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* Permanent address: Division of Mineral Chemistry, C.S.I.R.O., P.O. Box 175, Chatswood, New South Wales, Australia.

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Rare Gases, Hydrogen, and Nitrogen: Concentrations and Isotopic Composition in Lunar Material

Abstract. *The concentrations and isotopic abundances of the rare gases have been investigated in fines and three types of rocks. The results obtained from different grain-size fractions and from samples etched to different degrees with nitric and hydrofluoric acids demonstrate the strong concentrations of the solar-wind component in the surface layers of the grains. Exposure ages as well as gas retention ages have been determined in different types of Apollo 11 material. Hydrogen, nitrogen, and other gases have been analyzed by a high-resolution mass spectrometer. As compared with that in terrestrial water, deuterium is depleted by at least a factor of 3 in the investigated type C rocks.*

We have investigated the concentrations and isotopic abundances of the rare gases in fines and in three types of rocks. The results obtained are listed in Table 1.

A systematic decrease of the concentrations of all rare gases has been found with increasing grain size and with increasing loss of material in the etching experiments (Table 1; Figs. 1, 2). The rare gases in the fines are obviously concentrated predominantly in the outer grain layers. Among the light rare gases, Ar shows the greatest and He the smallest decrease of concentration with increasing weight of removed material (Fig. 2), which may be due either to a different distribution or different losses of these nuclides by diffusion or to different penetration depths for He, Ne, and Ar solar wind particles. On the basis of our experience with gas-rich stone meteorites, where the metal fraction invariably shows the least (or no) loss by diffusion, and of a comparison of the $^4He/^{20}Ne$ or $^4He/^{36}Ar$ ratios in these etched samples with ratios found in the selected iron grains, we believe that preferential loss of the He and Ne by diffusion is responsible. The Kr and Xe concentrations depend similarly on the grain size and on the amount of material removed by etching.

The abundance ratios with one nuclide abundantly formed by spallation and the other abundantly occurring in the solar wind (for instance, $^3He/^4He$, $^{21}Ne/^{20}Ne$, and $^{38}Ar/^{36}Ar$) show a strong increase with increasing grain size and with increasing degree of etching (Fig. 3).

In the 1 percent residuum of the strongly etched sample the ^{21}Ne is almost purely spallogenic. The amount, together with a production rate of $P_{21} = 0.2 \times 10^{-8}$ cm³/g (at standard temperature and pressure) times 10^6 years yields an exposure age of $T_{21} = 215 \times 10^6$ years. Furthermore, as the ^4He in this fraction is almost pure solar wind helium, the ^3He can be corrected to obtain the spallogenic component, which is 2.7×10^{-6} cm³/g at standard temperature and pressure. Hence, using a production rate of $P_3 = 1.3 \times 10^{-8}$ cm³/g (at standard temperature and pressure) times 10^6 years, we obtain the ^3He exposure age of $T_3 = 207 \times 10^6$ years, in good agreement with the ^{21}Ne exposure age.

The rare gas contents of type A, B, and C rocks are compiled in Table 2. For type C rock 10021.20, similar values have been found as for fines. In type A and B rocks all three components (solar wind, radiogenic, and spallogenic) have been detected. The results for radiogenic ^4H and ^{40}Ar, as well as for spallogenic ^3H and ^{21}Ne, are shown in the table. Exposure ages have been calculated, with production rates $P_3 = 1 \times 10^{-8}$ cm³/g times 10^6 years and $P_{21} = 0.12 \times 10^{-8}$ cm³/g

Table 1. Concentrations of rare gas in cubic centimeters per gram at standard temperature and pressure in the bulk material in various grain-size fractions and in acid-etched fractions of fines of sample 10084.18. The concentrations in acid-treated fines are given after 40 percent of the weight has been removed by HNO_3, 93 percent has been removed by HNO_3 and HF, and 99 percent has been removed by acid treatment. The concentrations in a few large grains (>250 μm) selected from the residuum of an acid-etched sample and those in a few milligrams of iron grains selected with a hand magnet are also listed.

Nuclide and ratios	Original fines	Grain-size fractions (μm)			Acid-etched fractions (removed weight in %)			Large grains	Iron grains
		30	30–100	100–250	40	93	99		
^3He	7.88×10^{-5}	1.06×10^{-4}	3.98×10^{-5}	1.80×10^{-5}	3.13×10^{-5}	5.83×10^{-6}	3.07×10^{-6}	2.75×10^{-6}	3.87×10^{-5}
^4He	2.01×10^{-1}	2.78×10^{-1}	1.02×10^{-1}	4.70×10^{-2}	8.72×10^{-2}	1.02×10^{-2}	9.51×10^{-4}	6.84×10^{-3}	9.80×10^{-2}
^{20}Ne	2.21×10^{-3}	3.34×10^{-3}	1.18×10^{-3}	5.85×10^{-4}	5.28×10^{-4}	4.04×10^{-5}	3.14×10^{-6}	3.35×10^{-5}	3.34×10^{-4}
^{21}Ne	5.65×10^{-6}	8.78×10^{-6}	3.42×10^{-6}	1.93×10^{-6}	1.76×10^{-6}	3.59×10^{-7}	4.37×10^{-7}	2.04×10^{-7}	9.44×10^{-7}
^{22}Ne	1.74×10^{-4}	2.69×10^{-4}	2.44×10^{-4}	4.77×10^{-5}	4.31×10^{-5}	3.57×10^{-6}	7.29×10^{-7}	2.82×10^{-6}	2.73×10^{-5}
^{36}Ar	3.71×10^{-4}	6.22×10^{-4}	2.36×10^{-4}	1.63×10^{-4}	3.05×10^{-5}	1.73×10^{-6}	9.46×10^{-7}	1.71×10^{-6}	5.11×10^{-5}
^{38}Ar	7.21×10^{-5}	1.20×10^{-4}	4.72×10^{-5}	3.22×10^{-5}	6.44×10^{-6}	6.96×10^{-7}	5.69×10^{-7}	4.46×10^{-7}	1.03×10^{-5}
^{40}Ar	4.09×10^{-4}	6.48×10^{-4}	3.04×10^{-4}	2.36×10^{-4}	6.60×10^{-5}	4.33×10^{-5}	2.76×10^{-5}	9.09×10^{-6}	7.69×10^{-5}
^{84}Kr	2.11×10^{-7}	3.34×10^{-7}	1.26×10^{-7}	8.87×10^{-8}	2.53×10^{-9}	2.3×10^{-9}	4.96×10^{-9}	1.62×10^{-9}	3.07×10^{-8}
^{132}Xe	2.87×10^{-8}	3.97×10^{-7}	1.82×10^{-7}	1.59×10^{-8}	6.09×10^{-9}	5.7×10^{-10}	1.13×10^{-9}	7.0×10^{-10}	5.5×10^{-9}
$^4He/^3He$	2550	2620	2560	2480	2790	1760	310	2450	2530
$^{20}Ne/^{22}Ne$	12.7	12.4	12.5	12.3	12.2	11.3	4.31	11.9	12.4
$^{22}Ne/^{21}Ne$	30.0	30.6	27.6	24.7	24.5	10.0	1.67	13.8	28.9
$^{36}Ar/^{38}Ar$	5.15	5.18	5.00	5.06	4.74	2.43	1.66	3.83	4.96
$^{40}Ar/^{36}Ar$	1.10	1.04	1.29	1.45	2.16	25	29.2	5.32	1.50

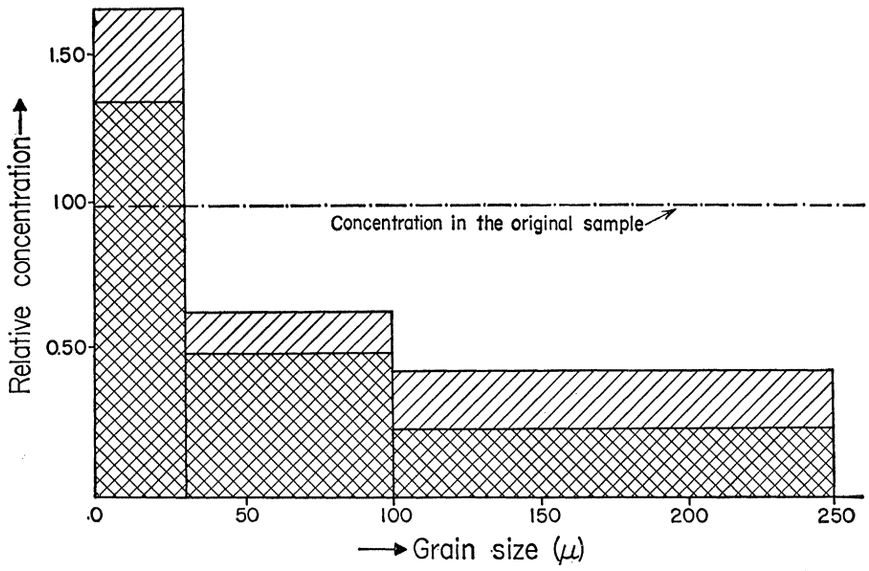


Fig. 1. Concentration of rare gases as a function of grain size.

Table 2. Rare gas concentrations in cubic centimeters per gram in rocks of type A, B, and C.

Nuclide ratios and ages	Type C	Type B			Type A	
	10021.20	10003.11	10017.33	10044.32	10049.20	10057.40
^{3}He	3.27×10^{-5}	1.13×10^{-6}	2.92×10^{-6}	6.37×10^{-7}	2.84×10^{-7}	4.39×10^{-7}
^{4}He	9.05×10^{-2}	2.24×10^{-4}	4.91×10^{-4}	1.49×10^{-4}	8.89×10^{-4}	6.76×10^{-4}
^{20}Ne	1.25×10^{-3}	1.05×10^{-6}	7.75×10^{-7}	1.18×10^{-7}	1.64×10^{-6}	5.49×10^{-7}
^{21}Ne	3.50×10^{-6}	1.29×10^{-7}	4.66×10^{-7}	6.71×10^{-8}	3.15×10^{-8}	5.83×10^{-8}
^{22}Ne	1.00×10^{-4}	2.13×10^{-7}	5.59×10^{-7}	8.38×10^{-8}	1.61×10^{-7}	7.95×10^{-8}
^{36}Ar	1.85×10^{-4}	2.86×10^{-7}	4.65×10^{-7}	9.54×10^{-8}	3.03×10^{-7}	1.16×10^{-7}
^{38}Ar	3.64×10^{-5}	2.20×10^{-7}	6.46×10^{-7}	1.24×10^{-7}	1.02×10^{-7}	8.15×10^{-8}
^{40}Ar	5.63×10^{-4}	2.63×10^{-5}	4.95×10^{-5}	4.47×10^{-5}	6.47×10^{-5}	4.19×10^{-5}
^{84}Kr	8.5×10^{-8}	2.8×10^{-10}	7.2×10^{-10}	2.0×10^{-10}	5.4×10^{-10}	4.2×10^{-10}
^{132}Xe	2.2×10^{-8}	9.8×10^{-11}	3.5×10^{-10}	1.1×10^{-10}	3.1×10^{-10}	1.5×10^{-10}
$^{4}He/^{3}He$	2770	197	168	234	3130	1540
$^{20}Ne/^{22}Ne$	12.6	4.93	1.39	1.41	10.2	6.91
$^{22}Ne/^{21}Ne$	28.4	1.65	1.20	1.25	5.11	1.36
$^{36}Ar/^{38}Ar$	5.08	1.20	0.72	0.77	2.97	1.42
$^{40}Ar/^{36}Ar$	3.04	92	106	496	214	341
^{3}He(spal)		1.1×10^{-6}	2.91×10^{-6}	6.37×10^{-7}	2.30×10^{-7}	4.22×10^{-7}
^{21}Ne(spal)		1.29×10^{-7}	4.64×10^{-7}	6.70×10^{-8}	2.7×10^{-8}	5.69×10^{-8}
^{4}He(rad)	4.5×10^{-3}	1.41×10^{-4}	4.63×10^{-4}	1.44×10^{-4}	7.45×10^{-4}	6.32×10^{-4}
^{40}Ar(rad)	3.7×10^{-4}	2.60×10^{-5}	4.95×10^{-5}	4.46×10^{-5}	6.47×10^{-5}	4.19×10^{-5}
K (ppm)			2060	860	2280	2010
U (ppm)			0.69	0.33	0.81	0.80
Th (ppm)			3.05	1.0		3.05
T_3 (10^6 yr)		110	291	64	23	42
T_{21} (10^6 yr)		108	387	56	22.5	47
T_4 (10^6 yr)			2550	1750	2950	2500
T_{40} (10^6 yr)			2600	3900	3200	2850

Table 3. Exposure ages and gas retention ages of Apollo 11 fines and rocks in million years.

Elements	Fines	Rocks type B			Rocks type A	
	10084	10003.11	10017.33	10044.32	10049.20	10057.40
			Exposure ages			
^{3}He	207	110	291	64	23	42
^{21}Ne	215	108	387	56	22,5	47
			Gas retention ages			
U/Th			2550	1750	2950	2500
K/Ar			2600	3900	3200	2850

times 10^6 years. The ^{3}He and ^{21}Ne exposure ages for individual samples agree within the experimental limits of error, but for different samples they differ by more than an order of magnitude, ranging from 20 to 400 $\times$ 10^6 years.

The Th/U ratio has been determined for three of the rock samples, and the average value of Th/U equal to 3.8 has been used in the calculation of the ages of the other samples as well. With the exception of rock type B 10044, where the U-Th/He age is more than a factor of 2 lower than the K/Ar age, both gas retention ages are concordant (Table 2). (The relative abundance of ^{40}K has been determined to agree within 1 percent with the value for a sample of terrestrial reagent potassium.) The Kr and Xe found in type A and B rocks possess a strong spallogenic component.

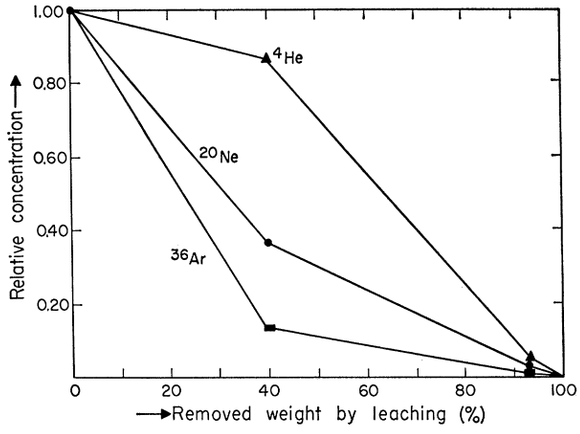
In addition to the rare gases, the concentrations and isotopic composition of H_2 and N_2 have been measured in a few selected rock specimens. Pulverized samples of 250 mg of the type C rock 10021.20 were heated in a Pt-crucible suspended within a quartz tube. The gases released were pumped continuously by means of a mercury diffusion pump into a Toepler pump to determine the total amount. Typically, 2.6 to 3.0 cm^3/g (at standard temperature and pressure) were given off by the samples upon heating to 1000°C, while additional amounts of less than 0.1 cm^3/g were released when the samples were subsequently heated to the melting point.

A partial analysis by mass spectrometry of the gases from one of the 250-mg samples gave the following results at standard temperature and pressure:

H_2 34.4%; 1.03 cm^3/g
He 17.4%; 0.52 cm^3/g; H/He$\approx$4
CO 13.1%; 0.39 cm^3/g
CO_2 5.0%; 0.15 cm^3/g
N_2 3.5%; 0.106 cm^3/g; H/N$\approx$10
Ar 0.092%; 0.0027 cm^3/g

The residual pressure was due to H_2O, NO, Ne, and minor components. Some isotopic ratios were $^{20}Ne/^{22}Ne = 13.2 \pm 0.3$, $^{36}Ar/^{38}Ar = 5.6 \pm 0.2$, $^{40}Ar/^{36}Ar = 2.65 \pm 0.10$, and $^{13}C/^{12}C \approx 0.012$.

To determine the isotopic composition of the hydrogen released from the samples a mass spectrometer (Varian Mat CH5) with a molecular flow inlet system and secondary electron multiplier was used. It permitted complete resolution of the triplet ^{3}He-HD-H_3. Hence, no treatment or operation of the



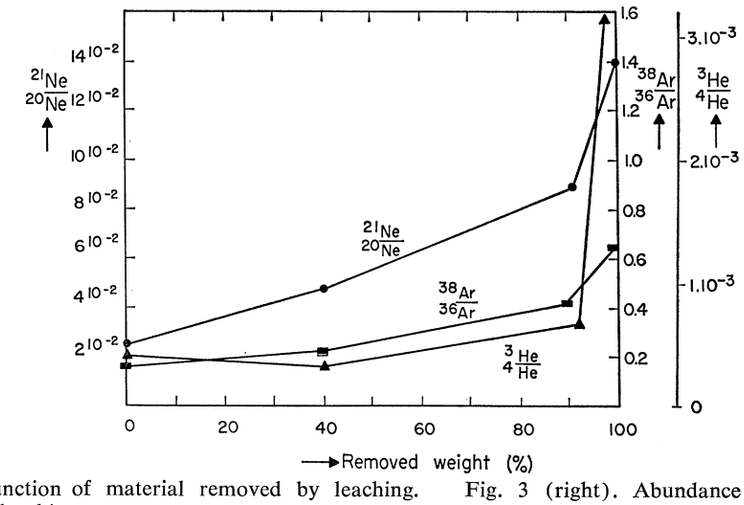


Fig. 2 (left). Relative concentration of rare gases as a function of material removed by leaching. Fig. 3 (right). Abundance ratios of rare gases as a function of material removed by leaching.

gases was required, but the accuracy of the isotopic ratio was still sufficient to measure the rather large deviations from terrestrial standard hydrogen.

Standard hydrogen samples were prepared from distilled tap water, from standard mean ocean water (SMOW) and standard normal ocean water (SNOW) (*2*) by reducing it over uranium at 700°C, and from cylinder hydrogen as well. Their D/H ratios were determined with a mass spectrometer (Varian Mat GD 150) with viscous gas inlet and double collector system. The absolute D/H ratios ranged from 41 $\times$ 10^{-6} for cylinder hydrogen to 156 $\times$ 10^{-6} for SMOW hydrogen (*1*). The standards and the gas samples from two different extractions of 250 mg of rock 10021.20 were alternately run with the CH5 spectrometer. Its resolution was 2500 (10 percent valley definition) at mass number 3. Corrections were made to allow for background and molecular flow. The results obtained from the two sets of measurements were:

$$(D/H)_1 = (1.08 \pm 0.30) \times (D/H)_{\text{H cylinder}} = (44 \pm 12) \times 10^{-6}$$

$$(D/H)_2 = 1/(3.5 \pm 0.4) \times (D/H)_{\text{SMOW}} = (45 \pm 5) \times 10^{-6}$$

The procedure was tested by also determining the $^4He/^3He$ ratio in the Apollo 11 gas as well as in an artificial H_2-^{3}He-^{4}He-mixture. The result thus obtained for He from rock 10021.20 is $^4H/^3He = 2660 \pm 200$, in reasonable agreement with independent determinations.

For several reasons the D/H ratio of 45 $\times$ 10^{-6} cannot be expected to reflect the exact solar ratio. It nevertheless shows quite clearly that on the solar surface the deuterium is depleted by at least a factor of three compared with SMOW in accordance with astronomical observations (*2*) and current theories (*3*). For example, the elemental ratios H/He = 4 and H/N = 10 will be even less representative for the solar surface or the solar wind. The abundance ratios of the rare gases have been already altered significantly by diffusion losses alone, and chemical properties will cause additional perturbations. An indication for this was found in a leaching experiment on lunar fines. Upon treatment of a sample with diluted sulfuric acid, less than 10 percent of the total nitrogen (about 100 ppm) evolves as gaseous N_2, while more than 65 percent is leached out in the form of NH_4^+, possibly indicating the existence of nitrides in the lunar material. An additional 15 percent was present as nitrate.

To get an idea about larger anomalies in the $^{15}N/^{14}N$ ratio another gas sample extracted from 250 mg of 10021.20 was run through a gas chromatograph; the isotopic ratio was determined in the nitrogen fraction by the CH5 mass spectrometer. Within the limits of error of this preliminary investigation the $^{15}N/^{14}N$ ratio agreed with that of a terrestrial N_2 sample.

H. Hintenberger
H. W. Weber, H. Voshage
H. Wänke, F. Begemann
E. Vilscek, F. Wlotzka
Max Planck Institut für Chemie (Otto Hahn Institute), Mainz, Germany

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Isotopic Analysis of Rare Gases from Stepwise Heating of Lunar Fines and Rocks

Abstract. *Highlights of a first effort in sorting out rare gases in lunar material are solar wind rare gases in abundance; variable $^{20}Ne/^{22}Ne$ but constant $^{21}Ne/^{22}Ne$ ratios in fractions of the trapped neon; cosmogenic rare gases similar to those found in meteorites, except for copious ^{131}Xe in one rock but not in another; at Tranquillity Base a rock 4.1 $\times$ 10^9 years old which reached the surface 35 to 65 million years ago, amid soil whose particles have typically been within a meter of the surface for 10^9 years or more.*

This paper describes the results of stepwise heating of three lunar samples. At each of a series of successively higher temperatures, all the rare gases evolved were examined in a glass mass spectrometer. The programmed heating was continued beyond the melting points of the samples until all gas had