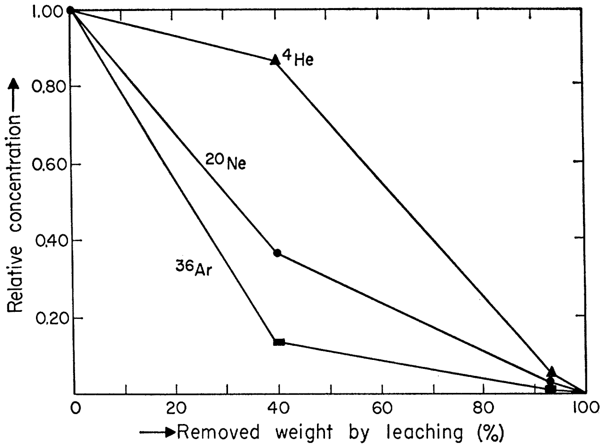

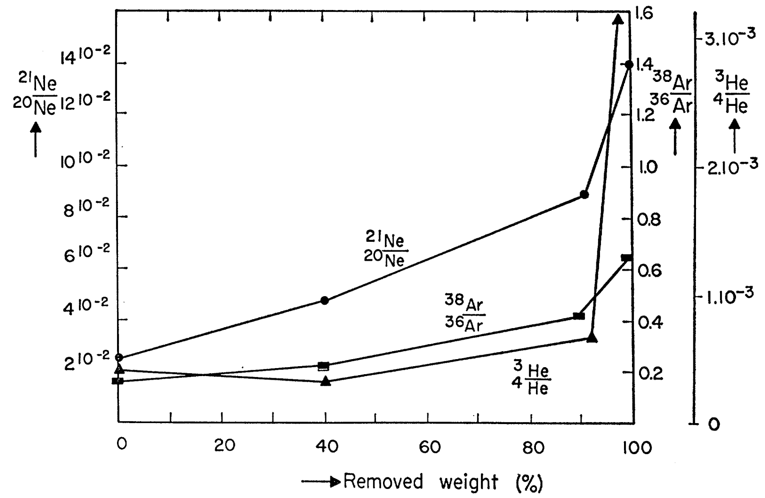

Fig. 2 (left). Relative concentration of rare gases as a function of material removed by leaching. Fig. 3 (right). Abundance ratios of rare gases as a function of material removed by leaching.

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 41×10^{-6} for cylinder hydrogen to 156×10^{-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:

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

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

The procedure was tested by also determining the $^4He/^3He$ ratio in the Apollo 11 gas as well as in an artificial H_2-^3He-^4He-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 45×10^{-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.

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4 January 1970

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 4.1×10^9 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

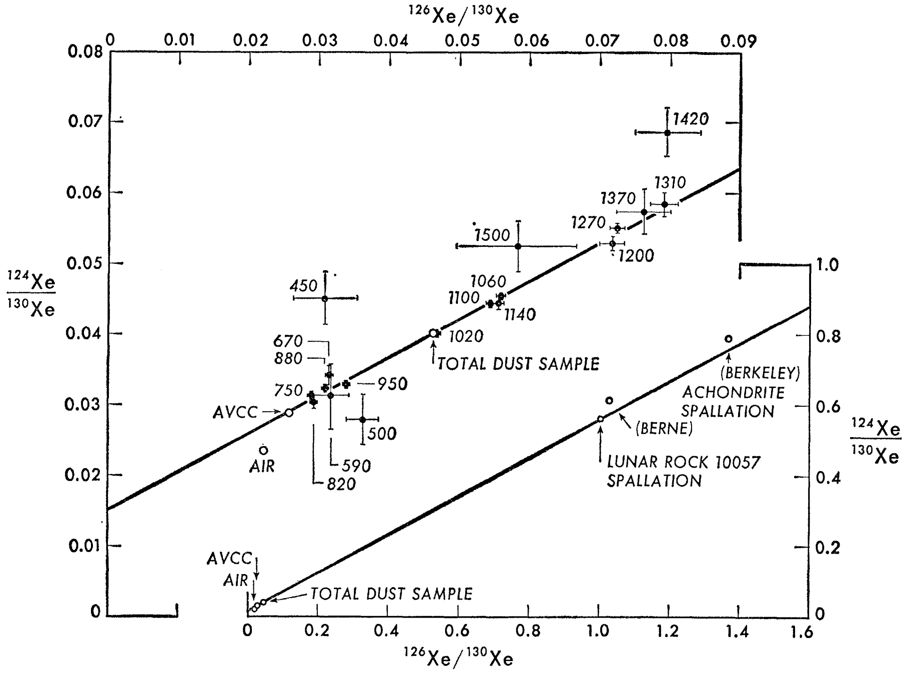

Fig. 1. Correlation of ratios $^{124}Xe/^{130}Xe$ and $^{126}Xe/^{130}Xe$ in lunar fines. The numbers are release temperatures in degrees Celsius for half-hour heatings. These isotopes belong to a two-component system. One component appears to have the AVCC ratios. The other is lunar spallation xenon as deduced from rock 10057. Note the similarity to spallation xenon in achondritic meteorites.

been extracted. Half-gram chips of rocks 57 (fine-grained crystalline) and 44 (coarser-grained crystalline) were studied in one system. A 0.09-g sample of lunar fines (sample 84) was studied in a second system. The lunar material was received at Berkeley in sealed, nitrogen-filled containers. All samples were handled in nitrogen; they were loaded into the vacuum systems without exposure to the atmosphere.

Attention is focused here on resolving the rare gas mass spectra into constituent components. As in meteorite studies, our basic technique has been to plot correlation diagrams for appropriate pairs of isotope ratios in the various temperature fractions from a sample. Two-component mixtures are characterized by straight lines on such a diagram, spanning end points corresponding to the two components. If the end points can somehow be inferred, relative concentrations of the two components can be deduced for each temperature fraction. Departures from a straight line indicate additional components. In particular, concentrations of additional monoisotopic components are easily deduced. The method of analysis should become clear upon discussion of examples.

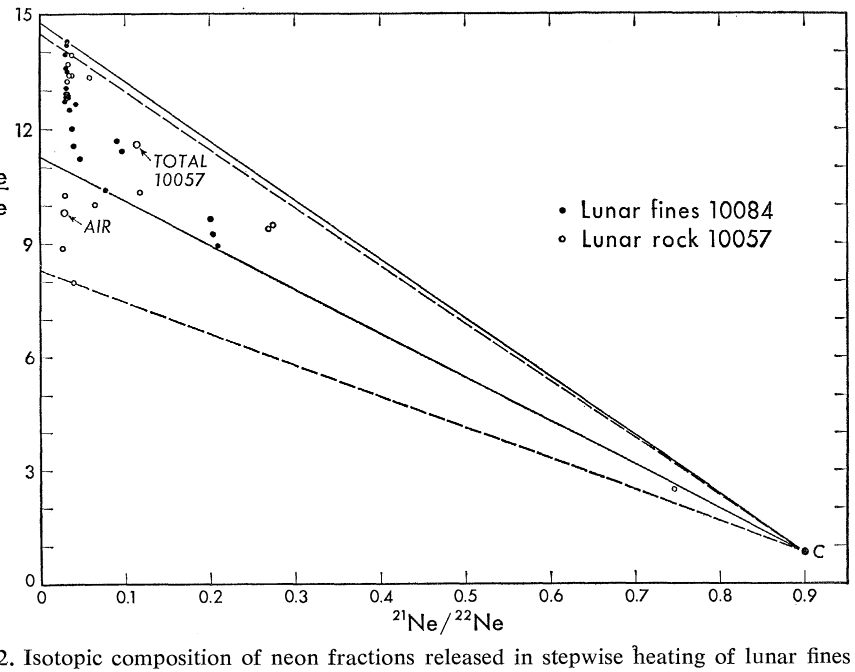

Fig. 2. Isotopic composition of neon fractions released in stepwise heating of lunar fines and rock 10057. The point *C* locates the composition of cosmogenic neon seen in a typical stone meteorite. The noncosmogenic neon composition in any fraction must lie toward the left on the line joining the observed composition with point *C*. Such lines have been drawn for the fractions of extreme composition. The trapped compositions are characterized by large variations in ratio $^{20}Ne/^{22}Ne$ but a nearly constant ratio for $^{21}Ne/^{22}Ne$.

Xenon in the lunar fines was detected in large concentrations and with an isotopic composition close to that predicted for solar-wind xenon by Marti (*1*) from his studies of xenon in the gas-rich achondrite Pesyanoe. The solar xenon is depleted in ^{134}Xe and ^{136}Xe relative to xenon seen in the carbonaceous chondrites. Our stepwise heating of the fines revealed an additional cosmogenic (cosmic-ray produced) xenon component, as shown in Fig. 1, which is a correlation plot of $^{124}Xe/^{130}Xe$ against $^{126}Xe/^{130}Xe$. The points define a line which spans the compositions of average-carbonaceous-chondrite (AVCC) xenon and spallation-type xenon as deduced from the 1200°C fraction from rock 57. The proximity of the most "southwesterly" points on this plot to the AVCC composition strongly suggests that the solar xenon has the AVCC ratios for the light xenon isotopes, although we have used the composition of the 820°C fraction in the fines for solar xenon in calculations in this paper. All numerical results in this paper are presented in Tables 1 and 2.

Neon both in the fines and in rock 57 is dominated by an abundant trapped component. Figure 2 shows the isotopic composition in the various temperature fractions. Although there is cosmogenic neon present, the spectra are dominated by neon for which the $^{21}Ne/^{22}Ne$ is relatively constant (at a value only slightly greater than the terrestrial value) but the $^{20}Ne/^{22}Ne$ is highly variable. Noncosmogenic neon in any fraction will have a composition somewhere "northwest" of the observed composition on the line joining that point with point *C*. On this basis the $^{20}Ne/^{22}Ne$ ratio for noncosmogenic neon in rock 57 varies from $\leqq 8.3$ to $\geqq 13.9$; similarly, the ratio in lunar fines

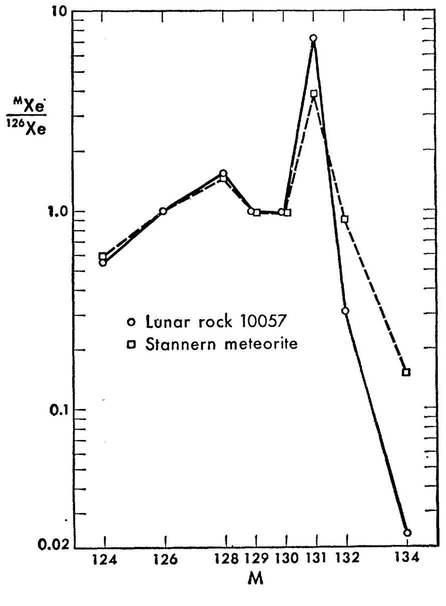

Fig. 3. Comparison of the mass spectrum of cosmogenic xenon in lunar rock 10057 with spallation xenon from the Stannern achondritic meteorite. A large and significant difference is seen for mass 131.

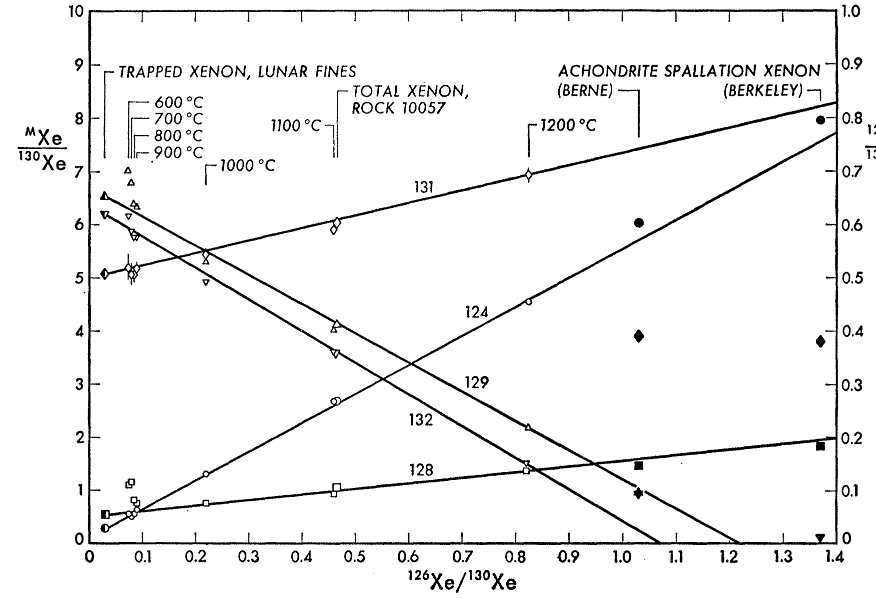

Fig. 4. Graphical analysis of the xenon released in stepwise heating of lunar rock 10057. Small corrections for fission have been made at masses 131 and 132. Isotopes 124, 126, 130, and 132 appear to belong to a simple two-component system (trapped and spallation xenon). Isotope 131 fits a two-component model but with a highly anomalous composition for the cosmogenic component. Isotopes 128 and 129 display excess amounts from 600° to 900°C inclusive.

ranges from ≦11.3 to ≧14.3. Effects of this type are known in stone meteorites (*2*), but have never been adequately explained. Their occurrence in lunar material is one of the most striking results of our study and places constraints upon future theories for their explanation.

Cosmogenic xenon in rock 57 presents a generally consistent picture. The 1200°C fraction is most strongly cosmogenic and has been used to deduce the spectrum. It was assumed that this fraction is a mixture of cosmogenic xenon and xenon with the composition seen at 820°C in the lunar fines. It was further assumed that there is no ^{136}Xe in the cosmogenic fraction. The cosmogenic spectrum is then easily obtained by subtraction. It fits (Fig. 3) the spallation xenon spectrum from the Stannern calcium-rich achondrite, as deduced by Marti *et al.* (*3*), more closely than it fits other published spallation spectra. The most striking difference between the spectra is at mass 131. Rock 57 contains an extraordinary excess of this isotope both in terms of absolute concentration and ratios! The differences at masses 132 and 134, which are small

Table 1. Rare gases from three lunar samples. The gas fractions for the stepwise heatings have been summed. All gas concentrations (boldface) are in units of 10^{-8} cm^3/g (STP). Errors in isotope ratios for total gas are about 1 percent. Errors in concentrations for total gas are about 10 percent.

Isotope	Lunar fines, sample 10084,59			Fine-grained crystalline rock, sample 10057,20					Medium-grained crystalline rock, sample 10044,20
	Total	Solar	Cosmic	Total	Trapped	Cosmic	Fission	Excess	Total
^{3}He/^{4}He	0.00047*			0.000545*†					
[^{4}He]	**2.9×10^{7}**			**83000†**					
^{20}Ne/^{22}Ne	12.85	12.90		11.58					3.72
^{21}Ne/^{22}Ne	0.0332	0.032		0.1152					0.710
[^{22}Ne]	**41000**	**41000**	**>360**	**81**	**73**	**8.1**			**10.3**
^{38}Ar/^{36}Ar	0.1925	0.183		0.237					
^{40}Ar/^{36}Ar	1.126	<0.82		39.1					
[^{36}Ar]	**50600**	**50200**	**400**	**388**	**373**	**15**			
^{78}Kr/^{82}Kr	0.0348	0.0315		0.10		0.23			0.164
^{80}Kr/^{82}Kr	0.2064	0.201		0.45		0.68	**0.0043‡**		0.486
^{81}Kr/^{82}Kr						0.0068			
^{83}Kr/^{82}Kr	1.003	0.997		1.06		1.35			1.10
^{84}Kr/^{82}Kr	4.91	4.91		3.57		0.47			2.91
^{86}Kr/^{82}Kr	1.503	1.496		1.02		0			0.786
[^{82}Kr]	**7.6**	**7.5**	**0.10**	**0.034**	**0.023**	**≡0.011**			**0.027**
^{124}Xe/^{130}Xe	0.0400	0.0302		0.265		0.57			0.59
^{126}Xe/^{130}Xe	0.0464	0.0293		0.465		1.03			0.94
^{128}Xe/^{130}Xe	0.530	0.515		1.048		1.61		**0.00031‡**	1.47
^{129}Xe/^{130}Xe	6.28	6.38		4.11		1.03		**0.00027‡**	2.85
^{131}Xe/^{130}Xe	4.98	4.98		6.05		7.50			4.55
^{132}Xe/^{130}Xe	5.97	6.06		3.58		0.32	**0.00008‡**		1.96
^{134}Xe/^{130}Xe	2.20	2.22		1.283		0.020	**0.00012‡**		
^{136}Xe/^{130}Xe	1.78	1.79		1.040		≡0	**0.00013‡**		0.439
[^{130}Xe]	**0.77**	**0.76**	**0.010**	**0.0052**	**0.0029**	**0.0023**			**0.0015**

*No discrimination correction was available for ^{3}He/^{4}He ratio. † Includes estimate for one gas fraction which was lost. ‡ Value is a concentration (not a ratio) for the isotope in the numerator for the row.

Table 2. Exposure ages of two lunar samples. Sample 10087,59 is lunar fines; sample 10057,20 is fine-grained crystalline rock.

Exposure age type	10084,59 (10^6 years)	10057,20 (10^6 years)
^{38}AR	3020	125
^{82}Kr	1600	64
^{130}Xe	720	63

in terms of absolute gas concentration, can perhaps be attributed to fission effects in the Stannern meteorite.

A comprehensive display of the xenon isotope variations in rock 57 is given in Fig. 4, where ratios ^{M}Xe/^{130}Xe are plotted against ^{126}Xe/^{130}Xe. For M equal to 124, 131, and 132, the points fall reasonably well on lines joining the 1200°C composition and the composition seen at 820°C in the lunar fines. Small corrections have been made for a fission contribution at masses 131 and 132 (see the following paragraph). Otherwise, these isotopes, with ^{126}Xe and ^{130}Xe, appear to belong to a two-component system of trapped and cosmogenic xenon. For M equal to 128 and 129, the values observed between 600° and 900°C fall above the lines containing the other points, as would occur if there were an excess of ^{128}Xe and ^{129}Xe being released at these temperatures. The correlation lines in Fig. 4 pass close to the compositions for cosmogenic xenon in calcium-rich achondrites, except at mass 131, where the correlation line observed has the opposite slope from that observed in meteorites.

Fission xenon in rock 57 was indicated, after subtraction of cosmogenic xenon, by higher values of ^{136}Xe/^{132}Xe and ^{134}Xe/^{132}Xe than in the lunar fines. The amount of fission xenon observed is approximately what should accumulate in 4.1×10^9 years (see below) of uranium decay in rock 57 (780 ppb uranium).

Argon from the samples is a mixture of radiogenic ^{40}Ar from ^{40}K decay, cosmogenic argon, and trapped argon, which can doubtless be ascribed to the solar wind. Values of the ratio ^{40}Ar/^{36}Ar as low as 0.82 were observed in argon fractions from the lunar fines, and provide an upper limit for this ratio in the solar wind. The much higher values of ^{40}Ar/^{36}Ar in gas fractions from rock 57 have to be attributed to ^{40}Ar from potassium decay. On that basis we compute a K-Ar age of $4.1 \pm 0.3 \times 10^9$ years for rock 57, using the preliminary value (*5*) for the potassium content of the rock.

Krypton exhibits a cosmogenic component in all samples, and an excess of ^{80}Kr in rock 57. Radioactive ^{81}Kr was observed in the highly cosmogenic 1200°C fraction of rock 57, permitting calculation of a ^{81}Kr/^{80,82}Kr age (*6*) of 37 million years for exposure of the sample to galactic cosmic rays. Crude exposure ages (Table 2) were calculated for rock 57 and for the fines from the cosmogenic contents of ^{38}Ar, ^{82}Kr, and ^{130}Xe. We used the production rates from Munk's (*7*) study of the calcium-rich achondrite Nuevo Laredo for this purpose, assuming targets of calcium, strontium, and barium, respectively. These ages for rock 57 exceed the ^{81}Kr/^{80,82}Kr age as they should; the results would agree only if that rock was abruptly shifted to its final location from a completely shielded location. The ^{38}Ar exposure ages are older than the others. For the soil, the ages represent an average for the fine-grained material, but much of the present surface soil material at Tranquillity Base has been within a meter or so of the surface for 10^9 years or so, according to our data.

Although we have not completely analyzed our results from rock 44, one important fact is immediately evident: in rock 44 the large excess of ^{131}Xe in the cosmogenic component is absent.

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Solar Wind Gases, Cosmic Ray Spallation Products, and the Irradiation History

Abstract. *The isotopic abundances of the rare gases in the fines are found to be similar to those previously reported for gas-rich meteorites. Relative to the heavy gases, neon and helium are depleted by factors of 2.5 and 10 respectively. Accurate krypton-krypton ages for rocks 10017, 10047, 10057, and 10071 were obtained covering a range of from 47 to 509 × 10^6 years. Varying relative production rates of the krypton and xenon isotopes in these rocks suggest different irradiation conditions and a complex history for at least some of the rocks.*

All 23 stable isotopes of the noble gases He to Xe and Kr^{81} with a half-life of 2.1×10^5 years have been determined in the soil (fines $\leq$ 1 mm) and in four rocks (10017, 10047, 10057, 10071) from the Apollo 11 mission. The results show that we are dealing with gases of different origin. The soil contains large amounts of trapped solar wind gases which almost completely mask other components. In the crystalline rocks, on the other hand, cosmic ray induced spallation and radiogenic gases are predominant. Small amounts of solar wind gases are found too in chips close to the rock surface. No trapped primordial or "planetary" gases were found in the rocks, which suggests that they were completely outgassed at the time of their formation. The relative abundances of the solar wind gases in the soil are given in Table 1. The heavier rare gases Ar to Xe show abundance ratios similar to those found in the Pesyanoe meteorite (*1*), and agree within factors of 2 to 3 with estimates from cosmic abundance calculations. Relative to the heavy gases, Ne and He in the fines are depleted by factors of about 2.5 and 10 respectively as compared with Pesyanoe, a typical gas-rich meteorite. The concentrations of the heavy gases in Pesyanoe are about 300 times lower and there is no evidence of saturation effects. Therefore the agreement between the abundance pattern of Ar, Kr, and Xe in lunar soil and in Pesyanoe is an important fact in the discussion of the origin of these gases.