
Introduction: Detailed studies of Apollo 15 green glass and related beads have shown they were formed in gas-rich fire fountains [1, 2]. As the magmatic fluid became super-saturated in volatile gases, bubbles or vesicles formed within the magma. These exsolved gases became trapped within vesicles as the glasses were ejected from the fire-fountain and subsequently quenched. One of the keys to understanding formation processes on the ancient moon includes determining the composition of volatile species and elements, including metals, dissolved in magmatic gases. Here we report the nature of mineral phases spatially associated with vesicles in a green glass bead from Apollo sample 15411.42. The phases reflect the composition of the cooling/degassing magmatic vapors and fluids present at the time of bead formation ~3 Ga ago [3].

Procedure and Results: Sample 15410 was collected in 1971 from the rim of Spur Crater at station 7. From this sample, subset 15411.42 was produced, a fraction of which was allocated to D.S. McKay. One partial green glass bead, ~250 × 200 μm, from this sub-sample was initially characterized by optical microscopy. It was subsequently coated with ~1 nm of Pt and analyzed by FESEM. The surface texture appeared smooth near the center of the bead, becoming bumpy and rough near the edges (Figs. 1A, B). The bumpy regions were composed of heterogeneously distributed, raised vesicles up to several μms in size (Fig. 1B). Some of the vesicles were intact while others exhibited holes in the tops and sides likely formed during the release of gas (Fig 1B). Vesicles contained single voids up to several μms in size (Fig. 1C) or multiple voids structured as a network of semi-circular holes of varying sizes (~0.1–1 μm ∅, Fig. 1D). Lining the interior walls of some of the vesicles were metallic Fe (Fe0) mounds ranging from ~10–100 nm ∅ (Fig. 1D). A FIB section was extracted from a region containing two intact vesicles, i.e., without holes (Fig 1B, yellow box; Fig. 1E). FESTEM analysis showed both vesicles contained multiple internal voids (Fig. 1E). Nanophase particles ranging from ~10 to 100 nm ∅ were embedded within the glassy matrix. The majority of particles was composed of Fe0 (Figs. 1F, G); they were identical in size and composition to the Fe-rich mounds lining the voids (Fig. 1D). A small fraction of particles contained S in varying amounts (Fig. 1G) indicating the presence of non-stoichiometric Fe-S. Some particles were located near the vesicle surface while others were heterogeneously distributed throughout the glassy matrix (Fig. 1F). The majority of particles was present in bands (up to several μms in length) that cross-cut the interior of the vesicle (Fig. 1F). The particles were not filling a fracture; rather they were completely encased within the glassy matrix with a composition typical for Apollo 15 green glasses. Occasional Ti-rich hotspots (Fig 1G) were observed in the glass matrix.

Discussion: The origin of nm-size Fe0 particles on the surfaces of lunar grains and inside agglutinates has been intensely debated with two main hypotheses proposed, or a combination thereof, to explain their presence: (1) irradiation (in situ formation via solar wind reduction/sputtering) [4]; (2) deposition (micrometeorite impact-induced heating resulting in re-condensation of Fe0) [5-7]; or (3) a combination of 1 & 2 [6, 7]. We suggest that during fire-fountaining, Fe0 and sulfide phases may have formed by graphite oxidation and the hydrogen reduction of the melt. Alternatively they may have formed by hot reducing gases containing Fe and Fe/S which formed bubbles in the ejecta which were subsequently quenched producing a foamy glass. Some bubbles collapsed resulting in deposition of metal and sulfide particles within the glassy matrix; other bubbles were preserved as voids providing surfaces for particle nucleation. The co-occurrence of Fe0 and Fe-S particles indicates the complex nature of the gas phase(s) and the heterogeneous conditions for gas reactions during eruption. Remarkably in our search for nucleation products, we did not detect many of the volatile elements previously reported to be associated with lunar magmatic activity [8 and references therein] including C-rich matter (e.g., amorphous, graphitic) derived from CO-rich volcanic gas, the primary gas assumed to be driving lunar eruptions [9]. Furthermore, we did not identify any phases construed to be formed in the presence of H2O vapor.

Figure 1: (A) SEM view of an Apollo 15 green glass bead. (B) Higher magn. SEM view of the region highlighted by the red box in A. Arrows denote location of vesicles. Region extracted by FIB highlighted by the yellow box. (C) Higher magn. view of a single void in a vesicle (see B, red arrow). (D) Multiple voids lined with Fe$^0$ mounds (bright spots) in a single vesicle. (E) STEM view of the FIB section containing two vesicles each with multiple voids. (F) Top of vesicle (blue box in E) containing Fe-rich particles (dark spots). (G) High magn. STEM view of region highlighted by the green box in E showing voids surrounded by Fe-rich particles. Glassy matrix is Si-rich with Ti-bearing hot spots. Corresponding element maps for the region in the green box (above) are shown for Si, S, Ti & Fe.