

# Single grain N-Ar analyses of lunar regoliths: Estimation of micrometeoritic flux at the Moon surface\*

Ko HASHIZUME<sup>1,2</sup>, Bernard MARTY<sup>2,3</sup> and Rainer WIELER<sup>4</sup>

1: Department of Earth & Space Sciences, Osaka University, Toyonaka, Osaka 560-0043, Japan

2: CRPG-CNRS, BP 20, 54501 Vandoeuvre-lès-Nancy Cedex, France

3: Ecole Nationale Supérieure de Géologie, 54501 Vandoeuvre-lès-Nancy Cedex, France

4: Institut for Isotope Geochemistry, ETH Zürich, Sonneggstrasse 5, CH-8092 Zürich, Switzerland

Corresponding email address: kohash@ess.sci.osaka-u.ac.jp

Surface of the Moon is irradiated or bombarded by various kinds of ions and objects, such as solar wind (SW), cosmic rays, and planetary materials like micrometeorites, comets or meteors. Absence of igneous activity at the recent Moon provides us a precious opportunity to obtain present and past information on, *e.g.*, chemical/isotopic composition of the Sun, production rate of cosmogenic nuclides, or flux and nature of planetary materials arriving onto the Moon, which are all necessary to understand the present situation and the history of formation of the solar system. Supply of these ions and objects onto the surface of the Moon is evidenced markedly by the highly volatile elements such as the rare gases, N, C, and H, those which are strongly depleted in igneous lunar rocks.

Among these elements, we are particularly interested in nitrogen, whose isotopic ratio  $^{15}\text{N}/^{14}\text{N}$  is observed to be largely variable among lunar regolith samples, and the cause of such variation had not been understood over the past three decades. Analyses of the nitrogen isotopic composition in lunar soils reveal at least two isotopically distinct trapped components (besides the in-situ component produced by cosmic rays) with  $\delta^{15}\text{N}$  ( $= \{[(^{15}\text{N}/^{14}\text{N})_{\text{sample}} / (^{15}\text{N}/^{14}\text{N})_{\text{terrestrial air}}] - 1\} \times 1000$ ) values varying widely between  $-200$  and  $+100$  ‰. Though the proportion of these components differs largely among different samples, it is commonly observed that these components coexist in the same soils, extracted at slightly different temperature by stepwise heating. The cause of the variation is a matter of debate. Some argue that the N isotopic composition of the solar wind changed during the last  $3 \times 10^9$  years (*e.g.*, Kerridge et al., 1993), while others claim that a significant fraction of the nitrogen in the lunar regolith is of non-solar origin (*e.g.*, Wieler et al., 1999). The latter view is also based on the fact that N in lunar soils is  $\sim 10$  times more abundant than one may expect from the concentrations of solar wind rare gases.

To decipher the complex lunar nitrogen archive, we have performed a series of microscopic N isotopic analyses at CRPG-Nancy aiming to precisely characterise the possible end-members contained in the lunar regoliths. Hashizume et al. (2000), using an ion microprobe, identified the N isotopic composition of the SW from the surface 100 nanometer layers of lunar regolith grains. The SW-N, associated with D-free H, a strong proof for its solar origin, showed a  $\delta^{15}\text{N}$  value as low as  $-240$  ‰, whereas non-solar N correlated with D-rich H possessed positive  $\delta^{15}\text{N}$  values, as high as  $+50$  ‰. Here in this study, we performed single mineral grain N-Ar isotope analyses to further tackle this problem. We analysed single grains, mostly of  $\sim 200$   $\mu\text{m}$  sized ilmenite, from Apollo 17 samples 71501, 79035 and 79135.

**Experimental:** In Nancy, a mass spectrometry system to analyse the isotopic composition of extremely small quantities of nitrogen has been developed, whose full detail is published elsewhere (Hashizume and Marty, 2001; Wieler et al., 1999). We analyse the N and Ar ( $^{38}\text{Ar}$  &  $^{36}\text{Ar}$ ) isotopic composition of the gas extracted from a single  $200$   $\mu\text{m}$  sized ilmenite grain. The gas is extracted from single grains with a  $\text{CO}_2$  laser in CW mode to minimize the blank gas. Stepwise analyses are performed by controlling the power of the laser. Though the temperature control is not accurate (presumably around  $100$  °C), we can constantly control the release of gas components:  $>90$  % of the trapped gas is released at low temperature ( $600$ - $1000$  °C), while  $>90$  % of the cosmogenic gas is released during the final fusion step.

## 1. Cosmogenic Nitrogen

In our analyses, the  $\delta^{15}\text{N}$  values varied in a range of  $-200$  ‰ to  $+2700$  ‰. The highest values are observed mostly in fusion steps, and are due to contributions of cosmogenic nitrogen ( $^{15}\text{N}/^{14}\text{N} \sim 1$ ). A good linear correlation between the amounts of cosmogenic  $^{15}\text{N}$  and  $^{38}\text{Ar}$  was obtained (Fig. 1) from which we were able to calculate the production rate ratio of these two nuclides. We obtained a value of  $^{15}\text{N}_c / ^{38}\text{Ar}_c = 14.4 \pm 1.0$  atoms/atoms for ilmenite grains. We are therefore, able to derive a  $^{15}\text{N}_c$  production rate in bulk lunar rock of  $10.4 \pm 0.7$   $\text{pg}^{-15}\text{N}/\text{g-rock}/\text{Ma}$ , when the following values are known: (i)  $^{38}\text{Ar}_c$  production rate in lunar ilmenites calibrated by the  $^{81}\text{Kr}$ -Kr age (Eberhardt et al., 1974), although for lunar rocks different from our sample; (ii) concentration of oxygen, the target element for  $^{15}\text{N}_c$  production, in bulk lunar rocks and ilmenites.

\*A paper presented at the 26th Symposium on Antarctic Meteorites (June 12-14, 2001 at NIPR, Tokyo) Abstract pp. 26-28.

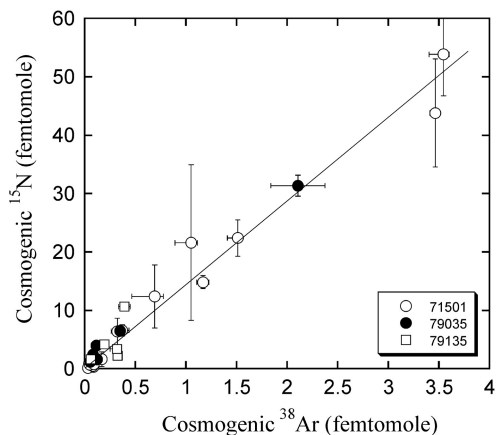
The obtained production rate is significantly higher than literature values of 3.6 (Becker et al., 1976), or 5.8 (Mathew and Marti, 2001). Such a discrepancy might be caused by differences in mean burial depths between the samples studied here and the rocks previously studied, combined with the significant difference in dependence of production rates of  $^{15}\text{N}_c$  and  $^{38}\text{Ar}_c$  on the burial depth.

## 2. Trapped Nitrogen – the trapping mechanism

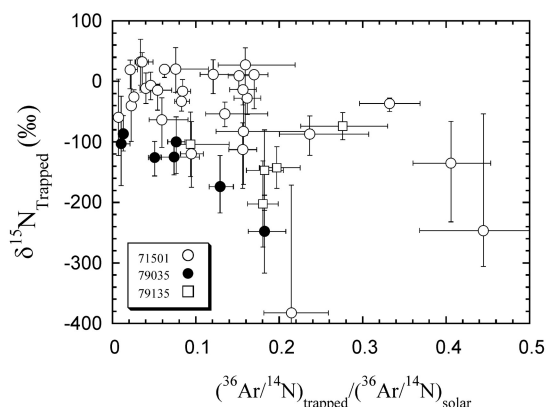
In the low temperature steps (600 - 1000°C), where the contribution of cosmogenic N is much smaller than in the fusion step, N with  $\delta^{15}\text{N}$  ranging from -200 to +100 ‰ and large amounts of trapped solar Ar were released. In Fig. 2, the  $\delta^{15}\text{N}$  values of the trapped components are plotted against the  $^{36}\text{Ar}/\text{N}$  ratios normalized to the solar abundance ratio. The general picture is consistent with previous works. All grains show  $^{36}\text{Ar}/\text{N}$  ratios much lower (0.01 - 0.45x) than the solar ratio. The mean  $\text{N}/^{36}\text{Ar}$  and  $\delta^{15}\text{N}$  values ( $\text{N}/^{36}\text{Ar} = 391$ ,  $\delta^{15}\text{N} = 0$  ‰ for 71501;  $\text{N}/^{36}\text{Ar} = 473$ ,  $\delta^{15}\text{N} = -60$  ‰ for 79035) for the ~200  $\mu\text{m}$  sized grains obtained by this study is not largely different from literature values for corresponding samples ( $\text{N}/^{36}\text{Ar} = 299$ ,  $\delta^{15}\text{N} = +18$  ‰ for 71501 ilmenites [Frick et al., 1988];  $\text{N}/^{36}\text{Ar} = 705$ ,  $\delta^{15}\text{N} = -78$  ‰ for 79035 ilmenites [Becker and Pepin, 1989]).

Single grains, which all experienced widely different exposure history, exhibit wide spread in the  $^{36}\text{Ar}/\text{N}$  ratios and the  $\delta^{15}\text{N}$  values, which must reflect mixture of multiple N-Ar components in various proportions. Those enriched in the solar component should show higher  $^{36}\text{Ar}/\text{N}$  ratio and lower  $\delta^{15}\text{N}$  value, as low as -240 ‰ (Hashizume et al., 2000), while those enriched in planetary components should generally be depleted in  $^{36}\text{Ar}$  relative to N (e.g.,  $(^{36}\text{Ar}/\text{N})_{\text{chondrite}} < 10^{-5} \times (^{36}\text{Ar}/\text{N})_{\text{solar}}$ ) and the  $\delta^{15}\text{N}$  higher than solar (e.g.,  $-100 < \delta^{15}\text{N}_{\text{chondrite}} < +1000$  ‰). Among the three regolith samples involved in this study, the 79035 ilmenite grains show the simplest and clearest trend in this diagram: A negative correlation ( $r = 0.93$ ) between the  $\delta^{15}\text{N}$  values and the  $^{36}\text{Ar}/\text{N}$  ratio can be explained by a binary mixing of two end-members, one of which with a  $\delta^{15}\text{N}$  value as low as -240 ‰, the upper limit for the solar value. An important point to be noted here is that the  $^{36}\text{Ar}/\text{N}$  ratio of the solar component trapped in the lunar sample seems to be significantly lower (~0.2 x) than the solar abundance ratio. Since SW is considered to possess almost the same  $^{36}\text{Ar}/\text{N}$  ratio (0.7 - 0.8 x) with the solar abundance ratio (Geiss et al., 1994), the only possible cause for the solar N enrichment in lunar samples is the preferential loss of solar rare gases from the lunar samples. However, Wieler et al. (1996) conclude, based on the single grain rare gas analysis of lunar samples where they found the relative abundances of Ar, Kr and Xe to be constant irrespective to their absolute concentration, that such loss is unlikely to have occurred by diffusion-like processes. We propose a three-stage SW trapping mechanism as follows to satisfactorily explain the observed N-rare gas abundance patterns in lunar grains.

I. The SW with substantially high energy (1KeV/nucleon) is implanted onto the surface of the lunar



**Fig. 1** Amounts of cosmogenic  $^{15}\text{N}$  plotted against those of cosmogenic  $^{38}\text{Ar}$  in Apollo 17 ilmenite grains. Each data represents fusion or 1000°C step of single grains. All fractions that show  $\delta^{15}\text{N}$  values higher than +100 ‰ are selected for this plot. The  $\delta^{15}\text{N}$  values for the trapped components are assumed to be  $-20 \pm 75$  ‰ for 71501 and  $-175 \pm 75$  ‰ for 79035/79135, which are the ones assumed by Becker and Pepin (1989). The assumed trapped  $^{38}\text{Ar}/^{36}\text{Ar}$  ratios are  $0.188^{+0.010}_{-0.004}$  for 71501 and  $0.190^{+0.016}_{-0.007}$  for 79035/79135. The mean values are calculated from the results of stepwise etching analyses by Benkert et al. (1993). Error bars represent  $1\sigma$  errors. Uncertainties assumed for the isotopic ratios of the trapped components are included in the error bars. Correlation factor for the best fit line is 0.97.



**Fig. 2** The  $\delta^{15}\text{N}$  value of the trapped component in Apollo 17 single ilmenite grains plotted against the  $^{36}\text{Ar}/\text{N}$  ratio normalized by the solar abundance ratio (0.0272). Each data represent averaged values taken from the  $\leq 1000^\circ\text{C}$  temperature steps of respective grains. Contribution of the cosmogenic  $^{15}\text{N}$  is subtracted from the measured  $\delta^{15}\text{N}$  values using the measured  $^{38}\text{Ar}/^{36}\text{Ar}$  ratios and the production rate ratio of  $^{15}\text{N}_c/^{38}\text{Ar}_c$  obtained in this study.

regoliths. The trapping probability of ions with an energy of several KeV or higher is considered to be unity (e.g., Manka and Michel, 1971). Therefore, no fractionation of solar rare gases to nitrogen will occur at this stage. **II.** As the surface of the mineral becomes saturated with the implanted SW, the implanted solar gases will be sputtered out from the mineral by high energy ions (SW, SEP or cosmic rays) continuously hitting the mineral surface. Such a process is known to be an all-or-nothing process, therefore, implanted ions are sputtered out from the sample without fractionation. **III.** The sputtered out solar gases, forming a dilute atmosphere at the lunar surface, are ionized by the high energy ions and re-implanted into the lunar regolith grains by a process so called Manka-Michel process (Manka and Michel, 1971). At this stage, the energy of the ions to be re-implanted should be substantially low compared to the original SW, where the implantation probability must be lower than unity. At such low energy range, implantation probability must be largely affected by the chemical nature of the elements to be implanted. Nitrogen behaves as a chemically active element at a reducing condition like the proton-rich surface layer of the lunar regolith.

### 3. Solar and Meteoritic N Association on the Moon – *Estimation of the micrometeoritic flux.*

We consider that the nature of the non-solar N trapped in the lunar regolith is the N contained in meteoritic solid material falling onto the Moon, most likely the micrometeoritic material like those on Earth which dominates the contemporary flux of extraterrestrial material on Earth. (See review by Engrand and Maurette, 1998.) The microimpactors at the Moon surface are melted or vaporized at the time of their impact, when the contained N is released into the lunar atmosphere. The meteoritic N will then be re-implanted, together with the sputtered-out SW component, by the process III we described above.

The trapping mechanism of the non-solar (micrometeoritic) N we propose here explains the general characteristics of the non-solar N trapped in the lunar regoliths, summarized by Kerridge (1993): (i) the non-solar N is extracted by stepwise heating at similar temperature with the solar N, suggesting that the non-solar and solar N are trapped at similar site and/or form in the minerals; (ii) abundance of bulk N in lunar regolith is roughly proportional to those of the solar heavy rare gases, even when the N is dominated by the non-solar component (i.e., when the bulk  $\delta^{15}\text{N}$  value is much higher than the solar value), because the implantation of the meteoritic component into the lunar mineral is driven by the SW.

Although the full detail of the N isotopes in micrometeorites on the Earth is yet unknown, study of those in interplanetary dust particles (IDPs) sampled in the stratosphere suggest that they contain N as abundant as the CI chondrites (~1000 ppm) (Keller et al., 1996), and are enriched in  $^{15}\text{N}$  relative to solar ( $-90 < \delta^{15}\text{N}_{\text{IDP}} < +480$  ‰; Messenger, 2000). The bulk  $\delta^{15}\text{N}$  values for the trapped lunar N, by our hypothesis, represent the mixing proportion of the solar and the micrometeoritic N flux accreting onto the Moon. The bulk  $\delta^{15}\text{N}$  value for various lunar samples covers roughly the entire range between the solar and IDP range ( $-200 < \delta^{15}\text{N}_{\text{lunar}} < +100$  ‰; reviewed by Kerridge, 1993), suggesting that the solar and micrometeoritic N supply rates on the Moon are comparable. The estimated SW  $^4\text{He}$  flux ( $7.2 \times 10^6$  atoms/cm<sup>2</sup>/sec; Manka and Michel, 1971) and the solar abundance ratios gives a SW N flux of  $1.6 \times 10^4$  atoms/cm<sup>2</sup>/sec, and a comparable rate for the micrometeoritic N flux. If IDP-like materials with 1000 ppm N have accreted on the Earth with the same rate, the accretion rate is calculated to be 67000 tons-material/year. Our estimated rate shows remarkable agreement with the estimated flux of  $40000 \pm 20000$  tons/year by direct measurements of IDPs in near-Earth interplanetary space (Love and Brownlee, 1993).

- Becker R. H., Clayton R. N. & Mayeda T. K. (1976) *Proc 7<sup>th</sup> Lunar Sci. Conf.*, 441-458.  
 Becker R. H. & Pepin R. O. (1989) *Geochim. Cosmochim. Acta* **53**, 1135-1146.  
 Benkert J-P., Baur H., Signer P. & Wieler R. (1993) *J. Geophys. Res.* **98**, 13147-13162.  
 Engrand C. & Maurette M. (1998) *Meteorit. Planet. Sci.* **33**, 565-580.  
 Frick U., Becker R. H. & Pepin R. O. (1988) *Proc. 18<sup>th</sup> Lunar Planet. Sci. Conf.*, 87-120.  
 Geiss J., Gloeckler G. & von Steiger R. (1994) *Phil. Trans. R. Soc. Lond. A* **349**, 213-226.  
 Hashizume K., Chaussidon M., Marty B. & Robert F. (2000) *Science* **290**, 1142-1145.  
 Hashizume K. & Marty B. (2001) In *Handbook of stable isotope analytical techniques*, Elsevier, In Press.  
 Keller L. P., Messenger S., Miller M. & Thomas K. L. (1996) *Lunar Planet. Sci. Conf.* XXVIII, 1811-1812 (Abstract).  
 Love S. G. & Brownlee D. E. (1993) *Science* **262**, 550-553.  
 Kerridge J.F. (1993) *Rev. Geophys.* **31**, 423-437.  
 Manka R. H. & Michel F. C. (1971) *Proc. 2<sup>nd</sup> Lunar Sci. Conf.* **2**, 1717-1728.  
 Mathew K. J. & Marti K. (2001) *Earth Planet. Sci. Lett.* **184**, 659-669.  
 Messenger S. (2000) *Nature* **404**, 968-971.  
 Wieler R., Humbert F. & Marty B. (1999) *Earth Planet. Sci. Lett.* **167**, 47-60.  
 Wieler R., Kehm K., Meshik A. P. & Hohenberg C. M. (1996) *Nature* **384**, 46-49.