

SIMULTANEOUS ANALYSIS OF ABUNDANCE AND ISOTOPIC COMPOSITION OF NITROGEN AND CARBON IN LUNAR BASALTS. J. I. Mortimer¹, A. B. Verchovsky¹, M. Anand^{1,2}, I. Gilmour¹, and C. T. Pillinger¹, ¹Planetary and Space Sciences, Department of Physical Sciences, The Open University, Milton Keynes, MK7 6AA, UK., ²Department of Earth Sciences, Natural History Museum, London, SW7 5BD, UK. james.mortimer@open.ac.uk

Introduction: In recent years, the search for lunar volatiles has attracted renewed interest; new analyses of lunar glasses and apatite crystals suggest initial magma volatile contents (prior to degassing) many times higher than previously reported (e.g. [1]), some with terrestrial-like volatile abundances [2, 3]. While much of recent lunar volatile research has focused on analysis of water and its hydrogen isotopic composition (e.g. [4, 5]), less attention has been paid to the geochemistry of other volatile elements such as N, C and noble gases in lunar samples, especially in lunar basalts.

Mare basalts provide an important window into the lunar interior, yielding data about the material from which the Earth-Moon system formed, and about the early geochemical evolution of the Moon. Post-emplacement history of mare basalts also provides a record of cosmogenic volatiles produced at the surface of the Moon over time, in addition to the indigenous lunar volatile components locked into the basalts at crystallisation.

In this new study, we combine stepped heating techniques at higher resolution than previous studies (e.g. [6, 7]), with simultaneous collection of data for more element and isotope systems (N and C (plus He, Ne, and Ar (see companion abstract at this meeting [8])) at each step, all from the same aliquot of lunar sample. Therefore, this new dataset represents a comprehensive, detailed inventory of volatiles in lunar basalts, building on and augmenting the results of previous studies.

Samples: Five Apollo basalt samples (10017, 12040, 12064, 14053, and 70035) were selected for this study, representing a range of crystallisation ages, cosmic-ray exposure (CRE) ages, and compositional variations, and covering each of the Apollo missions (except Apollo 16).

Methods: Sample preparation is outlined in a companion abstract [8]. Samples were analysed using the custom-built multiple static-mode mass spectrometer system 'Finesse' at the Open University [9] (also described in more detail in a companion abstract at this meeting [8]). N abundances (recorded as ng) were measured *via* calibration of the dedicated N mass spectrometer ion current at $m/z = 28$, and C abundances (recorded as ng of C) were calculated using the pressure of CO₂ measured on a calibrated MKS Baratron™ capacitance manometer.

Results: Nitrogen: All of the samples display the same general release profiles, with 67 – 84 % of the nitrogen being released at temperatures below 500 °C; average $\delta^{15}\text{N}$ values across this temperature range vary between -5.6 ‰ and +2.4 ‰, associated with terrestrial contamination. At the highest temperatures, very low amounts of nitrogen (blank level – 17 % of total N) are released, with a very distinct isotopic signature extremely enriched in ¹⁵N. This suggests that at high temperatures, nitrogen release is dominated by a cosmogenic N component (cosmogenic nitrogen containing a higher proportion of ¹⁵N relative to ¹⁴N). ¹⁵N enrichment is well-correlated with CRE ages; the most ¹⁵N enriched signatures are observed in basalts with the oldest CRE ages (Fig. 1), and *vice versa*.

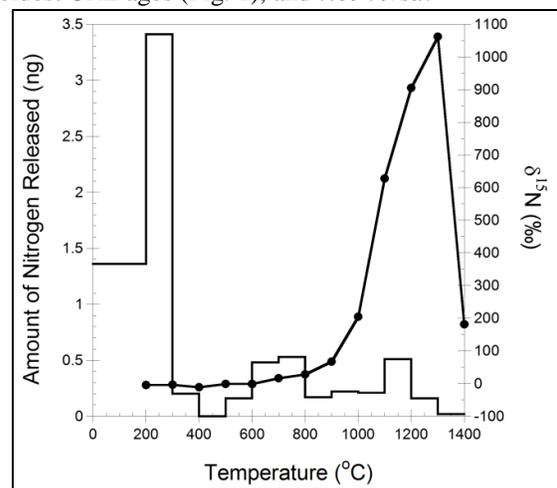


Figure 1: Step-plot for N release in basalt 10017, with the oldest CRE age, and the greatest ¹⁵N enrichment at high temperatures ($\delta^{15}\text{N} = +1062.3$ ‰)

The mid-temperature range (variable between different samples, based on analysis of each samples individual release profiles, but typically between 700 °C and 1000 °C) offers the best opportunity to investigate the isotopic signature of any indigenous N present in the basalt samples without interferences from either cosmogenic N or terrestrial contaminants. Between 15 % and 26 % of the N present is released at mid-temperature steps, and $\delta^{15}\text{N}$ values in this temperature range, attributed to a minor indigenous N component, vary between samples, from a maximum of +25.2 ‰, down to -4.5 ‰. This range of indigenous $\delta^{15}\text{N}$ values, while broad, yields an average value identical (within error) to an indigenous lunar basalt N signature

of 13.0 ± 1.2 ‰ across the same temperature range, as measured by [7].

Carbon: As with nitrogen, the samples show similar carbon release patterns. The majority (51 – 98 %) of C present is released below 600 °C, again associated with terrestrial organic contaminants. Between 1 % and 3 % of the carbon present is released at mid-temperature steps (typically between 650 °C and 1000 °C). In high-temperature combustion steps, very low amounts of C (< 1 % of total C) are released above system blank levels. Cosmogenic carbon, characterised by the high temperature enrichment in ^{13}C , can be recognised with certainty in most samples.

Indigenous lunar N and C: Using the mid-temperature ‘window’ between terrestrial contaminants and cosmogenic C (typically between 700 °C and 1000 °C), it is feasible to quantify the amount and isotopic composition of indigenous volatile components in lunar basalts. By comparing the release profiles of C and N in the five basalt samples studied, it is possible to identify several samples where the C and N are most likely co-located in the same phase, although the exact nature of this phase remains unidentified on the basis of release temperature alone. Since C and N are located in the same phase, it is possible to use the calculated C/N ratios for these indigenous volatile components to characterise the C and N properties of the lunar mantle, from which these basalts are derived.

The average C/N ratios of the indigenous components (Table 1) are relatively tightly constrained. All the basalts in this study show indigenous C/N ratios that are much lower than those measured for the present-day terrestrial depleted mantle ($C/N_{\text{mantle}} = 535 \pm 224$ [10, 11]), or even for bulk silicate Earth (BSE) ($C/N_{\text{BSE}} = \sim 40 - 50$ (calculated from data in [10])).

| Sample | C/N ratio |
|-----------------------------|---------------|
| 10017 | 21 |
| 12040 | 6 |
| 12064 | 9 |
| 14053 | 4 |
| 70035 | 11 |
| Terrestrial Depleted Mantle | 535 ± 224 |
| Enstatite Chondrites | 4.5 to 15 |

Table 1: C/N ratios, calculated for five lunar basalts analysed in this study, compared with C/N ratios for terrestrial depleted mantle and enstatite chondrites (as a proxy for primordial terrestrial mantle).

The large difference in C/N ratios between the terrestrial depleted mantle and indigenous lunar values can be explained by the significant influence of subducted sediments greatly increasing the C content of the Earth’s mantle compared to that of the Moon.

Therefore, a more relevant comparison might be made between primordial terrestrial mantle C/N and this indigenous lunar C/N data. Taking an enstatite chondrite composition as a proxy for the primordial terrestrial mantle [12], using enstatite carbon values averaging 3800 ppm [13] and the extremes of the nitrogen values proposed by [14] (254 - 850 ppm), C/N ratios of 4.5 and 15 are obtained.

Both of these C/N ratios for enstatite chondrites fall within or very close to the range found in this study for indigenous C and N in lunar basalts. However, there is a difference between the indigenous $\delta^{15}\text{N}$ signatures for these lunar basalts, and the values measured for enstatite chondrites (-29.2 ± 0.6 ‰ [14]), suggesting that indigenous lunar N does not come from an enstatite chondrite-type source.

Conclusions: Simultaneous measurements of N and C abundances and isotopic data from the same aliquot of sample, combined with high temperature-resolution stepwise combustion, permits an in-depth analysis of volatile components present in lunar samples. Results from this study suggest that indigenous lunar N, as present in mare basalts, has an average $\delta^{15}\text{N}$ value of around +12.6 ‰, consistent with results from previous studies (e.g. [7]).

The average C/N ratio of the indigenous lunar volatile component falls within the same range across all of the samples analysed in this study and is consistently much lower and therefore distinct from the C/N ratios of the present-day terrestrial depleted mantle or the bulk silicate Earth, consistent with the greater differentiation of Earth’s mantle volatile signatures due to tectonic recycling of material when compared to the Moon.

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