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Major and Trace Elements and Cosmic-Ray Produced Radioisotopes in Lunar Samples

Abstract. *Analytical data for 42 major and trace elements were mostly obtained by a combination of instrumental and radiochemical neutron activation analyses using both thermal and 14-million-electronvolt neutrons. Excesses of nitrogen and chlorine in the fines, compared with the rocks, are attributed to the solar wind. A striking similarity for contents of seven elements in lunar metal and metal from the calcium-rich achondrite Juvinas was noted. Fractional dissolution was used to separate five radionuclides produced by cosmic-ray bombardment in the fines and rock 57-40. Results for argon-39 from the reaction potassium-39 (n,p), and for argon-37, from the reaction calcium-40 (n,α), seem to require a neutron spectrum containing more neutrons below 2 million electronvolts than the evaporation spectrum or that given by Arnold, Honda, and Lal* (1) *or a strong time dependence for the neutron flux.*

The lunar samples were treated following our standard procedure for the analysis of major and trace elements in meteorites. Pulverized samples (grain sizes ≤ 60 μm) of 250 to 800 mg were first irradiated by 14 MeV neutrons produced by the (d, T) reaction for the determination of O, Si, Mg, and Al. The same samples were then irradiated in the TRIGA research reactor (of the University of Mainz) for 6 hours at a flux of 7×10^{11}n/cm^2 sec, and the γ-ray spectra were measured after various cooling periods by means of a high-resolution Ge(Li) detector. In this way concentrations of the elements Na, K, Ca, Sc, Ti, Cr, Mn, Fe, Co, La, Ce, Sm, Tb, Yb, Lu, Hf, and Ta were determined without dissolving the samples. The reproducibility of these determinations was usually better than 5 percent except for Ca, Ce, and Ta, where the errors are 10 to 20 percent.

Three weeks after their first reactor irradiation, the samples were irradiated for an additional 6 hours at the same flux and radiochemically processed as follows. After addition of carriers, the samples were decomposed under vacuum by Na_2O_2-fusion. The rare gases were purified and xenon, containing the isotope Xe^{135} from the fission of uranium, was isolated for β and β-γ coincidence counting. The melt was then further radiochemically processed for the isolation of individual elements and groups of elements, mainly by solvent extraction techniques. The procedure was similar to one described previously (*2*). Concentrations were determined by γ-ray counting with NaI and Ge(Li) detectors. Chemical yields were determined by reirradiation of samples. The elements determined by this procedure were Li, Cl, Ni, Cu, Ga, Ge, Rb, In, Cs, Pr, Nd, Gd, Dy, Ho, Er, W, Au, Th, and U, with standard deviations less than 10 percent. Portions (about 50 mg) of the samples were set aside before irradiation for the determination of boron by a specially developed fluorescence method (*3*).

Table 1 shows the results of all chemical analyses. Some remarkable features are the high concentrations of Ti (*4*), Zr, and Hf. All rare-earth elements are present in much higher concentrations than in any known type of meteorites. Compared with calcium-rich achondrites, the enrichment amounts to about a factor of 10, except for Eu which seems to be somewhat less enriched. On the other hand, sample 44-32, which shows the lowest concentration of La, has the highest Eu content of all lunar samples analyzed in this laboratory. The concentrations of U, Th, and, to a smaller extent, K are again higher than in any known meteorite. The weight ratio K/U of about 2600 is constant for all our samples and comes very close to that found in achondrites (3000 to 4000). There is a high excess of Cl and especially In in the fine material as compared to lunar rock. Although a possible contamination with In before the distribution of the samples cannot be excluded, the value of 0.75 ppm is only five times higher than the amount of In in the dark phase of the gas-rich meteorite Leighton. A leaching experiment showed that about 80 percent of both Cl and In can be leached out from lunar fines with dilute sulfuric acid (10 percent).

In a similar experiment (*5*), N and Ar were leached from fines in amounts exceeding those from the lunar rock 57-40 by 100 ppm and 1 ppm, respectively. As contamination by atmospheric nitrogen can have been only minor (*5*), we consider this similarity to suggest that not only the rare gases but at least part of the excess N and Cl must be attributed to the solar winds as well.

Some additional interesting information has been obtained from a few milligrams of metal particles, which had been magnetically separated from our sample of lunar fines 84-18. An instrumental neutron activation analysis yielded the following elemental concentrations (values for metal from the calcium-rich achondrite Juvinas are given in parentheses): Fe, 94.6 (96.5) percent; Ni, 4.7 (2.9) percent; Co, 0.52 (0.62) percent; Cu, 340 (150) ppm; Au, 0.83 (0.76) ppm; Ir, 2.6 (0.9) ppm; and W, 24 (21) ppm. Note the surprisingly high concentration of W. We were unable to find any similarly high concentration of tungsten in the metal of several other types of meteorites (calcium-poor achondrite, H and L chondrites). This emphasizes the striking parallelism of the content of trace elements in the lunar metal and that in Juvinas.

From the amount of H_2 evolved during the treatment of a sample of lunar fines with diluted sulfuric acid under vacuum, the amount of metal present in sample 84-18 was estimated to be 0.6 percent by weight. This means that the total amount of Ni (280 ppm) found in this sample (lunar fines) is present in the form of metallic Ni-Fe.

For the examination of cosmic ray isotopes, a technique for fractional dissolution was applied to a sample of the lunar fines (84-18) and the rock (57-40). The fines were processed without crushing; the rock was pulverized to pass a 60-μm sieve. Preliminary experiments on small samples showed hot HNO_3 to be a suitable solvent for the desired fractionation of the target elements of interest. It preferentially dissolves the feldspar, resulting in a fraction enriched in Ca and Al. In addition, in the case of the lunar fines, a considerable fraction of all mineral components was readily dissolved in cold HNO_3. As this effect was not observed for the rock sample, a possible explanation is radiation damage of the surface layers induced by the solar wind or the dissolution of the glass more abundantly present in the fines, or both. The HNO_3 - insoluble residue was decomposed with NH_4HF_2 and H_2SO_4, all steps being performed under vacuum.

After radiochemical purification, ^{22}Na was counted by γ-γ coincidence (NaI), ^{26}Al by high-resolution γ-ray spectroscopy (GeLi), ^{10}Be and ^{36}Cl by β^- counting of BeO and NaCl, and the Ar isotopes by internal gas counting. Table 2 gives the concentrations of the relevant target elements dissolved in the different steps as well as the normalized decay rates. The ^{22}Na and ^{26}Al activities in the total samples were determined before the dissolution as well. For ^{22}Na in the fines this total activity of 61 ± 15 dpm/kg is exactly the same as that obtained by summing the activities in the three fractions; for ^{26}Al, however, the agreement is not as good, the two values being 86 ± 12 dpm/kg and 121 ± 25 dpm/kg. With the exception of ^{39}Ar, the decay rates of all radioisotopes are higher in the fines than in the rock, although to a variable degree. The main reason is the different chemical composition, as discussed below.

In addition to the isotopes listed in Table 2, the ^{14}C content of the fines was measured as 39 ± 5 dpm/kg; a preliminary value for the ^{10}Be decay rate of 27 dpm/kg has been obtained from the cold HNO_3 fraction of the fines. Using the data of Table 2, we calculated the production rates of the radioisotopes on various target elements (Table 3). The high value for the production of ^{39}Ar on K is, as in the case of meteorites (*6*), clearly due to the reaction ^{39}K (n,p). The contribution from Ca can be neglected because for the reaction ^{40}Ca(n,2p)^{39}Ar, the *Q* value is −8.1 Mev, and the probability that only two

Table 1. Concentrations of elements in lunar samples.

Element	Type A (57-40)	Type B (17-33)	Type B (44-32)	Type C (18-22)	Type C (60-16)	Type D (84-18)
			Concentration (%)			
O	40.4	40.7	41.5	40.7	41.4	41.5
Mg	4.2	4.8	3.9	5.0	4.6	4.8
Al	4.0	4.4	6.3	6.1	6.2	6.9
Si	18.9	19.6	20.1	19.6	19.8	19.7
Ca	8.4	8.2	5.1			8.1
Ti	6.5	7.0	6.3	5.5	4.6	4.3
Fe	14.0	14.6	13.3	11.1	12.1	12.0
			Concentration (ppm)			
B	0.8	0.7	1.2			1.03
Li	14.0	23		13.3	10.4	10.4
Na	3000	3470	3580	3920	3600	3150
Cl	12.0	12.2		16.5	15.5	27.1
K	2010	2060	860	1320	1330	1090
Sc	87	86	92	69	70	61
Cr	2160	2310	1300	1900	1820	1830
Mn	1800	1480	2000	1050	1340	1560
Co	25.4	24.5	11.0	24.0	30.0	27.2
Ni	<10					280
Cu	4.3	7.7	4.2			8.2
Ga	5.2	4.2	5.1			4.9
Ge	<1	<1	<1			1.4
Rb	5.2	4.2	5.1			3.0
In	0.0027	0.138				0.75
Cs	0.20	0.12				0.12
La	25	21	12	18	18	15
Ce	107	76	80			63
Pr	9.6	7.8				5.3
Nd	60	58	50	60		47
Sm	12.6	11.9	11.3	8.5	8.7	7.6
Eu	1.80	1.89	2.69	1.68	1.61	1.67
Gd	30	19				18
Tb	5.0	4.6	4.5			2.8
Dy	24	19				17
Ho	5.5	3.8				4.6
Er	12	13				9.5
Yb	16.8	15.6	15.0	11.1	10.9	8.3
Lu	2.15	2.12	1.96	1.56	1.57	1.30
Hf	25.7	23.2	18.3			15.6
Ta	2.0	2.2	2.0	2.1		1.3
W	0.43	0.40	0.24			0.22
Au	0.0016	0.0087	0.0019			0.0021
Th	3.05	3.05	0.76			1.25
U	0.80	0.69	0.28			0.35

Table 2. Concentrations of relevant elements in lunar fines and rock dissolved in HNO_3, and normalized decay rates.

Element	Lunar fines 84-18				Lunar rock 57-40		
	HNO_3 (25°C)	HNO_3 (70°C)	Residue	Total	HNO_3 (90°C)	Residue	Total
				Chemical analyses (percentage by weight)			
O	10.6	3.0	27.1	41.5	4.8	35.6	40.4
Si	3.9	0.8	15.0	19.7	3.0	15.9	18.9
Al	3.92	1.66	1.12	6.9	3.4	1.2	4.6
Mg	1.89	0.14	2.77	4.8	0.4	3.8	4.2
Ca	3.63	1.58	3.61	8.82	2.27	5.60	7.87
Ti	0.49		3.81	4.30	0.33	5.35	5.68
Fe	4.22	0.66	7.12	12.0	1.27	13.03	14.3
K	0.045	0.014	0.050	0.109	0.057	0.144	0.201
				Activity (dpm/kg)			
^{22}Na	32 ± 5	10 ± 2	19 ± 3	61 ± 6	9 ± 2		24 ± 6
^{26}Al	57 ± 13	37 ± 15	27 ± 14	121 ± 25	25 ± 10		70 ± 10
^{36}Cl	6.5 ± 0.28	2.0 ± 0.7	6.13 ± 0.29	14.6 ± 0.8	3.30 ± 0.31	8.85 ± 0.38	12.15 ± 0.5
^{37}Ar	14.4 ± 0.9	4.7 ± 4.3	14.1 ± 0.9	33.2 ± 4.5	—		
^{39}Ar	2.43 ± 0.14	1.18 ± 0.43	3.86 ± 0.20	7.5 ± 0.5	1.99 ± 0.17	7.09 ± 0.23	9.08 ± 0.29

Table 3. Production rates of various radioisotopes in disintegrations per minute per kilogram of target material.

Isotope	Target element					
	Mg	Al	Si	K	Ca	Fe
^{22}Na	100 ± 50	600 ± 200	100 ± 50			
^{26}Al		1000 ± 400	100 ± 50			
^{36}Cl fine					175 ± 8	
^{36}Cl rock					152 ± 9	
^{37}Ar fine					394 ± 18	
^{37}Ar rock						
^{39}Ar fine				4400 ± 500		7.5 ± 1.5*
^{39}Ar rock				3100 ± 500		7.5 ± 2.2*

*The production rate of ^{39}Ar on Ti is assumed to be four times that on Fe, corresponding to a hardness exponent of n equal to 2.5 in the spallation formula.

protons are emitted is extremely small; proton-induced reactions are not possible at all.

Argon-37, on the other hand, is essentially produced from Ca by the neutron-induced reaction ^{40}Ca(n, α) ^{37}Ar. Within the accuracy of the present analysis, ^{36}Cl must be ascribed entirely to Ca as well, although the production rate on Ti and Fe will certainly be comparable to that of ^{39}Ar on these elements.

The ratio of 10 for the production rate of ^{39}Ar from K to that of ^{37}Ar from Ca is about five times higher than the ratio of the effective cross sections for any reasonable choice for the neutron energy spectrum (*1, 6, 7*). Hence, one must either assume that there is a peculiar neutron energy spectrum with an extremely large fraction of the neutrons having energies below 2 Mev, or that the neutron intensity is strongly time-dependent.

Sodium-22 and aluminum-26 cannot be assigned to the different target elements with the same accuracy as the previous isotopes. Nevertheless, it is obvious that for both isotopes Al is the most important target element, which is clearly one reason for the higher decay rates of these isotopes in the fines as compared to the rock. The production of ^{26}Al from ^{27}Al does not imply that the reaction ^{27}Al(n,2n) is solely or even predominantly responsible, as the reaction ^{27}Al(p,pn) is possible as well.

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