Phenocryst Growth and Compositional Inhomogeneity of Apollo 17 Glass Spherules

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Introduction: Volcanic glass spherules are a prominent feature of the regolith at the Apollo 17 landing site. A reinvigorated interest in these glasses has centered around their volatile contents [1] and the associated relationship to the primordial water content of the moon. This revised line of thinking about lunar evolution warrants a new look at the petrography and compositions of these materials. Ultimately, an understanding of the variations in internal compositions, phase equilibria and the trace element partitioning of the phases preserved within glass provides a unique insight into the structure and evolution of the moon as well as the processes associated with the differentiation of lunar materials.

Here we report on the geochemistry and petrography of glassy spherules collected from the top 10 cm of regolith on the rim of Shorty Crater during the Apollo 17 mission. These glasses have been well characterized to be the result of volcanic fire-fountains and associated with dark mantle deposits [2]. Glasses consist of whole and broken droplets with a median size of 40 μm [3]. Glasses demonstrate a degree of crystallization (e.g., olivine phenocrysts) controlled either by plume optical density segregation (i.e., quenching environment) and bead size [4,5] or by devitrification processes [6]. These glasses exhibit surface exposure ages between 25 and 40 Ma and the eruption age is estimated to range from 3.51 to 3.71 Ga [7]. A preliminary examination of 43, volcanic glasses from soil aliquot 74221,2 has been completed using both Field Emission Scanning Electron Microprobe (FESEM) and Electron Probe Micro Analysis (EMPA) instruments.

Methods: Hand picked glass beads were mounted in epoxy within 3 mm stainless steel cylinders, and were then hand polished using 25 μm diamond paste, to expose an internal cross section of each bead. Holding cylinders were cleaned with ethanol and carbon coated for imaging and analysis.

FESEM: Initial analysis of the 43 beads began with the JEOL JSM 6330F Field Emission instrument. The SEM used a 15.0 kV accelerating voltage, a beam emission current of 12 μA, and a working distance of 15 mm. Beads were imaged in both secondary electron (SEI) and backscattered electron (BSE) compound (COMPO) modes showing a distinct population difference between homogeneous spherules and beads exhibiting crystal growth. Of the beads examined, 28 (65%) show crystalline growth structures to sub-micron scales (Fig. 1-3) as opposed to homogenous samples that show no discernable structures at resolvable scales. Table 1 shows the textural categorization based on the degree of crystallization for the 43 beads examined herein. Glass beads were noted as being either orange or opaque in transmitted light; and all opaque glasses exhibited crystal growth.

Table 1: Degree of individual bead crystallization.

<table>
<thead>
<tr>
<th>Bead Crystallization Area (%)</th>
<th>Population (%)</th>
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<tbody>
<tr>
<td>0-25</td>
<td>10</td>
</tr>
<tr>
<td>25-50</td>
<td>15</td>
</tr>
<tr>
<td>50-75</td>
<td>20</td>
</tr>
<tr>
<td>75-100</td>
<td>45</td>
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* (n=43)

Glasses with crystalline structures exhibit repeatable patterns across all beads with such structures (e.g., spinifex textures). Figures 2-3 show ~50-100 μm olivine phenocrysts, around which are clustered 0.1-1.0 μm dendritic/feathery ilmenite and triangular/rectangular spinel crystals [4,5].

Fig. 1: Full bead BSE image of bead S2B1 showing individual EMPA shot locations and many parallel, dendritic and feathery olivine crystalline band structures emanating from different nucleation sites.
Fig. 2: A magnified BSE image of the central region of Fig. 1 (see box) showing an intersection of the olivine crystalline band structures, all bordered by small dendritic/feathery ilmenite and very small triangular/rectangular spinel crystalline structures [4,5].

Fig. 3: A magnified BSE image of glass sample S8B8 demonstrating olivine, ilmenite and spinel crystalline structures.

**EMPA.** Preliminary analysis of the same samples using a Cameca SX50-Electron Microprobe has also been performed. Samples were examined using a beam diameter of 10 μm, beam current of 20 nA, a 15.0 kV accelerating voltage and the glass reference KL2-g was probed before EMPA analysis run sets. Initial analysis shows a tighter clustering of compositional data for homogeneous glasses than for those showing growth structures, as should be expected (Fig.4).

**Discussion:** The crystallization of olivine phenocrysts, in particular with spinifex, feather and dendritic textures, is known to be a function of the undercooling of the magma post eruption [8], and of the location of settling of molten droplets within the volcanic gas plume surrounding the vent site (i.e., homogenous glasses cooling and quenching quickly away from the effects of venting gasses) [4]. The result is that substantial posteruptive compositional changes during crystallization may have (for example) increased the concentration of water in the residual liquid, and speeded its exit from the spherule.

Fig. 4: EMPA compositional analysis of 4 glass beads: samples S2B1 and S2B4 (blue and purple) demonstrate large variability when compared to homogenous beads S2B2 and S2B3 (red and green), a-d [1] and g-h [4] are a selection of average compositions reported in the literature. Similar dispersions are noted across all major elemental groups.

As noted by Delano [2], most authors publish average compositional analyses for lunar glasses, and do not take into account fractionation trends or the post-eruptive crystallization documented here which may be especially relevant for nonconservative volatile elements. The homogenous glasses, on the other hand, may be better suited for average composition reporting, and the investigation of lunar mantle evolution.

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