
Introduction: Primitive picritic lunar glasses such as the A17 orange glass and the A15 green glass are widely considered to be the products of lunar fire-fountaining [1,2,3,4,5]. Other processes such as meteoric impacts do not readily explain the primitive chemistry of the glasses relative to mare basalts, the homogeneity of individual spheres or the volatile-rich coatings on the glasses. The fire-fountaining hypothesis, however, leaves many unanswered questions: 1) What was the driving force for the lunar fire-fountainings? 2) What volatiles were present in these primitive lunar melts? 3) Have the melts suffered degassing, and if so, was the oxidation state of the glasses affected? [4,9] proposed that lunar eruptions were driven by oxidation of reduced-C and subsequent CO degassing upon magmatic ascent. The auto-reduction behavior of 74220 orange glass was interpreted as evidence for reduced-C and support for carbon's role as a reducing agent in lunar volcanism. This model is supported by recent analyses of CO-rich gas trapped in a green glass vesicle [6]. It merits further investigation because C-species and abundances have not been directly analyzed in primitive glass spheres, and because of the important implications of the model. An alternative model is suggested by the S-rich coatings on many volcanic glass spherules. [7] has suggested that fractionation of an FeS-rich phase from A15 green glass magmas is implied by their chemistry suggesting that the melts were sulfide-saturated at some point in their history. S-loss from lunar magmas has been suggested as a driving mechanism for mare fire-fountaining [8] although the plausibility of this model has been called into question [9].

A study of the volatiles in primitive lunar glasses has been initiated to investigate the above questions and to obtain more information about processes involved in their genesis and evolution.

Analytical: Seven green glass spherules from sample 15427,67 were obtained from Dr. J. Delano. Sections were prepared for FTIR analyses by grinding and doubly polishing each glass sphere down to a grit size of 0.05 μm. FTIR sections were, thus, central slices of each spherule and were diskoidal in shape. Each glass sample was either spherical or ellipsoidal in shape except for one sample which was rain-drop in form and another which appeared to be a glass fragment; this fragment (GGV-3) contained a vesicle = 8 μm in diameter.

Micro-FTIR analyses were performed according to procedures outlined in [10]. Spot sizes ranged from 80-20 μm; resolution was either 4 or 2 cm⁻¹ and either 128, 256 or 512 scans were taken. Major elements, S and Cl were analyzed by a Cameca electron microprobe with a beam current of 30 nAmps, a 5 μm focused beam and counting times of 100-300 sec for S and Cl.

Results: FTIR spectra were analyzed for the presence of vibrational bands attributable to dissolved C species which include: molecular CO₂ at 2350 cm⁻¹, molecular CO at 2160 cm⁻¹, carbonyl (2125-1700 cm⁻¹) and carbonate (1700-1300 cm⁻¹) regions. Pure and subtraction spectra were examined and found to be devoid of all C species; thus all seven samples showed no indication of the presence of C in any of the IR detectable forms. Fig. 1 is a typical green glass IR spectrum displaying a conspicuous absence of absorption peaks due to dissolved volatiles. The sloping background below 2000 cm⁻¹ is attributable to silicate network vibrations [10]. In addition, glass H₂O contents were determined and found to be free of IR detectable H₂O. These glasses are amongst the driest ever reported. In one sample, H₂O was slightly above detection (50 ppm); however, work is underway to determine if this water is a product of contamination.

In about half of the samples, sharp peaks are present in the 1000-600 cm⁻¹ area which are small or absent in sample cores and grow in intensity toward the rims. The peak assignments are uncertain but because of their sharpness and presence in the silicate network vibrational region it is possible that they are indicative of glass devitrification at the submicron scale; although, glasses were optically clear.

A spectrum of the vesicle in sample GGV-3 was taken and a thickness normalized glass spectrum was subtracted. The bubble appeared devoid of gasses in accordance with the findings of [6] who found vapor filled vesicles to be uncommon in 15426 green glasses.

EM results for S ranged from 100-350 ppm between glasses (min. detect. S=50 ppm). Except for near-rim concentrations of up to 400 ppm Cl in some spherules, Cl was below detectability (50...
ppm) in most samples although a few core analyses were as high as 100 ppm. The most significant EM finding was the existence in several samples of a spotty zonal decrease in S from core to rim; e.g., sample GGV-8 has a core-rim concentration gradient of 323-123 ppm S.

**Discussion:** The absence of C species in these glasses requires a rethinking of the C-model. The various gas driving mechanisms have been discussed by [9] who argues convincingly that C was involved, at least in some measure, in mare volcanism. Some C in the form of graphite could have survived the lunar magma ocean event since with increasing P the C-O oxidation surface becomes more oxidizing than the lunar mantle at depth; a change which stabilizes graphite and eliminates a C-O gas from the deep lunar interior.

It is possible that CO, the most abundant C-O species under lunar mare conditions [9], does not dissolve appreciably in basaltic melts. Our unpublished experimental results on basaltic melts at 1300°C suggest this as a distinct possibility. The data of [11] imply that even if CO dissolves as CO$^-$, as does CO$_2$, it has only a fraction of the effect of CO$_2$. Other data [12] suggest that molecular CO may dissolve somewhat in more silicic melts although like molecular CO$_2$ it should be small or absent in basaltic glasses. To test this hypothesis we have recalculated the fugacities of C-O-S species as a function of P, T and C activity assuming that S$_2$ is buffered by Fe-FeS. Like [9] we find CO to be the dominant gas species under lunar conditions represented by fO$_2$ near IW.

Under a green glass liquidus T of 1420°C [13] the graphite-saturated C-O-S surface is well below IW at 1 bar, at 100 bars the gas is comprised of 98% CO and at 1000 bars 86% of the CO phase is still CO; thus, unless CO dissolves appreciably as CO$_2$ or as an as yet unidentified reduced C species, the only contribution to C solubility in the melt will be from CO$_2$. This, however, will be quite small owing to a small fCO$_2$. For example, at P=1000 bars fCO$_2$ = 165 bars which implies a solubility of ~85 ppm CO$_2$. Besides being close to the limits of FTIR detectability, this magma would have to survive undevolatilized all the way to the surface; an unlikely scenario.

A further explanation for the absence of CO$_2$ is that over the course of 3.3 Ga, CO$_2$ may have diffused out of these glasses. We calculated the temperature necessary for CO$_2$ to diffuse through the glass the root mean square distance ($\langle X^2\rangle=2Dt$) of X=200 µm over 3.3 Ga and used the D$_{CO2}$ in basalt melt of D=3.995exp(-46600/RT) (R in cal/deg*mole) [14]. Our result is T = 200°C which represents the diffusion of 32% of the CO$_2$ from the green glass. This very low T results from the enormous amount of time given for the diffusion process to take place and assumes that D$_{CO2}$ in glass is comparable to that in melt. If over a protracted period of time the glass spheres were exposed to a T > 200°C this process becomes quite plausible.

The feasibility of magmatic volatile loss during ascent or upon cooling is attested to by the patchy zoning in S within the glasses. This would help explain the low S contents. As per [7] the possibility remains that these melts were at one time saturated in an Fe-FeS liquid which would imply a melt S content of ~2000 ppm [15]. A Ni-rich (61%) metal sphere found in sample GGV-3 may be the product of desulfurization of a Ni-rich sulfide.