

SIMULTANEOUS ANALYSIS OF ABUNDANCE AND ISOTOPIC COMPOSITION OF HELIUM, NEON, AND ARGON 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]. Most of these recent studies have focused on measuring abundances and isotopic composition of water (e.g. [4, 5]). Other lunar volatiles investigated include F, Cl, and S (e.g. [2, 6]). In contrast, relatively very few recent studies have been carried out on lunar samples for determining their C, N, and noble gas signatures (e.g. [7, 8]). In this contribution we report new data on abundances and isotopic composition of He, Ne, Ar in lunar basalts with the aim of better constraining the origin(s) and abundances of lunar volatiles.

Apollo lunar 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 include 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.

Samples and Methods: 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). Approximately 250 mg of a single chip of each mare basalt was crushed using an agate mortar and pestle, to produce a homogenous powder, necessary for sub-sampling; around 5 mg aliquots of each sample were placed in cleaned Pt foil buckets, and subsequently crushed into spheres for analysis.

In this study, we have utilized advances in stepped heating techniques to combine higher resolution (multiple steps, down to 50 °C intervals), with simultaneous collection of data for more element and isotope systems (He, Ne, and Ar (plus N and C described in a companion abstract at this meeting [9])) 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 were analysed using the custom-built multiple static-mode mass spectrometer system 'Finesse' at

the Open University [10]. Samples were heated incrementally inside a double-walled quartz-ceramic furnace in 100 °C steps from 200 °C to 600 °C, 50 °C steps from 650 °C to 950 °C, and 100 °C steps from 1000 °C to 1400 °C.

Gases released at each temperature were collected after each step, cryogenically separated using a system of liquid nitrogen cooled traps and molecular sieves, and Ar and Ne were purified using Ti-Al getters. Gases were transferred within the machine along high vacuum lines, controlled by a system of automated pneumatic valves [10]. He and Ne were analysed using the quadrupole mass spectrometer, and Ar using one of two magnetic sector mass spectrometers within the 'Finesse' instrument.

Results:

Radiogenic Noble Gas Isotopes: Radiogenic ^4He and ^{40}Ar are present in all of the samples studied. As expected, measured ^4He and ^{40}Ar concentrations correlate closely with bulk chemical composition of individual mare basalts (U & Th and K producing ^4He and ^{40}Ar *in situ* by radioactive decay), and also vary as a function of mare basalt crystallisation ages, with older samples releasing the greatest concentrations of radiogenic noble gases.

Close agreement between measured radiogenic noble gas concentrations in this study with literature values demonstrates the effectiveness of the extraction technique used here. Small variations in measured ^4He abundances compared to literature values can be explained by a heterogeneous distribution of the minor mineral apatite (a main carrier of U and Th) in these samples.

Cosmogenic Noble Gas Isotopes: Cosmogenic ^{21}Ne is released from all the basalt samples and is well-correlated with published CRE ages for lunar basalts. Comparison of measured ^{21}Ne concentrations reveals close agreement with literature values. As with radiogenic noble gases, this correlation confirms the reliability and stability of this stepped combustion method, as described above, across a range of samples.

Trapped Noble Gas Isotopes: One sample, 12064, after blank correction, displays cosmogenic neon mixing with a trapped neon component with an isotopic signature identical to the terrestrial atmosphere (Fig. 1).

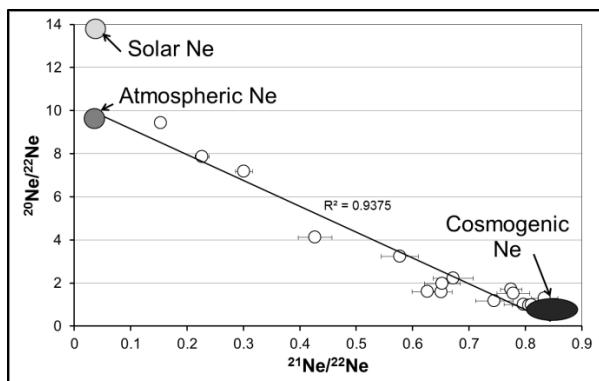


Figure 1: Neon components in sample 12064, displaying mixing between cosmogenic Ne and terrestrial-like trapped Ne components.

It is plausible that during sample crushing, terrestrial atmospheric gases were trapped in these samples, as previously observed by [11]. This is supported by the fact that in all of the samples for which Ne data were collected in this study, trapped ^{20}Ne is observed in greater abundances than in previously published studies, despite good agreements for cosmogenic ^{21}Ne values.

Although ^{20}Ne abundances in all mare basalts analysed in this study are higher than previously reported values, only 12064 displays a mixing trend between a cosmogenic Ne component and a terrestrial-like trapped Ne component. However, the abundance of ^{21}Ne in other samples is too low to enable identification of any mixing trend. Thus, trapping of terrestrial gases during sample preparation cannot be ruled out on the basis of Ne data alone.

On the other hand, noble gas components with terrestrial-like isotopic signatures have been previously observed in less processed samples [12]. Assuming indigenous lunar noble gases do indeed have terrestrial-like signatures, it may be possible that the neon isotopes measured in 12064 represent mixing of the minor cosmogenic neon component with an indigenous lunar neon component.

In order to further investigate the source of this atmospheric-like trapped Ne component, we have exploited the capability of the ‘Finesse’ instrument to collect data simultaneously for multiple elements in the same aliquot of sample, and examine the N data released from 12064 for any present-day terrestrial atmospheric N contribution, if trapping during sample preparation was the source of the observed terrestrial-like Ne isotope signature.

By knowing the relative abundances of N and Ne in the current terrestrial atmosphere and applying that ratio to the total abundance of trapped ^{20}Ne in sample 12064, the expected abundance of any trapped terrestrial N can be calculated (5710517 ng of N). However,

basalt 12064 releases only 42.52 ng of N (134302 times lower than the calculated expected abundance) and therefore, does not seem to show any evidence of significant trapped terrestrial atmospheric N.

The other trapped noble gas for which data were collected is ^{36}Ar ; again, as with any trapped atmospheric N, a higher abundance of ^{36}Ar might be expected if additional terrestrial atmospheric gases were introduced during sample crushing for this study. However, whilst a higher abundance of ^{36}Ar is observed in sample 14053 compared to published values, in most other samples in this study there is good agreement between these data and literature values, and in 12040, the amount of ^{36}Ar observed is lower than that measured in previous studies.

Thus, any potential trapping of ^{20}Ne during sample preparation cannot explain the observed mixing trend in 12064, and the addition of terrestrial atmospheric gases can be discounted based on co-collected N and Ar data in this study. This suggests that, at least within the lunar mantle source region for 12064, indigenous lunar Ne has a similar isotopic composition to the Earth.

Conclusions: Simultaneously measuring multiple element abundances and isotopic data from the same aliquot of sample, with high temperature-resolution stepwise heating techniques, permits in-depth analysis of the volatile components present in lunar samples. Close correlation between measured values in this study and published literature values demonstrate the effectiveness and reliability of this technique. Samples showing mixing of Ne components between a cosmogenic end-member and a terrestrial atmospheric-like composition potentially suggest that at least some indigenous lunar noble gases may have very similar compositions to terrestrial atmosphere.

Acknowledgements: CAPTEM is thanked for allocation of Apollo samples. STFC and OU are thanked for a PhD studentship to JIM. This research was partially supported by a STFC research grant to MA (grant No. ST/I001298/1).

References: [1] Saal A. E. et al. (2008) *Nature*, 454, 192-195. [2] Boyce J. W. et al. (2010) *Nature*, 466 (7305), 466-469. [3] Hauri E. H. et al. (2011) *Science*, 333 (6039), 213-215. [4] Greenwood J. P. et al. (2011) *Nature Geoscience*, 4, 79-82. [5] Tartèse R. et al. (2013) *Geochim. Cosmochim. Acta*, 122, 58-74. [6] McCubbin F. M. et al. (2011) *GCA*, 75, 5073-5093. [7] Barry P. H. et al. (2013) *LPS VII*, Abstract #2160. [8] Füri E. et al. (2012) *Icarus*, 218, 220-229. [9] Mortimer J. I. et al., this meeting, [10] Abernethy F. A. J. et al. (2013) *Meteoritics and Planet. Sci.*, 48, 1590-1606. [11] Niemeyer S. and Leich D. A. (1976) *LPS VII*, 587-597. [12] Lightner B. D. and Marti K. (1974) *LPS V*, 2023-2031.