Reports

Chemical Composition of the Lunar Surface in Mare Tranquillitatis

Abstract. *More precise and comprehensive analytical results have been derived for lunar material at the Surveyor V landing site from alpha-scattering data. The composition is, in general, basaltic; the low sodium and high titanium contents, however, are distinctly different from the abundances in meteorites or common terrestrial rocks.*

Preliminary chemical analyses of lunar surface material at three locations on the moon (two mare and one terra sites) have been reported (*1–3*). These analyses were obtained by the alpha-scattering technique on three of the Surveyor soft landings on the moon in 1967–1968. The data from Surveyor V, which landed in Mare Tranquillitatis, have now been processed more completely. This processing made use of more data from the mission than were available for the preliminary report (*1*), more detailed checks of data quality, more precise calibration information for the instrument, and improved calculational techniques for reduction of the data. In addition, a spare flight instrument has been used to analyze a series of terrestrial rocks of known composition, under conditions approximating those of the missions, in order to obtain a more current estimate of the reliability of this technique. This work has led to significantly more comprehensive and precise analytical results for Mare Tranquillitatis than reported in (*1*).

The alpha-scattering technique of chemical analysis and the Surveyor missions carrying this experiment have been described (*1–4*). In the studies reported here, the spare instrument was used to obtain a library of backscattered-alpha and proton spectra for pure elements and relatively simple chemical compounds. Spectra were also obtained from 11 powdered rocks of known composition, ranging from ultrabasic rocks to granites. The rock data were then treated by both the least-squares fitting techniques involving elemental libraries (*4, 5*) and a variant which uses libraries containing spectra from the most important oxide constituents of rocks. This latter approach minimizes the dependence of the results on empirical stopping-power relationships.

The accuracy of the results is appreciably better than previously reported (*4*). This is due to the use of higher quality Cm^{242} alpha sources, more stable detectors and electronics, and analysis in terms of oxides. For example, the accuracy is sufficient to distinguish between the two basalts (USGS W-1 and BCR-1) and between the two granites (USGS G-1 and G-2) included in the series of rocks. Comparison of the results of the alpha-scattering technique with those of conventional methods reveals small biases (0.7 atom percent high for carbon, 0.8 atom percent low for oxygen, $\leqq 0.3$ atom percent for other elements). The root-mean-square deviations of the alpha analyses from conventional analyses, after subtraction of these small biases, are taken as measures of the precision of the method and are given in column 3 of Table 1 for eight of the most important elements in rocks.

When a 21-component library is used to interpret the data from the rocks, it is found that the amounts calculated for the principal constituents are not affected appreciably. The sensitivity of the technique for elements such as B, N, F, P, Cl, and S is better than 1 atom percent. Under laboratory conditions, potassium and calcium are determined semiquantitatively; the results invariably show which of the two is the more abundant. Although all of the rocks examined contained less than 1 atom percent of titanium, the amounts of this element were adequately determined.

The Surveyor V mission data used for this report came from the original

Table 1. Chemical analyses on the Surveyor V mission. All values and errors are expressed as atom percent on a hydrogen-free basis.

Elements		Precision of the method	Standard glass		Mare Tranquillitatis surface material		
Mass range	Symbol		Composition	Alpha analysis*	Sample 1*	Sample 2*	Estimated errors†
12	C	±0.3			0.2 ± 0.3	0.9 ± 0.2	±0.8
16	O	±0.8	58.6	60.1 ± 3.2	61.6 ± 1.4	60.9 ± 0.8	±2.0
19	F				0.06 ± 0.09	0.05 ± 0.06	±0.2
23	Na	±0.2	7.7	7.1 ± 0.6	0.34 ± 0.14	0.45 ± 0.10	±0.4
24–26	Mg	±1.0	8.5	9.1 ± 1.4	2.8 ± 0.5	2.4 ± 0.2	±1.5
27	Al	±0.2	1.5	2.0 ± 0.7	6.2 ± 0.2	6.2 ± 0.2	±0.9
28–30	Si	±0.7	17.2	14.9 ± 3.9	16.3 ± 0.5	17.4 ± 0.4	±1.7
31–38	"S"				0.3 ± 0.7	0.0	±0.5
39–44	"Ca"	±0.4	0	0.4 ± 1.5	6.3 ± 0.4	5.4 ± 0.3	±0.9
45–51	"Ti"				1.9 ± 0.4	2.3 ± 0.3	±0.8
52–61	"Fe"	±0.2	6.5	6.9 ± 0.6	3.7 ± 0.2	3.7 ± 0.2	±0.6
62–72	"Zn"				< 0.16	< 0.09	
73–90	"Sr"				< 0.07	< 0.06	
91–117	Zr–In				< 0.05	< 0.06	
118–238	Sn–U				< 0.07	< 0.07	

* The values are the results of the least-squares treatment using an eight-element library for the standard glass and a 14-element library for the lunar surface samples. They have been corrected for the small biases of the method. The errors quoted here are the $1\ \sigma$ statistical errors. † The estimated errors include estimates of systematic as well as statistical errors, at the 90-percent confidence level.

recordings made at the tracking stations of the NASA Deep Space Network in Australia, Spain, and California. Overlap periods during which data were recorded at two stations or on different magnetic tapes at the same station were examined and found to have very few discrepancies. A nonredundant, chronological record of the individual alpha and proton events and of pertinent engineering data was then prepared. Detailed examination of these data lends confidence in the overall performance of the instrument.

Small adjustments in the energy scales of the spectra were made in order to correct for changes in instrument characteristics induced by temperature variations on the moon during measurements on a given sample. In the alpha mode, these corrections were based on the observed variation in the positions of the Es^{254} calibration peak and of the prominent O^{16} feature in the lunar spectra. In the proton mode the data of the electronic-pulser calibration were used. These corrections corresponded to a root-mean-square deviation in the gain of the instrument of only 0.4 percent.

After the energy-scale corrections were made, appropriate background spectra were subtracted from the lunar data. These spectra were constructed from the brief (192-minute) measurements in the background phase of the experiment on the moon, from the preflight measurements at Cape Kennedy, and from calculated cosmic-ray contributions. The contribution of the background to the lunar sample measurements has been illustrated in the preliminary report (*1*) and is, in general, small.

Table 2. An oxide composition* of lunar mare material calculated from Surveyor V results.

Oxide	Weight percent
Na_2O	0.6
MgO	4.4
Al_2O_3	14.4
SiO_2	46.4
CaO	14.5
TiO_2	7.6
FeO	12.1
	100.0

* Calculated from the mean values from Table 1, neglecting the apportionment of the apparent excess of 1.6 atom percent of oxygen.

After background subtraction, the lunar data were analyzed in terms of a library of spectra obtained with the spare instrument. This library was used, rather than that obtained a year before launch with the actual flight instrument, because it was more complete, was obtained with Cm^{242} alpha sources closer to flight quality, and agreed better with the brief preflight measurements made on several standard materials. The applicability of this more complete library is reinforced by the satisfactory results of the terrestrial rock analyses and of analyses of the standard glass sample on the moon.

Only 78.6 minutes of useful data were accumulated on this standard sample on the Surveyor V mission. The results of an eight-element analysis of these data are shown in Table 1. Because of the short measurement time, the statistical errors of the least-squares treatment are rather large, but the agreement with the known composition is adequate. This is further indication that the instrument was operating satisfactorily on the moon.

Two lunar samples were examined on the Surveyor V mission. The data from 1087 minutes of measurement (~ 90 percent of the available data) on the first sample passed tests of reliability. For the second sample, tested data from 2317 minutes of operation were used. After the small corrections to the energy scales were made and the backgrounds subtracted, the lunar-sample data were analyzed by a least-squares treatment using a library of 14 components. The library spectra for the elements Na, Mg, Al, Si, K, and Ca were those of the appropriate oxides; for all other components (including oxygen) they were elemental spectra.

Results of the data reduction of both lunar samples are included in Table 1. The value for each element in each sample is given along with its statistical error, as determined from the least-squares analysis. The correction for the bias of the method has already been applied. The last column in Table 1 presents estimates of the errors (at the 90 percent confidence level) that take into account possible systematic effects.

The results for the principal constituents do not change appreciably if the number of components in the library is increased from 14 to 21. Although, in the laboratory, the technique marginally distinguishes between K and Ca, the conditions of the lunar analysis are considered sufficiently uncertain so that values are quoted in Table 1 only for "Ca," the sum of the two. The situation is different in the case of "Ti," elements with mass numbers $45 < A < 51$. Here, even the raw data of both samples indicate their presence in significant amounts. The lunar-sample and calibration data were examined carefully for evidence of instrument malfunction which could contribute spurious events

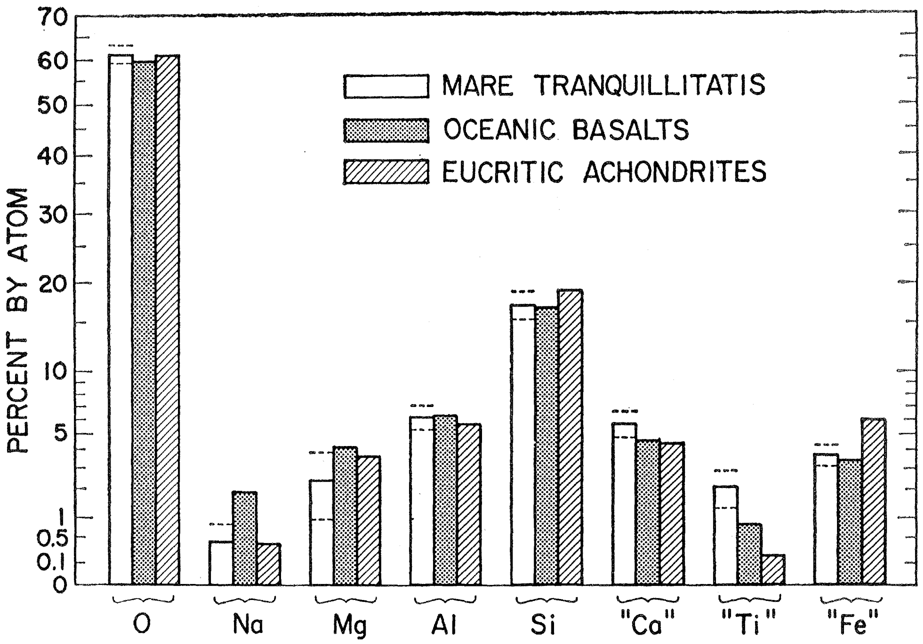

Fig. 1. Comparison of the chemical composition of lunar surface material in Mare Tranquillitatis with compositions of oceanic basalts and eucritic meteorites. The values are plotted on a square-root scale with estimated errors indicated for the lunar results. The lunar values are averages of samples 1 and 2; the values for basalts are from (*6*); for eucrites, from (*7*).

to the region sensitive to titanium. Although a minor misbehavior appeared in some of the data, it seems incapable of explaining the values obtained; data in periods not displaying this anomaly gave the same analytical results. Limits are given in Table 1 for groups of elements with masses greater than 61. In addition to the spectra of elements listed in Table 1, those of B, N, P, and Cl have been included in the libraries for the analyses, but have been found to make no contribution to the lunar-sample spectra.

The results presented in Table 1 for the composition of lunar surface material are within the ranges given in the preliminary report for Surveyor V (*1*). The errors assigned now, however, are considerably smaller.

In general, the data for the two lunar samples examined on the mission agree. A major disagreement is in the values for carbon. In view of the uncertainties uncovered in the analysis for this element in terrestrial rocks by this technique, it cannot be concluded that carbon has been detected in lunar surface material. Its abundance is almost certainly less than 2 atom percent.

The amount of sodium, reported earlier only as an upper limit of 2 percent, has now been set at a value of 0.4 percent. In addition, the presence of titanium in significant amounts has been established. The data on the other minor elements speak primarily to their absence in appreciable amounts.

The values for oxygen in Table 1 are slightly greater than required to oxidize the iron to FeO and all of the other metals to oxides. This slight excess of oxygen, if real, may be in the form of water, carbonates, or higher oxides of iron. If the mean values of the lunar surface analyses of Table 1 are converted to an oxide weight composition, the results in Table 2 are obtained.

The more precise results in Table 1 make even more certain most of the conclusions drawn in the preliminary reports: the chemical composition does not correspond to that of the nonvolatile components of the sun's atmosphere, to that of terrestrial ultrabasic rocks, or to that of the most common chondritic meteorites. The low silicon and high iron and calcium values rule out a granitic composition. The preliminary results indicated a similarity in chemical composition with that of terrestrial basalts and basaltic achondrites. The comparison of the present, more precise and comprehensive, data with these two classes of rocks is shown in Fig. 1. The three most abundant elements (oxygen, silicon, and aluminum) still agree within our estimated errors. On the other hand, the low value for sodium and high value for titanium appear incompatible with the composition of most terrestrial basalts; the high value for titanium and the relatively low value for iron are at variance with the content of these elements in eucrites and other calcium-rich achondrites. Thus, there appears to be no common material on earth that matches, in all respects, the chemical composition of lunar surface material at Mare Tranquillitatis. This uniqueness suggests detailed geochemical processes somewhat special to the history of this material. Moreover, the present, more complete, analysis of the Surveyor V data gives evidence that mare materials in different parts of the moon differ in at least one minor constituent. The alpha spectrum at the Surveyor VI mare site (Sinus Medii) differed slightly but significantly from Surveyor V spectra in the energy region sensitive to the presence of titanium (*2*). There is a clear indication that the titanium content at Sinus Medii is less than at the Surveyor V site.

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8. Work at the University of Chicago aided by NASA grant NGR-14-001-128; at the Jet Propulsion Laboratory, by NASA contract NAS-7-1000; and at the Argonne National Laboratory, by the AEC. Most of the experimental work and calculations were performed by T. E. Economou and K. P. Sowinski of the Enrico Fermi Institute, University of Chicago. Dr. J. A. Wood, Smithsonian Astrophysical Laboratory, provided data for the comparisons with terrestrial rocks and meteorites. Dr. N. Sugarman, University of Chicago, has assisted in the critical evaluation of Surveyor data.

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Rare-Earth Elements and High Pressures

Abstract. *Praseodymium, under very high pressures, shows a magnetic behavior similar to that of cerium at normal pressure.*

One can observe the magnetic behavior of solid solutions of the rare earths in ZrB_{12} under the high pressures exerted by the extreme rigidity of the boron lattice. Of all known dodecaborides, ZrB_{12} has the smallest lattice constant, $a_0 = 7.408$ Å (*1*). We have been able to substitute several atom percent of most rare-earth elements for Zr in ZrB_{12}. The atomic radius of Zr (1.60 Å) is much smaller than the atomic radii of the rare earths, which range from 1.86 Å for La to 1.72 Å for Lu. Since ZrB_{12} is superconducting at 6°K (*2*), an indication of the effect of this pressure on the magnetic configuration of the dissolved

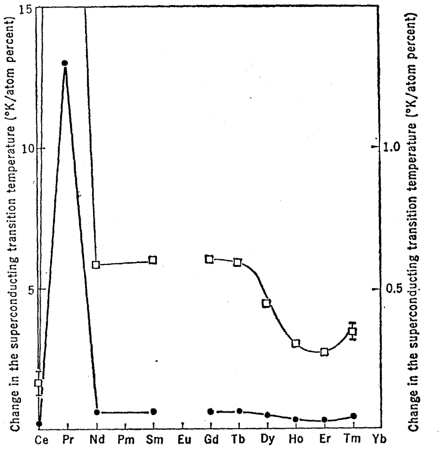

Fig. 1. Depression of the superconducting transition temperature of ZrB_{12} by rare-earth impurities; right scale (□) is an expanded version of the left scale (●).

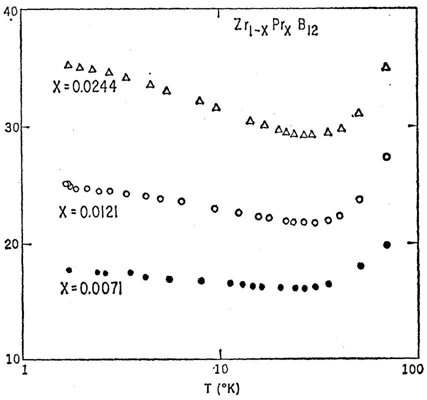

Fig. 2. Electrical resistivity (ρ) of $Zr_{1-x}Pr_xB_{12}$ alloys plotted against the logarithm of the temperature.