Table 2. Chemical composition of lunar breccia and soil fines (in percent by weight).

Constituent	10019	10048	10060	311079
SiO_2	41.1	42.2	41.5	42.2
Al_2O_3	13.7	12.9	11.8	14.1
Fe_2O_3	0.00	0.00	0.00	0.00
FeO	15.7	15.7	17.0	15.3
MgO	7.86	7.54	7.52	7.94
CaO	11.9	11.4	11.6	12.1
Na_2O	0.93	0.52	0.78	0.54
K_2O	0.14	0.17	0.18	0.14
H_2O^-	0.00	0.00	0.00	0.00
Total Ti as TiO_2	8.25	8.95	9.15	7.60
P_2O_5	< 0.2	< 0.2	< 0.2	< 0.2
MnO	0.22	0.22	0.23	0.21
Cr_2O_3	0.32	0.31	0.33	0.31
ZrO_2	0.03	< 0.03	0.04	0.03
NiO	0.02	0.02	0.02	0.02
Total	100.15	99.91	100.13	100.47
Total Fe as Fe_2O_3	17.4	17.4	18.9	17.0
R_2O_3	40.3	40.0	40.5	39.3

940 mg of $Li_2B_4O_7$. No heavy absorber was added to the mix. After cooling, the fused glass was brought to 1200 mg with powdered cellulose and then was ground. Three hundred milligrams of the fused mix was pressed into a ½-inch-diameter disc and Na, Mg, Al, and Si were determined with a soft x-ray spectrometer; P, K, Ca, Ti, Mn, Fe, Cr, and Ni analyses were made with an x-ray milliprobe. The rest of the fused mix was pressed into a 1-inch-diameter disc for determination of Si, Al, Fe, Ca, Ti, Mn, Zr, Cr, and Ni.

Chemical determinations were made on all samples for H_2O^-, SiO_2, Na_2O, MgO, R_2O_3, and total reducing capacity. FeO was determined, after catalytic oxidation, on the lunar fines (sample 311079).

The compositional data for the allocated samples are grouped according to rock type and numerical sequence in Tables 1 and 2. The samples listed in Table 1 are type B (gabbro) except for sample 10022, a basalt. Samples 10003, 10022, 10024, 10050, and 10062 were whole rock fragments. Samples 10047 and 10049 were pulverized at the Lunar Receiving Laboratory. Sample 10058 was received as a whole rock fragment and as a pulverized sample.

Chemical compositions of three samples of breccia and one of the lunar fines are given in Table 2. Of the breccias, 10019 was a whole rock fragment, and 10048 and 10060 were received as pulverized samples. These new data support the ranges of ferrous iron, titania, magnesia, and chrome previously reported (*2*). The overall similarity in major element composition for all the samples is apparent. Differences are noted in the minor element contents; for example, the fines and the breccia are characterized by a relatively high NiO (200 ppm) when compared to the igneous rocks (< 10 ppm). In contrast to the previously reported high values for ZrO_2 (*1*, *2*), the new data show that ZrO_2 abundances do not exceed 400 ppm in any of the samples but are more abundant in the breccias and lunar soil fines. As a minor constituent, chromium is relatively abundant (2100 to 4000 ppm Cr_2O_3).

Summations (Tables 1 and 2) for the samples tend to be high and, at first glance, appear to be attributable to metallic iron because it is analytically incorporated in the cited FeO values. Determinations of the total reducing capacity (*3*) of the samples (Table 3) were found to be as much as 4.6 percent higher (equivalent to 1.8 percent additional metallic iron) than can be accounted for by the total iron (as FeO) content obtained by x-ray fluorescence analysis. Optical examination, coupled with calculations based on the assumption that the NiO content is totally associated with meteoritic iron, indicate that the contribution from metallic iron and troilite is no greater than 0.5 percent. The excessive reducing capacity of the returned lunar materials suggests the presence of an element occurring as a major constituent and capable of existing in a lower valence state such as Ti(III). To eliminate the possibility of Ti(III) contributing to the total reducing capacity, a catalytic oxidation was made before a volumetric determination of total iron as FeO. Duplicate volumetric analyses on sample 311079 gave identical results for FeO as those obtained by x-ray spectroscopy.

Table 3. Comparison of total Fe (as FeO) determined by x-ray spectroscopy with total reducing capacity (as FeO) of the lunar materials (in percent by weight).

Sample	Rock type	Reducing capacity	FeO value	Difference (+) as FeO
10003	Gabbro	22.4	19.8	2.6
10019	Breccia	19.4	15.7	3.7
10022	Basalt	21.0	18.9	2.1
10024	Gabbro	22.3	18.5	3.8
10047	Gabbro	19.8	19.0	0.8
10048	Breccia	20.3	15.7	4.6
10049	Gabbro	21.8	18.7	3.1
10050	Gabbro	19.2	17.3	1.9
10058†	Gabbro	19.3	17.3	2.0
10058*	Gabbro	20.3	18.2	2.1
10060	Breccia	20.8	17.0	3.8
10062	Gabbro	20.5	18.3	2.2
311079	Fines	19.4	15.3‡	4.1

* Whole rock. † Pulverized. ‡ The total iron content (as FeO) of sample 311079 was also determined chemically and found to be 15.2_5 and 15.3_6 percent.

The excessive reducing capacity and high summations strongly suggest the presence of Ti(III) in the lunar samples. Investigations continue in this direction.

HARRY J. ROSE, JR., FRANK CUTTITTA
EDWARD J. DWORNIK, M. K. CARRON
R. P. CHRISTIAN, J. R. LINDSAY
D. T. LIGON, R. R. LARSON
U.S. Geological Survey,
Washington, D.C. 20242

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3. The total reducing capacity was determined by dissolution of the samples with 5:3:3 $HF:H_2SO_4:H_3PO_4$ in excess $(NH_4)_3VO_4$ (oxidant) and subsequent back titration of remaining vanadium (V). Two separate determinations of each sample gave identical results.
4. Publication authorized by the director, U.S. Geological Survey.

4 January 1970, revised 6 January 1970

Emission Spectrographic Determination of Trace Elements in Lunar Samples

Abstract. *Eighteen minor or trace elements were detected and determined by emission spectroscopy. Direct d-c arc excitation of powdered samples was used with three variations in the procedure. Thirteen lunar samples consisting of four fine-grained igneous rocks, one medium-grained igneous rock, seven breccias, and one sample of fines were analyzed. The zinc and nickel concentrations in the breccias were approximately one order of magnitude greater than the concentrations of these elements in igneous rocks.*

Thirteen Apollo 11 lunar samples were processed and analyzed spectrographically for 44 elements. The samples we analyzed can be classified into four groups: (i) four samples of type A, fine-grained, vesicular igneous rocks; (ii) one sample of type B, medium-grained vuggy igneous rock; (iii) seven samples of breccias; and (iv) one sample of fines less than 1 mm in grain size from the bulk sample. These sample groups have been described (*1*).

The 12 rock samples consisted of one or more chips and some accompanying

Table 1. Elements detected by emission spectrography. Elemental abundances, in parts per million, are arranged according to rock type and listed in approximate order of volatility in the d-c arc.

Sample*	Element																	
	Zn	Cu	Ga	Rb	Li	Mn	Cr	Co	Ni	Ba‡	Sr‡	V	Be	Nb	Sc	La	Y	Zr
								Rock type A										
57	†	5.7	5.0	4.7	17	2150	2790	30	6.1	440	140	65	3.3	29	99	26	165	635
69	†	8.7	4.9	5.5	18	2390	2760	30	6.7	420	130	72	3.3	20	94	27	164	566
71	†	14	4.8	5.2	17	2230	3060	33	7.0	470	140	78	3.0	24	97	27	162	644
72	†	6.7	4.5	5.0	16	2230	2860	30	6.6	430	130	76	2.7	23	96	25	155	530
								Rock type B										
03	†	6.7	4.7	1.0	9	2580	1860	15	2.7	160	150	82	1.5	21	94	15	113	380
								Rock type C										
18	23	12	4.4	3.6	12	1660	2340	32	197	220	110	60	1.8	25	66	15	97	429
21	24	12	4.6	4.0	13	1770	2480	33	184	270	130	60	2.0	28	72	22	113	424
59	29	21	4.6	3.0	12	1990	2380	33	222	240	120	57	1.7	18	66	19	102	369
61	27	16	5.2	3.4	11	1820	2730	35	241	270	130	60	2.4	21	67	18	103	393
65	23	14	5.0	2.8	12	1925	2390	30	169	260	140	57	2.2	25	69	16	103	390
68	22	12	4.7	3.3	14	2020	2600	33	205	250	130	58	1.9	31	71	21	108	482
73	23	19	3.7	2.1	11	1880	2330	29	199	240	160	66	2.1	14	64	21	89	322
								Rock type D										
84	19	10	3.8	2.7	11	1960	1740	24	185	210	130	50	1.6	18	56	16	81	273

* Last two digits of NASA laboratory number. † Not detected at limit of 4 ppm. ‡ Line width, < 5 percent transmission from oscillogram.

fines. Each sample was crushed and pulverized prior to testing. Six of the samples were crushed with a steel diamond mortar prior to grinding to an impalpable powder with an agate mortar and pestle. The remainder of the samples were both crushed and ground in the agate mortar. The sample of fines was quartered twice, and one quarter of the original sample was ground in the agate mortar. A 200-mg portion of each finely ground sample was mixed with 50 mg of graphite powder (*2*); the mixture was ground in an agate mortar and stored in polyethylene capsules.

Three modifications of d-c arc emission spectrography were used: (i) a sample mixed with graphite was excited by an arc at 15 amperes d-c in air with a 3.4-m Ebert spectrograph, and 38 elements in the spectral region between 2300 and 4800 Å were determined (*3*); (ii) a sample mixed with Na_2CO_3 buffer was excited in an argon atmosphere with a 3-m Eagle spectrograph, and nine volatile elements, including Zn, Pb, and Ag, were determined in the second-order spectrum from 2400 to 3650 Å (*4*); and (iii) a sample mixed with a K_2CO_3 buffer was excited in an arc in air with a 3-m Eagle spectrograph, and Cs, Li, and Rb were determined in the spectral region from 6500 to 9000 Å (*5*). The coefficient of variation of the determinations in case (i) is ± 15 percent of the amount present; in cases (ii) and (iii) the coefficient of variation is ± 10 percent of the amount that is present.

Table 2. Elements not detected by any of the three d-c arc techniques used.

Element	Detection limits (ppm)
Ag	0.2
As	4
Au	0.2
B	10
Bi	1
Cd	8
Ce	100
Cs	1
Ge	1
Hf	20
Hg	8
In	1
Mo	2
Nd	100
P	2000
Pb	1
Pt	3
Re	30
Sb	100
Sn	10
Ta	100
Te	300
Th	100
Tl	1
U	500
W	200

Table 3. Average elemental concentrations in type A and type C lunar rocks compared to concentrations in terrestrial rocks (concentrations in parts per million).

Element	Type A	Type C	Basalts (*6*)	Ultramafic rocks (*6*)
Zn	< 4	24	105	50
Cu	9	15	87	10
Ga	5	5	17	1.5
Rb	5	3	30	0.2
Li	17	12	17	.X
Mn	2250	1870	1500	1620
Cr	2870	2460	170	1600
Co	31	32	48	150
Ni	7	202	130	2000
Ba	440	250	330	0.4
Sr	135	131	465	1
V	73	60	250	40
Be	3	2	1	.X
Nb	24	23	19	16
Sc	97	68	30	15
La	26	19	15	.X
Y	162	102	21	.X
Zr	594	401	140	45

The results of the analyses are listed in Table 1. The most obvious demarcation in the trace element concentrations occurs between the igneous rocks of types A and B, as compared to the breccias of types C and D. The concentration of nickel is 30 times higher in breccias than in igneous rocks. The concentration of zinc is between five and seven times higher in breccias than in igneous rocks; the magnitude of this difference depends on how much below the limit of detection (4 parts per million) is the concentration in the igneous rocks. In addition, there are several elements for which there are real but smaller differences in concentrations between the igneous and brecciated rocks: (i) Cu is approximately twice as concentrated in the breccias as in the igneous rocks; (ii) Rb and Li are 1½ times more concentrated in type A igneous rocks than in the breccias; (iii) a trend similar to that exhibited by Rb and Li is shown by Sc, La, and Y; (iv) Ba tends to be concentrated in type A igneous rocks, whereas Sr maintains a fairly even concentration in all samples. Several other examples can be noted.

Table 2 lists the elements not detected; also given is the lowest detection limit for the most applicable method of determination for each element.

Comparison (Table 3) of our data with values for terrestrial rocks (*6*) shows that these lunar samples do not closely resemble average terrestrial basalts or ultramafic rocks.

CHARLES ANNELL
ARMIN HELZ

U.S. Geological Survey,
Washington, D.C. 20242

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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 $\leqq 60\ \mu$m) 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 feld-