THE EVASIVE LUNAR VOLCANIC GAS: NEW DISCOVERIES FROM APOLLO 17 ORANGE BEADS 50 YEARS LATER. Y. Liu[1], X. Su[2], Y. Zhang[2], C. Ma[3]. [1]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA. [2]Department of Earth and Environmental Sciences, University of Michigan, Ann Arbor, MI 48105, USA. 3 Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA. (yang.liu@jpl.nasa.gov).

Introduction: Soils and rocks on the Moon collected and returned by Apollo astronauts are gifts kept on giving. Among Apollo 17 samples, the orange glass beads have fascinated many generations of lunar scientists. These orange beads were studied intensely for ~10 years after their return to Earth. These studies showed these beads formed through fire-fountain eruption powered by volcanic gas. Bulk chemical and surface observations found these beads contain a thin layer of coating enriched in volatile-mobile elements, which are thought to be derived from condensed lunar volcanic gas [1-6].

The volatiles that power the eruption were not identified until 2008. Early studies hypothesized that CO could be the driving gas, but the technology in 1990s was not able to detect <1 ppm by weight of total dissolved C [7]. The study of volatiles (species of H, C, S, F, Cl) in lunar volcanic beads catalyzed the paradigm shift in our view of water on the Moon [8-10]. The presence of residual H and S inside the beads shows that H and S are more abundant than C in the pre-eruptive melt. This conclusion was further supported by observation of high amounts of H_2O, S, F and Cl in melt inclusions in olivine grains erupted with 74220 orange beads [11-14]. Modern analyses of isotopes of moderately volatile elements (MVEs such as Zn, Rb, Ga, Pb, K) also observed that these orange beads contain condensed vapor [15-19]. All of these findings further indicate that the volcanic gas associated with the pyroclastic eruption was non-negligible and possibly formed a transient atmosphere locally [20]. However, because of the enriched MVEs in bulk bead samples and the pervasive depletion of light isotopes of MVEs in lunar basalts (differentiated), a lasting debate is how representative lunar volcanic beads are of lunar mantle [17, 21]. Part of these uncertainties is caused by the unknown degassing mechanisms of moderately volatile elements. This had led some authors to suggest that isotope anomalies of K are due to giant impact not volcanic outgassing [19]. Here, we review new discoveries made on these beads.

New discoveries:

Pre-eruptive concentrations of various volatiles and MVEs in 74220 orange glass bead magmas [10-14,22]

Based on the studies of olivine-hosted melt inclusions (OHMIs) in 74220 samples, the pre-eruptive concentrations of various volatile elements have been found to be significantly higher than in orange glass beads. For example, pre-eruptive concentrations are higher than those in orange glass beads by about a factor of 287 for H_2O [11-13, 22], a factor of 65 for Cl [12, 13, 22], a factor of 14 for C [10, 22], 9 for Zn [14, 21, 22]-16], 7 for F and Cu [11, 12-14, 22], 2.4 for S [12, 13, 22]. Despite such high pre-eruptive concentrations of volatiles and MVEs, the concentrations of many volatiles and MVEs are still much lower than those in bulk glass beads [23].

Mineral forms of vapor condensates [24, 25].

Despite extensive studies, the mineral forms of vapor condensates on Apollo 17 orange beads were not discovered until recently. To date, we discovered two minerals, Na-K-sulfate and a Zn-chlorohydroxosulfate, on the surfaces of orange beads. These salt grains are euhedral with sizes up to a few microns and sit on a thin layer of coating. The textural information shows that Na-K-sulfate formed before Zn-chlorohydroxosulfate. As lunar volcanic gas is regarded to be highly reducing, these oxidized salt grains are unlikely the original condensates. Rather, since these samples were not sealed, these salt grains are likely formed through in situ alteration of original condensates. Since the chemical ratios of major elements are unchanged by alteration, the original condensates are inferred to be Na-K-sulfide and metallic Zn with a small amount of Na, $ZnCl_2$ and NaCl, or ZnS and Na_2S. These findings enable us to constrain the outgassing mechanisms of these MVEs, where Na, K, and Zn degas from lunar melt following the reactions:

$$NaO_{0.5,(l)} = Na_{(g)} + 0.25\ O_{2(g)},$$
$$KO_{0.5,(l)} = K_{(g)} + 0.25\ O_{2(g)},$$
$$ZnO_{(l)} = Zn_{(g)} + 0.5\ O_{2(g)}.$$

Subsequently, these elements in the gas condense following the reactions:

$$2Na(g) + S(g) = Na_2S$$
$$2K(g) + S(g) = K_2S$$
$$Zn_{(g)} = Zn$$

Such dissociative reactions indicate that isotope fractionations between light and heavy isotopes of these MVE elements are more complicated than a simple Rayleigh distillation which assumed the liquid and vapor species of the MVEs are the same.

In-gassing of moderately volatile elements Na, K, Cu in Apollo 17 orange beads [26-28]

Another unexpected discovery is U-shaped profiles of moderately volatile element Na, K, and Cu in orange beads. These elements show significant enrichment within ~25 μm from the edge of the bead and then uniform abundances at a distance >50 μm from the edge to the center. The uniform abundances in the interior are lower than those analyzed in olivine-hosted melt inclusions. These observations indicate that orange beads experienced significant outgassing that affected the center of the beads, and subsequently these beads experienced in-gassing from the lunar volcanic gas. Numerical modeling of both outgassing and in-gassing processes in individual beads matched observed profiles well, and showed that the U-shaped profile of each bead tracks the cooling history of the volcanic gas.

Synopsis

Collectively, orange glass beads show a systematic record of lunar volcanic gas, from degassed interior, to volatile enrichment near edge, a thin layer of vapor coating, to then larger vapor condensate minerals. All of these findings are consistent with a transient atmosphere formed by the lunar volcanic gas. More interestingly, even though these samples were not sealed under the lunar conditions, new science findings are still possible even at 50 years after they returned to Earth.

References

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