



Simultaneous analysis of abundance and isotopic composition of nitrogen, carbon, and noble gases in lunar basalts: Insights into interior and surface processes on the Moon



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ABSTRACT

Simultaneous static-mode mass spectrometric measurements of nitrogen, carbon, helium, neon, and argon extracted from the same aliquot of sample by high-resolution stepped combustion have been made for a suite of six lunar basalts.

Collecting abundance and isotopic data for several elements simultaneously from the same sample aliquot enables more detailed identification of different volatile components present in the basalts by comparing release patterns for volatiles across a range of temperature steps. This approach has yielded new data, from which new insights can be gained regarding the indigenous volatile inventory of the Moon.

By taking into account N and C data for mid-temperature steps, unaffected by terrestrial contamination or cosmogenic additions, it is possible to determine the indigenous N and C signatures of the lunar basalts. With an average $\delta^{15}\text{N}$ value of around +0.35‰, the indigenous N component seen in these samples is similar within error to other (albeit limited in number) isotopic measurements of indigenous lunar N. Average C/N ratios for indigenous volatiles in these six basalt samples are much lower than those of the terrestrial depleted mantle, or bulk silicate Earth, possibly suggesting much less C in the lunar interior, relative to N, than on Earth.

Cosmogenic isotopes in these samples are well-correlated with published sample exposure ages, and record the rate of *in situ* production of spallogenic volatiles within material on the lunar surface.

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1. 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 (mainly H, reported as either OH or H₂O) many times higher than previously reported (e.g., F \ddot{u} ri et al., 2014; Greenwood et al., 2011; McCubbin et al., 2010; Saal et al., 2008; Tartèse et al., 2013), some with terrestrial-like volatile abundances (e.g., Boyce et al., 2010; Hauri et al., 2011).

In light of these new data, and given the advances in analytical techniques made in the decades since the Apollo missions returned lunar samples to Earth, it is timely to reassess some other light volatile elements (C, N) and noble gases (He, Ne, Ar) in lunar samples, to constrain better their origin(s) and abundances.

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. Crucially, mare basalts (and associated pyroclastic glasses) are derived from the lunar mantle, and thus comprise a key sample set from which the indigenous volatile inventory of the lunar interior can be assessed. Furthermore, post-emplacement history of mare basalts also provide 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.

Stepped heating techniques have been used in analyses of lunar samples since the early 1970s, when the Apollo samples were first returned to Earth (e.g. Friedman et al., 1970), and so are well-established analytical methods for use with extra-terrestrial material.

For stepped combustion analyses, such as those presented in this paper, each lunar sample is incrementally heated in the presence of oxygen gas. As a sample is heated, the release patterns of

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the combustion products of carbon (CO₂) and the gases released by pyrolysis (N₂ and noble gases) are recorded; the isotopic compositions of all the gases are measured at each temperature step. This enables different components present in the sample, which are associated with different release temperatures and isotopic signatures, to be distinguished from one another.

Crucial for the study of extra-terrestrial material, such as the lunar samples, is the capability of this method to distinguish the abundance and isotopic signature of terrestrial contaminants, which are more labile components and released at lower temperatures, from any indigenous lunar volatile components released at higher temperatures. In a single-step combustion analysis, in which the entire sample is combusted at the same high-temperature, these components from different sources are not resolvable.

Stepped combustion experiments on mare basalt samples have been carried out by a number of groups over the last four decades, although not all of these studies collected isotopic data (Table 1 contains a list of some previous lunar basalt studies, which focus mainly on N, C, and He, some of which employed stepped combustion techniques, and others which used different methods). However, it is worth noting that even those studies using stepped heating methods were of limited resolution, typically collecting data in only a small number of steps across the temperature range.

In this new study, we combine higher resolution (multiple steps, down to 50 °C intervals), with simultaneous collection of data for more element and isotope systems (N, C, He, Ne, and Ar) 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.

2. Samples

For this study, six Apollo basalt samples were selected (Table 2), covering a range of crystallisation ages, cosmic ray exposure ages, and compositional variations (both high Ti and low Ti basalts). These samples cover all of the US sample return missions, apart from Apollo 16 which mainly sampled lunar highlands anorthositic rocks, rather than the mare basalts which are the focus of this work.

A second aliquot of 12064,138 (Run 2) was analysed for Ne approximately 6 months after the first aliquot (Run 1), for the purposes of confirming the Ne isotope ratio mixing trend observed in the first run (see Section 5.4.3 for further discussion).

3. Methods

Approximately 250 mg of a single chip of each mare basalt was crushed using an agate mortar and pestle, to produce a homogeneous powder, necessary for sub-sampling; around 5 mg samples were used for stepped-combustion analysis. In order to minimise any terrestrial contamination of the samples before analysis, the basalt powders were weighed out and transferred into 4 mm × 4 mm clean platinum foil buckets in a Class 100 clean room (Pt foil cleaning methods are as described in Abernethy et al., 2013). Tweezers and spatulas used to transfer the basalt powders from their respective vials to the platinum buckets were cleaned before use, and wiped with acetone using lint-free cloths between uses with separate samples.

The 'Finesse' mass spectrometric instrument used in this study is a custom-built mass spectrometer system, consisting of three dedicated static-mode mass spectrometers (one for carbon, one for nitrogen and argon, and a quadrupole for helium and neon), all linked *via* high vacuum lines to a common sample inlet and combustion furnace (see Wright et al., 1988; Wright and Pillinger, 1989; Verchovsky et al., 1997 for further details, and Boyd et al., 1997, for a review of the stepped-heating method).

Samples were combusted in oxygen, supplied from CuO, in a double-walled quartz-ceramic furnace for 30 min at each temperature step, followed by 15 min for oxygen desorption, before transfer of the gases produced to the clean-up section. For the initial batch of samples, only thirteen combustion steps were used, in 100 °C steps from 200 to 1400 °C. However, for the final three samples (12040, 12064 (Run 2), and 15555), a total of seventeen combustion steps were employed to acquire higher-resolution data across the mid-range temperatures, heating in 100 °C steps from 200 to 600 °C, then in 50 °C steps from 650 to 950 °C, followed by 100 °C steps from 1000 to 1400 °C. Gas fractions were cryogenically separated using liquid nitrogen cooled traps, some of which were filled with molecular sieves. Argon and neon were purified using Ti–Al getters, and nitrogen was purified using a CuO furnace to ensure no CO was present. Carbon yields (recorded as ng of C) were calculated using the pressure of CO₂ measured on a calibrated MKS Baratron™ capacitance manometer. Nitrogen yields (also recorded as ng) were measured *via* calibration of the mass spectrometer ion current at *m/z* = 28, with yields of noble gases also determined by calibration of mass spectrometer peak intensities at the appropriate *m/z* values. Gases were transferred to different

Table 1
Previous nitrogen, carbon, and noble gas analyses of lunar basalts. Sample numbers in bold refer to samples used in common with this study.

Author(s)	Year	Lunar basalt sample(s)	Volatiles	Method
Des Marais	1978	15058, 15555 , 70215, 75035	$\delta^{13}\text{C}_{(\text{VPDB})}$, $\delta^{15}\text{N}_{(\text{AIR})}$	Stepped combustion at 420 °C, 500 °C, and 1230 °C (varies between samples)
	1983	15016, 15058, 15499, 15555 , 70017, 74275	$\delta^{13}\text{C}_{(\text{VPDB})}$, $\delta^{15}\text{N}_{(\text{AIR})}$	Stepped combustion at 420 °C, 500 °C, and 1230 °C (varies between samples)
Friedman et al.	1970	10017	$\delta^{13}\text{C}_{(\text{VPDB})}$	Combustion to 1350 °C
	1971	12004, 12021, 12051	$\delta^{13}\text{C}_{(\text{VPDB})}$	Combustion to 900 °C
	1972	15555	$\delta^{13}\text{C}_{(\text{VPDB})}$	Combustion to 950 °C
Gibson and Andrawes	1978	15058, 15065, 15499, 15556, 70215, 74255, 74275, 75035, 78505	N (abundance only)	Crushing
	1971	10017 , 12022	C, N (abundance only)	Thermal gas release
Kaplan et al.	1976	15016, 15499, 15555	$\delta^{13}\text{C}_{(\text{VPDB})}$, $\delta^{15}\text{N}_{(\text{AIR})}$, He	Combustion
	2001	75075	$\delta^{15}\text{N}_{(\text{AIR})}$	Combustion at 400 °C, then stepped pyrolysis up to 1600 °C
Moore et al.	1970	10049, 10050	C, N (abundance only)	Combustion at 1600 °C
	1971	12002, 12022, 12040 , 12044, 12052, 12063, 12065	C, N (abundance only)	Combustion at 1600 °C
	1972	14310	C, N (abundance only)	Combustion at 1600 °C
	1973	15058, 15065, 15076, 15499, 15556, 15595	C (abundance only)	Combustion at 1600 °C
	1974	70215, 71055, 75035	C (abundance only)	Combustion at 1600 °C
	1974	70017, 70215, 74275, 75035, 75075	$\delta^{13}\text{C}_{(\text{VPDB})}$, $\delta^{15}\text{N}_{(\text{AIR})}$, He	Pyrolysis-combustion

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