trapped Xe if our estimate of the composition of fission-free trapped Xe, shown by the heavy curve, is correct. This depletion of fission Xe, coupled with the absence of excess ^{86}Kr in lunar Kr and its definite presence in average carbonaceous chondrite Kr, suggests that excess ^{86}Kr and fission Xe concentrations may correlate, both resulting from the addition of a fissiogenic Kr-Xe component.

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Cosmic Ray Production of Rare Gas Radioactivities and Tritium in Lunar Material

Abstract. *The argon radioactivities ^{37}Ar and ^{39}Ar were obtained by vacuum melting from interior and exterior portions of rock 10057 and from a portion of the fines from the bulk sample container. The release of argon and tritium as a function of the temperature was followed for the fine material. A comparison is made of the activities observed in the lunar samples with those expected from the spallation of iron, titanium, and calcium. From these data and the ^{38}Ar content, the cosmic ray exposure age of rock 10057 is deduced as 110 × 10^6 years.*

A measurement of the stable and radioactive argon isotopes in lunar material can give valuable information on cosmic ray interactions on the lunar surface and can be used to deduce cosmic ray exposure ages of fragmented material resting on the lunar surface. Of particular interest are the stable isotopes ^{36}Ar and ^{38}Ar, and the radioactive isotopes ^{37}Ar (half-life, 35 days) and ^{39}Ar (half-life, 269 years). These isotopes are produced primarily by high-energy bombardment of the relatively abundant elements iron, titanium, and calcium. The primary goal of the investigation discussed here was to measure the ^{37}Ar and ^{39}Ar in surface rocks and in the fine material. The argon is evolved from the solid by vacuum melting and is counted in a small low-level gas proportional counter. By using pulse height analysis the Auger electron spectrum from the electron capture of ^{37}Ar can be easily distinguished from the beta spectrum of ^{39}Ar, and the two isotopes can be measured simultaneously. Since ^{37}Ar has a half-life of only 35 days, the measurements were made at the Lunar Receiving Laboratory during the biological quarantine.

The vacuum melting technique used to evolve and count the argon radioactivities also allows a search to be made for radioactive isotopes of the higher rare gases—namely ^{81}Kr, ^{85}Kr, ^{127}Xe, ^{133}Xe, and ^{222}Rn. The isotope ^{81}Kr (half-life, 2.1 × 10^5 years) has been observed in meteorites (*1*) and has been attributed to high-energy spallation of Sr, Y, and Zr. Radon-222 arises from the decay of ^{238}U, and a measurement of the ^{222}Rn content can be used as a sensitive measurement of the uranium concentration.

Of special interest is the tritium radioactivity in lunar materials that is also released by vacuum melting. This isotope is produced by high-energy cosmic ray bombardment. The rate of tritium production is an essential quantity needed to determine the tritium-^3He cosmic ray exposure age. Of far greater interest is the possibility that some of the solar flare particles are tritons. Fireman and his associates (*2*) observed tritium in the Discoverer 17 satellite and in a sounding rocket that was exposed to the solar flare of 12 November 1960. An analysis of their measurements indicates that the tritium-to-hydrogen ratio in this event was about 10^{-3} (*2*, *3*). A search for tritium in material exposed on the surface of the moon may afford a unique opportunity to remeasure the tritium content of solar flare particles.

Three separate samples of lunar material were studied; an internal (weight, 7.65 g) and an external (weight, 10.6 g) fragment of rock 10057, and a 10.6-g portion of the fine material (10002,6) from the bulk sample. Among the lunar rocks, the one designated 10057 has been classified type A; this includes the crystalline, fine-grained, vesicular rocks. The external rock fragment and the fine material were processed and measured at the Lunar Receiving Laboratory during the quarantine period, and therefore had to be heat-sterilized. The internal rock chip was measured after the quarantine period had ended, and was not sterilized. The sterilization was conducted in a stainless steel container at a temperature of 120°C for a period of 24 hours. A search was made for ^{37}Ar and ^{39}Ar released from the fine material during the heating and less than 0.6 disintegration min^{-1} kg^{-1} (dpm/kg) was found. The tritium released during the sterilization of the fine material was not determined because it was considered very likely that, if hydrogen were released, it would be absorbed into the stainless steel of the container.

Samples of lunar material in an alumina-lined molybdenum crucible were heated by a radio-frequency induction heater. The gases evolved were collected in a Toepler pump and placed in a tube containing hot vanadium metal. The vanadium at 850°C serves as a getter to remove chemically active constituents. The vanadium was then cooled to room temperature to absorb hydrogen as

Table 1. Volumes of rare gases and hydrogen from lunar material.

Sample	Extraction temperature (°C) and heating period	Rare gases (cm^3/g, STP)	Hydrogen (cm^3/g, STP)
Fines	Sterilization, 120, 24 hr	Not meas.	Not meas.
1000.2,6	120 to 600, 64 min	0.145	0.67
1000.2,6	600 to 900, 73 min	0.068	0.12
1000.2,6	900 to 1200, 92 min	0.003	0.04
1000.2,6	1200 to 1600, 68 min	<0.0005	<0.007
Total	120 to 1600	0.217	0.84
10057,3 (exterior)	120 to 1600	Not meas.	~0.1
10057,3 (interior)	120 to 1600	Not meas.	~0.16

Table 2. Radioactivities of rare gas and tritium.

Sample	Radioactivity (dpm/kg)			Ratio $^{37}Ar/^{39}Ar$
	Tritium	^{37}Ar*	^{39}Ar	
	Fines, sample 10002.6			
Sterilization heating	Not meas.	$\leqslant 0.6$	–	–
Heat I: 120°–600°C	199 ± 12	$\leqslant 1$	–	–
Heat II: 600°–900°C	70 ± 3	6.7 ± 0.7	3.6 ± 0.2	1.84 ± 0.20
Heat III: 900°–1200°C	41 ± 3	11.3 ± 0.8	5.3 ± 0.3	2.14 ± 0.18
Heat IV: 1200°–1600°C	3 ± 2	$\leqslant 2$	–	–
Combined argon heats I and IV	–	0.7 ± 0.2	0.2 ± 0.2	–
Totals	314 ± 13	18.7 ± 1.2	9.2 ± 0.4	2.03 ± 0.16
	Rocks			
10057,3 (exterior)†	224 ± 15	18.5 ± 0.9	11.2 ± 0.3	1.65 ± 0.09
10057,27 (interior)†	214 ± 10	21.6 ± 4.1	13.5 ± 0.4	1.60 ± 0.30

* Values have been corrected for decay to 0000 hours, C.D.T., 21 July 1969. If reentry is taken as the true EOB time, the ^{37}Ar results should be decreased by a factor of 1.076. † Krypton radioactivities were measured for rock 10057: exterior sample, −0.5 ± 0.3; interior sample, 0.0 ± 0.3 dpm/kg.

vanadium hydride. The rare gases were removed from the vanadium tube, their volume was measured, and they were placed in a sample transfer bulb. The vanadium tube was then reheated to 850°C to dissociate the vanadium hydride. The hydrogen was collected with a Toepler pump, measured, and sealed in a second sample transfer bulb. The apparatus for vacuum fusion and extraction of the rare gases and hydrogen from the samples was located in the gas analysis laboratory behind the secondary biological barrier. The sealed glass ampules containing the rare gases and hydrogen were then sterilized and taken through the biological barrier to a purification and counter filling system outside the barrier.

The isolated rare gases were then separated by gas phase chromatography on a charcoal column with helium as the carrier gas. The separated argon, krypton, and xenon were placed in small gas proportional counters for the radioactivity measurements. The counters had a 0.0125-mm tungsten center wire in a cylindrical cathode of zone-refined iron enclosed in an envelope of silica glass. The counter had a thin window at one end to permit energy calibration of the multichannel analyzer with an external ^{55}Fe x-ray source. The active volume of these counters ranged from 0.3 to 0.6 cm^3. The counter was operated inside a ring of anticoincidence gas proportional counters inside a lead shield 10 cm thick. The shield was located 15 meters underground in the Radiation Counting Laboratory. Eight counters could be operated simultaneously, recording the spectra with 256 channel analyzers. The counter voltage was adjusted so that the 2.8 kev Auger electron from the decay of ^{37}Ar would center at channel 104. The counters had a 30 percent resolution (full width at half maximum) for these events. The amplifier was designed so that all events with energy greater than 6.8 kev were stored in channels 250 to 254 (hereafter referred to as "pileup channels"). This arrangement made it possible to distinguish clearly the events arising from the electron capture decay of ^{37}Ar, and the continuous beta spectrum (maximum energy, 570 kev) arising from ^{39}Ar decay. Individual counter efficiencies for ^{37}Ar and ^{39}Ar were measured by filling the counters with argon containing known amounts of these radioactivities. The exact efficiency of the individual counters was measured over the pulse height spectrum and the pileup channels. Their individual distributions depended upon their specific dimensions and gas pressure. In general they exhibited total efficiencies in the range of 50 to 70 percent for ^{37}Ar and ^{39}Ar. To measure krypton, xenon, and radon radioactivities, the counter was adjusted in the same way, so that these decays would be recorded primarily in the pileup channels.

Hydrogen was purified by passing the gas through a palladium metal thimble at 800°C, and the gas was placed in a gas proportional counter; the gas filling was a mixture of 90 percent argon and 10 percent methane. The counter operated at 1 atmosphere and contained less than 0.2 atmosphere of hydrogen gas. Counting was performed in the same system used in the rare gas counting, with the voltage on the counter adjusted so that all events from an externally placed ^{60}Co source occurred in the pileup channels. The cathode was made of copper, and the outer envelope of silica glass. It had an internal diameter of 1.0 cm and was 12.5 cm long.

Preliminary studies (*4*) showed that the fine material contained large quantities of rare gas that probably can be attributed to solar-wind bombardment. We therefore measured the amounts of rare gases and hydrogen evolved from this finely divided material with increasing temperature. As is mentioned above, this sample had been heated previously to 120°C for 24 hours; the quantity of gas released during this period was not measured. The sample was then heated in stages, reaching the maximum temperatures 600°, 900°, 1200°, and 1600°C; the volume of rare gas and hydrogen released at these temperatures, and the periods of time that the fines were maintained at the maximum temperature, are given in Table 1. Detailed studies of the rare gas composition of the fine material show that the rare gas is more than 98 percent helium (*4*, *5*). This gas evolution experiment shows that more than 67 percent of the helium and 80 percent of the hydrogen is removed from this fine material at 600°C. A temperature of 900°C releases the remaining quantities of these gases. We compared the H/He atom ratio of 7.8 measured from the fines to the H/He ratio in the sun. The recently accepted solar value (*6*) is 17, higher by a factor of 2 than the value obtained by heating the fine material. This may be explained by the preferential loss of hydrogen with respect to helium in these finely divided silicates. The volume of hydrogen observed in these measurements would correspond to a hydrogen abundance of 75 parts per million. The two fragments of rock 10057 were heated to 1600°C; they yielded 0.1 and 0.16 cm^3 of hydrogen (Table 1). The larger volume of hydrogen obtained from the interior sample can probably be accounted for

Table 3. Production cross sections for the argon isotopes in the lunar material.

Element	Percentage in sample		Thin target cross section for 600 Mev protons (millibarns)*			
	Fines	Rock 10057	^{37}Ar	^{38}Ar	^{39}Ar	^{42}Ar
Fe	12.4	15.5	5.6	12†	6.3	0.075
Ti	4.2	7.5	11.6	30‡	15.7	0.34
Ca	8.6	7.1	46.7	32‡	2.0	0.039
K	0.10	0.15	47.4	50§	6.3	0
Mn + Cr	0.5	1.3	5§	12§	5§	0.1§

* Absolute errors are in the range of 5 to 10 percent. † Value of Goebel *et al.* (*8*) normalized to the ^{37}Ar and ^{39}Ar values given above for Fe. ‡ Derived from the $^{38}Ar/^{39}Ar$ ratio measured with 380 Mev protons on Ti by Stoenner *et al.* (*9*), and with 3 Gev protons on Ca by A. A. Schaeffer (*10*). § These cross sections are rough estimates from nuclear systematics.

by the fact that this sample had been stored in air for several weeks prior to measurement. We conclude that the hydrogen abundance of the rock was less than or equal to 10 ppm.

The tritium activity released from the fine material in the various temperature intervals is given in Table 2. Sixty-three percent of the tritium was released at 600°C, closely paralleling the evolution of hydrogen (80 percent). The total tritium activity observed in the fine material was approximately the same as that observed in the rock. All of these samples have approximately the same amount of tritium actvity as that usually observed in stone meteorites (*7*)—namely 200 to 700 dpm/kg. It is clear that the high tritium content that one might expect from solar-flare tritons imbedded in an exposed surface is not observed. Perhaps the samples measured were not truly surface samples. The fines were well mixed, and, if there were a high tritium content on the surface, it could be highly diluted with deeper-lying material. The exterior rock sample did have micrometeorite pits on its surface, but it is not at all certain that this surface had been exposed during the last 20 years or so. The interesting observation of Fireman and his associates (*2*) of a triton component in solar-flare particles should be tested with lunar material known to have been exposed in recent years on the surface.

The release of ^{37}Ar and ^{39}Ar radioactivities from the fine material during the stepwise heating shows that the argon evolved almost completely in the temperature interval 600° to 1200°C. Measurements on the combined sample evolved below 600°C and above 1200°C (see Table 2) showed that less than 4 percent of both of these activities was released outside the 600° to 1200°C interval. This result indicates that the argon produced throughout this silicate material with an average particle size of 100 microns (*4*) is strongly retained. The total ^{37}Ar and ^{39}Ar activity measured in this material is approximately the same as that measured in the rock sample. Since the fine material contains large quantities of solar-wind argon, it is impossible to determine the ^{38}Ar produced by cosmic rays, and therefore an effective exposure age cannot be deduced.

The ^{37}Ar and ^{39}Ar activities produced in the fines and the rock were compared with those expected from cosmic ray bombardment. The magnitude of the activities almost exactly equals those observed in recently fallen meteorites (*7*). The meteorite samples studied are regarded as interior pieces of objects, weighing 10 to 100 kg, that receive an isotropic cosmic ray exposure. The surface lunar material might be expected to contain higher activities produced by low-energy solar and galactic cosmic rays, but on the other hand the lunar surface receives only about half the isotropic flux. Apparently the geometric and shielding effects nearly cancel. The ratio of the ^{37}Ar and ^{39}Ar activities can be compared to the ratio expected from cosmic ray bombardment. The cross section for producing these isotopes in thin targets (1 to 5 g cm^{-2}) of iron, titanium, calcium, and potassium at 600 Mev is given in Table 3, along with the chemical analysis of rock 10057 (*4*). On the basis of these data the calculated $^{37}Ar/^{39}Ar$ atom ratio, constant cosmic ray bombardment being assumed, is 3.2 for the fine material and 2.2 for rock 10057. The observed $^{37}Ar/^{39}Ar$ ratio for both of these samples is about 30 percent lower than the estimated cross-section ratios. To obtain an accurate model for the production ratio for these isotopes, a series of bombardments of thick targets of lunar-like material at several energies is required. Experiments along these lines are in progress, but for the present we must use the available information at 600 Mev. To deduce a cosmic ray exposure age based upon the ^{38}Ar content of rock 10057, one must evaluate the relative production rates of ^{38}Ar and ^{39}Ar. Using the cross sections listed in Table 3, we calculate an $^{38}Ar/^{39}Ar$ cross-section ratio of 2.8. The ^{38}Ar content of rock 10057 was measured, by Funkhouser and his associates (*5*), to be 7.1×10^{-8} cm³ (STP)/g. Using the measured ^{38}Ar and ^{39}Ar production rates and the calculated $^{38}Ar/^{39}Ar$ cross-section ratio, we calculate that rock 10057 was exposed for 110 million years on the lunar surface.

Since the lunar samples are high in Sr, Y, and Zr, it is possible that measurable amounts of ^{81}Kr and ^{85}Kr may be present. A search was made for krypton activities in rock 10057, but only an upper limit of less than 0.5 dpm/kg could be set. From the composition of the rock and an estimate of the production cross sections, we conclude that the level of both ^{81}Kr and ^{85}Kr activities is about 0.2 dpm/kg.

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Inert Gases in Lunar Samples

Abstract. *Sample 10084,40 (fines, less than 1 millimeter) contains substantial amounts of the inert gases. Their concentrations are inversely proportional to particle size; hence the gases appear to be surface-correlated in the soil fragments. The most likely origin of the gas is solar wind or solar cosmic rays. Glass and feldspar are generally poorer in gas than lithic fragments. Ratios of elements in the sample differ significantly from solar values. Ratios of isotopes in the sample are similar to those in meteorites. Argon-40 appears to consist of a radiogenic and a surface-correlated component. An apparent potassium-argon age of* $4.42^{+0.24}_{-0.28}$ *billion years is calculated.*

We have determined (mass-spectrometrically) the concentrations of the inert gases, and in all cases the isotopic compositions of He, Ne, and Ar in the following "splits" of sample 10084,40 ("fines," < 1 mm): 1 and 2, "bulk" of 10084,40 (weights 3.507 and 10.827 mg); 3, lithic fragment, ~800 μm