

served in lunar samples. The terrestrial basalts, however, are distinctly higher in In content than any lunar rocks. The highest Ir values in the lunar samples appear to be about an order of magnitude higher than those observed in basaltic rocks and achondrites.

On the basis of these limited data one can note that the samples collected in Mare Tranquillitatis are distinctly different from the logical comparison materials of Ca-rich (basaltic) achondrites and typical terrestrial rocks of basaltic composition. Our limited conclusions are: (i) Typical basaltic achondrites did not originate in the Mare Tranquillitatis area of the moon; and (ii) the lunar materials of basaltic composition differ from those found on the earth either as a result of differing fractionation processes or differing primitive starting materials, or both. These conclusions have been drawn previously (2).

The five Hawaiian rock samples are from the Waianae Volcano on the island of Oahu. Samples 6, 11, and 20 are from the lower member of this volcano [as described by MacDonald (10)] and were probably produced during a single stage of magmatic activity. Samples 31 and 178 are from the upper member of this volcano, and may not be as closely related to the former, more basic rocks. Nonetheless, it appears of some interest to consider all these rocks to be related and to attempt to define the behavior of Ga, Ge, and In during the course of magmatic activity. The five samples were chosen to form a suite of related rocks, extending from the most mafic sample, C-6, in order of increasing sample number to the most felsic sample, C-178. To observe possible trends through this suite, we plotted our data against the crystallization index defined by Poldervaart and Parker (11) (Fig. 1).

Gallium shows a pronounced enrichment during the course of magmatic fractionation [in disagreement with the data summarized by Prinz (3)]. Indium also appears to be enriched, although the C-31 point falls off a smooth curve fitted through the other points. The concentration of Ge does not appear to change appreciably during the fractionation process. Also shown are the concentrations of Na<sub>2</sub>O and TiO<sub>2</sub> in the same rocks as reported by MacDonald and Katsura (10). These are also enriched in the later differentiates, TiO<sub>2</sub> to about the same degree as Ga and In, and Na<sub>2</sub>O to a still greater extent.

One of the intriguing problems regarding the Mare Tranquillitatis samples

is their high TiO<sub>2</sub> content. The most plausible explanations of this observation are that the enrichment is the result of a high-temperature volatilization or partial condensation process or the result of magmatic fractionation, or some combination of these possibilities. If volatility is the major cause of the enrichment, one would expect a negative correlation between the contents of TiO<sub>2</sub> and of In, which forms relatively volatile compounds. If magmatic fractionation has established the trends in the lunar samples, our preliminary data indicate that a positive correlation between In and TiO<sub>2</sub> would result. We will search for evidence regarding these possibilities in the data to be published from these proceedings.

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## Multielement Analysis of Lunar Soil and Rocks

**Abstract.** Results for multielement analysis of lunar soil and of seven rocks returned by Apollo 11 are presented. Sixty-six elements were determined with spark source mass spectrography and neutron activation. U.S. Geological Survey standard W-1 was used as a comparative standard. Results indicate an apparent uniformity of composition among the samples. Comparison with solar, meteoritic, and terrestrial abundances reveals depletion of volatile elements and enrichment of the rare earths titanium, zirconium, yttrium, and hafnium. Although there is an overall similarity of the lunar material to basaltic achondrites and basalts, the differences suggest detailed geochemical processes special to the history of this material.

Chemical analyses of lunar soil and seven rocks from the Apollo 11 mission were performed with spark source mass spectrography (MS) and neutron activation analysis (NAA); this resulted in the determination of approximately 66 elements per sample. Both methods as used for terrestrial samples have previously been described (1). The U.S. Geological Survey standard diabase W-1 was again used as a multielement standard, and the same literature values were employed.

For the lunar analyses, a few changes have been made in these methods. One gram of each sample was crushed; then 200 mg was removed for NAA, and 500 mg was removed for MS. For the shorter irradiations in NAA, flux and irradiation times were changed to compensate for the smaller sample size. For the longer irradiations, the samples were inserted in the central thimble of the TRIGA reactor with a resultant flux of  $3.5 \times 10^{12}$  neutron/cm<sup>2</sup>-sec. In the case

of MS, the 500-mg samples were mixed with equal amounts of graphite (National Carbon Co. spectroscopic powder). Because of small sample size, accurate doping of an internal standard for MS was not possible. Zirconium present in the samples represented a suitable internal standard, and the NAA determination for this element was used in the MS calculations.

Results of the analysis of the eight lunar samples received at our laboratory are given in Table 1, along with the method employed. Results from the method having the better accuracy (as determined by past analyses of terrestrial and meteoritic materials) and the better analytical conditions (higher sensitivity, lower background, and so forth) were used. When these criteria were judged equivalent, an arithmetic average of the results of the two methods was reported. Since these multielement methods possess variations in precision for each element, only average values

are given. The relative standard deviation of the determinations by MS is 5 to 25 percent about the mean, whereas that of NAA is 10 percent or less. Accuracy, evaluated by analysis of terrestrial materials, is comparable to or

better than the precision. To complete the values for the major elements, Si was determined by atomic absorption spectrophotometry.

The results of both MS and NAA determinations depend on the accuracy of

published isotope ratios as applied to the lunar samples. In the determination of lead by MS, the isotope ratios did not correspond to published terrestrial values. Of the four stable lead isotopes, <sup>204</sup>Pb was obscured. A summation of

Table 1. Elemental abundances in the lunar samples studied. The results are grouped according to NASA sample type (2): A, fine-grained vesicular; B, coarse-grained crystalline; C, breccia; and D, soil. The sample of type D (84-55) is the fine fraction (<1 mm) of soil sample 10002. NAA, neutron activation analysis; MS, mass spectrography; AA, atomic absorption. Numbers used to designate samples are NASA laboratory numbers.

Element	Method	Type A rocks			Type B rocks		Type C rocks		Soil
		20-26	57-32	72-24	58-26	46-23	56-20	60-13	84-55
<i>Major elements (weight percent)</i>									
Si	AA	19.4	21.5	19.2	18.4	20.6	19.8	18.7	20.2
Al	NAA	5.9	4.0	4.0	5.4	6.2	5.7	6.0	7.3
Ti	NAA	6.1	6.5	6.7	5.8	5.0	5.6	5.1	4.1
Fe	NAA	14.7	15.7	15.4	15.2	13.2	14.8	13.8	12.5
Mg	NAA	5.0	3.7	4.3	3.4	5.5	2.8	4.6	4.6
Ca	NAA	10.3	10.1	10.3	11.0	9.8	11.0	10.4	9.6
Na	NAA	0.28	0.35	0.32	0.32	0.35	0.32	0.34	0.33
K	NAA	0.052	0.22	0.29	0.093	0.17	0.094	0.16	0.11
Mn	NAA	0.20	0.17	0.17	0.19	0.16	0.20	0.16	0.16
Cr	NAA	0.22	0.21	0.24	0.15	0.21	0.14	0.22	0.20
Zr	NAA	0.036	0.056	0.072	0.038	0.062	0.041	0.058	0.039
Ni*	NAA	0.006	0.004	0.003	0.008	0.007	0.005	0.007	0.017
V	NAA-MS	0.0059	0.0040	0.0062	0.0041	0.0068	0.0056	0.0062	0.0078
P	MS	0.070	0.041	0.070	0.024	0.10	0.033	0.060	0.14
<i>Trace elements (parts per million)</i>									
Li	MS	5	8	14	6	16	16	7	6
Be	MS	2	2.5	4	1.5	6	3	3	4
B	MS	1	4	4	2	9	2	3	2
N	MS	10	20	30	10	70	20	6	30
F	MS	85	70	100	50	220	30	80	66
Cl	MS	150	50	60	50	520	16	150	350
Sc	NAA	85	84	86	87	64	97	70	60
Co	NAA-MS	20	24	28	14	42	15	32	40
Cu	NAA	3.7	5.5	18	7.1	9.7	3.8	11	9.9
Zn	NAA	2.1	2.9	7.0	9.3	30	2.7	25	22
Ga	NAA	3.5	4.7	4.3	4.3	4.9	4.3	5.1	4.6
Ge	MS		1.3	1.1	1.2		1.2	1.4	0.7
As (~)	NAA	0.03	0.04	0.05	0.07	0.05	0.03	0.09	0.07
Se	MS	0.4				0.4		0.9	0.2
Br (~)	NAA	0.1	0.1	0.2	0.3	0.2	0.06	0.3	0.2
Rb	NAA-MS	2.8	4.8	5.7	1.2	3.6	2.0	4.0	4.4
Sr	NAA-MS	170	130	140	180	170	160	180	200
Y	MS	130	210	250	150	190	180	210	150
Nb	MS	36	42	45	47	38	37	45	33
Mo	NAA-MS	0.4	0.4	0.4	0.4	0.7	0.4	0.7	0.7
Pd	MS	0.09	0.1	0.1	0.2	0.1	0.1		0.04
Ag	MS	0.1	0.04	0.6	0.07	0.02	0.2	0.01	0.1
Cd	MS		0.9	1	0.7	0.8	0.9	0.3	0.3
In	MS		0.07	2	0.6	0.08	0.06		0.5
Sn	MS		0.6	0.4	1.2		0.3		0.7
Sb	NAA	0.01	0.005	0.01	0.01	0.005	0.005	0.005	0.005
Cs	NAA-MS	0.2	0.2	0.3	0.3	0.2	0.06	0.2	0.2
Ba	NAA-MS	96	280	300	140	280	100	250	220
La	NAA-MS	11	31	35	16	23	13	24	22
Ce	NAA-MS	34	83	96	45	67	42	62	50
Pr	MS	8.7	22	20	13	20	12	13	9
Nd	NAA-MS	43	84	120	72	70	82	96	46
Sm	NAA-MS	14	24	28	22	20	23	24	18
Eu	NAA-MS	1.6	2.1	2.2	3.0	2.0	2.5	2.0	1.9
Gd	NAA-MS	17	26	31	22	20	24	28	20
Tb	NAA-MS	3.5	5.6	6.8	5.4	4.5	5.4	5.0	3.8
Dy	MS	30	42	45	39	30	40	41	25
Ho	NAA-MS	7	8	10	9	9	9	10	6
Er	MS	19	32	35	36	23	27	30	15
Tm	NAA-MS	1.2	2.3	2.8	2.0	1.6	2.1	1.8	1.2
Yb	NAA-MS	15	26	28	22	20	20	22	12
Lu	NAA-MS	1.5	2.2	2.6	2.3	1.8	1.8	2.0	1.4
Hf	NAA-MS	11	15	18	13	11	11	13	9
Ta	NAA	1.3	1.2	1.8	1.0	1.7	2.2	1.7	1.3
W	NAA	0.13	0.42	0.42	0.36	0.35	0.15	0.35	0.25
Tl	MS								0.2
Pb	MS		3	3	3	2	1.2	3	6
Th	NAA-MS	1.5	4.5	4.8	1.1	2.8	1.4	3.0	2.3
U	NAA	0.14	0.56	0.50	0.20	0.58	0.21	0.60	0.48

\* Third decimal place approximate.

the intensities of the remaining three isotopes was used to compute the elemental concentration. In terrestrial basaltic samples, this would lead to a value 2 percent lower than expected, which is well within experimental error.

For the elements Ru, Rh, Te, and I, mass spectrographic determinations were limited by the lack of sensitivity factors. A comparison of the intensities shows that Ru and Te are approximately of the same concentrations as in terrestrial basaltic materials as exemplified by the USGS standard BCR-1; Rh is enhanced by a factor of 2 to 3; and I is depleted by a factor of 2. The elements Re, Os, and Ir were not observed; their detection limits are approximately 0.1 ppm for MS in these samples. Similarly, Hg was not detected by NAA at 0.02 ppm.

The accuracy of elemental determinations is dependent on the amount of possible contaminants. The values for N, F, Cl, Ag, and In may have been influenced by contamination before they were received. The samples were received under a dry nitrogen blanket and prepared for analysis in dry air; this resulted in the possibility of surface N<sub>2</sub> adsorption. On the lunar surface, the samples were sealed in Teflon bags, and the sample boxes were sealed with In-Al alloy O-ring. In addition, a microscopic examination of the samples as received from NASA revealed foreign material in the form of translucent fibers, possibly from the plastic packaging materials.

At the 2 $\sigma$  level of significance, there is neither general sample-to-sample variance, nor is there a sample type-to-type variation of elemental abundances (Table 1). When variations at the 1 $\sigma$  level are examined, division of the samples into two groups, based on the behavior of 13 elements, is possible. For example, if the samples are arranged in order of increasing potassium content, rocks 20, 58, and 56 fall into one group and rocks 60, 46, 57, and 72 fall into another group, with the lunar fine material 84 having intermediate values for these elements but approaching the second group. These groups do not follow the textural types suggested by the Preliminary Examination Team (2). However, it should be emphasized that such a compositional classification is possible only if the 1 $\sigma$  variation in values is regarded as significant.

Of the elements studied, there is greatest variation among the eight samples for P, K, Cl, F, In, Zn, and Cu. This variation cannot be attributed to

analytical imprecision and must be regarded as reflecting the variation of the samples received by this laboratory. In the case of Zr and Yb, our values are significantly different from the data reported for the same samples by the Preliminary Examination Team. At present, we are unable to assess the source of this discrepancy, apart from commenting on the possible sampling difficulties in the distribution of the samples by NASA.

Comparison of the average lunar elemental abundance data with those of solar (recalculated on a H, He-free basis) meteoritic and terrestrial crust values results in the following observations: In the lunar material, volatile elements such as Sb, As, Br, Cu, Zn and Hg appear depleted. Sodium and potassium are depleted when compared to terrestrial crust and basalts, and they are enriched when compared to solar abundances. The rare earth and refractory elements such as Ti, Zr, Y, and Hf appear enriched. The lunar rare earth abundances, when normalized against La, correspond approximately with solar abundances, are slightly higher than in achondrites, and are considerably higher than those of the terrestrial crust.

With regard to the major elements, the lunar samples more closely resemble basaltic achondrites and, to a lesser extent, terrestrial basalts, with the notable exceptions of Ti and Zr, which are sub-

stantially enriched in the lunar material. The trace element distribution in the lunar materials is also comparable to that in achondrites and basalts. Comparison with basalts shows that the trace elements, though dispersed, are evenly distributed about a 1:1 trend line. Comparison with achondrites shows that most trace elements are uniformly enriched in the lunar materials.

It is apparent that the lunar samples are compositionally different from all materials with which they have been compared. Although there is closer similarity to basaltic achondrites and basalts, the lunar material does not match them in all respects. This uniqueness implies detailed geochemical processes special to the history of this material.

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## Neutron Activation Analysis of Milligram Quantities of Lunar Rocks and Soils

**Abstract.** *A neutron activation scheme for determining 25 elements in lunar samples weighing 20 milligrams is described and applied to a suite of Apollo 11 lunar materials. Concentrations of titanium, chromium, scandium, tantalum, hafnium, and rare earths are higher than in average basalt, whereas cobalt, nickel, and copper are lower. Chemical variations show groupings of elements possibly associated with the major phases, pyroxene, plagioclase, and ilmenite. The high concentration of "refractory oxides" and low volatile content implies that the raw material for the Apollo 11 samples was condensed from the primitive solar nebula at high temperatures.*

The aim of our program of investigation of lunar material was to develop and employ a neutron activation analysis procedure for the analysis of 20 mg or less of rock or mineral for a large part of the periodic chart. The method we developed is of paramount importance when only small quantities of material are available for analysis. This situation may arise either from a paucity of sample or, more likely, in the analysis

of mineral separate fractions from lunar rock and soil. The procedure was adapted from the one described by Perlman and Asaro (1).

The general analytical scheme starts with a short neutron irradiation immediately followed by counting with a Ge(Li) diode detector, then proceeding to a longer irradiation and counting with the same system after longer waiting periods. Finally chemical separations of