Implications of a titanium-rich glass clod at Oceanus Procellarum

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Abstract

A friable clod consisting of spherules and conchoidal fragments of red-black glass with an exceptionally titanium-rich composition (~16 percent TiO_2) was discovered in the 2–4 mm fraction of Apollo 12 sample 12033. Despite a diligent search of the remaining Apollo 12 soils, no similar fragment has been found in the samples from that or any other lunar mission. By analogy with the glass spherule clods collected at the Apollo 15 and Apollo 17 sites, this unique clod of glass may represent a lunar magma of which no crystalline equivalent has yet been found.

The probability is small that magmas with the composition of the red-black glass could be parental to high-K titaniferous Apollo 11 basalt by low-pressure fractional crystallization. Red-black glass composition cannot be parental to any other lunar basalt types. If red-black glass is a magma type, and not an accidentally remelted cumulate, its existence requires that gross heterogeneity of TiO_2 characterize lunar magma source regions and/or that simple models of magma genesis cannot produce this type.

Occurrence

A friable spherule aggregate, which looked like a dollop of black caviar (Fig. 1), was recognized as an exceptional particle of lunar soil during a macroscopic survey of Apollo 12 sample 12033,66. The sample represented a layer of light gray soil that was exposed at a depth of a few centimeters in the walls of a trench the astronauts dug through the rim of Head Crater. The light color of the soil signaled an abundance of small ropy fragments of Kreep-rich glass coated with gray-white dust. The ropy glasses have been interpreted as either ray material from the crater Copernicus (Meyer *et al.*, 1971) or as shock-melted ejecta from a more local impact crater that penetrated thin mare flows and excavated noritic materials (Quaide *et al.*, 1971). Although the dark clod, which differed strikingly in texture and composition from all other particles in the Apollo 12 soils, occurred in a sample consisting of 40 percent ropy glass fragments, no genetic association between these particle types need be assumed. On the contrary, high values of titanium and chromium in the dark glasses

suggest an affinity with mare basalts rather than norites.

When the clod was discovered in the summer of 1971, it was immediately mounted in epoxy and cut into a thin section. As no more of the clod remains, the opportunity was thus lost to treat this 2-mm particle as a consortium rock (an approach that was developed later) in order to determine its age and trace element content and to analyse the spherule surfaces for micromounds of condensed volatiles, as was done subsequently on the Apollo 15 green spherules and the Apollo 17 orange and black spherules (for review see Butler and Meyer, 1976).

A single soil particle, regardless of how exotic its composition, hardly seems adequate for formulating a petrogenetic hypothesis. In order to find additional examples to be used for surficial analyses and other studies, an arrangement was made by U. B. Marvin in 1977 to examine and catalogue the Apollo 12 soils in storage in the Curatorial Facility at Houston (catalogue in preparation). A diligent search of all the fractions coarser than 0.55 mm failed to locate a single spherule or spherule aggregate of red-black

glass. Inasmuch as no similar clod has been found in any other lunar soil, the original clod remains unique.

Texture

In thin section the clod is nearly opaque in transmitted light, but the extra illumination provided by a substage condenser shows that the main constituent is a very dark red-black glass. A single 50-μm fragment of clinopyroxene is located near the center of the section, but most if not all of the many other small transparent phases are crystallites of olivine and pyroxene. Reflected light (Fig. 2a) reveals that the clod is a porous aggregate of spherules (5–130 μm dia.), conchoidal spherule fragments, and irregular chunks of glass. Some of these glass chunks and partially devitrified fragments of spherules have been compressed together into new aggregates, but clasts incorporating lithologies other than red-black glass and its partial devitrification products were not observed. About 35 percent of the glassy particles are brownish in color and contain well-developed crystallites of ilmenite, olivine, and/or pyroxene with a maximum size of 2.5 × 1.4 μm (Figs. 2b, 2c, 2d). The remaining 65 percent of the spherules and fragments are dark red and cloudy, with opaque submicron crystallites distributed uniformly or aligned in feathery patterns in the glass. The presence of these minute crystallites gives the dark glasses an exceptionally bright reflectivity which makes the mafic silicates look dull gray in comparison. This is the opposite of the usual reflectivity contrast between glasses and mafic silicates.

Composition

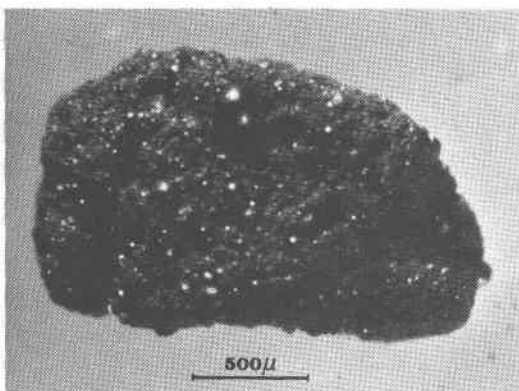Electron microprobe analyses of the homogeneous-appearing dark spherules and fragments show
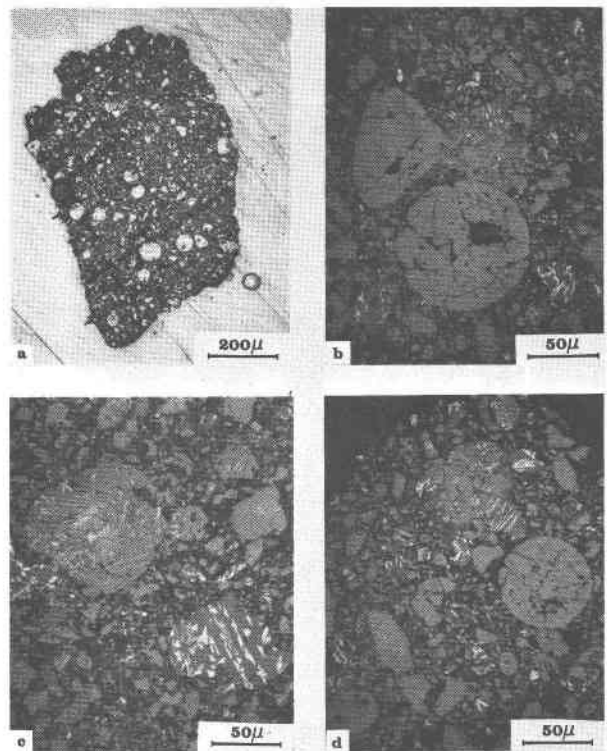

Fig. 2. Views in reflected light of the polished thin section of the glassy clod. (a) View of the entire particle showing the distribution of spherules in the porous matrix of conchoidal glass fragments. The dark diagonal streaks are pre-existing fractures. (b) A portion of the section illustrating the contrast between the highly reflective spherules and fragments containing minute, uniformly distributed opaque crystallites and the fragments of darker glass with prominent crystallites. (c) Two particles with crystallites in different stages of growth. The particle at the upper left has a delicate dendritic pattern of ilmenite. The one at lower left includes ilmenite crystallites plus one elongated olivine crystallite which occupies the band between the lobe at the left and the larger portion at the right. The remaining matrix material is brownish glass that partially covers the olivine, making it indistinguishable in this photograph. (d) A "homogeneous" spherule and an irregular mass of glass with the more uniform variety grading into the more coarsely crystalline type.

the narrow compositional range listed in Table 1 and plotted in Figures 3 and 4. The red-black glass is olivine-normative and contains about 31 weight percent of normative ilmenite. The growth of olivine, ilmenite, and a few clinopyroxene crystallites in the red-black glass produces a lighter-colored, quartz-normative, pyroxene–plagioclase-rich residual glass (Table 1). Most attempts to analyze the crystallites failed to yield mineral compositions unmixed with glass. However, two good crystallite analyses are of olivine (Fo_{71}) containing 0.3 percent Cr. This value of chromium in a lunar rock suggests a genetic relationship with mare basalts rather than with norites or

Fig. 1. The 2-mm clod of spherules and fragments of red-black glass from Apollo 12 sample 12033,66.

Table 1. Electron microprobe analyses of the glass clod

A. The average and range of values in 8 particles of red-black "homogeneous" glass
B. Bulk composition of the clod, derived from the average of 8 100 μm broad-beam analyses recalculated to 100 percent
C. The composition of 1 particle of brown quartz-normative, residual glass containing crystallites of olivine and ilmenite

	A Avg.	A Range	B	C
SiO$_2$	33.44	31.83 – 35.14	33.02	42.81
TiO$_2$	16.37	16.02 – 16.76	15.68	10.54
Al$_2$O$_3$	4.60	3.90 – 5.41	6.21	5.15
Cr$_2$O$_3$	0.84	0.71 – 0.98	1.00	0.22
FeO	23.87	23.42 – 24.43	23.64	20.88
MnO	0.30	0.24 – 0.36	0.30	0.30
MgO	13.00	12.04 – 13.87	12.57	8.15
CaO	6.27	5.14 – 6.90	6.69	10.74
Na$_2$O	0.05	0.00 – 0.13	0.15	0.30
K$_2$O	0.12	0.03 – 0.42	0.40	0.71
NiO	0.02	0.00 – 0.06	0.02	0.03
P$_2$O$_5$	n.d.		0.20	0.17
SO$_3$	0.08	0.01 – 0.16	0.12	0.09
Total	98.96		100.00	100.09

Glass spherules and clods

Impact and volcanism are both glass-forming processes, and both are generally believed to have contributed glassy particles to the lunar regolith. To distinguish impact from volcanic glass is sometimes a relatively straightforward exercise: impact glasses may have the composition of non-igneous target materials, whereas volcanic glasses should duplicate or show a close genetic relationship to the compositions of volcanic lavas. It becomes more difficult to distinguish between impact and volcanic origins when glassy particles are the product of impacts into igneous rocks or remelted breccias with large proportions of igneous clasts. Particles of either impact or volcanic glass would logically occur in association with unmelted fragments of equivalent composition. Thus many lunar glasses are not easily classified.

Spherules of clear glass in a wide spectrum of colors are ubiquitous in the lunar soils, and those individuals that mimic the composition of individual minerals or of bulk soils are readily ascribed to impact. If impact was the process responsible for producing aggregated spherule deposits, the highland soils should include *discrete layers or lenses* rich in
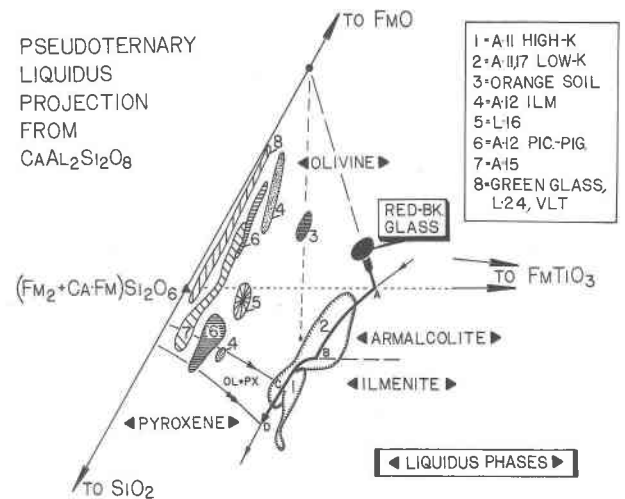
anorthositic gabbros (Marvin *et al.*, 1971). One analysis yielded a normative composition of 94 percent clinopyroxene (En$_{43}$Fs$_{44}$Wo$_{13}$). The single pyroxene fragment not occurring as a crystallite is more Ca-rich (En$_{49}$Fs$_{20}$Wo$_{31}$).

In an attempt to determine the bulk composition of the clod, a number of 100-μm broad-beam analyses were made at random on the section. The clod is highly porous, and the results (which were unexpectedly uniform) summed to about 84 percent. The average values, recalculated to 100 percent, are given in Table 1. We believe that the higher content of alumina in the bulk analysis (column B *vs.* A) represents small amounts of Al$_2$O$_3$ polishing compound trapped in pore spaces.

The analytical results show that the red-black glass is richer in TiO$_2$ by about 6 percent than the orange glass of the Apollo 11 and Apollo 17 soils, and by 4 to 5 percent than some red-black glasses from the Apollo 11 site analyzed by Keil *et al.* (1970). No mare basalts sampled have equivalent compositions. Thus the dark spherule clod represents an exceptional lunar composition. The clod is especially out of place at the Apollo 12 site, where the basalts of Oceanus Procellarum contain a maximum of only 5.5 percent TiO$_2$.

Fig. 3. Liquidus surface for a portion of the FmO–FmTiO$_3$–(Fm$_2$ + Ca·Fm)Si$_2$O$_6$ plane projected from CaAl$_2$Si$_2$O$_8$. Liquidus phase volumes for armalcolite, ilmenite, olivine, pyroxene, and olivine + pyroxene are shown from Walker *et al.* (1975). Equilibrium crystallization of red-black glass produces residual liquids which follow the heavy arrow to A, B, C, then D (see text). Numbers on composition fields are keyed in box to Apollo and Luna basaltic rock and glass types. The only possible suite of rocks that can be related to red-black glass by crystal–liquid fractionation at low pressure and low pO_2 (to which these liquid relations apply) is the titaniferous basalt suite of Apollo 11 and 17.

milky glass beads, produced by the cratering events that have sculptured the crustal anorthosites and anorthositic norites during the past 4 billion years. Yet no such concentrations were observed at the Apollo 14 or Apollo 16 sites, where the spherules that are present (including feldspar-rich glasses) are relatively dispersed components of the regolith. At the two sites where large volumes of spherules of uniform composition have been discovered, the glasses are highly mafic and not of highland-related compositions. In a negative way the absence of aggregates rich in feldspathic spherules in the highland soils, which have been generated by impact, lends support to the hypothesis of volcanic origin for the aggregated concentrations of green spherules near the rim of Mare Imbrium at the Apollo 15 site and the orange and black spherules at the margin of the Littrow Valley at the Apollo 17 site.

The hypothesis that these spherules originated by the eruptions of fire fountains along fissures at the rims of the mare-filled basins is primarily popular because of the large volumes and uniform compositions of the glasses, the presence in a few spherules of large euhedral olivine phenocrysts that must have existed in a larger volume of liquid prior to the dispersal of glass droplets, and the occurrence on the spherule surfaces of condensed volatile elements not found in comparable concentrations elsewhere on the moon. The hypothesis is popular in spite of the fact that mare basalts at the Apollo 15 and Apollo 17 sites neither duplicate the compositions nor show obvious genetic relationships to the glasses of the spherule deposits, as might be expected if the spherules were also of igneous origin. Both the Apollo 15 and Apollo 17 deposits include a few friable clods of spherules admixed with glass, mineral, and lithic fragments that aggregated after the spherules were deposited in the regolith. We suggest by analogy that the clod of red-black glass in sample 12033,66 was projected to the Apollo 12 site from a deposit rich in high-titanium glass spherules. In the following section we explore the inference that these spherules were volcanic in origin.

Petrogenesis of the red-black glass

The existence of red-black lunar glass of bizarre Ti-rich composition poses the following questions for lunar petrogenesis. (1) If substantial quantities of magma of this composition existed, is it possible that this material could have been parental to other known magma types by fractional crystallization? (2) If such is the case, is the red-black glass parental to
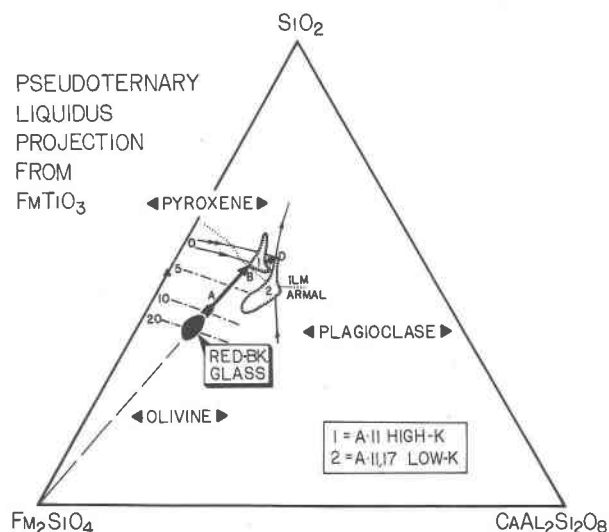

Fig. 4. Liquidus surface for SiO_2–Fm_2SiO_4–$CaAl_2Si_2O_8$ projected from $FmTiO_3$. Liquidus phase volumes for plagioclase, olivine, pyroxene, and olivine + pyroxene are shown from Walker *et al.* (1975). The trace of the armalcolite/ilmenite reaction is shown for low pO_2 and low total pressure. Crystallization of red-black glass produces residual liquid which follows the heavy arrow from A to B to D (same letters as in Fig. 3). This sequence intersects the high-K titaniferous basalt suite from Apollo 11. Numbers on compositional fields are keyed in box to titaniferous basalt types. The displacement of the olivine+pyroxene phase boundary is shown for total pressure of 5, 10, and 20 kbar as well as at low pressure. Red-black glass would intersect this equilibrium at 15–20 kbar or about 300–400 km depth on the moon.

any of the other types? (3) What is the origin of this chemical type, irrespective of the glass-forming process responsible for its distribution around the lunar surface?

To address these questions, red-black glass compositions are plotted in Figures 3 and 4, which are liquidus projections appropriate to titaniferous basalt petrogenesis taken from Walker *et al.* (1975). Figure 3 projects from $CaAl_2Si_2O_8$ onto the plane FmO–$FmTiO_3$–$(Fm_2 + Ca \cdot Fm)Si_2O_6$ (FmO is combined FeO and MgO), which includes olivine, pyroxene, armalcolite, and ilmenite. The plane is subdivided into liquidus crystallization fields for these phases; arrows indicate the direction of decreasing temperature on multiple saturation curves separating liquidus phase spaces. Red-black glass lies in the olivine primary phase volume and crystallizes olivine until the titaniferous oxide saturation surface is reached at A, in this case the one for armalcolite. Equilibrium crystallization of red-black glass commences with olivine, which is subsequently joined by armalcolite. Continued crystallization results in the reaction relation between armalcolite and liquid, producing ilme-

nite at the expense of armalcolite at B. Further crystallization drives the residual liquid further down on the diagram until pyroxene saturation is reached from C to D.

Figure 4 shows liquidus relations in the part of SiO_2–$CaAl_2Si_2O_8$–Fm_2SiO_4 space appropriate to titaniferous basalts, projected from $FmTiO_3$. Again one can follow the equilibrium crystallization sequence olivine → pyroxene in this diagram. Note the trace of the armalcolite → ilmenite reaction on this liquidus. This projection shows that the last major phase to crystallize under equilibrium conditions will be plagioclase. This saturation curve is reached as crystallization advances the residual liquid along the olivine + pyroxene intersection. Olivine remains in the final recrystallization product of ilmenite, pyroxene, and plagioclase (even though it is in reaction relation to the final liquids) by virtue of the high normative olivine content of red-black glass.

An important feature of this crystallization sequence is that the residual liquid from crystallization of red-black glass intersects the composition field of some of the Apollo 11 titaniferous basalt samples, namely the high-K suite. It does not intersect either the Apollo 11 or the Apollo 17 low-K titaniferous suites (see Fig. 4). Subtraction of ~50 percent olivine and ~10 percent armalcolite would be necessary to bring the residual liquid to the appropriate compositions where olivine and armalcolite react with the liquid to give pyroxene and ilmenite. Minor pyroxene fractionation may be required, but plagioclase would play no role in this differentiation. The red-black glass compositions appear to be suitable parents to the high-K Apollo 11 suite with regard to K_2O content as well as with respect to major element chemistry. The K_2O content of red-black glass is variable but may be as high as 0.42 percent. In this respect the red-black glass makes a more suitable parent for high-K material than the Apollo 17 orange glass, which appears to be uniformly low in K_2O. From major element considerations alone, Apollo 17 orange glass could also be parental to the high-K Apollo 11 group by simple olivine fractionation at low pressure. However, neither orange nor red-black glass compositions can be parental to the closely associated low-K series from Apollo 11 and 17. The failure of either glass type to be able to produce the associated low-K series by crystal fractionation at low pressure casts doubt on the proposition that the red-black glass is, in fact, parental to the high-K suite. The lack of intermediate differentiates between red-black glass and its supposed differentiates also diminishes the credibility of the hypothesis. Furthermore, the singular occurrence of red-black glass in the Apollo 12 soil, where the bedrock is not high-Ti basalt, and the lack of reports of this material at Apollo 11 and 17, where titaniferous basalt is common, does not encourage the view that there is any intimate genetic connection.

It may be useful to inquire whether crystal–liquid fractionation at high pressure is capable of producing the low-K parental magma from either the orange or red-black glass. In this inquiry, then, one must assume that the answer to the third question posed is: "the red-black glass originates by direct partial melting at depth within the moon." This could be accomplished by partial melting of an olivine–pyroxene assemblage at 300–400 km. This can be deduced from Figure 4, which shows that the olivine–pyroxene cosaturation curve intersects the red-black glass compositions at 15–20 kbar pressure. Slow ascent to the lunar surface of such a magma, if it maintained equilibrium with its olivine–pyroxenite source region, would result in modification of the melt composition in response to the shift of the olivine/pyroxene saturation boundary to less olivine-normative compositions with decreasing load pressure. In this situation pyroxene fractionation in the 5–10 kbar pressure range (100–200 km) could yield magmas with major element chemistry similar to the parent of the low-K suite. The residuum in this case would be ilmenite-saturated. On the other hand, if the ascent of magma segregated from the residue at 15–20 kbar were rapid and essentially adiabatic, eruption of the titaniferous red-black glass could result. This could then give rise to the high-K suite by fractional crystallization as described above.

This complex scheme involving partial melting of olivine pyroxenite with subsequent fractionation of pyroxene, olivine, ilmenite, and armalcolite at different depths is capable in principle of generating the major element chemistry of the titaniferous basalts as daughter products of the red-black glass composition. A family of such schemes is possible with differing degrees of melting, depths of segregation, and subsequent crystal fractionation. Unfortunately this family of models does not appear to be consistent with the incompatible element abundances. A feature common to all of the models is that the low-K suite must be the result of either the larger degree of fractional crystallization or the smaller degree of partial melting when estimated on major element criteria. This conclusion results because the low-K suite is more aluminous than the high-K suite. The fractiona-

tions discussed involve crystalline phases less aluminous than the participating liquid. Hence liquids resulting from a process leading to a smaller proportion of liquid should be more aluminous. For instance, the product of a greater amount of fractional crystallization should be more aluminous. However, the greater enrichment of the alkali and REE elements, which suggests a smaller proportion of liquid, in the high-K group, is contradicted by the less aluminous character of this group which suggests a process leading to a higher proportion of liquid.

Alternate proposals which derive red-black glass by advanced degrees of melting of shallow source regions similar to those that give titaniferous basalts by lesser degrees of melting may be considered. However, these proposals are also unable to give in detail a coherent account of the relation between the red-black glass and the other two titaniferous magma types, for the same reasons. Evidently there is no such simple relation of the magma types, or else the source regions producing various related batches of magma are heterogeneous with respect, at least, to their incompatible element content. Just this sort of dilemma has led Green *et al.* (1975) to postulate that mare basalt source regions are heterogeneous with respect to TiO_2 content.

In summary, there exist several possibilities of relating other titaniferous basalt types to a red-black glass parental liquid generated within the lunar interior by partial melting. However, in detail most of the proposals are unsatisfying, suggesting that simple models are not viable. It is possible that the red-black glass could result from some process as complex as the Ringwood-Kesson dynamic assimilation model (1976), or, in view of the very limited occurrence, other serendipitous processes such as impact-remelting of titaniferous cumulate rocks may have generated the red-black glass.

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[1] *PLC, 1, 2, etc.* = Proceedings Lunar Science Conference, 1st, 2nd, *etc.*