

IN SEARCH OF THE MOON'S INDIGENOUS VOLATILES: NOBLE GASES AND NITROGEN IN VESICULAR LUNAR GLASSES

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An accurate knowledge of the elemental and isotopic composition of the volatile inventory initially acquired during lunar formation is of considerable importance in elucidating the origin and evolution of the Moon. Unfortunately, it has proven quite difficult to acquire this information owing to the extreme paucity of indigenous volatiles at the lunar surface, and the heavy overprint of implanted solar wind particles and cosmic ray produced nuclides which tends to mask the signatures of any lunar gases that are present. In recent years however, in a search for "bottles" that may have retained analytically resolvable quantities of primordial volatiles, attention has been focused on green and orange glass spherules which have been found at several of the lunar landing sites. Despite some initial controversy most investigators now agree that these glasses resulted from the rapid quenching of molten silicate droplets which were ejected into the lunar "atmosphere" during the explosive volcanic eruption of ultramafic magmas onto the lunar surface (1,2). It appears that the source regions for these magmas may have been at depths as great as several hundred kilometers (2), that is, in regions that may not have experienced substantial melting and concomitant loss of volatiles during the "magma ocean" phase of lunar evolution some 4.4AE ago. Indeed, studies of the cooling histories (3) and surficial sublimate coatings (4) of these glass spherules have shown that it is probable that the initially molten droplets cooled during free-fall through a gaseous medium which presumably accompanied the erupting magmas to the lunar surface. It was surmised therefore, that the rapid quenching of the silicate droplets may have precluded the near-quantitative degassing of volatiles that is typical of mare basalts for example. The noble gas contents of several of these glasses (5,6) and other samples (7) were therefore analyzed by several investigators, but the results of these attempts to isolate a pristine volatile component, indigenous to the Moon, have generally proven to be inconclusive due to relatively low gas contents, complex sample histories and difficulty in separating the desired component from the radiogenic, cosmogenic, reimplanted lunar atmosphere, and solar wind components which are all present in varying degrees in these glasses. Subsequently however, it was found that a small fraction of the lunar glass spherules contain sealed vesicles on the order of 10^{-6} to 10^{-8} cm³ in volume (8,9). While there is no certainty that these vesicles currently contain a free volatile phase, or even that these vesicles are the result of a volatile vapor phase exsolving from a liquid magma, the possibility that a sample of primordial lunar gas is trapped in the interior of these unusual glasses is certainly tantalizing. This abstract reports the first results of a study of the noble gases and nitrogen contained in these vesicular lunar glasses.

Lunar green glass breccia 15427 was collected at the rim of Spur Crater during the Apollo 15 mission, and Ar-Ar dating of the glass spheres, which comprise ~60% of the breccia, has yielded gas retention ages of 3.79 ± 0.08 (10), 3.38 ± 0.06 (6), and 3.29 ± 0.06 AE (11). A 5gr. aliquot of this breccia was carefully handpicked by J.W. DeLano with the result that twenty four vesicular green glass spheres were isolated, characterized by electron microprobe, and assigned to the various chemical groups defined by previous analyses of lunar glasses (8). Four of the spherules containing the largest vesicles, along with six additional nonvesicular glasses, were selected and individually analyzed for noble gas and nitrogen contents by stepped heating and mass spectrometry. Weights of the individual spherules ranged from 27 to 130 μ g. and vesicle volumes were between 0.45 and 1.44×10^{-6} cm³. It was anticipated that, due to the very small sample sizes, the amounts of gas available for analysis would be quite small, and this in general proved to be the case. Despite these limitations, it was decided to employ stepped heating techniques (3 steps/sample) in an attempt to remove any surface implanted solar wind and/or orphan ⁴⁰Ar that might otherwise mask volatiles trapped in the vesicle interior. Instrumental blank and interferences were therefore quite high (commonly >50%) relative to the small gas releases, for ⁴He, ²⁰Ne, ²²Ne, ⁴⁰Ar, N₂, Kr and Xe.

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Preliminary analysis of the experimental data has revealed a number of interesting features. Despite the fact that all ten glasses were taken from the same 5gr. clod of 15427, it is evident that all had experienced different precompaction and irradiation histories. The first of these conclusions was reached earlier (5) for spherules from breccia 15426 (essentially identical to 15427). Considerable variation in total gas yields, elemental ratios and amounts of surface impregnated SW from sphere to sphere are evident, and cosmogenic ^3He , ^{21}Ne and ^{38}Ar excesses vary by nearly an order of magnitude between samples, pointing to considerably different shielding from the cosmic ray flux. These results indicate that misleading results might be obtained if attempts are made to deconvolute elemental and isotopic spectra obtained from batch analyses of groups of spherules. Yields of ^{36}Ar from the ten spherules varied widely, ranging from 2×10^{-5} to 5×10^{-5} cc(STP)/g, but the distribution is discontinuous and a bimodal distribution is evident. The L(low)-group of glasses consists of one vesicular and five nonvesicular spherules, and shows relatively low measured ^{36}Ar concentrations, in the range 2 to 7×10^{-7} cc/g. The H(high)-group however, which comprises one nonvesicular and three vesicular glasses, shows much higher Ar releases of 0.9 to 5×10^{-5} cc/g. Similar differences are noted for Ne, while He, Kr and N₂ variations are less clearly defined. The L-group glasses cluster precisely in the Ar concentration range previously defined by Lakatos *et al.* (5) for clod spherules from 15426. The H-group however, lie at much higher concentration values and overlap the high Ar end of their field shown for glasses separated from lunar fines (0.4 to 2×10^{-5} cc/g). Two interpretations are therefore possible. Either the H-group glasses are essentially the same as other measured spherules, regardless of source, and all happen to lie at the high end of their Ar content range, or the vesicular glasses (taken from a breccia interior) are rich in Ar because the sealed vesicles contained a free volatile phase. N/Ar ratios for this group are clearly distinct from solar values and suggest the presence of a second component characterized by an isotopically light nitrogen signature. $^{40}\text{Ar}/^{36}\text{Ar}$ ratios for the H-group glasses cluster in the range 3-7 after correction for in-situ radiogenic ^{40}Ar production, and are similar to ratios reported in (5). Unlike ^4He and trapped Ne, the major ^{36}Ar releases from the H-group glasses do not occur at 750°C. An elemental fractionation is evident as the Ne/Ar ratios are clearly nonsolar, despite a solar isotopic composition for Ne. One H-group spherule shows somewhat different release characteristics which may indicate that this glass was exposed to the solar wind prior to compaction, and was later remelted with the surface solar wind component being incorporated into the glass interior. Trapped Ne, Ar and Kr releases do not correlate linearly with vesicle volume (they are in correct order), but this would not be expected unless closure T and P were identical for all glasses and no subsequent leakage had occurred. At present, data analysis is still incomplete. We expect to soon be able to further constrain the nature of the volatiles trapped in these unusual glasses.

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