High-titanium lunar basalts: A possible source in the Allende meteorite

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Abstract—The high content of titanium and many refractory trace elements is a remarkable feature of many lunar basalts, and its origin is imperfectly understood. A unique titanium-rich pyroxene in the Allende meteorite shows an abundance pattern for Ti, Ba, Sr, rare earth elements, Y, Zr, Hf, and Nb paralleling that for the high-titanium lunar basalts. Its probable origin as a high-temperature condensate from the primitive solar nebula indicates that it may have been an important phase in the original accretion of the Moon. A small degree of partial melting of material containing this phase would give a magma with abundance patterns for these elements comparable to those measured in basalts collected on the Apollo 11 and 17 missions; the younger and less Ti-rich basalts of other missions can plausibly be explained by a greater degree of partial melting and dilution with other phases.

The high titanium content (averaging 12% TiO_2) of the basalts returned by the Apollo 11 mission was the greatest geochemical surprise of the first manned lunar landing, although it had been foreshadowed by the alpha-scattering data from the unmanned Surveyor V landing (TURKEVICH *et al.*, 1969). Terrestrial basalts average about 2% TiO_2 and very few contain as much as 5%. Meteorites contain comparatively little titanium; the commonest class, the chondrites, average 0.11% TiO_2 , and the highest figure is 2.2% TiO_2 in the unique achondrite Angra dos Reis. The high Ti content of the Apollo 11 (and Apollo 17) basalts is positively correlated not with any of the major elements but with refractory trace elements such as Ba, Zr, Hf, Nb, and the rare earths.

Coincidental with the first Apollo landing was the fall of the Allende meteorite, a Type III carbonaceous chondrite, in northern Mexico on February 8, 1969. The ready availability of this meteorite, its unusual composition, coupled with the impending arrival of lunar samples resulted in its intensive investigation in many laboratories. The Allende meteorite (CLARKE *et al.*, 1970) consists of a fine-grained matrix (~60%) of iron-rich olivine (~50 mole percent Fe_2SiO_4) which encloses Mg-rich olivine-pyroxene chondrules (~30%), coarsely crystalline Ca,Al-rich chondrules (~5%), and finely crystalline Ca,Al-rich aggregates (~5%). The Ca,Al-rich chondrules and aggregates have attracted particular attention, since they are made up of minerals (spinel, melilite, pyroxene) identified as early high-temperature condensates from the primitive solar nebula (MARVIN *et al.*, 1970; GROSSMAN and CLARK, 1973).

I have separated a number of these Ca,Al-rich chondrules from this meteorite, and their analyses (MARTIN and MASON, 1974) show a notable titanium content ($\text{TiO}_2 = 1.0 \sim 1.5\%$). The meteorite has the normal TiO_2 content (0.15%) for a Type III carbonaceous chondrite, and most of this titanium evidently resides in the Ca,Al-rich chondrules

and aggregates. Microprobe analyses show that the principal host mineral for the Ti is the pyroxene, spinel containing only minor amounts of this element and melilite being essentially Ti-free; this has been observed by other investigators (MARVIN *et al.* 1970; FUCHS, 1971).

The pyroxene in the Allende chondrules has a unique composition, quite different from any known terrestrial pyroxene. Microprobe analyses show a considerable composition range, from chondrule to chondrule, in individual chondrules, and within single grains (MASON, 1974). The ranges measured (weight percent) are: SiO_2 31~43, Al_2O_3 14~23, TiO_2 3~18, MgO 5~12, CaO 24~26; FeO and Na_2O are uniformly low, <0.1. In terms of pyroxene components, the analyses correspond to 30~65% $\text{CaMgSi}_2\text{O}_6$, 5~30% $\text{CaAl}_2\text{SiO}_6$, 5~20% $\text{CaTiAl}_2\text{O}_6$, and 0~40% CaTiAlSiO_6 . The presence of the last component, which has Ti in the trivalent state, in the Allende pyroxene was established by DOWTY and CLARK (1973).

Recently I separated a small amount of this pyroxene from an Allende chondrule and analysed it for minor and trace elements by spark source mass spectrography (MASON and MARTIN, 1974). The trace element concentrations are considerably higher than in previously-analysed meteoritic pyroxenes (ALLEN and MASON, 1973), and the pattern of distribution is somewhat different. Significantly, however, the distribution pattern shows a remarkable parallelism, for some 20 elements, with that of the lunar high-Ti basalts from the Apollo 11 and 17 missions, as illustrated in Fig. 1. This figure compares the data for the Allende pyroxene with those for basalt 10003 from the Apollo 11 mission, but other basalts from that and the Apollo 17 mission show closely similar element distribution patterns. Of particular significance is the marked negative Eu anomaly in both materials. The Allende pyroxene analysed had a relatively low Ti content (3.9% TiO_2); other Allende pyroxenes, with higher TiO_2 , would probably give parallel trace element distribution patterns even closer to that of 10003.

The possible connection between the Allende pyroxenes and the high-Ti lunar basalts is fortified by evidence from phase relations at liquidus temperatures in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-TiO}_2\text{-SiO}_2$ (MUAN and OSBORN, 1965). At compositions comparable to those for the Allende Ca,Al-rich chondrules, pyroxene is the only phase containing an appreciable amount of Ti, and is the final phase to begin crystallizing on cooling a melt, at about

Fig. 1. Chondrite-normalized elemental abundances for Apollo 11 basalt 10003 (upper curve) and Allende pyroxene (lower curve). The data for the Allende pyroxene are from MASON and MARTIN (1974), for 10003 from GAST *et al.* (1970) and ANNELL and HELZ (1970).

1,250°C. The textural relations of the Allende chondrules, with the pyroxene occupying the interstices between the earlier-crystallized melilite and spinel, are consistent with the laboratory evidence. Therefore, if the Moon aggregated from solid material similar to that making up the Allende meteorite, and if this material were subsequently heated, the initial melt would incorporate much of this pyroxene, thereby partitioning most of the Ti and refractory trace elements into the liquid phase. Further melting, with the incorporation of melilite, olivine, and spinel, would result in dilution of the Ti and trace elements and the diminution of the negative Eu anomaly (since melilite has a strong positive Eu anomaly). This would give Ti and trace element concentrations characteristic of the younger basalts collected on the Apollo 12 and 15 and Luna 16 missions. The age-sequence of the lunar basalts and their Ti content appear to be interrelated (Table 1), although the number of sample locations is inadequate for categorical statements. Titanium contents are relatively uniform for all basalts from each lunar site, and possibly for all lunar basalts of similar age. Thus Apollo 11 and 17 basalts are similar in age and composition, although separated by over 600km on the lunar surface; and Apollo 12 and 15 basalts have a comparable relation, although separated by about 1,000km. It thus appears that the Ti content of the lunar basalts is age-controlled rather than spatially controlled.

Table 1. Age and average TiO_2 content of lunar basalts

Mission	Age ($\times 10^9$ y)	TiO_2 (weight %)
Apollo 11	3.7	12.2
Apollo 17	3.7	12.1
Luna 16	3.4	4.9
Apollo 12	3.2	3.2
Apollo 15	3.2	2.2

Further evidence favoring the origin of lunar basalts by the partial melting of material with composition similar to that of the Allende pyroxene comes from a consideration of the Rb-Sr isotopic data. Most of the lunar basalts have a whole-rock model age of 4,600 million years, although their age of solidification is much younger. This implies that the source material had an initial Sr 87/86 ratio close to 0.6990, the primordial value for this ratio as found in basaltic achondrite meteorites. HURLEY and PINSON (1970) deduce that the source material of the Apollo 11 basalts had an Rb/Sr ratio not greater than 0.006 ± 0.004 , about a fifth that of average Earth and a fortieth that of average chondrites. In the analysed Allende pyroxene Rb is 0.07ppm and Sr 30ppm, giving an Rb/Sr ratio of 0.002. GRAY *et al.* (1973) have found that material from the Allende Ca,Al-rich chondrules has the lowest Sr 87/86 ratios yet found, indicating that it is a primitive condensate from the solar nebula unmodified by the addition of radiogenic strontium. A magma derived in large part from such material would provide the characteristic Rb/Sr isochrons of the lunar basalts.

The origin of the lunar basalts was certainly more complex than the melting of material similar to the Allende pyroxene. In order to produce the Fe/Mg ratios of the lunar basalts the pyroxene would have to contain considerable amount of iron, or iron would have to be introduced from another phase. The iron-rich olivine of the Allende matrix would satisfy this requirement. Several groups of investigators have proposed model Moons based on varying proportions of primitive condensates similar to the materials

of the Allende meteorite. GANAPATHY and ANDERS (1974) have a compositional model incorporating six components, of which early condensate (similar to the Allende Ca,Al-rich chondrules) comprises 23.5% and remelted silicate (largely olivine) comprises 63.4% and thus provide the major part. WÄNKE *et al.* (1974) propose a model with 60% HTC (high-temperature component, equated with Allende chondrules) and 40% ChC (chondritic component, largely olivine and pyroxene).

The ideas put forward in this report have a considerable bearing on a major controversy regarding lunar basalts, as to whether they originated by partial melting of an initial solid or represent residual liquids from an extensive sequence of fractional crystallization. RINGWOOD and GREEN (1974) have strongly supported the partial melting hypothesis, and interpret the available data to indicate that Apollo 11 and 17 basalts represent 2~5% partial melts, Apollo 12 basalts 10~15%, and Apollo 15 basalts 10~20%. O HARA *et al.* (1974) argue that the Ti-rich basalts represent residual liquids remaining after the fractional crystallization of anorthite-bearing cumulates. The hypothesis of partial melting, to an increasing degree in going from Apollo 11 and 17 to the Apollo 12 and 15 basalts, is consistent with the proposition that material similar to that of the Allende pyroxene provided the initial melt. The progressive decrease in Ti and other refractory elements, and in the Eu anomaly, is understandable in terms of progressive dilution of an initial liquid enriched in these elements and with a marked negative Eu anomaly. The relationship between age and composition of the lunar basalts agrees with this sequence, whereas progressive fractional crystallization should result in enhanced content of Ti and trace elements in the later, i.e. younger, lunar basalts.

The geochemical evolution outlined here for the lunar basalts also has significant implications for the overall development of the Moon. It suggests the following sequence of events. The Moon was formed about 4,600 million years ago by the accretion of solid particles formed by condensation in the primitive solar nebula. Whether the accretion was homogeneous, i.e., the material was of uniform composition throughout, or heterogeneous with some chemical fractionation during accretion, is a moot point. The interior was relatively cool and remained solid, whereas the outer layers were heated to the melting point and beyond by the heat produced from the kinetic energy of the infalling material. A molten layer perhaps of the order of 100km thick formed on the surface of the Moon, cooled, and fractionally crystallized to produce an anorthite-rich crust (now represented by the lunar highlands) with increasing amounts of ferromagnesian minerals (olivine and pyroxene) towards the base. This crust was intensively impacted by infalling bodies, producing the cratered terrain and the large mare basins. This period of evolution terminated about 3,900 million years ago, with the formation of the Imbrium basin, probably the last of the mare-producing events. During this period of catastrophic events at the lunar surface, the temperature of the interior was slowly increasing by the accumulation of radiogenic heat. Melting began at considerable depths (perhaps 200~300km) about 3,800 million years ago and the resultant magma rose to the surface through zones of weakness (probably connected with the mare basins), and eventually broke through and flooded these basins with a series of lava flows. This period of lunar history continued for some 600 million years, until cooling from the surface depressed the zone of melting until the magma could no longer penetrate to the surface. At this period (about 3,200 million years ago) lunar volcanism effectively terminated. Since then the Moon has been

essentially a passive object modified only by external influences such as the solar wind and meteoritic bombardment. This is in marked contrast to the earth, which developed a stable crust about 3,800 million years ago and has continued to be geologically active.

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