centers. These variations may be real, a possibility supported by the systematic albedo patterns in Mare Serenitatis (*5*) and more indirectly by the work of Soderblom (*4*), who found several spectral subtypes of both "red" and "blue" maria. However, two factors confuse the picture at this time. First, because of the relatively large field of view of the x-ray experiment, intensity readings near mare rims include contributions from the nearby highland areas. Second, the mare regolith near the borders may contain substantial amounts of ejecta from nearby highlands. Study of the prime data, taken at 8-second intervals, may clarify this result.

4) The Imbrium ejecta blanket [Fra Mauro and Alpes Formation (*6*)] and possibly other ejecta blankets may be chemically different from the highlands outside such ejecta blankets. An obvious interpretation of this difference, if it is real, is that the mare basin ejecta blankets represent less Al-rich material derived from some depth in the moon. However, the ejecta blanket areas covered by the x-ray spectrometer, in particular in the Haemus Mountains south of Mare Serenitatis, included substantial areas of highland mare material [shown as Eratosthenian mare by Wilhelms and McCauley (*6*)]. It is thus unwise at this time to draw firm conclusions about the composition of the mare basin ejecta.

5) The x-ray data support the belief that the moon has a global Al- or plagioclase-rich crust whose formation was the first major geochemical event of the moon's geologic evolution after its formation. The data tend to support the suggestion of Wood (*7*) of widespread cumulates of plagioclase. Despite the preliminary nature of these data, one can pinpoint areas on the lunar highlands that have Al/Si ratios corresponding to analyzed materials rich in plagioclase. As shown in Table 1, the anorthositic gabbros have Al/Si ratios of 0.64, gabbroic anorthosites 0.82, and anorthositic fragments 0.89.

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Primordial Radioelements and Cosmogenic Radionuclides in Lunar Samples from Apollo 15

Abstract. Two basalts, two breccias, and two soils from Apollo 15 were analyzed by nondestructive gamma-ray spectrometry. The concentrations of potassium, thorium, and uranium in the basalts were similar to those in the Apollo 12 basalts, but the potassium : uranium ratios were somewhat higher. Primordial radioelements were enriched in the soils and breccia, consistent with a two-component mixture of mare basalt and up to 20 percent foreign component (KREEP). The abundance patterns for cosmogenic radionuclides implied surface sampling for all specimens. The galactic cosmic-ray production rate of vanadium-48 was determined as 57 ± 11 disintegrations per minute per kilogram of iron. Cobalt-56 concentrations were used to estimate the intensity of the solar flare of 25 January 1971.

The Apollo 15 mission has presented a unique opportunity to study the geochemistry of lunar surface materials by nondestructive gamma-ray spectrometry. The area explored was large and geologically diverse, and the improved sample documentation was supported by live television coverage. In addition, the Apollo 15 manned lunar landing, unlike previous missions, was not closely preceded by an intense solar flare. Thus, the Apollo 15 material could be used in a study of the galactic cosmic-ray production rates of some short-lived radionuclides that previously were produced chiefly by solar cosmic rays. Finally, since no quarantine requirements were imposed on samples from Apollo 15, the preliminary examination at the Lunar Receiving Laboratory (LRL) was supplemented by measurements at other laboratories.

The first Apollo 15 samples for radioactivity determination (15016,0 and 15101,1) were received from the LRL on 11 August 1971, about 9 days after lift-off from the moon. Two weeks later another pair of samples was received (15495,0 and 15601,2). Additional samples (15285,0 and 15455,0) gave valuable data on long-lived radionuclides, but because of the long decay interval before measurement they yielded little information concerning short-lived species.

The equipment and techniques of nondestructive gamma-ray spectrometry are essentially those we developed for use during the Apollo 11 and Apollo 12 missions at the LRL (*1–3*). Spectrum libraries for all the samples except 15455,0 were obtained from replicas that accurately reproduced the electronic and bulk densities of the lunar samples. The radioactive concentrations of the major components are given in Table 1; a more detailed analysis for components with lower concentrations is in progress. The bulk densities shown in Table 1 were obtained from the known sample weights and the measured volumes of the replicas.

The samples used in this study are representative of the varied geology associated with the Apollo 15 landing site. The locations at which they were found are shown in Fig. 1, which is a simplified map of Hadley Base drawn from the preliminary field geology reports (*4*). Excellent documentation exists on these samples. For the benefit of later discussion, brief sample descriptions (*5*) are given below.

Sample 15016,0 is a vesicular, porphyritic basalt. Its low density of 2.4 g/cm^3 suggests that it contains nearly 20 percent void space. Sample 15495,0 is a coarsely crystalline mare basalt. Its density suggests that it contains 5 to 10 percent void space due to vugs. Sample 15285,0 is a breccia of apparently homogeneous composition, with various amounts of glass coating on its surfaces. Sample 15455,0, the "black and white rock," is a dark breccia with white norite clasts. Soil sample 15101,1 from St. George Crater consists of fines of low density (about 1.2 g/cm^3) with diameters of less than 1 mm. Soil sample 15601,2 from the "terrace" of Hadley Rille consists of fines less than 1 mm in diameter and has the higher density (about 1.7 g/cm^3) characteristic of mare soils from the Apollo 12 site.

The concentrations of the primordial radioelements K, Th, and U in the six samples are listed in Table 1. Since a large number of samples from previous Apollo missions have been studied by gamma-ray spectrometry, detailed comparisons with the results in Table 1 can be made.

The values of the mass ratio K/U for the earth and the moon fall into separate groups whose averages are characteristic of each planet (*1, 2*). The constancy of the ratio of K (a volatile element, depleted on the moon) to U (a refractory element) appears to be the result of early chemical fractionation not affected by later igneous processes. Values of K/U for lunar material are separable into the groups shown in Fig. 2, which is redrawn from our systematics (*2*) of Apollo 11 and Apollo 12 sample data, with the addition of recent results for Apollo 14 samples (*6, 7*). The K concentrations in Fig. 2 are not normalized to 18 percent Si. The correlation between the K and U concentrations implies that there is a similar relationship between K and Th, because values of the concentration ratio Th/U are nearly constant in lunar material (typically 3.6 to 3.8).

The two Apollo 15 basalts, 15016 and 15495, have K concentrations that are similar to those of the Apollo 11 low-K basalts and the Apollo 12 basalts. However, for the Apollo 15 basalts we have measured, the average value of K/U is about 2800, compared to about 2000 for the Apollo 11 and Apollo 12 basalts of the same concentration of K. In Fig. 2 the eucrite zone slightly overlaps the data region for 15016 and 15495. In fact, the K and U concentrations for the Nuevo Laredo eucrite (*8*), respectively, 390 and 0.14 parts per million (ppm), are almost identical to those of rock 15016.

As was the situation for the Apollo 12 samples (*2*), the soils and breccia from Apollo 15 are much higher in K, Th, and U than the basalts. Therefore, the soils and breccia are very likely mixtures of basalt and a foreign component high in these elements. If we assume a simple, two-component model for the soils and breccia with Apollo 15 mare basalt as one end member, then from Fig. 2 the most likely candidate for the second component is KREEP [a material high in potassium, rare earth elements, and phosphorus (*9*)] because the other possibilities would yield higher K/U ratios than those observed in the

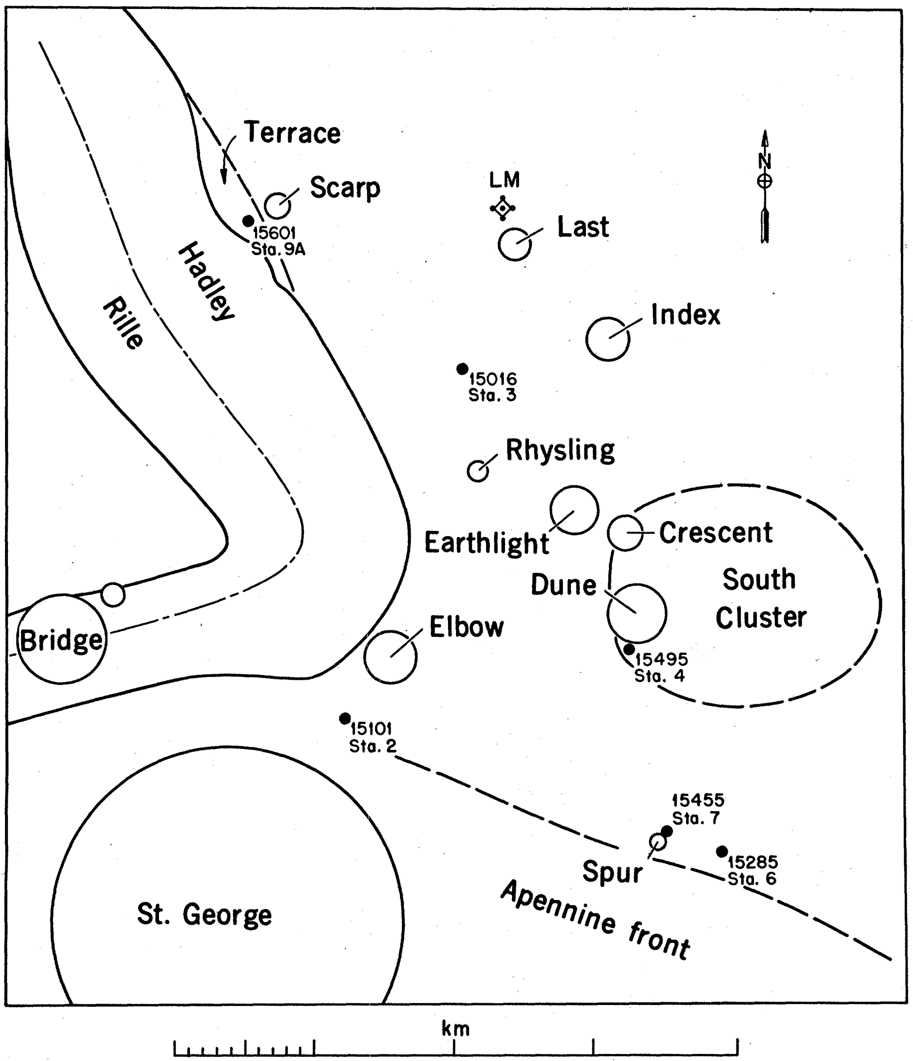

Fig. 1. Original locations of the samples described in this report. Craters are shown as open circles, and sampling stations are shown as solid black circles. The coordinates of the lunar module (*LM*) are 25.8°N 3°E.

Table 1. Concentrations of primordial radioelements and cosmogenic radionuclides in Apollo 15 lunar samples. The values for the short-lived nuclides have been corrected for decay to 1711 hours G.M.T., 2 August 1971.

Measurement	Sample number					
	15016,0	15495,0	15285,0	15455,0	15101,1	15601,2
Petrologic type	Basalt	Basalt	Breccia	Breccia*	Fines	Fines
Weight (g)	923.7	909.0	251.3	832.8	115.6	204.3
Bulk density (g/cm^3)	2.4	2.9	2.4		~ 1.2	~ 1.7
K (ppm)†	374 ± 20	495 ± 25	1610 ± 80	900 ± 150	1484 ± 74	900 ± 45
Th (ppm)†	0.52 ± 0.02	0.60 ± 0.03	3.4 ± 0.1	2.0 ± 0.3	3.1 ± 0.3	1.8 ± 0.2
U (ppm)†	0.15 ± 0.01	0.16 ± 0.01	0.93 ± 0.05	0.53 ± 0.08	0.86 ± 0.08	0.51 ± 0.05
^{26}Al (dpm/kg)	82 ± 4	69 ± 3	85 ± 4		120 ± 12	112 ± 11
^{22}Na (dpm/kg)	29 ± 2	29 ± 3	50 ± 4		44 ± 5	55 ± 6
^{48}V (dpm/kg)	10 ± 2	Trace			9 ± 6	
^{56}Co (dpm/kg)	16 ± 3	11 ± 2			11 ± 6	28 ± 9

* "Black and white" breccia; analysis given for dark portion by assay with Ge(Li) detector. † Terrestrial isotopic abundances and equilibria of the Th and U decay series were assumed in the standardization for assay of K, Th, and U.

soils and breccia. Even the presence of 30 percent anorthosite in the soil, because of the proximity to the lunar highlands (*10*), would not alter the conclusion that KREEP is the most likely foreign component, since anorthosites are very low in K, Th, and U and would simply act as diluents. Any lunar material rich in KREEP, such as the Apollo 14 samples (*7*), might also serve as the source of the foreign component.

Breccia 15285 is similar in composition to soil 15101 and is most likely a breccia of local origin produced by meteorite impact. Estimates based on a two-component mixture of mare basalt and KREEP suggest that these samples contain about 20 percent KREEP. Sample 15455, the "black and white rock," is a more complex, inhomogeneous breccia. Samples 15455 and 15601 have similar concentrations of primordial radioelements and appear to be lower in KREEP (about 10 percent).

The rille soil (sample 15601) contains much less K, Th, and U than the soils and soil breccia from most of the other locations at Hadley Base (Table 1) (*11*). Sample 15601 was collected about 20 m from the edge of Hadley Rille. One explanation for the lower concentrations of K, Th, and U in this sample is that this area earlier was covered by a layer of lunar material as rich in KREEP as the adjoining region (up to 20 percent), but that erosion by meteorite impacts at the edge of the rille removed a large part of the layer. The effect of such impact erosion is much greater at an edge than on a horizontal plane, because the eroded material tends to fall inside the rille. It was reported that in the region under discussion the regolith was almost absent 25 m from the edge of the rille (*4*).

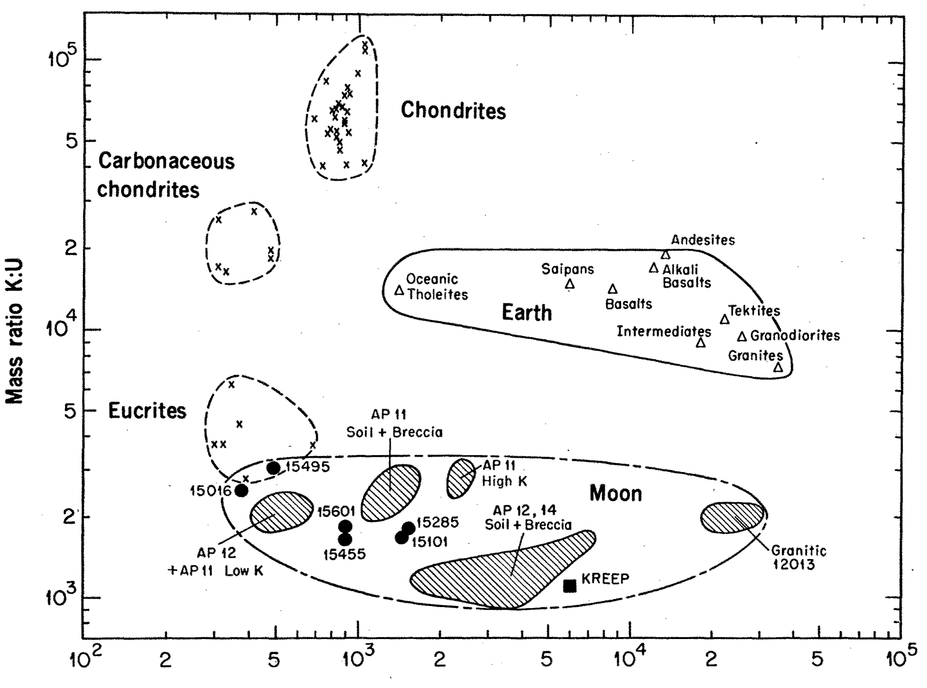

Fig. 2. Values of the mass ratio K/U as a function of the concentration of K.

The general concentration patterns for ^{22}Na and ^{26}Al resemble those observed on previous Apollo missions. The abundance of 2.6-year ^{22}Na is a measure of the exposure to solar and galactic cosmic rays over approximately the past 10 years; the concentration of ^{26}Al is a measure of the exposure over about 2×10^6 years. Because chemical analyses are lacking for most of the samples we have examined, it is not possible to make detailed interpretations of the concentrations of ^{22}Na and ^{26}Al. However, there are no measurements that suggest strongly that the yield of ^{26}Al has not attained saturation. Further, the cosmogenic radionuclide yields, especially of ^{56}Co, suggest that the rocks were collected from the surface, in agreement with preliminary documentation.

Both soil samples also appear to have been taken from near the surface. The high concentrations of ^{22}Na, ^{26}Al, and ^{56}Co are consistent with a sampling depth of about 3 cm for 15101 and a somewhat shallower depth of 1.5 to 3.0 cm for 15601, if it is assumed that their chemical composition is similar to that of the Apollo 12 soils.

During the preliminary examinations of the Apollo 11 and Apollo 12 samples in the LRL, we detected two relatively short-lived nuclides (*1*, *3*); 5.7-day ^{52}Mn was determined in four rocks and 16-day ^{48}V in six rocks. The concentration of ^{48}V was well correlated with the Ti concentration of the rocks, as would be expected if most of the ^{48}V was produced by solar-flare protons through the $^{48}Ti(p,n)$ reaction. From the ^{48}V content of rock 12062, which appeared to have been buried, we inferred a yield from galactic proton bombardment of about 40 ± 20 disintegrations per minute (dpm)/kg Fe.

As shown in Table 1, we determined ^{48}V quantitatively in the first two Apollo 15 samples received, 15016 and 15101. However, the results on 15016 were superior because weak components of the gamma-ray spectra of mare basalts suffer less interference from the Th and U decay series than do the spectra of lunar soil and breccia. The concentration of ^{48}V in 15016 leads to a galactic production rate for ^{48}V of 57 ± 11 dpm/kg Fe, based on an FeO concentration (*11*) of 22.6 percent. This result agrees well with our earlier estimate of 40 ± 20 dpm/kg Fe, within the experimental errors, and with the value 90 ± 45 dpm/kg determined by Honda and Arnold (*12*) for the yield of ^{48}V in the iron meteorite Aroos.

Although no intense solar flare directly preceded the Apollo 15 mission, 77.3-day ^{56}Co was detected in some of the samples. Since ^{56}Co is almost totally produced by solar-flare protons through the $^{56}Fe(p,n)$ reaction, the ^{56}Co detected in Apollo 15 samples was produced in the solar flare of 25 January 1971. No measurements of the intensity of this flare have been published, but a comparison of the present ^{56}Co concentrations with those of the Apollo 12 samples (*3*) suggests that the flare of 25 January 1971 was approximately 30 percent more intense than the well-characterized event of 3 November 1969.

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16 November 1971

Mars: An Evolving Atmosphere

Abstract. *Photochemical reactions in the martian exosphere produce fast atoms of oxygen, carbon, and nitrogen and provide large escape fluxes of these elements. They appear to play a crucial role in the evolution of the martian atmosphere. The relative outgassing rates of H_2O and CO_2 on Mars are comparable with terrestrial values, although absolute rates for Mars are lower by a factor of 10^3. Nitrogen is a trace constituent, less than 1 percent, of the present martian atmosphere.*

We now understand that the atmospheric pressure at the surface of Mars is about 5 mb and that the atmosphere is composed mainly of CO_2, with trace amounts of H_2O and CO (*1*). We expect significant amounts of O_2 and O_3, produced as photochemical by-products of CO_2. Nitrogen is surprisingly rare. Analysis of data from Mariners 6 and 7 suggests an upper limit on the mixing ratio of N_2 relative to CO_2 (by volume) of 5 percent but indicates that the probable abundance is much less than this value (*2*). The outer atmosphere contains small amounts of atomic hydrogen, carbon, and oxygen (*2a*), and the planet is losing hydrogen by thermal evaporation at a significant rate, about 10^8 atoms cm^{-2} sec^{-1} (*3*). Some implications of these data regarding the possible evolutionary history of Mars are discussed in this report.

The escape rate of H, inferred from the Mariner data, is particularly significant. The escaping atoms are supplied at the expense of atmospheric water, dissociated by sunlight near the martian surface at an average rate of about 10^9 molecules cm^{-2} sec^{-1}. According to Hunten and McElroy (*4*), H_2O is reformed at the surface with an efficiency of about 90 percent, and approximately 10 percent of the H_2O dissociation events lead to formation of H_2. The escaping atoms are produced by reactions involving H_2, notably

$$O(^1D) + H_2 \rightarrow OH + H$$

$$CO_2^+ + H_2 \rightarrow CO_2H^+ + H$$

$$CO_2H^+ + e \rightarrow CO_2 + H$$

and photodissociation

$$h\nu + H_2 \rightarrow H + H$$

To a good approximation, the escape flux of H is proportional to the abundance of H_2. Hunten and McElroy estimate a mixing ratio, H_2 to CO_2, of order 10^{-6}.

Integrated over the age of the planet, about 5×10^9 years, the present escape rate of H would imply a loss of H equivalent to about 10^{25} molecules of H_2O per square centimeter of martian surface, enough to supply a surface pressure of H_2O equal to about 0.1 atm. By way of comparison, the total amount of H_2O evolved by Earth over geologic time corresponds to an average column density of 10^{28} molecules cm^{-2} (*5*). If O atoms released on Mars by H_2O photolysis and differential escape of H were to remain in the atmosphere they would supply an abundance of O_2 equal to the present observational limit in less than 10^5 years. We shall argue that the excess O is in fact lost to interplanetary space, the escape energy being supplied to O atoms in the exosphere by dissociative recombination of molecular ions.

The martian ionosphere, first detected by Mariner 4 (*6*), is produced by photoionization of CO_2. Its chemical composition is determined by competition between

$$CO_2^+ + O \rightarrow O_2^+ + CO \qquad (1)$$

and

$$CO_2^+ + e \rightarrow CO + O \qquad (2)$$