Gas Analysis of the Lunar Surface

Abstract. *The rare gas analysis of the lunar surface has lead to important conclusions concerning the moon. The large amounts of rare gases found in the lunar soil and breccia indicate that the solar atmosphere is trapped in the lunar soil as no other source of such large amounts of gas is known. The cosmogenic products indicate that the exposure ages of the 17 lunar rocks measured vary from 20 to 400 million years with some grouping of the ages. The most striking feature is the old potassium-argon age which for the 14 rocks analyzed varies from 2.5 to 3.8 billion years. It is concluded that Mare Tranquillitatis crystallized about 4 billion years ago from a molten state produced by a large meteorite impact or volcanic flow.*

The rare gases offer important clues to the history of the lunar surface layers. Variations in isotopic abundances and absolute amounts of the noble gases indicate that a separation from the primordial gas component took place early in the moon's evolution such that subsequent additions of rare gases are rather easily traced. We now have evidence that the processes that add rare gases to the moon include radioactive decay and solar wind, solar flare and cosmic ray implantation, and nuclear reactions induced by the higher energy particles. Interpretation of rare gas measurements leads to surface exposure ages, the time of crystallization of rocks, and insight into the composition of the solar surface.

Most of the gas analyses were made with a 6-inch, 60° magnetic deflection mass spectrometer. A number of the "gassier" samples were analyzed on a less sensitive 5-inch, 180° instrument.

Standard techniques of gas extraction, chemical purification with hot titanium, and separation were employed (*1*). All samples were initially degassed at 125° to 150°C for 5 to 24 hours prior to introduction into the vacuum system. Subsequent adsorption of atmospheric rare gases was considered negligible in most samples after we observed the small amount of gases released at 400° to 450°C in several of the samples.

The 6-inch spectrometer was operated at a sensitivity of 2×10^{-10} cm^3/mv for He, Ne, Ar and 3×10^{-13} cm^3/mv for Kr and Xe. The 1650°C-furnace blank comprised most of the background and it normally amounted to $< 5 \times 10^{-9}$ cm^3 ^{3}He, 1×10^{-7} cm^3 ^{4}He, 9×10^{-9} cm^3 ^{20}Ne, 7×10^{-8} cm^3 ^{40}Ar, 6×10^{-12} cm^3 ^{84}Kr, and 2×10^{-12} cm^3 ^{132}Xe. Long term reproducibility determined from daily standards, was within $\pm$ 5 percent for all five noble gases. Isotopic ratios were corrected for mass spectrometer discrimination and are accurate to $\pm$ 2 percent for the gases He, Ne, and Ar and less than 1 percent for the gases Kr and Xe. The accuracy in the absolute amount of each gas is estimated to be within $\pm$ 20 percent.

The high gas content of the fines and breccia allowed the use of milligram size samples. Only interior portions of crystalline rocks were analyzed and these were mechanically cleaned of contaminating fines; nevertheless, some degree of solar contamination was unavoidable. Most samples of the crystalline rocks measured ranged from 10 to 100 mg.

Because of the large amounts of solar gases in the fines and breccia (Table 1), surface exposure and K-Ar ages could only be calculated for the crystalline rocks (Table 2) plus two lithic fragments handpicked from two different breccias. Both the radiation and K-Ar ages are depicted (Fig. 1). Corrections for determining spallation gases were applied in the normal manner using solar ratios measured in the fines and breccia. No atmospheric ^{40}Ar was assumed present in the calculation of radiogenic Ar, and the solar correction was negligible in most all cases.

The breccia and fines contain extraordinarily large amounts of noble gases which are derived predominantly from the solar wind. Compared to relative cosmic abundances, depletion of the major elemental isotope decreases with increasing atomic weight, as would be expected, invoking loss by diffusion and sputtering-saturation mechanisms. The average relative abundances of ^{4}He, ^{20}Ne, ^{36}Ar, ^{84}Kr, ^{132}Xe in both the fines and breccia samples, normalized to ^{36}Ar (100), are 42,000; 660; 100; 0.054; 0.020, respectively. Both the absolute and relative amount of gas varies by a factor of three, even within a single sample, yet the isotopic abundances vary only slightly. The ratio ^{4}He/^{3}He is about 2800, in agreement with estimates of solar abundances (*2*). The average value for ^{20}Ne/^{22}Ne is 12.4 and for ^{22}Ne/^{21}Ne, about 30.7 (corrected for spallation ^{21}Ne). Both these ratios are similar to those in gas rich meteorites. The high, yet variable, ^{20}Ne/^{22}Ne ratio, relative to the terrestrial atmosphere, might be attributed to ^{23}Na (p,α) ^{20}Ne reactions generated by solar flares in the surface layers of the lunar fines. Shock or some similar process apparently tends to homogenize the noble gases throughout the fines and breccia on a small scale as indicated by temperature release patterns. Yet millimeter-size lithic fragments removed from the breccia contain only small amounts of cosmic noble gases.

The breccias returned by Apollo 11 generally contain more gas than the fines. The isotopic ratios are similar with one notable exception: ^{40}Ar/^{36}Ar is about 1.1 in the fines, but averages 2.2 in the breccia samples. Theoretical

Table 1. Rare gas content of fines and breccia (concentration in units of 10^{-8} cm^3/g).

Sample	Helium		Neon			Argon			^{84}Kr	^{132}Xe
	^{4}He	4/3	^{20}Ne	20/22	22/21	^{36}Ar	40/36	36/38		
				Fines						
10010	11,000,000	2430	200,000	12.4	31.6	35,000	1.1	5.20	21	10
10010	19,000,000	2540	313,000	12.8	29.4	34,000	1.2	5.17	20	4.1
				Breccia						
10018	24,000,000	2650	480,000	13.4	27.8	72,000	2.1	5.16	35	12
10021	37,000,000	3300	750,000	12.4	30.6	100,000	2.1	5.13	28	10
10023	25,000,000	2570	350,000	12.7	29.3	52,000	2.4	5.15	24	11
10027	15,000,000	2930	320,000	12.2	29.9	67,000	2.2	5.08	41	12
10048	21,000,000	2600	350,000	11.1	28.6	55,000	2.1	5.22	31	12
10061	47,000,000	3400	710,000	12.1	30.0	89,000	1.8	5.14	48	11
10068	25,000,000	2780	330,000	12.2	29.0	42,000	2.7	5.22	20	7.5

calculations for elemental synthesis predict an $^{40}Ar/^{36}Ar$ ratio of less than 0.01 percent (*2*), thus the large amounts of ^{40}Ar observed must be of radiogenic origin, not produced by *in situ* decay of ^{40}K but adsorbed and/or injected into the fines and breccia in characteristically different amounts. Perhaps the breccia were not derived locally, but from fines with a higher $^{40}Ar/^{36}Ar$ ratio in another site. The $^{36}Ar/^{38}Ar$ ratio is a remarkably constant $5.28 \pm .06$.

The major Kr and Xe component in the fines and breccia is ascribed to a solar wind origin. The isotopic composition among these samples varied only slightly and showed an average composition for xenon 124/126/128/129/130/131/132/134/136 of 0.57/0.65/8.5/104/16.5/82.5/≡100/37.1/30.4, and an average composition for krypton 78/80/82/83/84/86 of 0.72/4.10/20.4/20.4/≡100/30.8. The lighter isotopes of Kr and Xe show a variable excess in the fines and breccia over the Kr and Xe trapped in carbonaceous chondrites. Xenon-134 and -136 appear depleted by several percent in the solar xenon component from that observed trapped in carbonaceous chondrites. This particular xenon isotopic pattern in lunar fines and breccia is consistent with the trapped plus fission two-component xenon found in temperature release studies of carbonaceous chondrites but shows values for the 134/132 and 136/132 ratios lower than any temperature release performed to date on these chondrites (*3*). The $^{129}Xe/^{132}Xe$ ratio in the solar component is the same as that found in typical carbonaceous chondrites.

The breccias have many of the characteristics of gas rich meteorites. It is not unreasonable, then, to suggest that gas rich meteorites were formed in a manner similar to the lunar breccia; that is, on a surface of a large body irradiated by solar and cosmic particles, with a certain amount of surface mixing, and then lithified by shock generated by meteoritic impact.

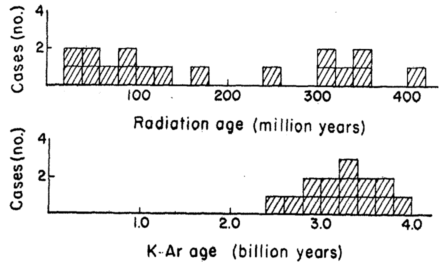

Fig. 1. Histograms of radiation ages (upper) and K-Ar ages (lower) of crystalline rocks.

All the crystalline rocks measured contain noble gases produced by spallation reactions. The amount of the spallogenic gases depends on the time the sample was exposed to cosmic rays, whereas the relative isotopic abundance reflects both the chemistry and the degree of radiation shielding of the sample. Elemental isotopic abundances of 15 crystalline rocks show an average value of 9 for $^{3}He/^{21}Ne$ and 0.9 for $^{21}Ne/^{38}Ar$.

Assuming 2π-geometry for the lunar surface rocks and, therefore, a production rate of 1.0×10^{-8} cm^3 per million years for ^{3}He, then absolute radiation ages can be assigned to the different samples. Production rates, relative to ^{3}He, have been derived for ^{21}Ne and ^{38}Ar from excitation functions applied to the average chemical composition of the crystalline rocks. The variation in the measured $^{3}He/^{21}Ne$ ratio appears to be dependent upon the effective energy spectrum rather than chemical composition. The ^{38}Ar is generated primarily from Ca, and the production rate is also a strong function of radiation hardness. The calculated $^{21}Ne/^{38}Ar$ ratio is rather uncertain because of limited cross-section data for Ca. Nevertheless, exposure ages determined from the calculated production rates of ^{21}Ne and ^{38}Ar agree within 20 percent of the ^{3}He based radiation age in almost all of the 17 samples measured.

Production rates of ^{21}Ne based on the measured ^{22}Na content of three rocks (*1*) agree well with calculated values as does a ^{3}He-T age on a crystalline rock that was analyzed for tritium (*4*). This fact, the general concordancy of the ^{3}He, ^{21}Ne, ^{38}Ar ages, and the concordant K-Ar and U-He ages (discussed later) imply that no widespread diffusive gas loss has occurred for the spallogenic gases in the crystalline rocks.

The radiation ages (Fig. 1) range from 20 to 400 million years and fall into two rather amorphous groups at about 100 and 350 million years. Spallation gases in lithic fragments from two breccia samples indicate radiation ages of approximately 350 million years. Thus, the breccia and the rocks were scattered on the surface of Mare Tranquillitatis by few, but distinct, events, most probably meteoritic impact. The estimated thickness of the regolith in the vicinity of the Apollo 11 landing site (*1*) and an assumed age of the basement rock of about 4 billion years leads to an average rate of "soil" formation of 1 to 2 mm per million years. In addition, the fact that even the rocks with the youngest surface ages exhibited rounding and that no rocks were found with radiation ages greater than about 400 million years again implies a combined erosion and surface coverage rate of 1 to 2 mm per million years. Some degree of turnover in the top meter of the regolith must be assumed in order to provide lunar rocks older than a few tens of million years that still remain uncovered.

Table 2. Rare gas content of crystalline rocks (concentrations in units of 10^{-8} cm^3/g).

Sample	^{3}He	^{4}He	^{20}Ne	^{21}Ne	^{22}Ne	^{36}Ar	^{38}Ar	^{40}Ar	^{84}Kr	^{132}Xe
10017	310	58,000	110	47	56	37	47	4100	0.080	0.040
10018 *	420	260,000	5,100	76	460	690	230	6100	0.51	0.17
10020	110	20,000	72	14	20	20	19	1800	0.046	0.031
10022	350	63,000	210	52	67	59	50	5700	0.13	0.063
10024	260	50,000	220	32	76	75	68	4100	0.46	0.39
10032	150	15,000	750	16	73	98	32	7400	0.071	0.041
10044	82	34,000	250	8.8	27	36	15	2500	0.094	0.046
10047	96	25,000	210	15	30	43	19	1500	0.090	0.036
10049	25	77,000	73	2.6	8.7	11	5.0	5600	0.059	0.021
10050	440	80,000	900	51	110	150	73	2500	0.35	0.21
10057	44	64,000	110	5.7	14	19	9.7	4800	0.020	0.013
10058	58	21,000	64	7.1	12	15	12	3700	0.015	0.007
10061 *	350	95,000	13,000	74	1000	2300	620	8200	1.58	0.46
10069	28	69,000	38	4.0	7.0	6.0	5.4	6500	0.007	0.005
10070	110	98,000	790	11	68	110	32	2400	0.071	
10071	320	73,000	177	37	52	36	34	6100	0.050	0.029
10072	190	75,000	235	26	44	41	36	7600	0.033	0.012

* Lithic fragments handpicked from breccia.

The lunar crystalline rocks show a wide isotopic variation in krypton and xenon, all characterized by excesses of xenon 124–132 and krypton 78–84 relative to ^{136}Xe and ^{86}Kr, respectively. These excesses are attributed to cosmic-ray spallation reactions in the rocks, mainly on Ba, Sr, Y, and Zr. The spallation spectrum for the various rocks are all similar and are (normalized to $^{126}\text{Xe} \equiv 1$ and $^{83}\text{Kr} \equiv 1$): 124/126/128/129/130/131/132/134 $\equiv$ 0.55 $\equiv$ 1/1.5/1.7/1.07/6.3/0.9/0.07, and 78/80/82/83/84 $\equiv$ 0.2/0.48/0.76 $\equiv$ 1/0.38. These spectra are quite similar to the spallation spectra found in achondrites except for a much higher ^{131}Xe and a somewhat lower ^{84}Kr. The higher 131 yield is probably an effect of low energy protons as barium is the major target for spallation Xe production, and 730-mev proton spallation of barium does not show this high ^{131}Xe yield (*5*). The amounts of ^{126}Xe and ^{83}Kr in the rocks vary by almost an order of magnitude among samples because of the differing exposure histories, yet these amounts correlate reasonably well with the spallation ^{38}Ar. The slight isotopic excesses of the lighter isotopes of Kr and Xe in the lunar fines and breccia over that in carbonaceous chondrites is also probably due to spallation reactions. Not only is the amount of excess ^{126}Xe in different breccia variable, but in amount it is only slightly greater than the spallation ^{126}Xe found in those crystalline rocks with the longest exposure history.

Radiogenic Ar and He are apparent in all crystalline rocks examined. K-Ar ages were obtained for 14 rocks and fragments for which K was known (*1*). Potassium was determined by emission spectroscopy but not from aliquots used for noble gas analysis. The K-Ar ages, including two from lithic fragments from two breccia samples, range from 2.5 to 3.8 billion years (Fig. 1). The U-He ages are subject to large errors because of the solar wind correction to the measured ^{4}He and the uncertainty in the U-Th content derived from the K values (*1*); nevertheless, most of the ages are concordant within this error with the K-Ar data. Thus, the spread in the K-Ar ages is probably real to some extent, and not just caused by variable leakage of radiogenic Ar.

Mare Tranquillitatis, then, probably first crystallized about 4 billion years ago from a large molten body produced either by meteoritic impact or volcanism. Subsequent large impacts or volcanic events would further mold the mare to its present form and produce younger rocks. Despite the time spread of approximately 1 billion years in volcanic events, it appears that the features of the moon at Mare Tranquillitatis were well delineated at least 2 billion years ago.

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Solid State Studies of the Radiation History of Lunar Samples

Abstract. *Particle track densities up to > 3 × 10⁹ per square centimeter have been measured in different samples. Rocks 17, 47, 57, and 58 have VH (Z >22) galactic cosmic ray ages of 11, 14, 28, and 13 × 10⁶ years, respectively. Rock 57 has a calculated erosion rate of ≲ 10⁻⁷ centimeter per year. Near-surface track versus depth data in rock 17 can be fit with solar flare particles that have a differential energy spectrum ∝E⁻³; lunar samples can be used to study the history of solar activity. The uranium in the crystalline rocks occurs principally in small regions <10 to ~100 micrometers in size. The (low) thermoluminescence of the fines increases with depth in core 10004. With one possible exception, x-ray studies have not shown pronounced radiation damage effects. The total energy release upon heating is small up to 900°C and occurs in three broad regions.*

We have measured particle tracks, thermoluminescence, x-ray distortions, U distributions, and energy release patterns in lunar samples. Table 1 gives a summary of track data. The lower track densities were measured with an optical microscope and the higher densities with a Cambridge Mark IV stereo-scan electron microscope. A series of cross calibrations (Fig. 1) have convinced us that the geometrically shaped, deep surface holes normally counted in the stereo-scan are essentially equivalent to the long tracks seen in the optical microscope after etching.

Track densities versus depth were measured in rocks 17 and 57. For the following reasons we believe that the tracks found at $\gtrsim$ 5 mm from an external surface are due primarily to VH nuclei ($Z > 22$) from galactic cosmic rays: (i) the uranium concentrations are too low to give an appreciable spontaneous fission track density; (ii) the tracks are frequently anisotropically distributed and have a length distribution characteristic of VH tracks studied in meteorites; (iii) long tracks attributable to VVH nuclei ($z \gtrsim 31$) are observed with an abundance of $\sim 10^{-3}$ of the total density; and (iv) deeper than 5 mm, there is an accord between theory and experiment for the depth profile of galactic tracks.

Using feldspar data from interior portions we calculate the following VH exposure ages: (i) 10017, $11 \pm 1 \times 10^6$ years, (ii) 10047, $14 \pm 4 \times 10^6$ years, (iii) 10057, $28 \pm 5 \times 10^6$ years, (iv) 10058, $13 \pm 2 \times 10^6$ years. The quoted errors are statistical. Greater uncertainties arise from the lack of precise sample position in the rocks. Our calculations are based on previous theoretical treatments (*1*) using a modified low energy spectrum (*2*). Because all the surfaces, including "tops" and "bottoms," have high densities compared with densities of interior samples, we use a "rolling stone model" in which the irradiation is uniform on all sides.

The VH exposure ages are all approximately equal and are in striking contrast to the proton spallation ages that can be inferred from the rare gas data reported in the preliminary examination. From both ^{3}He and ^{21}Ne data, rock 17 has the oldest spallation age, probably $\gtrsim 200 \times 10^6$ years. Rock 57, in contrast, has the youngest spallation age, probably $\gtrsim 40 \times 10^6$ years.