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Predominantly non-solar origin of nitrogen in lunar soils

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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 five lunar soils.

Noble gas isotope ratios show that the majority of noble gases are derived from a solar wind source; for example, at peak release temperatures of 500–600 °C, $^{21}\text{Ne}/^{22}\text{Ne} = 0.0313 \pm 0.0007$ to 0.0333 ± 0.0007 , and $^{20}\text{Ne}/^{22}\text{Ne} = 11.48 \pm 0.05$ to 12.43 ± 0.07 , with values at the lowest temperature steps less fractionated during implantation from, and therefore even closer to, solar values ($^{21}\text{Ne}/^{22}\text{Ne}_{\text{SW}} = 0.03361 \pm 0.00018$ and $^{20}\text{Ne}/^{22}\text{Ne}_{\text{SW}} = 14.001 \pm 0.042$ (Pepin et al., 2012)). Despite the co-release of nitrogen and solar wind argon, measured nitrogen isotopic signatures at each temperature step, whilst variable, are significantly more enriched in ^{15}N compared to the measured solar wind nitrogen value from the Genesis mission. Therefore, mixing between a ^{15}N -enriched non-solar planetary nitrogen source with solar wind nitrogen is required to explain the measured isotopic values from the stepped combustion analysis of lunar soils. Binary mixing calculations, made under different assumptions about the degree of loss of solar wind ^{36}Ar , reveal that the majority (up to 98%) of the nitrogen released is derived from a non-solar source. The range of modelled non-solar end-member nitrogen compositions required to satisfy the measured $\delta^{15}\text{N}$ values varies between samples and temperature steps from +5‰ up to +300‰, or between +87‰ and +160‰ for bulk samples. This range of modelled isotopic compositions for the non-solar source of nitrogen encompasses measured values for several different groups of carbonaceous chondrite, as well as IDPs.

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Keywords: Moon; Regoliths; Cosmochemistry; Solar wind; Meteorites

1. INTRODUCTION

For decades, there has been debate about the source(s) of nitrogen in lunar soils; since noble gases in lunar soils are predominantly solar, and nitrogen is both well correlated with these solar components, and likewise, co-located on soil grain surfaces (Wieler et al., 1999), a predominantly solar source for nitrogen was expected. However, stepped heating analyses of lunar regolith have

consistently revealed a similar release profile across all Apollo and Luna soils, with low temperature, ^{15}N -enriched nitrogen preceding a mid-temperature, ^{15}N -depleted component, which is then followed at the highest temperature steps by a second ^{15}N -enriched release (e.g. Brilliant et al., 1994; Assonov et al., 2002). This pattern of heavy-light-heavy ('V-shaped') nitrogen, with large-scale variations in nitrogen isotopic composition of around 300‰ (Becker and Clayton, 1975; Kerridge, 1975, 1993; Clayton and Thiemens, 1980; Frick et al., 1988; Brilliant et al., 1994; Wieler et al., 1999; Assonov et al., 2002; Furi et al., 2012), coupled with the observation that nitrogen isotopic variations correlate with $^{40}\text{Ar}/^{36}\text{Ar}$ ratios (which are taken as a proxy for soil antiquity, or when in

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the past a soil was exposed at the lunar surface) (Füri et al., 2012), led many to suggest that the composition of the solar wind must have changed over time, becoming progressively more enriched in ^{15}N (Kerridge, 1975; Becker and Clayton, 1975; Clayton and Thiemens, 1980).

In contrast, solar noble gases as measured in lunar soils display very minor variations in comparison to nitrogen isotopic compositions (e.g. Kerridge, 1989, 1993), inconsistent with a secular variation hypothesis for nitrogen. Further, $\text{N}/^{36}\text{Ar}$ ratios measured in lunar soils (Frick et al., 1988; Kerridge, 1993; Wieler et al., 1999; Assonov et al., 2002) are around ten times greater than the solar elemental abundance ratio of 37 (Anders and Grevesse, 1989). Whilst ^{15}N -depleted ('light') nitrogen is correlated with the release of solar wind D-depleted hydrogen from the outer rims of lunar soil grains, ^{15}N -enriched ('heavy') nitrogen correlates with the release of D-enriched hydrogen from a planetary source (Hashizume et al., 2000). Thus, the observed trend of higher average $\delta^{15}\text{N}$ values with decreasing soil antiquity may not be caused by a secular variation in solar wind composition, but instead may be recording a change in the relative contribution of a planetary nitrogen source to the lunar surface (Hashizume et al., 2002). Therefore, current evidence suggests that nitrogen in lunar soils represents mixing between a 'heavy' planetary nitrogen component and a solar wind component of 'light' composition (Geiss and Bochsler, 1982; Wieler et al., 1999; Hashizume et al., 2000, 2002; Assonov et al., 2002; Marty et al., 2003; Ozima et al., 2005; Füri et al., 2012). This has been supported by recent direct measurements of solar wind nitrogen implanted into the Genesis Solar Wind Concentrator target, which gave a modern-day $\delta^{15}\text{N}$ value for solar wind of $-407 \pm 7\text{‰}$ (Marty et al., 2011), comparable to the composition of protosolar nitrogen ($-383 \pm 8\text{‰}$ (Marty et al., 2011)), and to that of the Jovian atmosphere (Owen et al., 2001).

In light of this, Füri et al. (2012) calculated that most of the nitrogen released from Luna 24 soil grains is from a non-solar source with a planetary composition of between $+100\text{‰}$ and $+160\text{‰}$, assuming binary mixing with ^{15}N -depleted solar wind, with the highest proportional contribution from a non-solar source being found in recently exposed Apollo soils (with $^{40}\text{Ar}/^{36}\text{Ar}$ ratios ≤ 1.5).

Characterising the source(s) of volatiles being delivered to the lunar surface is essential for a broader consideration of how volatiles can be transported around the Solar System and added to the surfaces and atmospheres of other rocky Solar System bodies after initial planetary formation. Indeed, the volatile elements included in this study form the majority of most terrestrial planet atmospheres. Thus, to begin to understand planetary atmospheric evolution, any likely exogenous volatile source(s) must be identified and their contributions taken into account. Further, volatiles present at the surface of the Moon and other airless bodies, such as larger asteroids, may prove vital to the further human exploration of the Solar System, providing resources to support life beyond Earth. From this perspective, knowledge of which volatiles are present must be coupled with information about where they originated, thereby

enabling resource reservoir estimation and replenishment rate consideration.

To this end, a diverse set of Apollo lunar soils have here been analysed by stepped combustion, with the released gases simultaneously analysed for nitrogen, carbon, and noble gases (He, Ne, and Ar) in order to better constrain the contribution of non-solar nitrogen by taking into account multiple isotope systems, and their variations over discrete temperature increments.

2. SAMPLES

Five Apollo lunar soils, representing both extremely mature (e.g. $I_s/\text{FeO} = 94$) and immature (e.g. $I_s/\text{FeO} = 5.7$) samples, and covering a range of collection locations, from Apollo 12, 14, 15, 16, and 17, and including both shaded soils and samples collected at the surface of the regolith in unshaded locations, were chosen for stepped combustion analyses. Note that sample 12070 was analysed twice. (Table 1). Soil maturity is expressed as the ratio of observed ferromagnetic intensity of the sample (I_s) divided by its total Fe content (FeO); ferromagnetic intensity increases as a sample is exposed at the lunar surface *via* the production of non-charged Fe microparticles, termed nanophase Fe or np-Fe⁰, resulting from reduction or sputtering processes acting upon lunar regolith materials to remove oxygen from ferrous Fe. Thus, the larger the ratio of I_s/FeO , the more mature the soil.

3. METHODS

For stepped combustion analyses, samples were weighed out and transferred into 4 mm × 4 mm clean platinum foil buckets in a Class 100 cleanroom (Pt foil cleaning methods are as described in Abernethy et al., 2013). Tweezers and spatulas used to transfer the sample fines from their respective vials to the platinum buckets were cleaned before use, and wiped with acetone using lint-free cloths between usages 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 gas clean-up sections, and combustion furnace (e.g. Mikhail et al., 2014, and references therein).

3.1. Stepped combustion procedure

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 released gases to the clean-up section. For Run 1 of soil 12070, twelve combustion steps were used, in 100 °C steps from 300 to 1400 °C. However, for Run 2 of soil 12070, fifteen combustion steps were employed to acquire higher-resolution data, heating in 100 °C steps from 200 to 700 °C, then in 50 °C steps from

Table 1

List of five lunar soil samples chosen for stepped combustion analysis (^aMorris, 1978).

Apollo Sample	Weight (mg) (Combustion)	Maturity (I_s/FeO)	Description
12070	Run 1: 2.063 Run 2: 5.211	Sub-mature (47 ^a)	Collected as part of the contingency sample, taken from a location in front of the Lunar Module (LM)
14141	7.637	Immature (5.7 ^a)	Coarse soil, collected from near the rim of Cone Crater
15040	5.662	Mature (94 ^a)	Collected at Station 8, from the surface at the top of a trench
69921	5.377	Mature (90 ^a)	Skim soil, collected from top 1 cm of regolith in shaded area next to a small (0.5 m) boulder at Station 9
72501	4.710	Mature (81 ^a)	Collected from landslide at Station 2, at the base of the slope of the South Massif, close to Nansen Crater

750 to 850 °C, followed by 100 °C steps from 900 to 1400 °C. All other soil samples were combusted in seventeen temperature steps, in increments of 100 °C from 200 to 600 °C, then in 50 °C steps from 650 to 850 °C, followed by 100 °C steps from 900 to 1400 °C. During stepped combustion analyses, C, N, He, Ne, and Ar data were collected.

Gas fractions released during stepped combustion analyses were processed in the same way for each sample. First, the released gases were cryogenically separated using liquid nitrogen cooled traps, one of which was filled with a molecular sieve. 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 parts of the machine using a system of computer-controlled pneumatic valves. For each temperature step, the isotopes and abundances of C, N, ⁴He, Ne, and Ar were measured sequentially, taking approximately 1.5 h to complete the cycle for all five elements. Once all measurements were complete, the high vacuum line was pumped before the gases released in the following temperature step were transferred from the furnace. In order to reduce the contributions from CO₂⁺⁺ and ⁴⁰Ar⁺⁺ to measurements of ²²Ne and ²⁰Ne respectively, a low ionisation voltage of ~40 V was used in the quadrupole ion source. Also, Ar present in the system was cooled down on the molecular sieves and the Ti–Al getter was open to the mass spectrometer chamber during Ne measurements.

Isotopic data are expressed using the delta (δ) notation, as parts per thousand (‰) deviations from standards (Vienna Peedee Belemnite_(VPDB) for C, and terrestrial air_(AIR) for N). System blanks were monitored between sample analyses by putting an empty clean Pt foil bucket through the same stepped combustion procedure used for the lunar samples and collecting both abundance and isotopic data. Typical system blank levels for stepped combustion were <10 ng for C and <1 ng for N. Typical system

blanks for ⁴He were <1E-7cc, for ²⁰Ne were <6.5E-10cc, and for ⁴⁰Ar and ³⁶Ar were <8E-9cc and <1.2E-10, respectively. All data presented in this paper have been corrected for the contribution of system blanks (unless otherwise stated), and any isotopic averages presented are calculated as weighted averages.

4. STEPPED COMBUSTION RESULTS

4.1. Nitrogen and carbon

Stepped combustion analyses in this study reveal volatile releases that are in excellent agreement with previous combustion work. For all soil samples, N is released in the characteristic heavy-light-heavy isotopic profile (as previously observed by Brilliant et al., 1994; Assonov et al., 2002 etc.) (Table A; Fig. 1).

For each soil, the most ¹⁵N-depleted ('lightest') isotopic signature is measured at 850–900 °C (apart from 12070 Run 1 (Panel A, Fig. 1), where most of the N in the 900 °C step was lost). It must be noted that the combustion steps releasing the lightest nitrogen component are not coincident with the maximum N abundances, but instead are associated with some of the lower released abundances (relative to combustion steps at temperatures either side of 850–900 °C). Given a solar wind N isotopic signature of around –407‰ (Marty et al., 2011), this indicates that the main contributor to N abundances in lunar soils must be from a non-solar source with a much more ¹⁵N-enriched ('heavier') isotopic composition, mixing in varying proportions with the less abundant light N component most likely derived from the solar wind (see Discussion section).

In contrast to N releases, hundreds of ng of C are released from the first few temperature steps, up to 500–600 °C. This is most likely associated with the release of terrestrial contaminants from the samples. However, above this temperature, two further releases of C are observed in all soils; one at roughly 600–900 °C, and a second at temperatures above 1000 °C (Table B; Fig. 2). Although large uncertainties are associated with some of these C releases, C isotopic composition varies considerably; in some samples (14141, 15040, and 72501) there is an apparent relative depletion in ¹³C associated with the 600–900 °C release

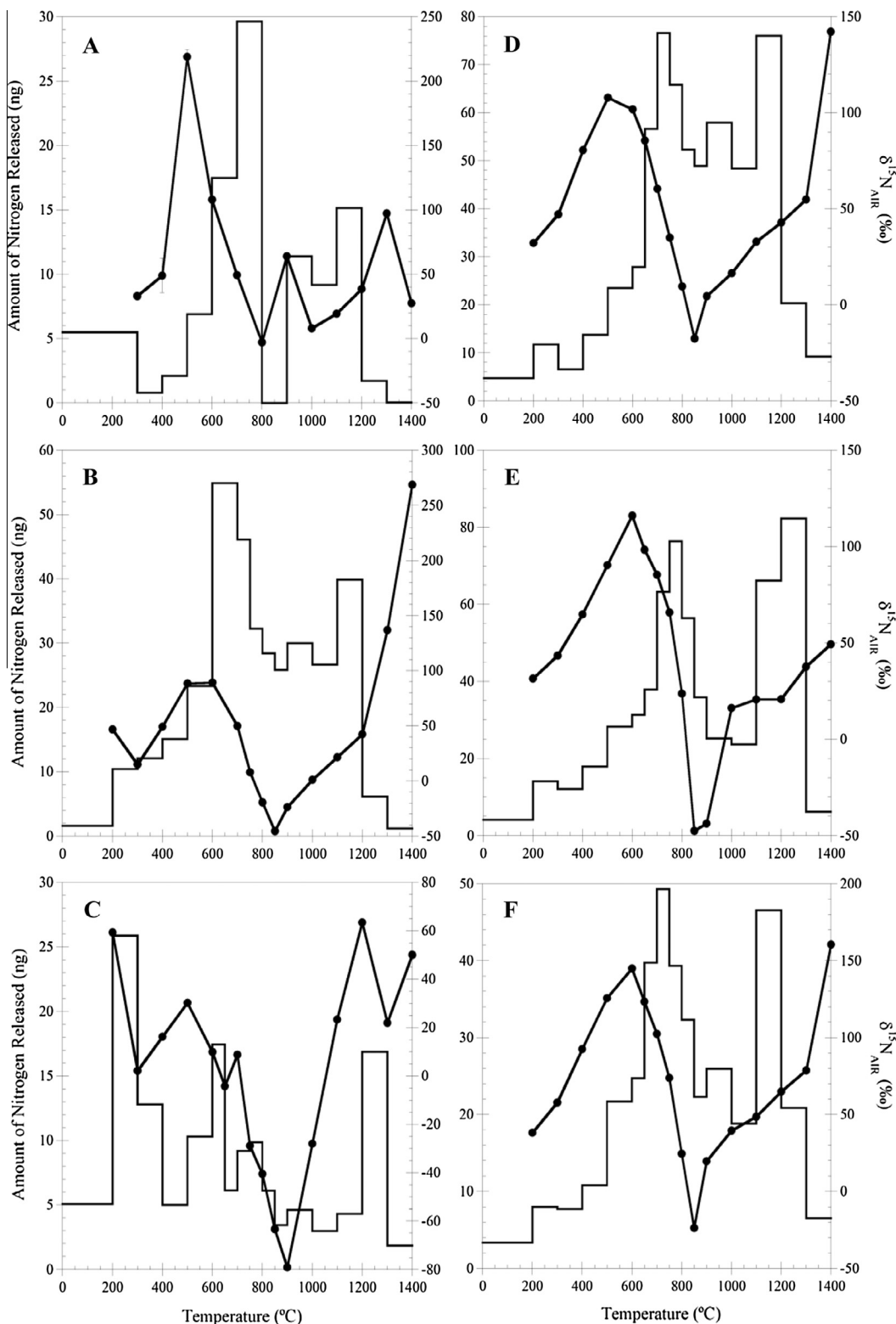


Fig. 1. Step plots showing nitrogen release profiles for all soils analysed by stepped combustion. Abundances, measured on left-hand axis, are displayed as a histogram, and isotopic compositions, measured on the right-hand axis, are displayed as a line graph. Errors in many cases are smaller than the symbol size. (A = 12070 Run 1; B = 12070 Run 2; C = 14141; D = 15040; E = 69921; F = 72501).

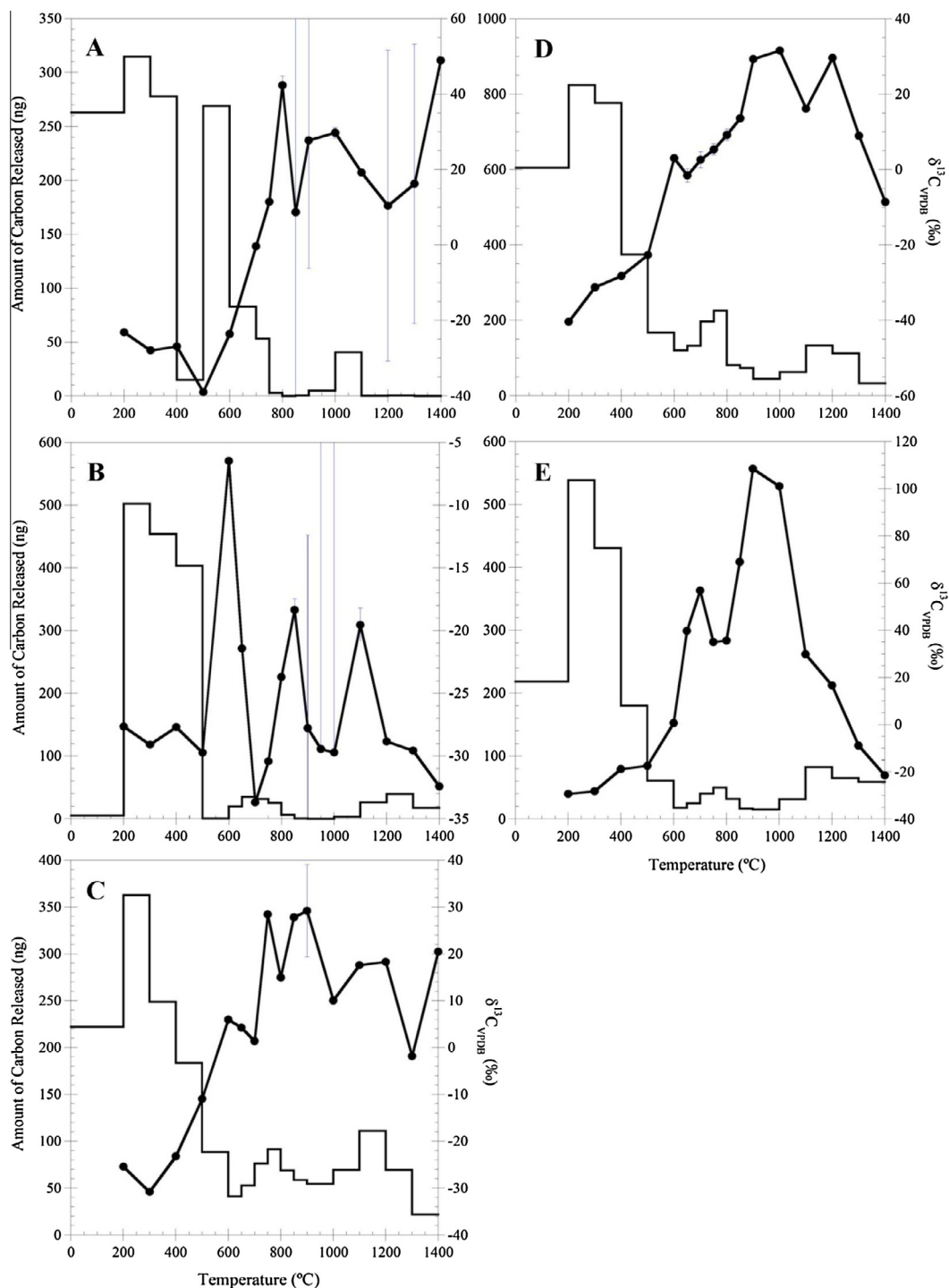


Fig. 2. Step plots showing carbon release profiles for soils analysed by stepped combustion. N.B: No carbon data was collected for 12070 Run 1. Abundances, measured on left-hand axis, are displayed as a histogram, and isotopic compositions, measured on the right-hand axis, are displayed as a line graph. Errors are shown in pale blue. (A = 12070 Run 2; B = 14141; C = 15040; D = 69921; E = 72501). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

peak of C, but in general, despite variations in isotopic composition, $\delta^{13}\text{C}$ values for C released above around 600 °C are positive (i.e. ^{13}C -enriched). The exception to this observation is 14141, which is the least mature soil in our

sample set. Whilst this soil shows a similar isotope profile to the other, more mature, soils, in this case, $\delta^{13}\text{C}$ values remain between -35‰ and -20‰ , lower than for the other samples.

4.2. Noble gases (Argon)

Again, as previously noted by others (e.g. [Hohenberg et al., 1970](#); [Brilliant et al., 1994](#); [Assonov et al., 2002](#)), ^{40}Ar , ^{36}Ar , and N are co-released in all samples ([Figs. 3 and 4](#)), albeit with an additional release peak of ^{40}Ar at lower temperatures (typically between 400 °C and 600 °C) that is not observed in releases of ^{36}Ar , which gives rise to the elevated $^{40}\text{Ar}/^{36}\text{Ar}$ ratios at these lower temperatures ([Table C](#)). [Assonov et al. \(2002\)](#) explain this low temperature ^{40}Ar release as being attributable to terrestrial atmospheric contamination and/or re-implantation of ^{40}Ar liberated to the lunar atmosphere during regolith reworking events (this re-implanted ^{40}Ar being much more loosely fixed at the surfaces of grains which have experienced little or no reworking than the bulk of the argon contained in the soils, which, after soil reworking, is immured deeper within grains; thus re-implanted ^{40}Ar is liberated at lower temperatures during analysis). As noted in previous studies (e.g. [Assonov et al., 2002](#)), atomic N/ ^{36}Ar ratios above $\sim 650^\circ\text{C}$ are relatively constant, at around ten times the solar ratio (as estimated by [Anders and Grevesse, 1989](#)).

4.3. Noble gases (Helium and Neon)

Typical release patterns for ^4He and ^{20}Ne from lunar soils analysed in this study are shown in [Fig. 5](#). The majority of the Ne released by combustion appears to be from a solar source, which is fractionated from the pure solar values (taken from [Pepin et al., 2012](#)) upon implantation into the lunar surface ([Fig. 6](#)). This dominant solar Ne component is also mixed with a much less abundant cosmogenic Ne component in some samples, although even the highest temperature steps still appear to be a mixture of solar and cosmogenic Ne ([Table F](#); [Fig. 6](#)). The $^4\text{He}/^{20}\text{Ne}$ ratios, which are comparable to those observed in other lunar soils, suggest that the majority of He is of solar wind origin as well.

5. DISCUSSION: SOLAR VS NON-SOLAR NITROGEN

Although spallation processes generated by incoming cosmic rays lead to a significant enrichment in ^{15}N progressively over time as a sample resides at or near to the lunar surface, stepped combustion analyses of lunar basalts have demonstrated that such cosmogenic N is only present in very low abundances of between 0.20 ppm and 0.25 ppm ([Mortimer et al., 2015](#)). Lunar soils contain much greater abundances of total N, ranging from 18.56 ppm N in immature soil 14141, up to 108.04 ppm N in mature soil 69921, and so the effect of a cosmogenic N component on measured isotopic compositions of lunar soils will be negligible. Similarly, stepped combustion analyses of lunar basalts reveal a minor indigenous lunar nitrogen component (at $+0.93 \pm 9.39\%$, and present in abundances of between 0.13 ppm and 0.90 ppm ([Mortimer et al., 2015](#) and additional data that is contained in the [Appendix](#) to this present study ([Table I](#))), or <0.1 ppm to 0.5 ppm ([Füri et al., 2015](#)); this is volume-correlated, and as with any cosmogenic N, is

several orders of magnitude less abundant than the total N released from lunar soils, which is mostly surface-correlated (e.g. [Hashizume et al., 2000](#)). Therefore, for the purposes of the following calculations, we assume that inputs from both cosmogenic and indigenous lunar N are so low in relation to the total N release from lunar soils that they have essentially no impact on weighted average (across all temperature steps) N isotopic compositions for each soil sample.

Assuming instead that the total N released from lunar soils represents a binary mixture of solar and non-solar nitrogen components, and taking into account the isotopic composition of the solar wind as measured by Genesis (at -407% ([Marty et al., 2011](#))), it is possible to carry out similar calculations to those of [Füri et al. \(2012\)](#) using data from this study, working backwards from the measured (mixed) N values to derive estimates for both the percentage contribution from a non-solar source of N to the lunar surface, and the likely isotopic composition of this non-solar extra-lunar contributor.

Weighted average nitrogen isotopic values ($\delta^{15}\text{N}_{\text{tr}}$) for the soils in this study vary between $+1.0\%$ and $+65.7\%$, with average atomic $^{36}\text{Ar}/\text{N}$ ratios (normalised to the solar $^{36}\text{Ar}/\text{N}$ value of 0.02714, taken from [Anders and Grevesse, 1989](#)) varying between 0.12 and 0.17 times the solar value ([Table 2](#)). The relative proportions of solar and non-solar N are calculated using the following equation:

$$\delta^{15}\text{N}_{\text{tr}} = \frac{\delta^{15}\text{N}_{\text{SW}} + f_{\text{P}}\delta^{15}\text{N}_{\text{P}}}{1 + f_{\text{P}}}$$

where $\delta^{15}\text{N}_{\text{SW}}$ and $\delta^{15}\text{N}_{\text{P}}$ are the end-member isotopic compositions of solar wind nitrogen and non-solar ('planetary') nitrogen, respectively. f_{P} is the mixing proportion of non-solar to solar nitrogen, and is defined thus:

$$f_{\text{P}} = \frac{N_{\text{P}}}{N_{\text{SW}}}$$

Clearly, with $^{36}\text{Ar}/\text{N}_{\text{tr}}$ values varying between 1/9th and 1/6th of the solar ratio, either $^{36}\text{Ar}_{\text{SW}}$ has been lost as a result of impact and gardening processes at the lunar surface (with N_{SW} being preferentially retained as a result of implantation into grains and its greater reactivity with common elements within soil grains), or a significant proportion of non-solar nitrogen (N_{P}) has been added to that derived from a solar source (negligible amounts of ^{36}Ar are added from the non-solar source, as evidenced by the majority of other noble gases (i.e. Ne) being derived from solar and not planetary sources). Whilst the preferential loss of solar noble gases over solar nitrogen is certainly an important factor, average $\delta^{15}\text{N}_{\text{tr}}$ values measured in lunar soils by stepped combustion methods display considerable enrichment in ^{15}N relative to the solar end-member value, which strongly suggests that the majority of the N measured in lunar soils comes from a non-solar source. Therefore, assuming that no loss of $^{36}\text{Ar}_{\text{SW}}$ has taken place, and that the difference between measured and solar $^{36}\text{Ar}/\text{N}$ values is caused by the addition of non-solar N alone, should give an upper limit to the proportion of non-solar N present and provide the lower limit of the isotopic composition of the non-solar end-member.

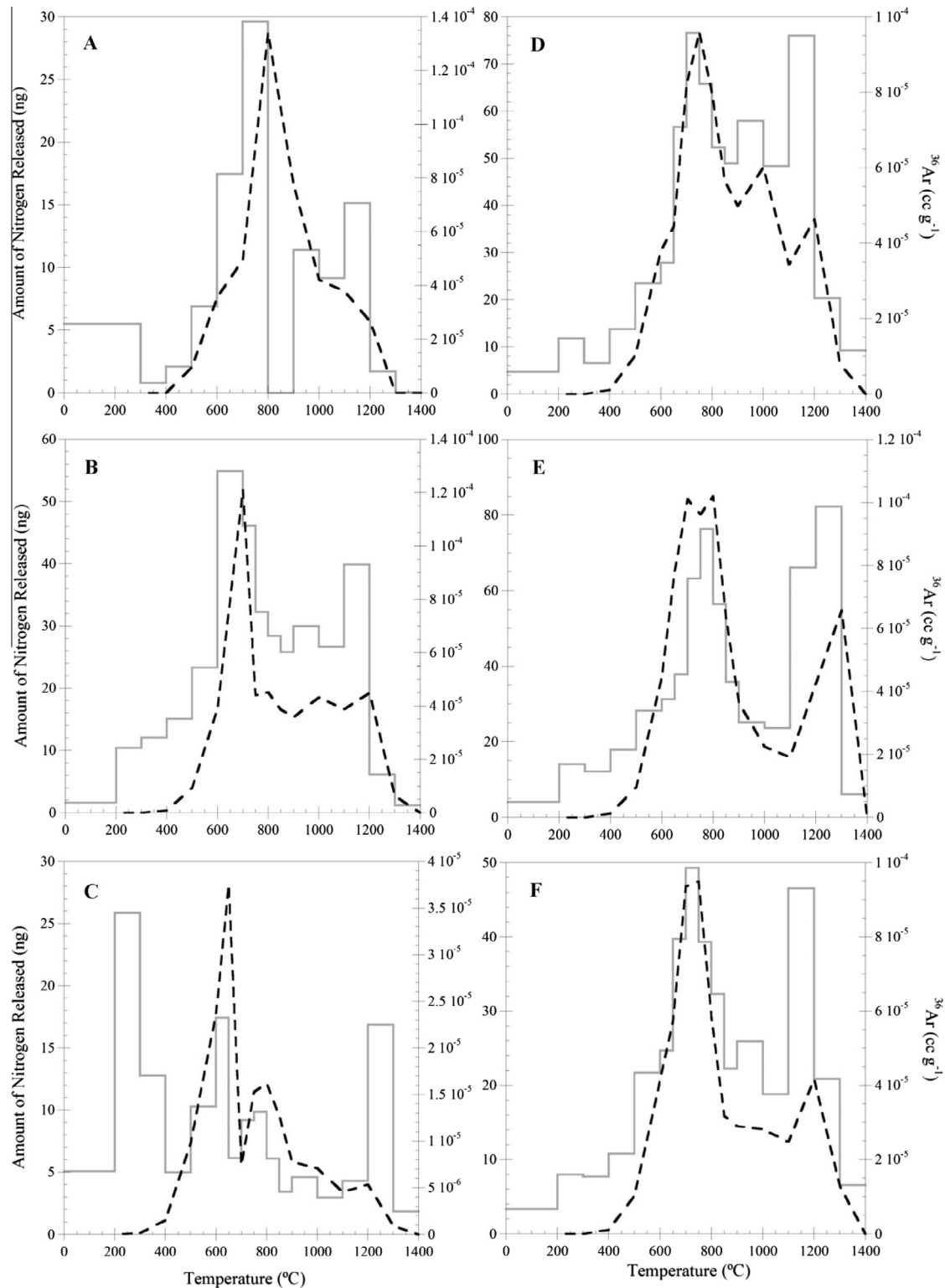


Fig. 3. Release patterns for nitrogen (grey histogram, measured on the left-hand axis) and ^{36}Ar (dotted black lines, measured on the right-hand axis) abundances, showing the co-release of ^{36}Ar and N above $\sim 400^\circ\text{C}$. (A = 12070 Run 1; B = 12070 Run 2; C = 14141; D = 15040; E = 69921; F = 72501).

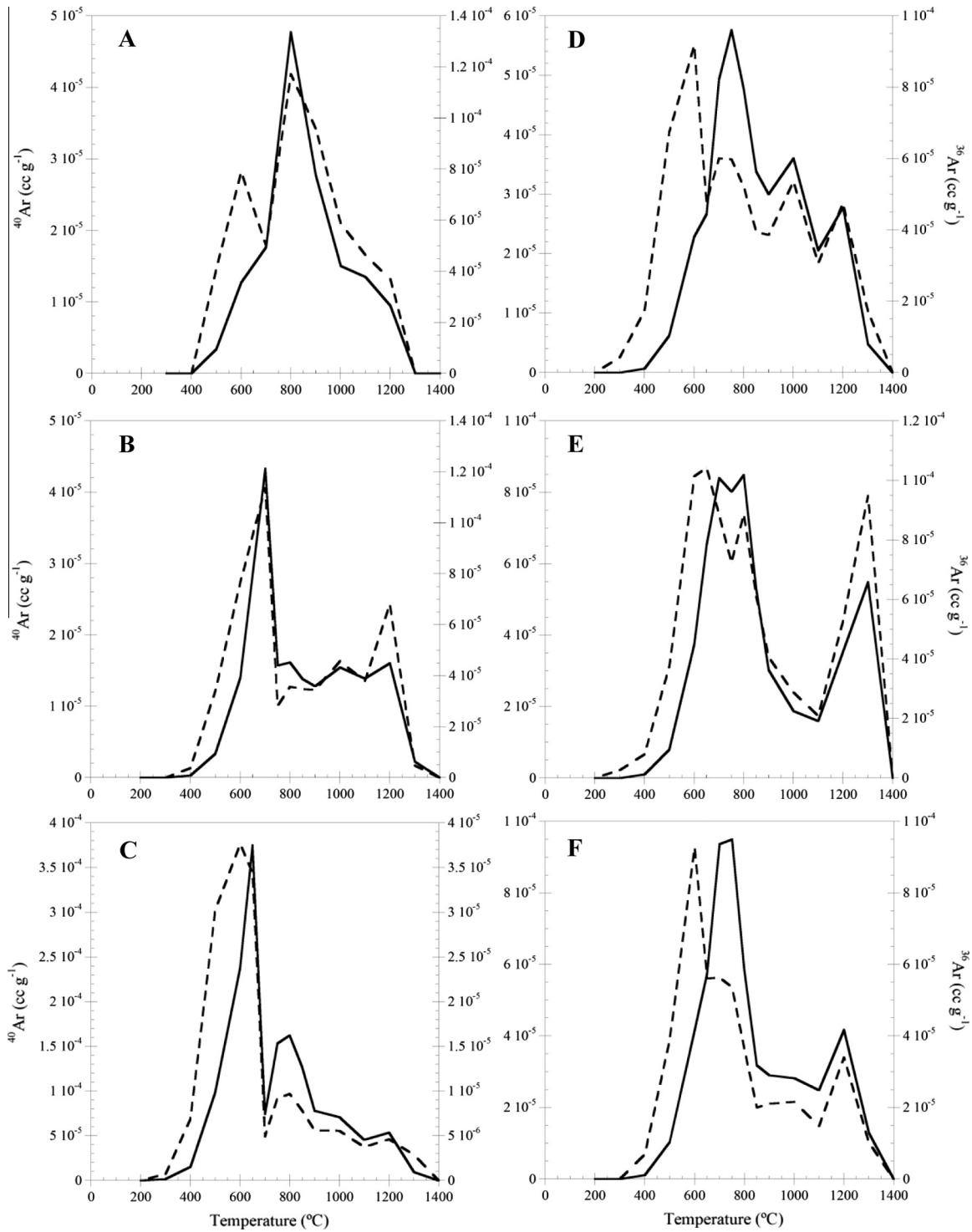


Fig. 4. Release patterns of ^{40}Ar (black dotted lines, measured on left-hand axis) and ^{36}Ar (solid black lines, measured on right-hand axis), showing co-release of both isotopes at temperatures over approximately 650 °C. (A = 12070 Run 1; B = 12070 Run 2; C = 14141; D = 15040; E = 69921; F = 72501).

Thus, to calculate the mixing proportion (f_P) of non-solar to solar N (N_P/N_{SW}), the following equation is used:

$$\frac{(^{36}\text{Ar}/\text{N})_{\text{tr}}}{(^{36}\text{Ar}/\text{N})_{\text{SW}}} = \frac{1 - f_R}{1 + f_P}$$

where $(^{36}\text{Ar}/\text{N})_{\text{tr}}$ is the average measured ratio for the soil sample, $(^{36}\text{Ar}/\text{N})_{\text{SW}}$ is the solar ratio taken from [Anders and Grevesse \(1989\)](#), and f_R is the fraction of solar gas lost.

To assess the likelihood of preferential loss of solar wind ^{36}Ar , a solar wind Ar/Xe atomic ratio of 23,360, calculated

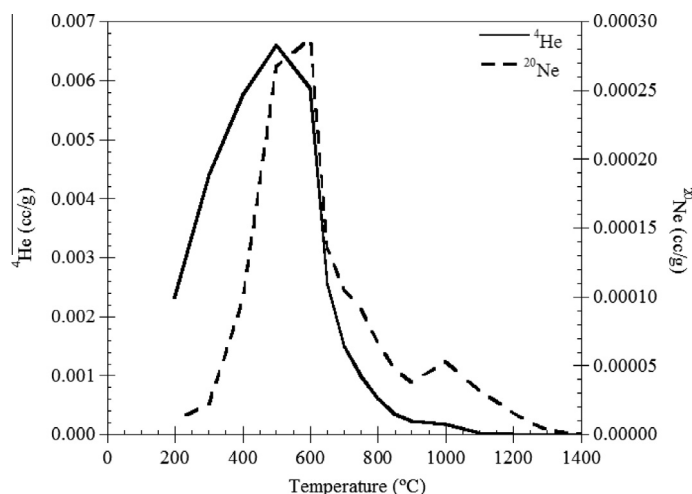


Fig. 5. Stepped combustion release profiles of ^4He and ^{20}Ne from soil sample 69921.

from data contained in Vogel et al. (2011) using direct measurements of the solar wind made with the Genesis Cz-Si targets, can be compared with Ar/Xe atomic ratios calculated from the bulk ^{36}Ar abundances in this study and bulk Xe abundances from published literature for the same samples. Taking ^{132}Xe abundances from Hintenberger et al. (1971) and Heymann et al. (1974), Ar/Xe = 23,400 for soil sample 12070 (Run 2), and Ar/Xe = 20708.66 for soil 72501, respectively. With Ar/Xe ratios so close to the directly-measured solar wind value, it seems that very little, if any, loss of solar wind ^{36}Ar from lunar soils has occurred, relative to Xe which has the highest retention among the noble gases. Assuming no loss of $^{36}\text{Ar}_{\text{SW}}$ means that a range of N_{P} end-member isotopic compositions are required for these samples, from +87‰ for 12070 (Run 2), up to +140‰ for 72501 (Fig. 7). However, this range of isotopic compositions results in a much tighter range of mixing proportions between N_{P} and N_{SW} , with the non-solar nitrogen source contributing 77.15% of the total N in soil 14141, up to 87.25% of the total N in soil 15040 (Table 2). It is interesting to note that, although most sub-mature and mature soils have a similar proportion contribution from a non-solar source (at approximately 86–87% of the total N in the soils), the sample with the lowest maturity, 14141, also has the lowest contribution from non-solar sources of N, at 77.15%. Therefore, it seems that N contributions from non-solar sources are increasingly dominant as a soil matures at the lunar surface. Furthermore, despite slight differences in the mixing proportions of solar and non-solar nitrogen sources between samples, it is clear that in all lunar soils, solar N only accounts for a small proportion of the total N present (<23% solar N). This conclusion is in agreement with those of Füri et al. (2012), who state that between 60% and 83% of the N present in low-antiquity ($^{40}\text{Ar}/^{36}\text{Ar}$ ratios ≤ 1.5) Apollo soils comes from a non-solar source. All of the Apollo soils used in this study have $^{40}\text{Ar}/^{36}\text{Ar}$ ratios ≤ 1.5 , except 14141, which has a $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of 10.92. The range of N_{P} isotopic compositions suggested here is also in close agreement with values

(+90‰ to +130‰) proposed by Füri et al. (2012) for Luna 24 samples.

If, however, we assume that some degree of $^{36}\text{Ar}_{\text{SW}}$ loss is also occurring alongside addition of non-solar N, theoretical mixing lines can be constructed between a solar N end-member (at ~ -400 ‰) and a non-solar (N_{P}) end-member composition of +140‰ (the value suggested by negligible loss of $^{36}\text{Ar}_{\text{SW}}$ from the most ^{15}N -enriched soil, 72501) (Fig. 7). In this case, 12070 (Run 2) has experienced the largest loss of $^{36}\text{Ar}_{\text{SW}}$, at $\sim 40\%$ loss ($f_{\text{R}} = 0.42$) (Table 2).

Soil maturity (I_{s}/FeO) is roughly positively correlated ($R^2 = 0.58$) with weighted average $\delta^{15}\text{N}$ values (Fig. 8), indicating that, as a soil undergoes progressive processing at the lunar surface, this seems to be driving the variations observed in $\delta^{15}\text{N}$ values. If, then, the potential loss of $^{36}\text{Ar}_{\text{SW}}$ from all soil samples is also taken into account, and a non-solar end-member isotopic composition of +160‰ is assumed (as proposed by Füri et al., 2012), the range of relative contributions from a non-solar N source remains largely the same (71.6%, up to 83% non-solar N) (Table 2), confirming that non-solar N is the major contributor to the total N present in lunar soils, and that solar N contributes only around a quarter of the total N abundance. A non-solar composition of +160‰ requires losses of $^{36}\text{Ar}_{\text{SW}}$ of between 18% and 48%, which again fits well with the calculations of Füri et al. (2012) (Fig. 9).

Although the binary mixing calculations based on the bulk measurements of Apollo soils already discussed in this paper are in excellent agreement with conclusions reached for Luna samples (Füri et al., 2012), both in terms of relative proportions of N_{SW} and N_{P} , and the range of isotopic compositions suggested for the non-solar end-member, the stepped heating data in this study can go further to consider how the relative proportions of N_{SW} and N_{P} change with the well-documented variations in nitrogen isotopic compositions as a sample is heated in discrete temperature steps. It must be noted, however, that such calculations can only be made for temperature steps that represent a two-component mixture of nitrogen. Therefore, temperature

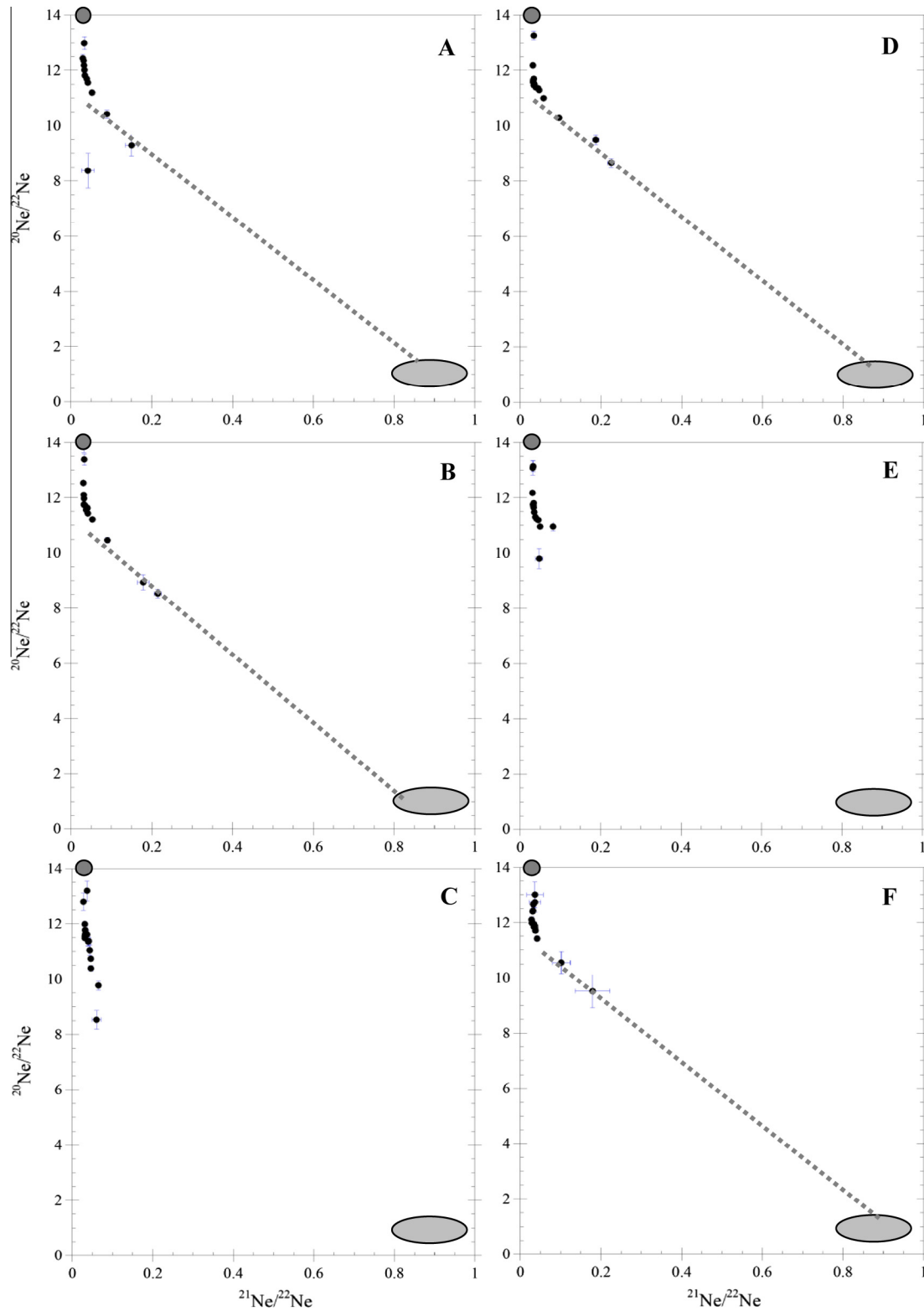


Fig. 6. Neon isotopic compositions for stepped combustion analyses of lunar soils. Most of the neon released is from a solar source, fractionated from true solar values during implantation. In some soils, this fractionated solar neon component is mixed with a minor cosmogenic neon component (grey dotted lines indicate mixing trend). Solar and cosmogenic end-member compositions are represented by dark circles and light grey ellipses (respectively). Instrument errors are 5%. (A = 12070 Run 1; B = 12070 Run 2; C = 14141; D = 15040; E = 69921; F = 72501).

Table 2

Comparing mixing proportions of solar and non-solar N end-members in 3 different scenarios (no loss of $^{36}\text{Ar}_{\text{SW}}$ and variable N_{P} compositions; variable loss of $^{36}\text{Ar}_{\text{SW}}$ and $N_{\text{P}} = +140\text{‰}$; variable loss of $^{36}\text{Ar}_{\text{SW}}$ and $N_{\text{P}} = +160\text{‰}$).

	12070 Run 1	12070 Run 2	14141	15040	69921	72501
<i>Assuming 0% loss of $^{36}\text{Ar}_{\text{SW}}$</i>						
Weighted average isotopic composition ($\delta^{15}\text{N}$, ‰)	32.3	23.3	1.0	36.2	34.6	65.7
Non-solar end-member isotopic composition ($\delta^{15}\text{N}$, ‰)	120	87	120	100	100	140
Contribution of non-solar nitrogen (%)	83.15	86.90	77.15	87.25	86.90	86.25
Contribution of solar nitrogen (%)	16.85	13.10	22.85	12.75	13.10	13.75
Loss of solar wind ^{36}Ar (%)	0	0	0	0	0	0
f_{R}	0	0	0	0	0	0
f_{P}	4.935	6.634	3.376	6.843	6.634	6.273
$(1 - f_{\text{R}})/(1 + f_{\text{P}})$	0.1685	0.1310	0.2285	0.1275	0.1310	0.1375
$(^{36}\text{Ar}/\text{N})_{\text{tr}}/(^{36}\text{Ar}/\text{N})_{\text{SW}}$	0.1685	0.1270	0.2319	0.1206	0.1282	0.1325
<i>Assuming $N_{\text{P}} = +140\text{‰}$</i>						
Weighted average isotopic composition ($\delta^{15}\text{N}$, ‰)	32.3	23.3	1.0	36.2	34.6	65.7
Non-Solar end-member isotopic composition ($\delta^{15}\text{N}$, ‰)	140	140	140	140	140	140
Contribution of non-solar nitrogen (%)	80.05	78.40	74.26	80.80	80.15	86.20
Contribution of solar nitrogen (%)	19.95	21.60	25.74	19.20	19.85	13.80
Loss of solar wind ^{36}Ar (%)	15	42	10	37	35	4
f_{R}	0.15	0.42	0.10	0.37	0.35	0.04
f_{P}	4.013	3.630	2.885	4.208	4.038	6.246
$(1 - f_{\text{R}})/(1 + f_{\text{P}})$	0.1696	0.1253	0.2317	0.1210	0.1290	0.1325
$(^{36}\text{Ar}/\text{N})_{\text{tr}}/(^{36}\text{Ar}/\text{N})_{\text{SW}}$	0.1685	0.1270	0.2319	0.1206	0.1282	0.1325
<i>Assuming $N_{\text{P}} = +160\text{‰}$</i>						
Weighted average isotopic composition ($\delta^{15}\text{N}$, ‰)	32.3	23.3	1.0	36.2	34.6	65.7
Non-Solar end-member isotopic composition ($\delta^{15}\text{N}$, ‰)	160	160	160	160	160	160
Contribution of non-solar nitrogen (%)	77.2	75.6	71.6	77.9	77.6	83
Contribution of solar nitrogen (%)	22.8	24.4	28.4	22.1	22.4	17
Loss of solar wind ^{36}Ar (%)	25	48	18	45	42	20
f_{R}	0.25	0.48	0.18	0.45	0.42	0.2
f_{P}	3.386	3.098	2.521	3.525	3.464	4.882
$(1 - f_{\text{R}})/(1 + f_{\text{P}})$	0.1710	0.1269	0.2329	0.1215	0.1299	0.1360
$(^{36}\text{Ar}/\text{N})_{\text{tr}}/(^{36}\text{Ar}/\text{N})_{\text{SW}}$	0.1685	0.1270	0.2319	0.1206	0.1282	0.1325

steps which may contain a third nitrogen component (whether terrestrial atmospheric N or cosmogenic N) and steps that released no measurable abundance of ^{36}Ar are not included in the following binary mixing calculations. Therefore, assuming that measured nitrogen isotopic compositions for temperature steps between 500 °C and 1200 °C (inclusive) represent binary mixing of N_{SW} and N_{P} , and assuming that the most ^{15}N -enriched steps within this range have experienced no loss of $^{36}\text{Ar}_{\text{SW}}$, the variable isotopic compositions for each temperature step within a sample can be reconciled with an N_{P} end-member composition that is more enriched in ^{15}N than bulk data would suggest, with separate samples indicating N_{P} end-member compositions between +210‰ and +300‰ (Fig. 10 and Table G). These N_{P} end-member isotopic compositions are more ^{15}N -enriched than measured values for most carbonaceous chondrite groups (Pearson et al., 2006), but are within the range of values measured in bulk IDPs, which also display ‘hotspots’ reaching up to +1300‰ (Floss et al., 2006), as well as being within the range of values measured in the chondrite Isheyevo, up to +4900 ± 300‰ (Briani et al., 2009), and the stony-iron meteorite Bencubbin, which has a maximum $\delta^{15}\text{N}$ of +1033‰ (Franchi et al., 1986).

Within an individual sample, the proportion of N_{P} to N_{SW} changes with each temperature step, with the largest contributions from N_{SW} observed at 850 °C to 900 °C, coincident with the least ^{15}N -enriched measured isotopic compositions. However, even at these temperature steps where N_{SW} contributions are greatest, in most samples, the majority (between 50% and 61%) of the nitrogen released is derived from the non-solar N_{P} source (Fig. 11). The one exception to this is 14141, which is the least mature of the soil samples analysed in this study; here, at 900 °C, a non-solar N_{P} component with an end-member composition of +260‰ contributes only 49% of the nitrogen released in that temperature step, with the remaining 51% of the released nitrogen being derived from a solar source. It therefore seems that stepped combustion data confirm the conclusions reached based on bulk data that the majority of nitrogen in lunar soils comes from a non-solar source in all but the most immature samples.

If, however, the original assumption of little to no preferential loss of solar wind ^{36}Ar is revisited, evidence from the bulk sample Ar/Xe atomic ratios of soil samples is further supported in the stepped combustion data by the close correlation of ^{36}Ar and nitrogen releases across the entire

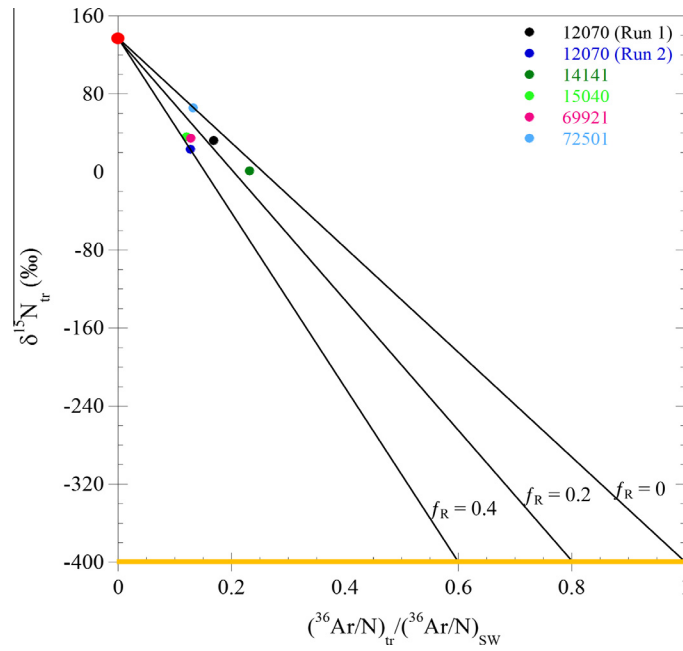


Fig. 7. Isotopic composition of nitrogen released from lunar soils (weighted average across all temperature steps) versus measured $^{36}\text{Ar}/\text{N}$ ratios in samples, normalised to the solar ratio (taken from [Anders and Grevesse, 1989](#)). The large red circle at $+140\text{‰}$ on the y -axis indicates the end-member isotopic composition of the non-solar N contribution, assuming no loss ($f_R = 0$) of $^{36}\text{Ar}_{\text{SW}}$ from the most ^{15}N -enriched sample (72501), and a maximum of 40% loss ($f_R = 0.4$) of $^{36}\text{Ar}_{\text{SW}}$ from the least ^{15}N -enriched sample (12070 run 2). The yellow bar at -400‰ represents the composition of solar nitrogen. Solid black lines are theoretical mixing lines between solar and non-solar N end-members, assuming different fractions of $^{36}\text{Ar}_{\text{SW}}$ loss.

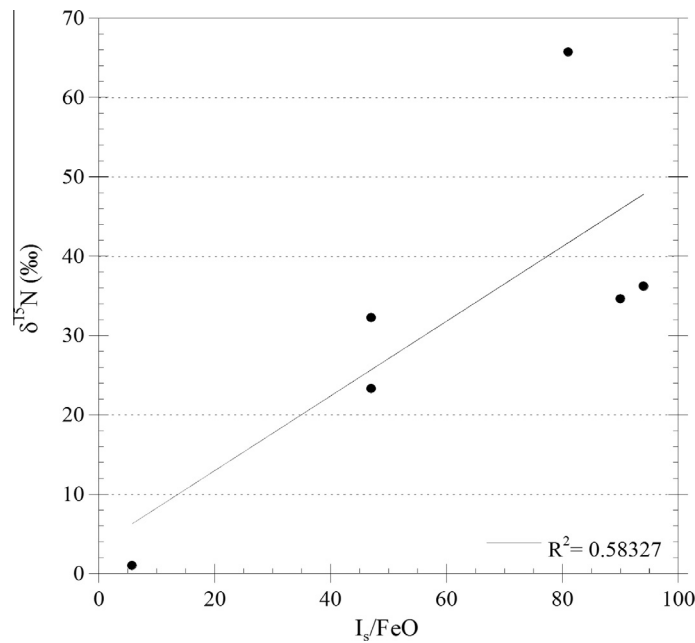


Fig. 8. Positive correlation between soil maturity (I_s/FeO) and weighted average measured nitrogen isotopic composition for bulk soils.

temperature range used in this study ([Fig. 3](#)). This pattern of co-release suggests that both species are located in sites with similar energies required for gas release to occur, and consequently, if there has been any partial loss of gas, this would be expected to have happened to both

^{36}Ar and nitrogen equally. Therefore, the range of N_P end-member compositions required to satisfy measured $\delta^{15}\text{N}$ values for each temperature step has been calculated based on an assumption of no loss of ^{36}Ar ([Fig. 12](#), [Table H](#)). In this case, the non-solar end-member composi-

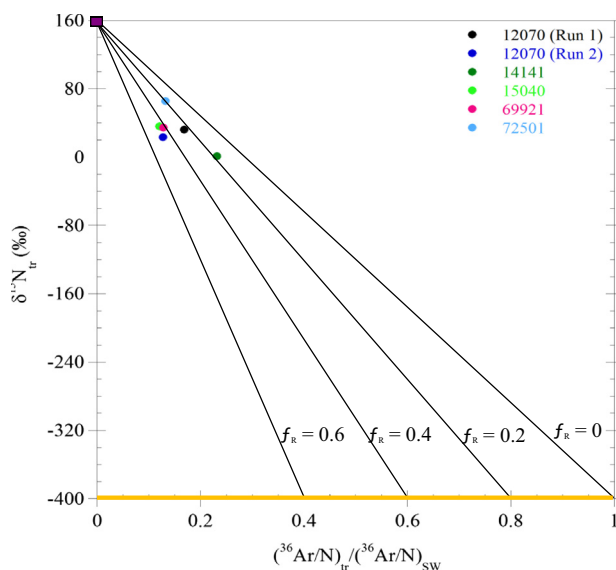


Fig. 9. Isotopic composition versus $(^{36}\text{Ar}/\text{N})_{\text{tr}}/({}^{36}\text{Ar}/\text{N})_{\text{sw}}$ ratios. The purple square at +160‰ on the y-axis indicates the end-member isotopic composition of N_p , taken from Füri et al., 2012. The yellow bar at -400‰ represents the composition of solar nitrogen. Solid black lines are theoretical mixing lines between solar and non-solar N end-members, assuming different fractions of $^{36}\text{Ar}_{\text{SW}}$ loss.

tion varies between +5‰ and +300‰, again with the majority of the measured nitrogen being derived from a non-solar source. These values are more consistent with those calculated for bulk samples, suggesting that a range of chondritic and/or IDP sources could be delivering nitrogen to the surface of the Moon.

However, it is also possible that the non-solar component may represent a mixture of different sources in addition to chondrites, including N from cometary ices. Since cometary ice N is extremely ^{15}N -enriched, its possible contribution allows a wider range of chondritic groups to be included as possible contributing sources (e.g. CO, CI, CM, CV), despite their average $\delta^{15}\text{N}$ values being lighter than the majority of the N_p end-member compositions suggested here. Taking a value of +700‰ as a lower estimate for cometary ice N (Füri and Marty, 2015), and mixing this with average values for CO, CI, CM, and CV chondrites (taken from Barnes et al., 2016 and references therein), gives the maximum possible cometary contribution to the mixed non-solar component. For bulk soil samples, assuming no loss of $^{36}\text{Ar}_{\text{SW}}$, the maximum cometary contributions to the N_p component are between 6% and 11% dependent upon the sample and chondrite group chosen, which equates to between 5% and 18% of the total lunar soil N abundance. Therefore, even with the possible addition of cometary N, the main source of N being delivered to the lunar surface remains a chondritic and/or IDP source.

6. CONCLUSIONS

Simultaneous measurements of carbon, nitrogen, and noble gases in lunar soils by stepped combustion analysis

reveal the characteristic release pattern of heavy-light-heavy nitrogen, as well as reconfirming that ^{40}Ar , ^{36}Ar , and N releases are well-correlated (above 650 °C). An excess of ^{40}Ar (relative to releases of ^{36}Ar) at low temperatures is most likely caused by terrestrial atmospheric contamination, or possibly by the re-implantation of liberated ^{40}Ar from the lunar atmosphere. Neon isotopes measured by stepped combustion reveal that the majority of neon in lunar soils comes from a solar source, with a minor cosmogenic component released at only the highest temperature steps.

However, the release of ^{15}N -enriched nitrogen from soils shows that it is not purely solar in origin (given a solar wind nitrogen signature of -407‰), and calculations reveal that up to 87% of the nitrogen measured in bulk lunar soils could come from a non-solar/planetary source, with an isotopic signature of between +87‰, up to +160‰. Taking measured nitrogen isotopic compositions and abundances of ^{36}Ar and N for each temperature step, more ^{15}N -enriched non-solar end-member compositions of between +210‰ and +300‰ are required to explain the measured values, assuming varying levels of $^{36}\text{Ar}_{\text{SW}}$ loss, with the largest contributions from N_{SW} occurring at 850 °C to 900 °C, coinciding with the most ^{15}N -depleted releases. However, even at temperatures where N_{SW} contributions to the total nitrogen release are greatest, the majority of the nitrogen being released (between 50% and 61%) is still derived from a non-solar source in most soils. The exception is 14141, which is the least mature soil analysed in this study ($I_s/\text{FeO} = 5.7$); in this sample, N_{SW} contributes 51% of the total nitrogen release at 900 °C.

Alternatively, Ar/Xe ratios measured in soils are very similar to those measured for the solar wind, suggesting that there has been no significant loss of $^{36}\text{Ar}_{\text{SW}}$ from soil samples. Furthermore, the matching release patterns of ^{36}Ar and nitrogen across the whole temperature range used in this study suggest that no preferential loss of $^{36}\text{Ar}_{\text{SW}}$ has occurred. Therefore, a model of nitrogen mixing based on this alternative assumption is considered to be most likely. Following on from this, if the fraction of solar gas lost is taken to be zero ($f_R = 0$), and the equation $\frac{1-f_R}{1+f_P} = R$, the end-member composition of the non-solar source (N_p) can be calculated using the following relationship:

$$\delta^{15}\text{N}_{\text{tr}} = \frac{(\delta^{15}\text{N}_p + (\delta^{15}\text{N}_{\text{SW}} - f_R - \delta^{15}\text{N}_p) \times R)}{(1 - f_R)}$$

With no loss of $^{36}\text{Ar}_{\text{SW}}$, a wider range of non-solar end-member compositions (N_p values between +5‰ and +300‰) is required, although this is perhaps expected when the range of material being delivered to the lunar surface from different sources is considered. Again, the majority of the nitrogen measured in lunar soils is derived from a non-solar source, with the calculated N_p end-member isotopic compositions being consistent with a likely IDP source for the N_p component, in agreement with the conclusions of Füri et al. (2012), and/or consistent with various carbonaceous chondrite sources of nitrogen. Possible additions from a cometary source mixing with a chondritic source cannot contribute more than ~10% to the N_p non-solar component.

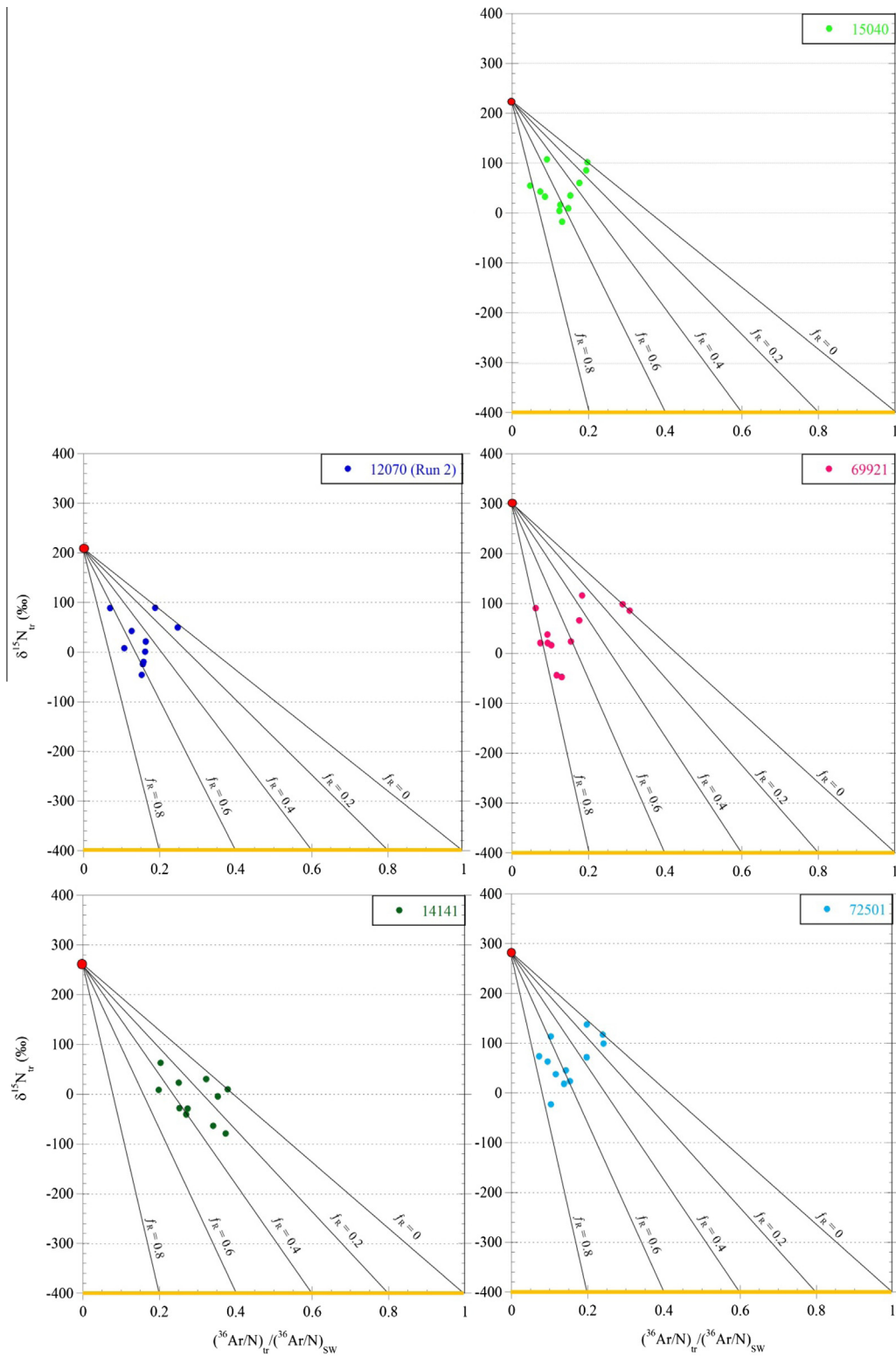


Fig. 10. Isotopic composition at each temperature step taken to indicate binary mixing only versus $(^{36}\text{Ar}/\text{N})_{\text{tr}} / (^{36}\text{Ar}/\text{N})_{\text{SW}}$ ratios. For each sample, the yellow line indicates N_{SW} end-member composition, and the red circle indicates the N_{P} end-member composition required, which varies between samples from +210‰ to +300‰. Solid black lines are theoretical mixing lines between N_{SW} and N_{P} end-members, assuming different fractions of $^{36}\text{Ar}_{\text{SW}}$ loss. See Table G for data.

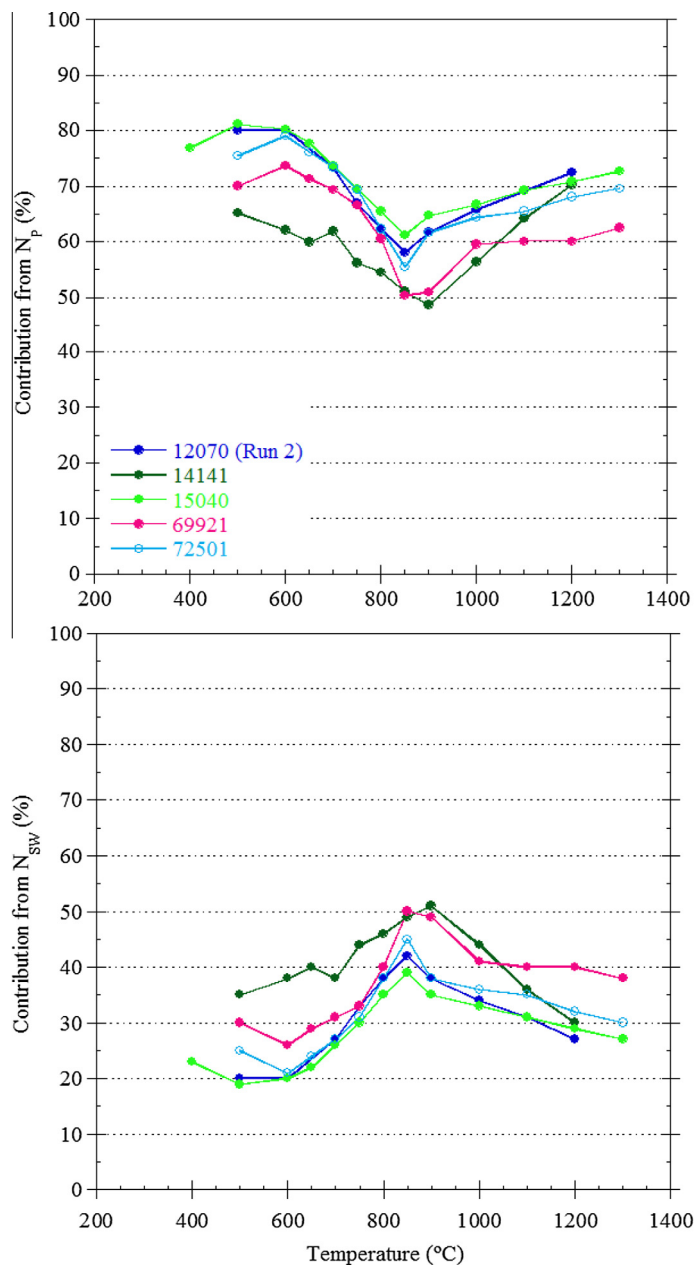


Fig. 11. Variations in the percentage of nitrogen released from lunar soils derived from a non-solar planetary source (N_P) and from a solar source (N_{SW}) at individual combustion temperature steps, assuming some degree of solar wind loss has occurred. Note that the lowest contribution from N_P (and therefore the greatest contribution from N_{SW}) occurs at 850 °C to 900 °C in each soil sample.

What is clear from these results is that there is an apparent decoupling between the sources of volatiles and their release temperatures and profiles following processing of material at the lunar surface. Although the most solar-like Ne compositions are released at the lowest temperatures, additions of non-solar N, mixing with solar N, results in the greatest proportion of solar N being released at higher temperatures of around 900 °C. Further, despite ^{36}Ar being purely solar and N being derived from a mixture of solar and non-solar sources, both are well-correlated and

co-released across the whole temperature range. Therefore, the sites volatiles are initially delivered to are not necessarily the sites where they are ultimately stored and later released from during analysis.

A further implication of these findings is that, assuming the Moon's surface has experienced volatile additions from similar sources to the Earth's atmosphere, chondritic and/or IDP sources appear to play the dominant role in the formation of planetary atmospheres, not comets, at least in the case of nitrogen.

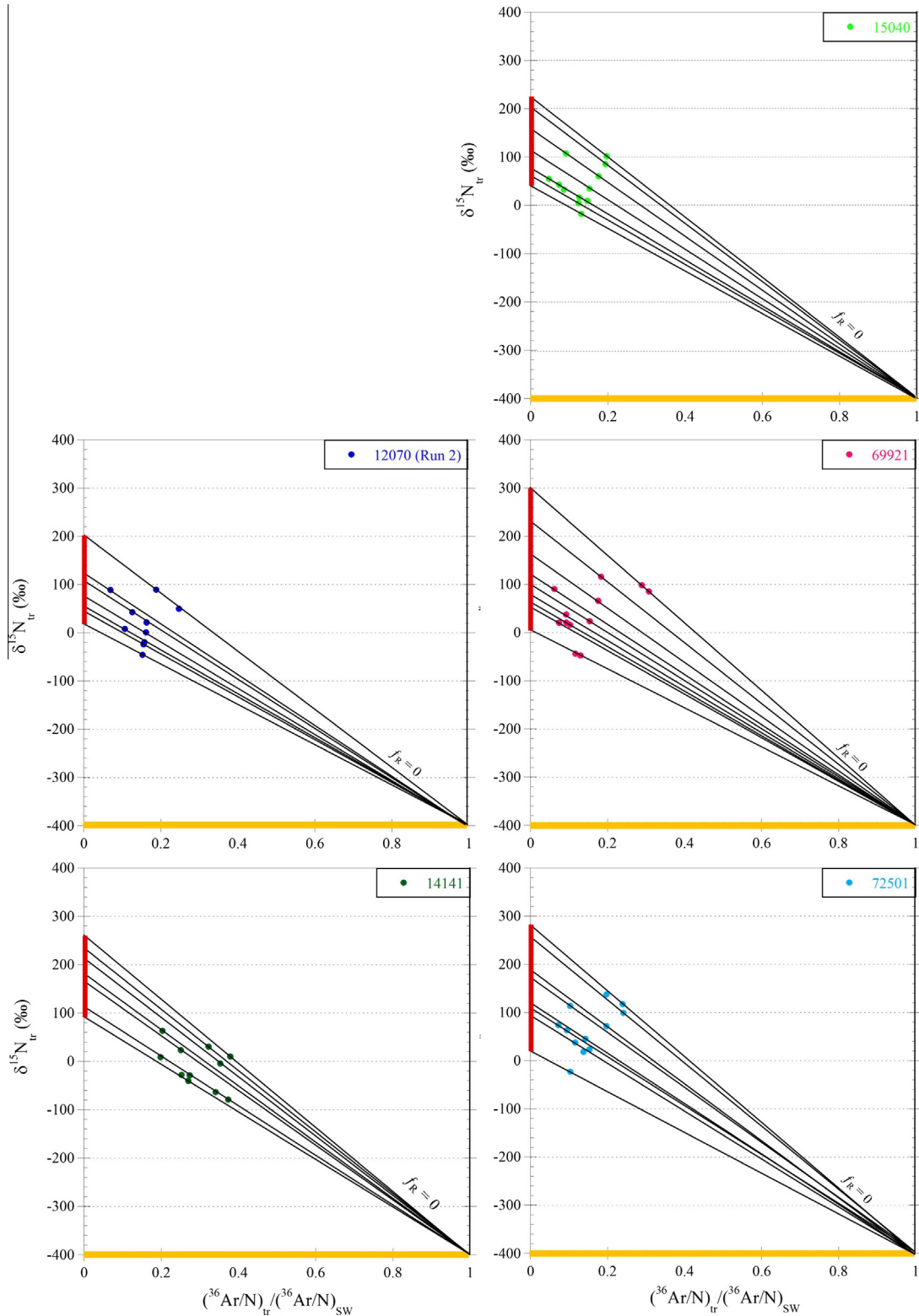


Fig. 12. Isotopic composition at each temperature step taken to indicate binary mixing only versus $(^{36}\text{Ar}/\text{N})_{\text{tr}} / (^{36}\text{Ar}/\text{N})_{\text{SW}}$ ratios. For each sample, the yellow line indicates N_{SW} end-member composition, and the red line indicates the N_{P} end-member composition required, which varies both within and between samples from +5‰ to +300‰. Solid black lines are theoretical mixing lines between N_{SW} and N_{P} end-members, assuming no loss of $^{36}\text{Ar}_{\text{SW}}$. See Table H for data.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.gca.2016.08.006>.

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