

INDIGENOUS LUNAR NITROGEN. P. H. Barry¹, D. R. Hilton², K. Marti³ and L. A. Taylor¹. ¹Planetary Geosciences Institute, Dept. of Earth and Planetary Sciences, University of Tennessee, Knoxville, TN 37996, USA (peter.barry@utk.edu), ²Fluids and Volatiles Laboratory, Scripps Institution of Oceanography, University of California, San Diego, La Jolla, CA 92093, USA, ³Department of Chemistry and Biochemistry, University of California San Diego, La Jolla, CA 92093, USA.

Introduction: Lunar surface samples display significant nitrogen isotope variability between ~ -234 ‰ and $+177$ ‰ [1]. This extremely wide range in $\delta^{15}\text{N}$ is best explained by mixing of isotopically distinct components which are either intrinsic to the Moon, deposited on the lunar surface by solar wind or have originated from some unknown source [2, 3]. Identifying the compositions and sources of the various components is a primary objective of this study and will help shed light on planetary accretion processes and atmosphere evolution models.

Lunar nitrogen can be broadly divided into two groups: endogenic and exogenic components. Endogenic (i.e., indigenous) nitrogen represents the residual component remaining following Moon formation. However, to date, this component is poorly constrained due to extremely low N_2 concentrations (>1 ppm) in primitive lunar samples. Recent improvements in analytical techniques [4, 5] have enabled better quantification of this component. More accurate isotopic constraints on the indigenous lunar component may reveal important information about the evolution of lunar N_2 and its initial characteristics. In addition, this information may prove useful for reconstructing the Earth-Moon formation history.

In contrast, exogenic (i.e., secondary) lunar nitrogen results from the accretion of solar wind particles and possibly implantation from other volatile sources. Exogenic lunar nitrogen has been more extensively studied [2-4] as it is several orders of magnitude more abundant than the endogenic component.

The goal of this pilot study is to determine if we can effectively measure nitrogen isotopes in pristine lunar basalts, in order to determine the indigenous lunar nitrogen isotope component.

Previous Studies of Indigenous Lunar N_2 : Igneous lunar rocks are reported to contain less than 1 ppm nitrogen [6-12] and previous attempts at determining the isotopic signature of indigenous lunar nitrogen have been unsuccessful in many instances. An additional and potentially complicating factor is that at such low concentrations there is possible contamination from cosmogenic nitrogen ($^{15}\text{N}_\text{C}$). Initial nitrogen studies [6-7] focused on Apollo 12 and 17 samples, determining the indigenous component to be $\sim +10$ ‰ [7]. Subsequently, Barraclough and Marti [9] measured indigenous

nitrogen in vesicular lunar glasses collected from the Apollo 15 mission. Murty and Goswami [10] investigated nitrogen in the lunar meteorite MAC88105 and determined a $\delta^{15}\text{N}$ value of $+17 \pm 3.4$ ‰ for indigenous lunar N_2 . Kerridge et al., [11] studied double drive core samples from the Apollo 17 mission (74001/74002) and interpreted nitrogen trapped on fumarolic glass particles ($\delta^{15}\text{N} = \sim +14$ ‰) to be representative of the elusive indigenous component. Later, Mathew and Marti [12] considered a variety of samples including an old ferroan anorthosite 60025 and an anorthosite breccia 67915 from North Ray Crater, volcanic glasses from 74001 near Shorty Crater and Apollo 17 basalt sample 75075, collected near the Camelot Crater. The average nitrogen isotope value determined for Shorty crater samples was $\sim +13 \pm 1.2$ ‰. A summary of previous studies is given in Fig 1.

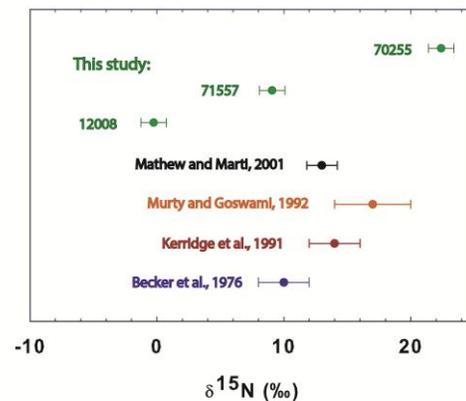


Fig. 1: Nitrogen isotope results of this study versus findings of previous studies.

Sample Selection and preparation: Using a combined petrology and geochemistry approach a total of three mare basalts were selected for nitrogen isotope analysis. Careful consideration was given to the pristine nature of the basalts, which was not always appreciated in the past. Apollo 12008 is an olivine vitrophyre basalt, Ar/Ar dated at 3.2 b.y., with an exposure age of less than 50 m.y. [13]. 70255 is a fine-grained, Ti-rich, blocky, subangular and relatively homogeneous basalt with 1-2 % vugs, containing both olivine and silica resulting from rapid cooling [14]. 71557 is a

coarse-grained basalt where large plates of plagioclase poikilitically enclose crystals of pyroxene, olivine and ilmenite [15]. The Apollo 17 samples are also dated at > 3.8 b.y., with minimal exposure ages [16].

Approximately 1 gram of lunar mare basalt sample was ultrasonically cleaned in a 50:50 acetone-methanol bath for one hour, then dried and loaded into one of two crushers which were then are baked at 100 °C overnight in order to remove any adsorbed atmospheric nitrogen. Simultaneously, the whole nitrogen extraction and purification line was also baked at 120 °C.

Experimental Techniques: Nitrogen isotopes were measured on a modified VG-5440 mass spectrometer. Prior to inlet into the mass spectrometer, sample gases were processed through a nitrogen extraction and purification vacuum line constructed of stainless steel and Pyrex glass cold fingers. For purification purposes sample gases are reacted with pure O₂ in the presence of a hot platinum foil catalyst in order to promote the oxidation of carbonaceous (CO, C₂H₄) and nitrogenous (NO) species to CO₂ and NO₂, respectively. Crushing is the favored bulk nitrogen extraction method for terrestrial and lunar basalts over conventional stepped-heating [17, 18] and sealed tube extraction methods [19, 20]. This method minimizes blank contributions and, as in the former case, helps avert any potential nitrogen losses or fractionation effects associated with hot molybdenum furnaces [21]. Following cleanup, gases were inlet into the mass spectrometer where m/z = 28, 29 and 30 are simultaneously measured using fixed triple collection mass spectrometry. The stability provided by the static triple collection approach improves the overall precision of the isotopic measurement and simultaneously allows for a comprehensive CO correction to be applied to all data, which also greatly improves the precision, resulting in better overall standard and sample reproducibility [5].

Results: We present new nitrogen isotope data for lunar mare basalts (n=3) from the Apollo 12 and 17 missions. In addition, we report N₂/Ar ratios for the same samples. All samples have previously been described petrologically and age dated. Our aim is to better constrain the indigenous nitrogen isotope signature of the Moon by targeting pristine lunar basalts.

Nitrogen isotopes ($\delta^{15}\text{N}$) range from +22.40 ‰ to -0.25 ‰, and suggest a possible regional variability between Apollo 12 and 17 sites (Fig. 1). Uncertainties are estimated to be lower than 1 ‰ based on the reproducibility of both internal and external running standards during the course of the sample run. Nitrogen concentrations range from 2.57 to 6.98 × 10⁻⁶ cm³ STP/g [N₂]. N₂/Ar ratios vary between 162 and 196 and are more than double the canonical air value observed on Earth. Furthermore, N₂/Ar values exhibit a positive

correlation with nitrogen isotopes, indicating that relatively high N₂/Ar ratios may be coupled with a high $\delta^{15}\text{N}$ endmember component. Importantly, we report relative blank contributions between 37 and 64 %.

Discussion: A better understanding of the elemental and isotopic composition of the initial volatile lunar inventory is important for deciphering the evolution of the Moon. To this end, we have targeted primitive lunar basalts in an order to better quantify the indigenous lunar nitrogen component. To date, data are limited due in part to the 1) scarcity of indigenous volatiles, 2) low N₂ concentration in lunar basalts and 3) the overprinting of solar wind particles and/or secondary nuclides produced by cosmic ray exposure. The preliminary results of this study confirm previous findings and expand the limited database for indigenous lunar nitrogen. Importantly, we show a possible distinction between Apollo 12 (low $\delta^{15}\text{N}$) and Apollo 17 (high $\delta^{15}\text{N}$) samples. However, analytical difficulties (i.e. high blank contributions) still persist as sample access is limited and N₂ concentrations in lunar basalts are extremely low. Only with access to larger sample quantities and/or further analytical improvements will the indigenous lunar nitrogen isotope component continue to be more tightly constrained. Considering the current limitations, additional and repeat analyses are planned for the future.

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