

A "dry" versus a "wet" Moon. The effect of potential indigenous water on the composition of lunar volcanic gases and sublimates. C.K. Shearer¹, Z.D. Sharp², A. Brearley², P.L. King¹, and T. Fischer². ¹ Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico. Albuquerque, New Mexico 87131 (cshearer@unm.edu), ² Department of Earth and Planetary Sciences, University of New Mexico. Albuquerque, New Mexico 87131.

Introduction:

One of the long held premises concerning the Moon is that its mantle was considered "dry" with a water content at the ppb level or less [1-4]. Arguments for a relatively "dry" lunar mantle have been summarized in great detail since the return of lunar samples [e.g. 2-4]. This low water content has profound implications for the nature of volatile species in lunar gases associated with fire-fountaining [2,5-8] and products of sublimation that occur on the surfaces of pyroclastic glasses. More recently, based on new measurements of volcanic glasses and potentially hydrous and nominally hydrous mineral phases, several researchers have concluded that the water content of the lunar interior and basaltic magmas produced through melting of the lunar mantle are perhaps several orders of magnitude higher than previously considered [9-11]. If correct, these new results have profound implications for the origin and thermal-magmatic history of the Moon. As another perspective for evaluating this controversy between a "wet" and "dry" Moon, we are examining the effect of variable water content on the composition of lunar volcanic gases and sublimation products. The intent of this study is to combine previous reported thermodynamic models of lunar volcanic gas compositions [2,5-8] with additional modeling to better understand the nature of volatile coatings on glass beads that have been documented in previous studies [e.g. 12-14] and are currently being made by our group.

Modeling and Analytical Approaches:

Our initial foundation for attempting to understand the potential effect of water on lunar volcanic gases and sublimates is based on the studies of [2, 5-8]. Additional modeling of eruptive gas composition at approximately IW-1 and at variable H₂O concentrations and resulting sublimation products are being made using SOLVGAS and GASWORKS software [15]. In these models, we are using initial eruptive gas starting compositions of Fegley [5] with increasing H₂O while remaining between f_{O₂} conditions of IW and IW-1.

The deposits on the surfaces of individual Apollo 15 and 17 glass beads are being characterized by several analytical approaches. Cl isotopic compositions of coatings on glass beads are being measured using the approach of Sharp et al. [16]. Mineralogy and chemistry of coatings are being analyzed and prepared by FIB. To gain a fuller appreciation of the availability of

water in the lunar magmas, mid- to near-IR spectra were collected on several types of volcanic glass spherules. For these measurements, all samples were prepared as doubly polished wafers ~30-80 microns thick. Samples were placed on a NaCl window in a chamber purged with dry air. Analyses were made using either a KBr or CaF₂ beamsplitter, Globar or white light source, and an MCT-A* detector (higher detectability than a standard MCT-A detector). Analyses were made for at least 300 scans, at a spectral resolution of 4 cm⁻¹.

Sublimation coatings on lunar glass beads:

Mineralogy and chemistry: Numerous studies of pyroclastic glasses have identified small deposits on their surfaces that have been attributed to vapor condensation during fire-fountaining. These surface deposits are enriched in a variety of volatile elements relative to the interior of the glass beads [e.g. 12,13]. More recently, high resolution microscopy has suggested that these deposits may preserve a sequence of sublimation deposition. For example, Wentworth et al. [14] defined layering of S, Fe, and Zn within the surface deposits on A15 Green glass. Because of compositional differences between high-Ti and very low-Ti lunar basalts may control solubility of volatile elements, it is anticipated that the gases associated with these two types of pyroclastic eruptions should also be different. Therefore, the mineralogy and layering of the sublimates on these glass surfaces will also be different.

Cl isotopic systematics: Results for the analyses of δ³⁷Cl for a small number of lunar basalts and breccias were reported by Sharp et al. [17]. The δ³⁷Cl composition for lunar materials ranges from -0.74 to 16.0 and has been attributed to both space-lunar surface interactions and fumarole processes. The δ³⁷Cl composition of leachate chloride was measured from two splits of A17 orange glass. One split consisted of hand-picked glass beads, while a second split was a bulk A17 pyroclastic deposit sample. The leachate from the hand-picked sample had a Cl content of 80 ppm and a δ³⁷Cl composition of -0.74. The leachate from the bulk sample had a Cl content of 50 ppm and a δ³⁷Cl of +8.59 to +9.32 [17]. The Cl isotopic composition of coatings on A15 Green glass separates is being determined. Other elements that occur in the sublimates (Fe, Cu, Zn, and Cd) are enriched in their light isotopes [18,19].

Micro-FTIR. Water bands were not observed in olivine-rich areas of the spherules. However, we have documented a water band in glass at $\sim 3400\text{ cm}^{-1}$ that is related to symmetric stretching of Si-OH + HOH + 2* bending of HOH [e.g., 20]. We did not observe molecular H₂O bands at 1630 cm^{-1} or 5200 cm^{-1} , which is consistent with the low inferred total H₂O content and other data for basaltic glasses indicating that hydroxyl should be the major H-O species at low total H₂O contents [e.g. 20]. Quantification of the $\sim 3400\text{ cm}^{-1}$ band awaits determining the IR extinction coefficients (ϵ_{3500}) for lunar glass compositions because the effect of Ti on the IR extinction coefficient for that band may be significant [21].

The effect of water indicated from previous studies and current modeling:

Composition of volcanic gases: Previous observations [e.g. 22] and models for lunar gas compositions [2,5] are guiding our preliminary calculations for evaluating the effect of varying amounts of indigenous water on gas compositions. In models [2,5] for lunar magmas with extremely low water content (<1ppm), HF and HCl were the dominant H compounds in the gas phase, although the dominant halogen species were Cl₂, CCl₄, SCl₂, and CF₄ [2,5]. S occurs primarily as COS, CS₂ and S₂, while H₂S and H₂O are virtually absent in the gas phase [2,5]. Colson [8] suggested that in a CO-rich volcanic gas resulting from the oxidation of graphite in lunar magmas [23,24], the halogens could also occur as COCl₂ and COCl. As the water content in the basalts increases (10s ppm) and the gas phase has higher H, the HF and HCl are still the dominant hydrogen species and they becomes increasingly more abundant as halogen-bearing species at the expense of Cl₂, CCl₄, and CF₄. Still H₂S and H₂O are virtually absent in the gas phase [2]. As expected, the gas composition changes dramatically with a melt composition that has a water content similar to that of MORB. HCl and HF are the dominant halogen species with H₂S the important S species. It appears that with the increasing water content in the lunar magmas, the HCl/H₂S should decrease. Changes in the volcanic gas composition should have profound implications for the stability of sublimates on the surfaces of the volcanic glass beads [6-8].

Sublimates Interpretation of previous modeling and our preliminary results illustrate how H₂O content of mare basalts would affect the composition of the volcanic gases driving lunar fire-fountaining. Our more detailed modeling will also take into account varying amounts of S and Cl. How will the changes in gas composition affect the stability of compounds that form sublimates on the surfaces of the glass bead and

the depositional history of these surface coatings? The effect of gas composition on the mineralogy of volcanic glass sublimates were explored in a series of papers [6-8] using slightly different gas compositions ranging from water absent [6,8] to minor amounts of water [7]. These results and our analysis identify numerous effects of H₂O on sublimation products and their sequence of sublimation. For example, at relatively high H₂O, FeS and ZnS are stable sublimates in a cooling vapor. With decreasing H₂O, the HCl/H₂S ratio should increase resulting in FeS and ZnS becoming less stable as the gas environment cools. At very "dry" conditions where hydrogen species of S and Cl are low to virtually non-existent, ZnS and perhaps FeS are unstable at relatively low temperatures for virtually all values of S species/Cl species. The extent of isotopic fractionation of Cl, Cd, Fe, Cu, and Zn will be partially dependent on the stability of species in the gas and compounds in the sublimation products.

Conclusions:

Combining results of previous studies with our preliminary observations suggest that differences in water content of lunar magmas will affect both the composition of the volcanic gas and the stability and condensation sequence of sublimation products on the surfaces of pyroclastic glass beads. Therefore, observations related to mineralogy, chemistry, and isotope chemistry can be placed within the context of gas compositions and will shed light on the water content of lunar magmatism and indigenous water in the lunar interior.

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