

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 N₂ 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 σ 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 σ 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 σ 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

Table 1. Chemical composition of Apollo 11 lunar rocks and soil. Values in parts per million except Fe and Ti in percentage. A blank indicates that no determination was made. Explanations for the notes in column 2 are as follows: (1) Irradiation B in highly thermalized neutron flux of 4.5×10^{12} neutrons $\text{cm}^{-2} \text{sec}^{-1}$ for 30 minutes. Counting began 3 hours after removal from pile. Irradiation in type 2 planchet, counting in type 1 planchet. (2) Irradiation B, uranium determined by spark counting of induced fission tracks in Lexan clamped on type 2 planchet. (3) Irradiation B, counting began 18 hours after removal from pile. Irradiation in type 2 planchet, counting in type 1 planchet. (4) Irradiation A in core of reactor at thermal neutron flux of 3×10^{13} neutrons $\text{cm}^{-2} \text{sec}^{-1}$ and large fast neutron component for 3 days. Counting began 8 days after removal from pile. Irradiation and counting in type 1 planchet. (5) Irradiation A, counting began 30 days after removal from pile. Normalization to europium values from irradiation B. (6) Chemical separation and counting as described in text. (7) Probably contaminated.

Element	Note	Vesicular basalt 10020	Gabbro 10044	Breccia 10046	Gabbro 10056	Gabbro 10062	Soil 10084	Breccia 10021	Vesicular basalt 10049	Vesicular basalt 10057
Na	3	2680*	3630*	3720*		2990*	3000*	3470	3800	4050
K	3	1260*	1090*	1200*		230*	1000*	1720	2350	3610
Mn	1	2130*	2290*	1760*	2140*	1510*	1250*	1580	1790	1930
Cu	3	35*	47*	47*		30*	38*	46*	48	60
Dy	1	18*	36*	20*	34*	22*	17*	23	31	37
Eu	3	1.5*	3.0*	1.9*	2.9	1.8*	2.0*	1.8	2.1	2.5
Sm	3	7.6*	18*	13*	17	10*	8.7*	12	18	17
La	4	7.7	14	18	12	12	20			
Yb	4	6.6	9.5	8.7	8.3	6.3	9.5			
Lu	4	0.81	1.3	1.2	1.2	0.87	1.3			
Ce	6	47	86	78	75	48	79			
Fe (%)	5	14	13	12	13	12	14			
Cr	5	2400	1600	1970	1410	1310	2220			
Co	5	21	13	30	14	13	33			
Ni	6	160*		35*	37*		320*			
Sc	5	98	100	71	109	76	80			
Ti (%)	4	5.1	3.7	3.9	3.6	3.9	4.4			
Hf	5	6.6	13	11	11	10	11			
Zr	6	260*	660*	370*			380*			
Ta	5	2.2	2.7	1.8	2.6	1.8	1.8			
U	2	0.25*	0.47*	0.72*	0.45*	0.32*	0.33*	0.39*	0.74	0.48
Ag	6, 7	1.3	0.41*	1.3	0.16*	0.17	0.25			

*Single determination. All others are the average of duplicate determinations.

specific fractions are performed on the sample, and counting is done by either Ge(Li) detector or NaI(Tl) detector, depending on efficiency and purity requirements.

Approximately 250 mg of a lunar rock or soil sample is crushed and ground in an Alundum mortar. Accurately weighed 20-mg aliquots are mixed in a small agate mortar with 80 mg of chromatographic grade cellulose and pelletized with a standard KBr pelletizer under 280 bars pressure. The diameter of the pellet is 1.3 cm, and its thickness is less than 1 mm.

Initially our procedure involved the transfer of the pellet to an accurately weighed high purity (99.9999 percent) aluminum foil planchet just large enough to receive the pellet. The planchet was capped and crimped to form a thin disk. This planchet we shall designate as the type 1 planchet. A standard silicate-matrix material (the "standard pot" made and analyzed by Perlman and Asaro and analyzed by us independently) was treated in identical fashion. In our initial irradiation sequence (called "irradiation A") the samples and standard were placed radially on edge around a cylinder and irradiated. During irradiation the cylinder is rotated around the axis to guarantee a homogeneous flux for all samples and standards.

In irradiation A using type 1 planchets the samples and the aluminum planchets were counted as a whole, and subtraction for the contaminants in the aluminum was made using a blank. The high amounts of ^{24}Na produced in the aluminum, the presence of a large amount of copper and a variable gold contamination in the aluminum foil, as well as the desirability of determining uranium by fission track counting (2), led us to develop a new removable container for the pellets. The new planchet is constructed so that an aluminum ring clamps a sheet of Lexan plastic (to detect induced uranium fission tracks) over the pellet seated in a machined slot. This planchet, hereafter designated the type 2 planchet, was used in a second irradiation sequence (irradiation B).

Throughout all the irradiations the cellulose binder, although blackened, maintains its cohesive role, and the pellet can be transferred without loss.

The detailed program of irradiations and countings is given below. All irradiations were performed at the Union Carbide "swimming pool" reactor at Sterling Forest, New York, a 2-hour drive from New Haven, Connecticut, and the counting was done at Yale.

1) The samples are given a 30-minute irradiation in type 2 planchets in a highly thermalized portion of the reactor at a flux of about 4.5×10^{12} neutrons

$\text{cm}^{-2} \text{sec}^{-1}$. Three hours later, after removal from the pile and after separation of the Lexan, which is etched and spark-counted for induced fission tracks from uranium (2), the pellet is transferred to a type 1 planchet and counted for Mn and Dy. Because of excess interference of Ga with the Mn peak in the standard pot, the USGS standard diabase W-1 was used as the standard. Decay for 18 hours is then followed by counting for Na, K, Cu, Sm, and Eu. The Ge(Li) diode detector is used for this part.

2) A long irradiation of the samples in type 1 planchets is next done for 3 days in the core of the reactor with a thermal neutron flux of 3×10^{13} neutrons $\text{cm}^{-2} \text{sec}^{-1}$ and a large fast neutron component. After 8 days cooling following removal from the pile, the total planchet is counted for short-lived (2- to 4-day half-lives) nuclides. Thirty days after removal from the pile the samples in the planchets are counted again to obtain results for the long-lived nuclides. The Ge(Li) diode detector is used for this part.

3) After the Ge(Li) detector counting sequence is over, the samples are transferred from the type 1 planchet to a nickel crucible, mixed with 500 mg of a solid carrier mixture charge containing the elements sought as oxides, and fused with 10 g NaOH and 10 g Na_2O_2 for half an hour. The fused mass is disag-

gregated in boiling water and centrifuged several times to separate the water-soluble components from the insoluble residue. The residue is dissolved in hydrochloric acid and passed through a column (15 cm long by 3 cm in diameter) containing Dowex-1 resin (50–100 mesh) in chloride form. Two column volumes each of the following acid solutions were passed and collected sequentially: 12N HCl carries the rare earths, Ag; 8N HCl carries Ti, Zr, Hf; 4N HCl carries Co; 0.1N HNO₃ carries Hg. Other elements, of course, are also removed from the column with the sought elements. From the appropriate fraction the following elements are separated, purified if necessary, and counted: Silver is separated and counted with the NaI detector, chemical yield is determined and compared with a silver standard; the remaining solution containing Sc and the rare earths is evaporated to dryness on a planchet and counted on the Ge(Li) detector. The Ce/Sc count ratio combined with the previously determined Sc concentration gives the Ce concentration, as compared with the standard pot, without the necessity of yield determination or further purification. The cobalt fraction containing ⁶⁰Co and ⁵⁸Co from n,p on ⁵⁸Ni is purified and counted on the NaI detector, the count ratio ⁵⁸Co/⁶⁰Co is compared with the standard pot, and the previously determined cobalt concentration gives the results for nickel. The Zr- and Hf-bearing fraction is evaporated to dryness and counted on the Ge(Li) detector, and the Zr/Hf count ratio combined with the previously determined Hf concentration gives the Zr concentration as compared with the standard pot without yield determination or further purification.

Selenium is separated from the water-soluble fraction by passing SO₂ through the acidified solution. Counting is done on the Ge(Li) detector.

The results of our analyses to date are listed in Table 1. Because of probable weighing problems in the irradiation A suite between samples and standards (suspected first by the low Ti results), all the numbers obtained from this irradiation sequence were corrected by the use of data from irradiation B. All values from irradiation A are normalized to the europium determined carefully together with the other short-lived nuclides in irradiation B.

Duplicate results indicate an error of about 5 to 10 percent (coefficient of variations determined from the ranges of a pooled sample). We think that most

of this error is due to heterogeneities or sample handling since the counting errors in most cases are lower.

Many of the distinctive chemical properties of the Apollo 11 materials were outlined in the published preliminary results (3). We confirm the high rare earth, Ti, Zr, and Cr contents and the low Mn, Co, and Ni contents. In addition, the results given in Table 1 show a deficiency of europium relative to other rare earths as compared with chondrites. Tantalum and hafnium are considerably higher in Apollo 11 site materials than in terrestrial basalts.

The elemental abundances vary among the several Apollo 11 site materials we have examined. Roughly, it appears that three coherent groups exist. One group varying together is Mn, Sc, Ta, Hf, and the rare earths; a second group appears to be Fe, Ti, Co, and Cr; and a third group is Na and U. If we conceive of Apollo 11 material as being composites of different proportions of three dominant phases, pyroxene, ilmenite, and plagioclase, the trace element groupings may be crudely explained as strong associations with these phases. Separated portions must be analyzed before this point can be made explicit.

Although it is premature to present a quantitative model for the chemical makeup of Apollo 11 site materials, several constraints are imposed by the data. The low cobalt and nickel concentrations relative to chromium and scandium, and the low abundance of metallic iron, implies that these components were either not accumulated or were separated out by a secondary process. The high abundances of Ti, Cr, Sc, Ta, Hf,

and rare earths imply that the raw material for Apollo 11 material could be a condensate from the solar nebula at temperatures between the higher temperature for the condensation of metallic iron and nickel and the lower temperature for the condensation of sulfides and proton-rich materials, a general model suggested by several people (4). The phases and their variations now observed may be due to the redistribution of the elements at the time of impact or as the result of some other magma-producing process.

The analytical procedure we have described is being modified to include an initial x-ray fluorescence scan of the pellet in the type 2 planchet before irradiation. Hence, on the same 20-mg sample we should obtain useful data for Ca, Fe, Ti, Sr, Y, and Zr on the specific sample to be analyzed by neutron activation. Our method is most suitable for small samples and, in particular, may be valuable for the analysis of separated mineral phases and glass beads. Results on a sample as small as 5 mg may be adequate for many problems.

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Elemental Composition of Lunar Surface Material

Abstract. *Elemental abundances, so far obtained, derived from the analysis of Apollo 11 lunar material are reported. Similarities and differences exist between lunar material, the eucritic achondrites, and the augite achondrite Angra dos Reis, the analysis of which is also reported.*

We present here the results of our initial analytical work on (i) lunar fines (sample 10084), (ii) lunar rock (sample 10060,26), (iii) glassy spheres (sample 10085/30/5) received, respectively, on 19 September, 23 October, and 19 November 1969. We also give some data on the elemental abundances in the augite achondrite Angra dos Reis, of which we were able to get 240 mg (BM 63233). In order to give approximate results in an initial survey of as many

elements as possible, we used the following methods: spark source mass spectrography (SSM), emission spectrography (E), and x-ray fluorescence spectrometry (XRF). To give more accurate results for a smaller number of elements, we used activation analysis (AA; instrumental, neutron, activation analysis, INAA; radiochemical, neutron activation analysis, RNAA; radiochemical, high-energy gamma, activation analysis, RGAA) and mass spectrometric isotope