rich rock types (high MgO in ilmenite, high bulk Mg). The generally higher temperature of crystallization for the basalt relative to the metamorphic temperatures of the plagioclase-rich breccia.

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**Fig. 5.** Plot of Mg/(Mg + Fe) in armalcolite types vs Mg/(Mg + Fe) in coexisting olivine. Points labeled Apollo 14 are from Steele and Smith (1972). Point labeled 14310 is from Peckett, Phillips, and Brown (1972); the Mg value for a hypothetical olivine was inferred from the most Fe-rich of the low-Ca pyroxenes in 14310, and a large error should be expected. Points labeled Albee are from Albee, Gancarz, and Chodos (1973); point labeled Tarosov is from Tarosov et al. (1973); point labeled Brown is from Brown et al. (1973) – uncertainty in position is because of basaltic nature of this fragment. Ferropseudobrookite points were based on Mg/(Mg + Fe²⁺) values; one sample coexists with two olivines, hence the indicated range. Apollo 11 (A-11) armalcolite range was collected from many sources, but most values lie in cross-hatched rectangle. Horizontal lines from this range indicate range of olivine which might coexist with these armalcolites.
would tend to increase the MgO content of the basaltic ilmenite (higher $K_p$), but this effect would be small (see before).

**Armalcolite**

Two armalcolite types, “Zr-,” and “Cr–Zr–armalcolite,” were found in the recrystallized breccia; both types of armalcolite were recognized previously by Haggerty (1972) and the occurrence of “Cr–Zr–armalcolite” was discussed by Levy et al (1972), Peckett, Phillips, and Brown (1972), Steele and Smith (1972), and Haggerty (1973a).

The two armalcolite types coexist with silicates which have a rather wide range of $mg$ values. Armalcolite compositions from Table 2b are plotted on Figure 5 as Mg/(Mg + Fe) in armalcolite vs Mg/(Mg + Fe) in coexisting olivine; some data were obtained from the literature (see caption for details). Figure 5 demonstrates the positive correlation between the $mg$ value of olivine and the $mg$ of both armalcolite types. Several interesting points can be made. (1) “Cr–Zr–armalcolites” and “Zr–armalcolites” have different distribution coefficients with respect to olivine $K_{D_{Cr-Zr- arm}} = 0.29$, $K_{D_{Cr-Zr- arm}} = 0.12$. This may arise simply from the influence of appreciable Cr$_2$O$_3$ and ZrO$_2$ in the “Cr–Zr–armalcolite”; however, optical data (Levy et al, 1972) suggest that “Cr–Zr–armalcolite” is cubic rather than orthorhombic, and a real structural difference might well cause the difference in distribution coefficients. (2) Limited data for terrestrial ferropseudobrookite phenocrysts coexisting with olivine phenocrysts from Kilauean lava flows (Anderson and Wright, 1972) fall near the “Zr–armalcolite” trend on Figure 5 and thus suggest a similarity in stoichiometry as well as structure (Lind and Houseley, 1971). (3) The Apollo 11 type armalcolites (see range at right of Figure 5), which are similar to “Zr–armalcolites” except mainly for the lower ZrO$_2$ content, should be in equilibrium with olivines with an $mg$ value of 0.74 to 0.78. This range corresponds to the most Mg-rich olivines found in ilmenite basalts, consistent with joint crystallization. Anderson (1971) argued for an exotic origin of some Apollo 11 armalcolite, but he gave no evidence from mineral compositions to support or refute this proposal. Based on the present data, Apollo 11 armalcolite could have crystallized from the Apollo 11 ilmenite basalt. (4) Anderson (1973) reported armalcolite in association with a Mg-rich assemblage in a peridotite 15445.10, but direct evidence of a genetic association was not present. The $mg$ value of this armalcolite (ZrO$_2$ < 0.1 wt percent) suggests that it is in equilibrium with olivine of $mg = 89$ (Fig. 5). Within experimental error this agrees with the value of $mg = 91$ for the olivine of 15445. Hence the armalcolite could be genetically associated with the Mg-rich assemblage and need not be exotic. (5) Armalcolite and olivine from a terrestrial ultramafic nodule (Cameron and Cameron, 1973) plot on the “Zr–armalcolite” trend of Figure 5.

The armalcolite types described here and in the literature always seem to coexist with Mg-rich silicates. When olivine has $mg > \sim 75$, armalcolite appears to be stable rather than ilmenite. This relationship was also seen in the armalcolites from mare-type basalts; initial crystallization yielded Mg-rich olivine ($\sim$Fo 75-80) and armalcolite, but with further crystallization armalcolite reacted to give ilmenite. With olivine of $\sim$Fo 75, both ilmenite and armalcolite coexist (e.g., 78462.2-7; also see Albee, Ganczarz, and Chodos, 1973). The Ti-oxide reactions as described by Haggerty (1973a) probably occur in assemblages with $mg$ near 75; otherwise either ilmenite or armalcolite would be stable.

**General Discussion**

The association of Mg-rich silicates and armalcolite has important implications regarding the chemistry of the Moon. If the mantle of the Moon formed during an initial differentiation and thus consists of Mg-rich silicates, one or more armalcolites would be expected as the coexisting Ti-oxide(s). The occurrence of an early crystallizing Ti-oxide phase may have effectively concentrated titanium in the mantle, and later partial melts derived from this region (e.g., Fe–Ti–basalts?) could be expected to be Ti-rich. The upper limit of stability for armalcolite in ilmenite basalts is about 3 kbar (Ringwood and Essene, 1970), but this limit may not apply to Mg-rich assemblages. In addition, if “Cr–Zr–armalcolite” has a different crystal structure (see before), the phase relations might be quite different.

The REE-bearing “Cr–Zr–armalcolite” probably is not a primary liquidus phase because of its enrichment in trace elements; it may result only from

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2 The 14310 point on Figure 5 appears to be an exception, but this rock is probably hybrid, formed from melting of heterogeneous regolith (Morgan et al, 1972).
metamorphism of polymict breccia incorporating REE-rich material (KREEP component?). In any case, the partial-melt products, particularly the REE content of such a partial melt could possibly result from the extent to which armalcolite contributes to this liquid.

Armalcolite appears, at least in one case (excluding ilmenite basalts), to be a primary igneous phase; Anderson (1973) interpreted 15445 as an igneous assemblage. Possibly igneous “Zr-armalcolite” was more common, but reactions such as those suggested by Haggerty (1972, 1973a) have erased most evidence.

A detailed experimental examination of armalcolite phase relations probably would do much to establish the role of the various armalcolite types in the Moon.

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