

## TRAPPING OF ATMOSPHERIC GASES DURING CRUSHING OF LUNAR SAMPLES.

A. B. Verchovsky<sup>1</sup>, J. Mortimer<sup>1</sup>, A. I. Buikin<sup>2</sup> and M. Anand<sup>1,3</sup>, <sup>1</sup>School of Physical Sciences, The Open University, Milton Keynes, MK7 6AA, UK; <sup>2</sup>Vernadsky Institute RAS, Moscow, Russia; <sup>3</sup>Department of Earth Sciences, Natural History Museum, London, SW7 5BD, UK ([sasha.verchovsky@open.ac.uk](mailto:sasha.verchovsky@open.ac.uk))

**Introduction.** The presence of terrestrial atmospheric noble gases in lunar samples has been known since the early analyses of lunar samples delivered by the Apollo program [1-4]. Some lunar samples contain trapped gases with clear terrestrial atmosphere Xe isotopic signatures [3, 4]. As a part of the sample preparation procedure some of them have been crushed before analyses. Therefore, it was thought that trapping of the atmospheric gases happened at this stage. However, the terrestrial atmospheric gases have been found also in the samples that have not been crushed prior to analysis [3]. Nevertheless, even in these cases the origin of the trapped gases has been attributed to terrestrial contamination, though the mechanism by which they are trapped remains unclear.

In the present study, we investigated this issue by taking into consideration nitrogen, which is the most abundant atmospheric constituent, and is also more chemically active than noble gases. Along with analyses of N in lunar samples which have an excess of atmospheric noble gases [5], we performed several crushing experiments to see in what proportion noble gases and nitrogen can be trapped and compared this with their abundance in the lunar samples.

**Experimental.** For the analyses of noble gases, nitrogen and carbon we used the ‘Finesse’ instrumentation [6], which allows simultaneous measurements of abundances and isotopic compositions of different species present. First, we analyzed each sample as it is, using stepped combustion and vacuum crushing. More than 10000 strokes cumulatively were applied during crushing, resulting in production of a fine-grained powder. The crushed samples were subsequently removed from the crusher and an aliquot of the sample was then analyzed by stepped combustion. The transfer from the crusher to the combustion furnace includes brief exposure of the crushed material to the atmosphere. In a separate experiment, we crushed (3000 strokes) one of the samples (69921) under atmospheric conditions i.e. without evacuation of air from the crusher, and then analyzed the crushed material using stepped combustion.

Altogether, three lunar soils (12070, 14141 and 69921) were used in this study. The nitrogen, carbon and noble gas step-combustion data for these samples have been published previously [7].

**Results and discussion.** Based on our initial analysis of nitrogen in the lunar rock, 12064, which showed a clear excess of atmosphere-like Ne, we found [5] that

the  $(N_2/Ne)_{tr}$  ratio is lower than the terrestrial atmospheric ratio by a factor of  $6 \times 10^4$ . This indicates that atmospheric nitrogen is much less efficiently trapped by crushing than Ne, contradicting the general idea that chemically active atmospheric species should be trapped during crushing of silicate materials in air with higher efficiency than the inert ones. This result can be considered as evidence for a non-atmospheric origin of the trapped Ne in this sample.

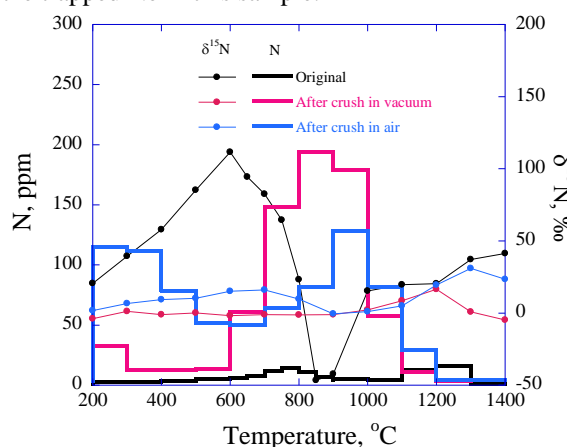


Figure 1. Release patterns of N and  $\delta^{15}N$  variations during stepped combustion of the original, crushed in vacuum, and crushed in air lunar soil 69921.

The experiments in which we analyzed crushed materials were designed to shed more light on the process of trapping of atmospheric species during crushing.

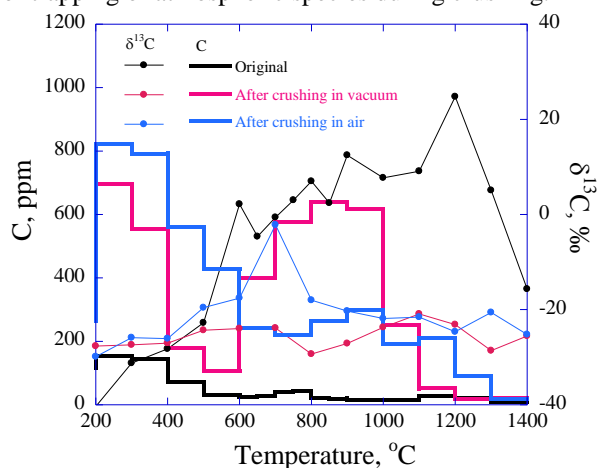


Figure 2. Release patterns of C and  $\delta^{13}C$  variations during stepped combustion of the original, crushed in vacuum, and crushed in air lunar soil 69921.

The most important result of the experiments is that in both cases, exposing the crushed material to air after crushing and crushing in air, shows a significant increase in N (by a factor of 6-14) and C (by a factor of 6-11) concentrations in the crushed residues compared to the original samples. The release patterns of N and C trapped from the atmosphere are complex and consist of low- and high-temperature components (Figs. 1, 2). The latter is released in the range from 600 to 1200 °C with maximum at 900-1000 °C. The ratio between amounts of N and C released at low and high temperatures is different for the crushing experiments, being higher for the sample crushed in air. Isotopically, N becomes more atmospheric-like and C more organic-like ( $\delta^{13}\text{C}$  about -25‰) after crushing compared to the original compositions.

If nitrogen, trapped during exposure of the crushed material to air or crushed in air, can come from air, then where did carbon come from? The concentration of  $\text{CO}_2$  in the atmosphere is many orders of magnitude lower than that of nitrogen. Isotopically, atmospheric  $\text{CO}_2$  is also different from that found in our samples.

C/N ratios (4-15) for the gases, released during combustion of the crushed samples, points to an organic material as the potential source. Such organic material is always present in any solid samples we analyze by stepped combustion. Usually it is a low temperature (200-500 °C) component, representing micro particles from air adsorbed on the sample's surface. If N and C in the crushed samples represent the same organic material, then we need to consider two questions: 1. How is this organic material remain unoxidized until such high temperatures? 2. Why is the organic material trapped more efficiently than the atmospheric gas molecules? For the latter, chemical reactions with freshly formed surfaces during crushing can result in very strong trapping due to annealing of surface defects in which they were trapped, thereby requiring more energy for subsequent releases than surface adsorbed species require. It is much more difficult to imagine this process working for small particles. Blank experiments with the crusher, when strokes were applied to its empty surfaces, did not show any N and C above the normal non-operational system blank level (0.5 and 5 ng respectively).

The majority of solar noble gases are lost during both types of crushing, but the amounts of trapped atmospheric noble gases are extremely low and can barely be seen in the residual materials (Fig. 3). The  $^{36}\text{Ar}/^{40}\text{Ar}$  ratio is a very sensitive indicator of the presence of atmospheric Ar, since this ratio in the samples analysed is significantly different from that in the atmosphere. The results shown in Fig. 3 indicate almost no difference in the  $^{36}\text{Ar}/^{40}\text{Ar}$  ratio between the original and crushed samples in spite of a huge difference in  $\text{N}_2/^{40}\text{Ar}$  ratio. N and C are trapped much more efficiently, however. Whatever the mechanism of trapping and the source of

C and N in the crushed samples, this result is in a sharp contradiction with the relative abundance of N, C and noble gases in the lunar rocks with trapped atmosphere-like noble gases [5].

As an extension of the work, we plan to apply similar crushing experiments to lunar rocks.

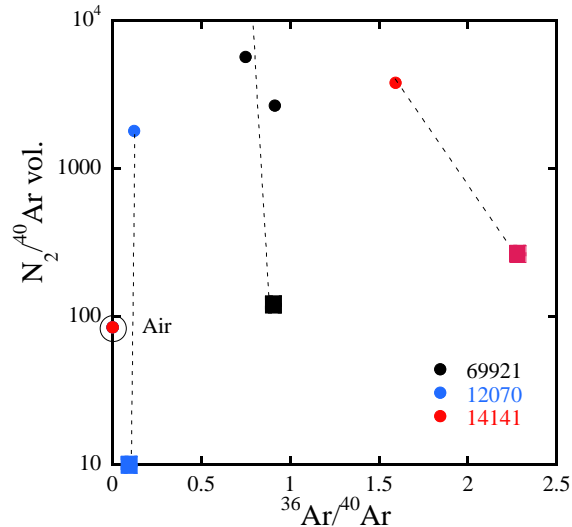


Figure 3. Bulk compositions of the original (squares) and crushed (circles) lunar soil samples.

**Conclusion.** Our crushing experiments demonstrated a very high efficiency of trapping for N and C, compared to that of noble gases. The mechanism of trapping and the source of N and C (apart from the fact that they come from air) is not clear. However what is clear is that lunar rocks with trapped atmosphere-like noble gases do not show such high concentrations of N and C and, therefore, their noble gases do not seem to have been trapped from air as a result of crushing.

**References.** [1] Lightner B. D. & Marti K. (1974) *Proc. 5<sup>th</sup> LPSC*, 2023-2031; [2] Leich D. A. and Niemeyer S. (1975) *Proc. 6<sup>th</sup> LPSC*, 1953-1965; [3] Niemeyer S. and Leich D. A. (1976) *Proc. 7<sup>th</sup> LPSC*, 587-597; [4] Niedermann S. and Eugster O. (1992) *GCA* 56, 493-509; [5] Mortimer J. et al. (2014) *Icarus* 255, 3-17; [6] Verchovsky A. B. et al. (2002) *EPSL* 199, 243-255; [7] Mortimer J. et al. (2016) *GCA* 193, 36-53.

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