EVOLUTION OF ISOTOPIC SIGNATURES IN LUNAR-REGOLITH NITROGEN: NOBLE GASES AND N IN ILMENITE GRAIN-SIZE FRACTIONS FROM REGOLITH BRECCIA 79035

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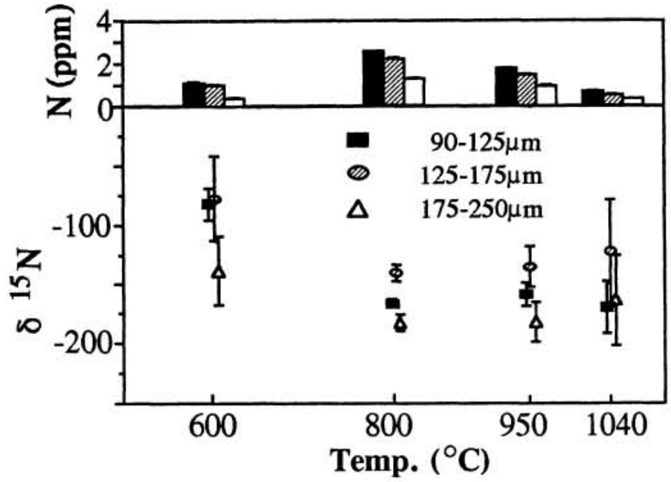
Our aim is to obtain a chronology of the N isotopic signature on the lunar surface. Regolith breccia 79035 is of interest in this regard because it contains some of the lightest N yet found in lunar samples [1-4]. A low $^{15}N/^{14}N$ ratio is commonly taken to be a signature of ancient surface exposure [e.g.,5,6]. Previous work had revealed a distinct difference in minimum $\delta^{15}N$ value between ilmenite ($-176^{o}/oo$[1]) and bulk samples (-243[3]), which we wished to investigate further using grain-size separates. Also, despite general agreement concerning the antiquity of its exposure, the compaction age of 79035 is poorly constrained and we hoped to shed more light on that issue.

We report here analyses of three ilmenite grain-size fractions: 90-125µm; 125-175µm; and 175-250µm. Aliquots were analysed by (1) one-step pyrolysis for He, Ne, Ar [7]; (2) stepwise pyrolysis for N, Xe; (3) stepwise closed-system etching for He, Ne, Ar [7]. We focus here on results from experiments (1) and (2); see [7] for experimental details of (1). Our analysis for N and Xe employed a combustion step at $400^{o}C$ for removal of possible carbonaceous contaminants, followed by pyrolysis at 600, 800, 950 and $1040^{o}C$. Becker & Pepin [1] previously studied a single ilmenite fraction (25-150µm).

As expected, N in ilmenite is predominantly surface correlated, and N/Xe ratios varied between 3 and $9x10^{6}$, i.e., within a factor of 3 of solar [e.g., 8]. This is in contrast to [1] in which pronounced enrichment of N was observed at low release temperatures. However, because of differences in grain-size distribution and methods of extraction, abundance differences cannot be directly compared. Minimum $\delta^{15}N$ values for surface-correlated N were about $-180^{o}/oo$, Fig.1, in good agreement with [1], confirming the difference between ilmenite and bulk, in which minima as low as $-243^{o}/oo$ have been reported [3]. Systematic shifts in $\delta^{15}N$ values for the intermediate size fraction suggest presence of a relatively heavy component amounting to roughly 20% of the N in that fraction, with a temperature release profile similar to that of ilmenite. Our results therefore agree with the conclusion of Carr *et al.* [3] that 79035 contains multiple N components with markedly different $\delta^{15}N$ values. Data for the intermediate size fraction suggest that at least one of those components is remarkably ^{15}N-enriched compared with most N in 79035.

Using the ordinate intercept in a $[^{36}Ar]^{-1}$ plot, Fig.2, the linear array of the three size fractions, plus additional data from [1] and [9], yields a trapped $^{40}Ar/^{36}Ar$ ratio of 1.44+/-0.1. (Use of the ordinate-intercept approach is justified by similar irradiation histories for different size fractions, manifested by similar $\delta^{15}N$ values and internal agreement of cosmic-ray exposure ages.) By contrast, bulk data for 79035 [10] reveal significantly more scatter and a distinctly higher trapped value of 2.08, suggesting that some component(s) in 79035 received surface exposure before the ilmenite. Using the calibration of Eugster *et al.* [11] (for bulk samples), the ilmenite values correspond to a nominal antiquity of 1.3Gyr, the bulk value to about 1.7Gyr. This appears to be the first determination of a well-defined minimum $\delta^{15}N$ value and a trapped $^{40}Ar/^{36}Ar$ ratio on the same mineral fraction.

In earlier work [1], low-temperature release of the heavy Xe isotopes revealed evidence for a fissiogenic component; our 400-$600^{o}C$ step was designed to explore the possibility of using this component as a chronometer. However, we found no evidence for such fissiogenic Xe at any temperature.



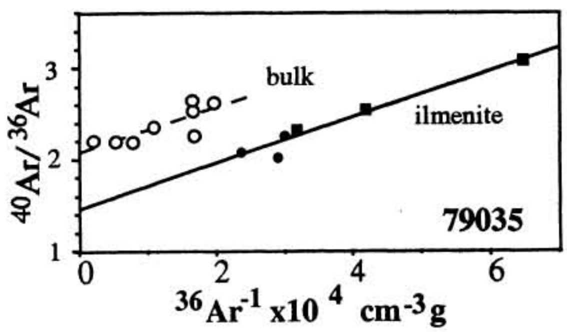


Fig. 1. N yield and $\delta^{15}N$ values for ilmenite grain-size fractions from 79035.
Fig. 2. $^{40}Ar/^{36}Ar$ ratios vs $[^{36}Ar]^{-1}$; ilmenite data from present work (square symbols) and [1,9]; bulk data from [10].

This is in marked contrast to some other apparently ancient regolith breccias which do contain a labile parentless fission component [e.g.,12].

By comparing $(^{3}He/^{38}Ar)_{spall}$ for 79035 ilmenite (~16) with that for ilmenite in 10071 (~11.6 [13]), which received its cosmic-ray exposure at a nominal depth of 50-60g/cm^2, we calculate a nominal cosmic-ray exposure depth of 5-10g/cm^2 for ilmenite in 79035. Adopting a mean value of 1.7-1.8wt% for the Mg content of primary ilmenite in Apollo 17 basalts [14], and a cosmogenic ^{21}Ne production rate of 1.77×10^{-10}ccSTP g^{-1} Myr^{-1} [15], we derive a nominal cosmic-ray exposure age of 960Myr for the ilmenite in 79035. Alternatively, $(^{3}He/^{21}Ne)_{spall}$ for 79035 ilmenite indicates an average Mg content of 1.1-1.2wt%, leading to an exposure age of 1240Myr. These are broadly consistent with the ^{21}Ne age calculated for the bulk-sample data of [10] using production rates from [15] (976Myr), and with the trapped $^{40}Ar/^{36}Ar$ data given above. Note that this age reflects integral regolith exposure and that there is no evidence for a heavily shielded irradiation. We also find little or no evidence for preirradiation of the ilmenite, relative to the bulk rock.

We conclude that N in 79035 ilmenite is distinct from that in the bulk breccia, which apparently contains components with different exposure histories. Whether distinct carriers or different histories can explain the internal variability among N isotopes in 79035, especially within the context of a long-term increase in $^{15}N/^{14}N$ ratio for lunar-surface N [5,6], is still unclear. Ilmenite in 79035 may have acquired N with $\delta^{15}N$=-180^{o}/oo not much more than 1Gyr ago, significantly closer to the present than generally believed. By contrast, black glass in 74001 apparently acquired at least two relatively heavy (extralunar) components ($\delta^{15}N$=-36 and +18) at 3.7Gyr ago [16].

[1] Becker R.H. & Pepin R.O. (1989) GCA 53,1135. [2] Clayton R.N. & Thiemens M.H. (1980) Ancient Sun, 463. [3] Carr R.H. et al. (1985) Meteoritics 20,622. [4] Frick U. et al. (1988) PLPSC18,87. [5] Geiss J. & Bochsler P. (1982) GCA 46,529. [6] Kerridge J.F. (1989) Science 245,480. [7] Benkert J.P. (1989) Ph.D. Thesis #8812, ETH Zurich. [8] Anders E. & Grevesse N. (1989) GCA 53,197 [9] Wieler R. et al. (1983) PLPSC13,A713. [10] Hintenberger H. et al. (1974) PLSC5,2005. [11] Eugster O. et al. (1983) Lunar Planet.Sci.XIV,177. [12] Swindle T.D. et al. (1986) In:Origin of the Moon, 331. [13] Eberhardt P. et al. (1974) GCA 38,97. [14] El Goresy A. et al. (1974) PLSC5,627. [15] Hohenberg C.M. et al. (1978) PLPSC9,2311. [16] Kerridge J.F. et al. (1991) PLPSC21, in press.