Fine Particles, Glasses, and Shock Effects

Silicate Liquid Immiscibility in Lunar Magmas, Evidenced by Melt Inclusions in Lunar Rocks

Abstract. *Examination of multiphase melt inclusions in 91 sections of 26 lunar rocks revealed abundant evidence of late-stage immiscibility in all crystalline rock sections and in soil fragments and most breccias. The two individual immiscible silicate melts (now glasses) vary in composition, but are essentially potassic granite and pyroxenite. This immiscibility may be important in the formation of the lunar highlands and tektites. Other inclusions yield the following temperatures at which the several minerals first appear on cooling the original magma: ilmenite (?) liquidus, 1210°C; pyroxene, 1140°C; plagioclase, 1105°C; solidus, ~1075°C. The glasses also place some limitations on maximum and minimum cooling rates.*

Ever since certain silicate systems were found to exhibit liquid immiscibility, there have been numerous attempts to apply this process to explain certain rocks. In 1927 Greig (*1*) showed that the unusual compositions and unreasonably high temperatures made immiscibility unlikely as a process in the origin of igneous rocks. Roedder (*2*) then described silicate immiscibility in the system leucite-fayalite-silica, and in the parent quaternary system K_2O-FeO-Al_2O_3-SiO_2, at more geologically reasonable temperatures and compositions. Recent work has also resurrected this hypothesis for certain syenite-gabbro associations (*3*).

Although normal, primary silicate melt inclusions are not rare in lunar rocks; other more unusual primary inclusions provide abundant evidence of immiscibility. Such evidence can be found readily in loose grain mounts, but is most obvious in thin sections. All 58 thin sections (or probe mounts) of 15 crystalline rocks (numbers 03, 17, 20, 22, 24, 29, 44, 45, 47, 49, 50, 57, 69, 71, and 72) showed such evidence under brief examination, although it was relatively sparse in sections from rocks 20 and 71. The fragments of crystalline rocks in many of the sections of breccias examined (33 slides from 11 rocks) showed similar evidence, as did most sections of 29 fragments from the lunar soil (sample 85) (*4*).

Normal silicate glass inclusions, representing the trapping of a *homogeneous* melt, were found in plagioclase, ilmenite, pyroxene, and olivine. Those in olivine were by far the largest and most abundant per unit of mineral volume. As in similar melt inclusions in earth rocks, failure to nucleate stable phases frequently prevented the attainment of equilibrium on cooling.

Most plagioclase crystals are remarkably free of inclusions, but a very few, such as 20-29 (*5*), contain in their cores one large inclusion or groups of amoeboid inclusions of dark brown glass of high index of refraction. In addition to the glass, there is usually a bubble (from shrinkage on cooling) and one or more opaque masses, presumably ilmenite. These inclusions were probably trapped by the nucleation and rapid growth of a skeletal plagioclase crystal in a portion of melt otherwise free of plagioclase nuclei at the time. The proportion of ilmenite appears to be approximately equal to that in the rock.

Many ilmenite crystals are skeletal, so most of the apparently unconnected blebs of silicate seen in them are not actually isolated. Some blebs of silicate melt were isolated by the growth of ilmenite, however, yielding large inclusions. On cooling, these generally have formed brown glasses, either isotropic or containing a mass of minute, feathery birefringent crystals, presumably pyroxene. A few also contain large crystals of tridymite.

Some growth phenomenon has resulted in the trapping of melt inclusions in many, if not most, of the larger olivine crystals. These inclusions vary from a small fraction of a micrometer (in secondary, healed fractures) (*6*) to 655 μm, and the present phase assemblage is, to a degree, a function of this size. The smallest are all glass, or have nucleated only a shrinkage bubble or one or two opaque phases (Fig. 1a). The larger ones are generally more crystalline, and contain up to six phases (Figs. 1b and 2); in effect, these present us with a sample of the magma and a documented model of its future evolution, starting at the time of trapping.

A series of heating experiments were performed on the inclusions in olivine. Individual tiny grains of olivine containing suitable multiphase inclusions were held in iron foil envelopes *in vacuo* for hours or days at various temperatures and then quenched and reexamined (Fig. 2). These experiments, to be reported in full elsewhere, provided the following data on the homogenization temperatures: ilmenite (*7*) liquidus, 1210°C; joined by pyroxene, 1140°C; joined by plagioclase, 1105°C; solidus, ~1075°C. As these runs were all made in "containers" of olivine, they represent liquids saturated with olivine. There are small amounts of volatile constituents in these inclusions, as more pyroxene crystals are present in inclusions open to the furnace vacuum than in adjacent, completely sealed inclusions in the same grain, at near-liquidus temperatures.

Heating experiments that result in the formation or melting of daughter minerals in such inclusions in olivine permit us to place some limits on both the maximum and the minimum cooling rates (*8*). This is complicated by what appear to be large differences in the ease of nucleation of the various phases, and the present data are partly contradictory, but the epitaxial nature of the daughter minerals in the multiphase inclusions (Figs. 1 and 2) suggests that the original cooling from the temperature of trapping to somewhat below 1100°C must have been very slow. The frequent lack of nucleation of pyroxene in the glass remaining after crystallization of ilmenite and plagioclase and the presence of dendritic crystals in those that did nucleate suggest that further cooling of the magma containing these phenocrysts was rapid. It may be possible to select laboratory cooling rates that will duplicate these textures in previously homogenized inclusions, but this has not yet been achieved.

When the rocks were approximately 90 to 98 percent crystallized, as a mush of ilmenite, olivine, plagioclase, and pyroxene, the residual silicate melt between the crystals, still very mafic in composition, started to form minute immiscible globules of a second, high-silica, high-potassium melt. The main evidence for this *heterogeneous* mixture of two silicate melts lies in the following facts:

1) Residual masses of high index glass that is brownish, clear, and isotropic or in part devitrified occur in the angular interstices between late plagioclase crystals and contain various sizes of almost spherical blebs of colorless, isotropic, low index glass and occasionally a vapor bubble. The larger of such low index blebs in turn have minute spherical masses of high index glass toward their centers. Similar examples of the reverse situation, the angular interstices between plagioclase crystals being filled with low index glass containing spherical masses of high index glass, were found in several rocks, particularly 03-37; 50-31; and 72-36 (Fig. 7b). Similar phenomena are frequently seen effectively in two dimensions in the form of exceedingly thin platelike inclusions between subparallel plagioclase crystals. In some of these the high index glass has crystallized to a small amount of an opaque phase (ilmenite?), and a much larger amount of a fine-grained or single-crystal, birefringent, high-index phase, presumably pyroxene, that contains a row of circular masses of colorless, low index glass (Fig. 5a).

2) The compositions of the two liquids, as determined by electron microprobe (to be detailed elsewhere), do not differ greatly from certain immiscible liquid pairs found in the synthetic system leucite-fayalite-silica (*3*). The nature of the lunar samples made accurate analysis difficult, and the compositions vary significantly from rock to rock, but most cluster closely about the following weighted averages of 37 complete microprobe analyses (high- and low-silica glasses, respectively): SiO_2 76.1, 47.8; Al_2O_3 11.7, 3.2; FeO 2.5, 31.4; MgO 0.3, 2.3; CaO 1.9, 11.2; Na_2O 0.4, 0.1; K_2O 6.6, 0.3; TiO_2 0.5, 3.7. In composition these glasses are essentially potassic granite and pyroxenite.

3) A synthetic charge, closely approximating a mixture of equal portions of the two glasses, fused in a pure iron container *in vacuo* at 1450°C, formed a homogeneous melt (n of glass 1.569 ± 0.005). Portions of this glass held in pure iron *in vacuo* in the range 1135° to 1075°C formed two immiscible liquids, one yellow brown, with high n, the other colorless, with low n, with or without crystals of silica (cristobalite?) and pyroxene (Fig. 8).

4) The most common, and obvious, evidence for immiscibility is found in the low-index glass inclusions in the outer margins of many late plagioclase crystals. This feature is present in all the rocks, including the fragments in the breccias, but is relatively rare in rocks 44, 50, and 71. In section these inclusions appear as rows of closely spaced, rounded or elongate blebs, with an almost regular spacing of 5 to 15 μm between centers, and almost always near a contact with pyroxene (Figs. 5b and 6). A few are connected with an external residual film of glass lining a vug, but many are found to be completely within a single plagioclase crystal (Fig. 6, a and b). They may make a zone about 20 μm wide that starts abruptly (presumably from the onset of immiscibility) at a growth zone near the edge of the crystal and extends to just a few micrometers from the contact with pyroxene. Only rarely are these blebs as large as 15 μm in diameter. The larger ones tend to bifurcate, and almost always contain 1- to 2-μm specks with a high index of refraction (pyroxene or high index glass?) on their surfaces and centers (Fig. 6, a and b). The occasional chance section

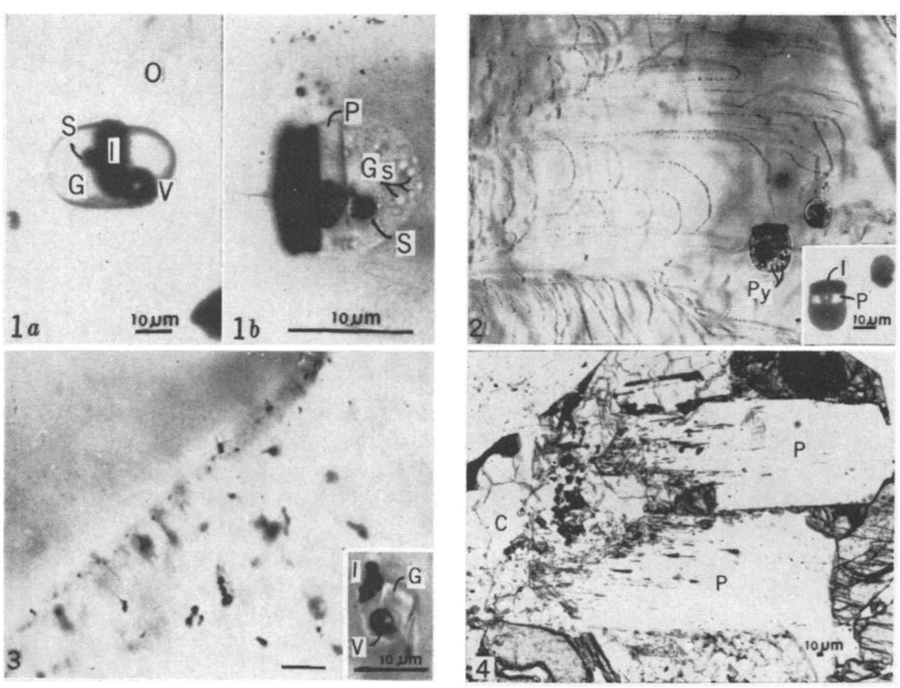

Fig. 1. (a) Unusually large inclusion of glass (G) in olivine (O) with daughter minerals ilmenite (I) and sulfide (?) (S), and shrinkage bubble (V). Slide 71-28. (b) Similar but also contains daughter crystal of plagioclase (P), and minute globules of much lower-index, high-silica glass (Gs). With rare exceptions, the plate-like ilmenite and plagioclase daughter crystals are always arrayed parallel to (100) of the enclosing olivine—a case of "internal epitaxy." The sulfide (?) grain (S) is spherical. Slide 45-32. Fig. 2. Pair of inclusions in olivine, similar to Fig. 1, before (inset) and after 2 days at 1110°C. The plagioclase has melted, and the almost opaque devitrified glass has recrystallized to a few coarser pyroxene crystals (Py) in clear glass. A series of dislocation loops (?), almost invisible in the original grain, have become decorated with minute, unidentified grains. Loose grain A-8 from olivine phenocryst, rock 20–41. Fig. 3. Pyroxene single crystal, in part inclusion-free (upper left), with a sharply delineated zone rich in glass inclusions (lower right). The upper left shows uniform extinction, but that of the lower right is blocky and irregular. Individual inclusions in such zones (inset) may have glass (G), opaque daughter crystal (I, ilmenite?), and shrinkage bubble (V). Slide 72-36. Fig. 4. Plagioclase crystals (P), rich in inclusions, near a mass of late, interstitial cristobalite (C), ilmenite, apatite, and high-silica glass (at left). Slide 47-7576.

parallel to the pyroxene-plagioclase contact shows them to be circular in cross section. Gelatin-slide mounts of crushed fragments show indices of refraction in the range 1.486 to 1.515 for these glasses. Many of the microprobe analyses were of such blebs in plagioclase.

5) A sharply delineated zone consisting of large numbers of tiny colorless silicate glass inclusions of very low index of refraction occurs near the margins of some pyroxene crystals (Fig. 3). In those rocks having strongly zoned pyroxenes, these inclusions start at the zone of most rapid increase in birefringence. Many of these inclusions contain an opaque daughter crystal, but most are so small that they have not even nucleated a bubble on cooling. Unlike the inclusions of mafic melt in olivine, not even the larger ones show any evidence of crystallization or devitrification to form silicates from this glass.

6) Large numbers of inclusions occur in both pyroxene and plagioclase within about 100 μm of most vugs and miarolytic cavities, and adjacent to or at the contact with *late* interstitial crystals of tridymite, cristobalite, and apatite (*9*). In pyroxene these inclusions are round or vermicular; in plagioclase they are generally thin tubes parallel to the length of the laths, and contain birefringent, high-index crystals (presumably pyroxene) as well as blebs of low-index glass (well displayed in rock 47; Fig. 4). In pyroxene these may be seen even though no other evidence of zoning is visible. Early crystals of tridymite and cristobalite, which are sharply euhedral against single-crystal pyroxene, plagioclase, and ilmenite (particularly in rocks 44 and 47), have no such inclusion zones in the minerals along their borders.

7) Inclusions of dark greenish or yellowish brown, high-index glass were found in late cristobalite. Some of these occur as globules in low-index glass (Fig. 7b). Others are large, spherical to elongate, curving blebs with indices of refraction much higher than the low-index glasses described above, and most of the larger ones contain birefringent, higher-index crystals, presumably pyroxene, that are either equant, solid, single crystals or long feathery dendrites. A few of the blebs contain minute blebs of colorless, very low-index glass within the high-index glass (*10*).

8) Almost perfectly circular masses of cristobalite in late, inclusion-rich plagioclase were found in or near some vugs (47-16). These presumably represent the crystallization, essentially in place, of round blebs of high-silica glass.

9) Three inclusions were found in ilmenite, from three different rocks, each consisting of dark brown, high-index glass and colorless, low-index glass.

10) Tiny blebs of very low-index glass (maximum 0.3 percent by volume) were found on the walls of three small undevitrified glass inclusions in olivine from rocks 20 and 45 (Fig. 1b). These are believed to represent immiscibility in metastable glass, in that pyroxene should have grown in these inclusions.

The immiscibility seems to occur too late in the crystallization to be helpful in explaining the odd bulk composition of these rocks, but, if the samples from the Sea of Tranquillity are at all representative of the maria, it is possible that this same splitting has occurred on a large scale in the early history of the moon, and that, as a result of the rising of such low-density liquid globules, the lunar highlands may be, in effect, partly "granitic" in composition. If so, the 30- to 100-fold increase in potassium should result in gross differences in heat flow and surface radioactivity. Any such surface mass would also greatly simplify the problem of a possible lunar origin for tektites, as the compositions of the siliceous glasses are obviously very much closer to tektites than are the compositions of the bulk rocks returned by Apollo 11.

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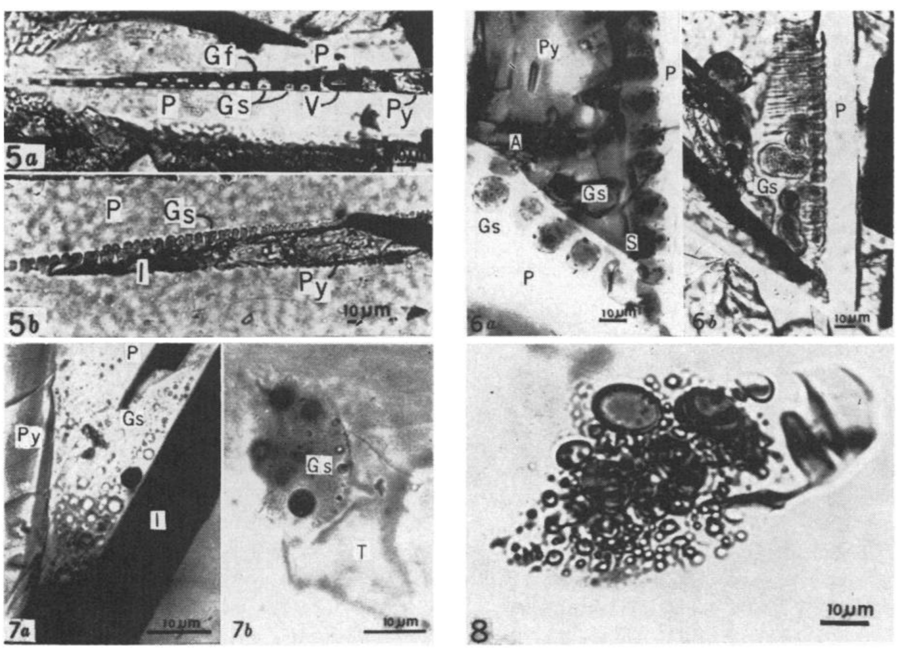

Fig. 5. (a) Wedge-like inclusion between two parts of single plagioclase crystal (P), now consisting of coarse pyroxene (Py), shrinkage bubble (V), isotropic (but devitrified?) low-silica, high-iron glass (Gf), and blebs of high-silica glass (Gs). Slide 71-32. (b) Similar wedge-like inclusion in plagioclase (P), but consisting of coarse pyroxene (Py), opaque mineral (I), and teeth-like row of high-silica glass blebs (Gs). Slide 72-46. Fig. 6. (a) Completely isolated blebs of high-silica glass (Gs) embedded in plagioclase single crystals (P). Each bleb has numerous much smaller blebs of high index (high-iron glass?), mainly on the interface with plagioclase. The pyroxene (Py) is strongly zoned, compositionally, and contains many blebs of high-silica glass (Gs), apatite (A), and sulfide (S) near its contact with plagioclase. Slide 72-36. (b) Somewhat similar, with mass of blebs of high-silica glass (Gs) all embedded in a single crystal of plagioclase, crystallographically continuous with the inclusion-free part (P). The center bleb is one of the largest such inclusions found. All show many minute, high-index blebs. Slide 45-32. Fig. 7. (a) Spheres of dark, high-index, high-iron glass in colorless, low index, high-silica glass (Gs). The glasses interfinger with plagioclase (P), between ilmenite (I) and pyroxene (Py); the largest sphere (dark) has devitrified, but the others are isotropic. Slide 72-36. (b) Similar, but with spheres of high-index glass (now devitrified and dark except for one small, bright, isotropic one), in a rounded mass of high-silica glass (Gs) in tridymite (T). Gelatin-slide mount of grain from rock 50-32, in 1.479 oil. Fig. 8. Synthetic melt, previously homogeneous, after 30 minutes at 1135°C. This grain of colorless glass, $n = 1.513$, is mounted in a matching oil, and contains many blebs of brownish, high-index glass plus a few crystals of silica (cristobalite?). The bar in the lower right of each photograph is 10 μm long.

References and Notes

1. J. Greig, *Amer. J. Sci.* (ser. 5) **13**, 1 (1927); *ibid.* **15**, 375 (1928). The term is used here to mean immiscibility between two silicate melts. There is ample evidence of immiscibility between silicate melts and: liquid iron; liquid sulfides; dense, supercritical CO_2 [E. Roedder, *Amer. Mineral.* **50**, 1746 (1965)]; and dense $NaCl$-H_2O fluids [E. Roedder and D. S. Coombs, *J. Petrol.* **8**, 417 (1967)].
2. E. Roedder, *Amer. Mineral.* **36**, 282 (1951); *Geol. Soc. Amer. Bull.* **64**, 1466, 1554 (abstracts) (1953).
3. A. R. Philpotts and J. A. Philpotts, *Geol. Soc. Amer. Abstracts 1969* (part 7), 176 (abstract) (1969).
4. Some of the inclusion types found raised still unanswered questions, owing to the small inclusion size, inclusion rarity, and hence lack of optimum orientation for observation, the necessary prohibition of destructive testing with these sections, and the obvious lack of time. As a result, many of the findings are too tentative to present here, but we believe the evidence for silicate immiscibility is conclusive.
5. During the examination of many of these rocks at the Lunar Receiving Laboratory, the individual thin sections or probe mounts of each rock were identified by the appropriate five-digit rock number followed by a dash and a six-digit section container number (for example, 10072-64-7668). When these sections were released to the principal investigators, NASA replaced these container numbers with new, two-digit section numbers such as 10072, 46). To aid other investigators in checking the specific sections examined, we give the container numbers where section numbers are not currently available, or both when there is ambiguity. We have omitted the "100" of the sample number and the "64" of the container number, and changed the comma to a hyphen to avoid ambiguity in serial listing. For some of these sections, we understand that a complete tabulation of container numbers and their equivalent section numbers cannot be made until the sections are returned to NASA.
6. A few very small secondary inclusions in olivine in samples 03-37 and 20-29 contained only gas, and this gas may be CO_2. Only destructive tests or the discovery of larger inclusions will permit more positive identification. Small amounts of noncondensable gases were found in some of the bubbles in glass fragments from samples 84 and 85, but most bubbles held only a vacuum.
7. All that is known about the identity of the phase at the liquidus is that it is the last portion to dissolve of an opaque phase remaining in the position of the original daughter ilmenite crystal. It could also be the ferropseudobrookite found at the liquidus in one synthetic lunar magma (R. Tuthill and M. Sato, personal communication).
8. Similar but very rapid vacuum heating experiments on minute fragments and spheres of glass from the lunar soil (sample 84) show that the dark glasses, with indices above 1.70, devitrify throughout within a few seconds in the range 1000 to 1100°C, but under these same conditions colorless glasses of index <1.60 may develop only a thin surface film of crystals. Such devitrification experiments may permit placing semiquantitative limits on the cooling history of some lunar materials, as similar devitrification textures are seen in some of the fragments of the breccias and soil, including well-developed chondrule-like features in some former glass spheres.
9. This interstitial occurrence of high-potassium glass and apatite may explain some of the biological growth effects reported for lunar soil. The silica crystals occur as close to olivine as a few hundred micrometers in several rocks, indicating nonequilibrium.
10. As a result of the need for multiple impregnations with epoxy (diluted with toluene) and the use of several epoxy resins with different indices of refraction in the preparation of these sections, there are many examples of apparent immiscibility (for example, filling of inclusion shrinkage bubbles with epoxy where they are cut by the section surface, or filling of the bubbles left in vugs by shrinkage of the previous impregnation), and of real immiscibility (residual globules of one epoxy component in another). These artifacts (and several other types) occur in cracks within grains, between grains, and, most confusingly, in the microvugs where evidence of actual magma immiscibility is most apt to be found.
11. Much of the preliminary work was done at the Manned Spacecraft Center, Houston. We are indebted to the personnel of the Lunar Receiving Laboratory for courtesies extended during this hectic period.

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Petrology of Unshocked Crystalline Rocks and Shock Effects in Lunar Rocks and Minerals

Abstract. *On the basis of rock modes, textures, and mineralogy, unshocked crystalline rocks are classified into a dominant ilmenite-rich suite (subdivided into intersertal, ophitic, and hornfels types) and a subordinate feldspar-rich suite (subdivided into poikilitic and granular types). Weakly to moderately shocked rocks show high strain-rate deformation and solid-state transformation of minerals to glasses; intensely shocked rocks are converted to rock glasses. Data on an unknown calcium-bearing iron metasilicate are presented.*

Evidence of impact metamorphism is widespread in the lunar sample. The fine material and breccias contain abundant small fragments of shocked crystalline rocks and mineral grains and particles of shock-melted rocks; only in the large rock fragments are the shock effects negligible. Moreover, some fragments have a history of multiple impact (for example, fragments of older breccia in younger breccia, and spherules of shock glass coated by different shock glass).

In order to study the effects of shock in the returned lunar samples, it is necessary to know in detail the rock textures and mineralogic variations characteristic of the unshocked crystalline rocks. On the basis of rock modes, mineralogy, and textures, we have classified these rocks into two suites: a dominant ilmenite-rich suite and a subordinate feldspar-rich suite. All the large samples and the bulk of the smaller rock fragments and mineral grains in the fines and breccias are from the ilmenite-rich suite; rocks of the feldspar-rich suite are found only as small fragments in the fines and breccias.

In the ilmenite-rich rocks, the major mineral constituents are clinopyroxene, calcic plagioclase, and ilmenite. Olivine is a common minor constituent, and cristobalite, troilite, and native iron are accessory and trace constituents of nearly all rocks. Interstitial glass is present in many rocks. The rocks are dominantly volcanic; both the presence of vesicles and vugs in all large samples and the rock textures suggest that they crystallized from magmas at or near the lunar surface (*1*).

Most of the ilmenite-rich rocks have one of three types of texture: (i) intersertal, (ii) ophitic-subophitic, and (iii) hornfels (*2*).

Intersertal rocks (Fig. 1A) have abundant interstitial glass that contains skeletal plagioclase grains, fine myrmekitic intergrowth of plagioclase and glass, and minute grains of pyroxene. Olivine forms sparse phenocrysts marginally reacted to clinopyroxene or small rounded cores in pyroxene grains. Ilmenite grains are subhedral. Clinopyroxene grains tend to be subhedral, but locally they form subophitic patches partly enclosing ilmenite. Patches of micrographic intergrowth of pyroxene and plagioclase fill some interstices. Grain size is typically fine and ranges from about 0.05 to 0.2 mm.

Ophitic rocks (Fig. 1B) are characterized by ophitic to subophitic intergrowth of clinopyroxene and plagioclase; plagioclase forms subhedral laths, and pyroxene is anhedral and partly encloses plagioclase. Olivine occurs as phenocrysts or as partly resorbed cores in pyroxene grains, and the pyroxene grains may be pigeonitic or contain cores of pigeonite. Interstitial myrmekitic intergrowth of plagioclase with glass is common. Grain size is highly variable and ranges from about 0.05 to 1 mm.

Hornfels (Fig. 1C) are characterized by reduced size of pyroxene and ilmenite grains and growth of coarse poikiloblastic grains of plagioclase. The ilmenite grains are equant rather than bladed; the pyroxene grains are equant and subhedral, or rounded, or form a mosaic of minute grains. The rocks may be highly inequigranular; ilmenite and pyroxene range from about 0.02 to 0.15 mm, and poikiloblastic plagioclase may be up to 3 mm across. Locally, primary rock texture is preserved in relict patches.

In nearly all the ilmenite-rich rocks, troilite (containing minute droplets of native iron) forms irregular patches or globules between grains. Minor cristobalite (locally intergrown with tridymite)