NITROGEN IN LUNAR IGNEOUS ROCKS

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The abundance and isotopic composition of the light elements hydrogen, helium, carbon, nitrogen and neon in fine-grained regolith samples of the moon demonstrate that the major portion of these elements is derived from implantation by the solar wind. This contribution is easy to detect because lunar rocks, which are the main source material of lunar fines, are, in general, strongly depleted in light volatile elements.

In previous papers we reported on chemically bound nitrogen concentrations in various lunar samples from the Apollo 11 through Apollo 17 landing sites by using the Kjeldahl method (1-3). This technique detects nitrogen only in a bound state and discriminates against molecular nitrogen N_2 of atmospheric or indigenous origin. We were able to show by the analysis of grain-size fractions and leach-experiments that the main amount of nitrogen in fines is derived from implantation by the solar wind and that the major portion of nitrogen is present in a bound state. The total range of Apollo 11 through Apollo 17 fines $<$ 1 mm varies from 23 to 124 ppm N.

On the other hand, lunar igneous rocks contain, in general, much less nitrogen than fines. For most of the rocks analysed so far in our laboratory (1), (3), only an upper limit of about 10 ppm N could be given due to insufficient sensitivity of the conventional Kjeldahl procedure. Also literature data on nitrogen in lunar igneous rocks are sparse, because of problems in the analytical determination of the low contents.

In a recent paper, Werner and Tölg (4) reported on the optimisation of the Kjeldahl method for the determination of nitrogen in high-purity metals, and also for the exact analysis of the smallest amounts of nitrogen in many inorganic and organic matrices. Discussion with those authors and Dr. E. Grallath, and replicate nitrogen analyses of U.S.G.S. standard rocks diabase W-1 and granite G-2 revealed that the optimised, program-controlled Kjeldahl method appeared to be most promising for the application to lunar rocks of low nitrogen content.

Six lunar igneous rocks, one clastic rock and two Apollo 15 fines have been selected for replicate analysis of bound nitrogen. Typical sample size for one run was about 150 mg for igneous rocks, and around 50 mg for the fines. After decomposition of the powdered sample with 1 ml of an acid mixture HF and H_2SO_4 (10:1) under pressure at 150°C for 6h in a PTFE bomb, the ammonium produced is separated via ammonia by steam distillation

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in a special micro circulating distillation apparatus, and absorption in dilute sulphuric acid. The determination is performed directly in the absorption vessel on only 2 ml of solution by coulometric titration with OBr^- and biamperometric end-point detection. The whole procedure is program-controlled, with the exception of the sample decomposition. Determining amounts of 0.1 to 1000 μg N, the coefficients of variation were found to be from $\pm$ 10 to $< \pm$ 1 %, respectively.

The results are compiled in Table 1, and compared with previous results which have been obtained by the conventional Kjeldahl method (1-3). There is satisfactory agreement for diabase W-1 and the two Apollo 15 fines between both methods. The variation of replicate analyses obtained with the optimised Kjeldahl method is distinctly smaller than that with the conventional one. Most of the lunar igneous rock samples are quite uniform in chemically bound nitrogen content, except vesicular basalt 15556. The range is only about 3 to 5 ppm N for samples of various types and from different Apollo missions. The small nitrogen concentrations of igneous rocks imply that indigenous nitrogen and/or ammonia was very low in abundance at the time of mineral and rock formation billions of years ago. If ammonia and/or nitrogen in reducing environment had been present, chemical reactions leading, for example, to nitride formation would have taken place. The low nitrogen content demonstrates once more the rigorous loss of volatile elements in the early history of the moon. Obviously, magmatic gases, if present at all, were low in nitrogen and nitrogen compounds at the formation of those rocks. Vesicular basalt 15556, which was collected near the Hadley Rille at station 9a, shows, however, a surprisingly high nitrogen content of 126 ppm. The discrepancy in the values obtained with the conventional and optimised method may be due to inhomogeneous distribution of bound nitrogen in this rock; different chips of the sample were analysed. A similar difference was found for Apollo 11 vesicular basalt 10057 and Apollo 14 clastic rock 14303, the analyses of which were also performed on separate averages of the rocks. Certainly, more data on vesicular and dense igneous rocks, and on clastic rocks are needed to reach a conclusive solution to this problem.

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Sample No.	Sample Type	Chem.bound N (ppm) by the Kjeldahl method Conventional	Optimised
10057,80	Vesicular basalt	64	6.3; 4.2
12053,96	Porphyritic basalt	-	3.1; 5.0
12063,112	Microgabbro	$<$ 10	-
15556,25	Vesicular basalt	$<$ 10	125; 127
70215,21	Fine-grained basalt	$<$ 8	3.0; 3.0
77017,32	Crushed anorthositic gabbro, brecciated & invaded by glass	$<$ 8	5.0; 5.1
79155,24	Homogeneous gabbro, partially coated with glass	$<$ 8	4.5; 4.5
14303,13	Clastic rock	31	7.9; 8.8
15012,14	Fines, SESC-1	108 (s=5.3; n=3)	110
15013,11	Fines, SESC	110 (s=5.4; n=3)	93.4; 94.0
W-1	Diabase, U.S.G.S. standard	14 (s=1.0; n=4)	14.0 (s=0.7; n=5)
G-2	Granite, U.S.G.S. standard	-	8 (s=2; n=3)

Table 1 Chemically bound nitrogen concentrations in various Apollo lunar samples and terrestrial standard rocks, using optimised and conventional Kjeldahl method. (-) not determined. s=standard deviation; n=number of determinations.

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