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# The Chemical Composition of the Lunar Surface

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In the last 5 years the chemical composition of the material making up the lunar surface has been determined at eleven locations on the moon. This type of information was first obtained, in 1967-1968, from the unmanned Surveyor missions which employed a new method of chemical analysis, a method based on the interaction of  $\alpha$  particles with matter. Since these Surveyor missions, both manned (Apollo) and unmanned (Luna) missions have brought back samples from the moon for chemical analysis on earth. In situ measurements have also been made using an X-ray fluorescence technique on the Soviet roving unmanned vehicle, Lunokhod. The dates of these missions, the places on the moon at which chemical analytical information is available, the type of terrain, and the technique of analysis used are summarized in Table I. Finally, measurements from orbiting spacecraft are beginning to provide information on the distribution of certain chemical elements over the lunar surface.

This Account reviews the  $\alpha$  particle technique of chemical analysis, the results obtained on the Surveyor missions, and the conclusions derived therefrom. It then summarizes the results obtained on subsequent missions and the status of information about the chemical nature of the lunar surface.

The emphasis in this Account is on the principal chemical elements. These are defined as the elements that are usually present in rocks in amounts greater than about 0.5% of the atoms. They are the elements that determine the gross chemistry, the minerals present, and the average density of a natural material. This emphasis is not to minimize the importance of the less prevalent elements, whose abundance patterns and variations contain much

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important information about the nature and history of the lunar surface.

Similarly, this Account is limited to the chemical composition of the lunar regolith—the fine-grained material that makes up most of the lunar surface. Rocks and fragments greater than a few millimeters in size are relatively rare in most places on the lunar surface. The powdered material has a median particle size of about 100  $\mu$  and is generally considered to be the product of the breakup of lunar rocks by micrometeorites and other objects and particles hitting the moon. The presence of many particles of glass in this fine material, as well as the evidence of shock deformation in many of the particles, support this idea. Because of the large distance of transport of particles on the moon resulting from the lack of an atmosphere and because of the low gravity, the powdered material at a particular location represents an average of a large area, probably many square kilometers.

The samples returned by the Apollo astronauts, as well as, to a lesser extent, those brought back by the automated Soviet missions, have larger fragments and rocks. Such rocks contain exceedingly important evidence about the times at which various processes occurred on the moon. They also contain detailed mineralogical information about the magmatic history of the rocks. These topics, however, are outside the scope of this Account.

### The $\alpha$ Particle Technique of Chemical Analysis

The  $\alpha$  particle technique of chemical analysis, as used on the Surveyor lunar missions, represents an application of two of the most important physical discoveries of this century: Lord Rutherford's proposal of the nuclear structure of the atom to explain the scattering of  $\alpha$  particles by matter, and his discovery of the artificial transmutation of nuclei by the observation of the  $^{14}N(\alpha,p)$  nuclear reaction. The application to chemical analysis grew out of a suggestion by S. K. Allison that the energy spectra

<sup>†</sup>This Account is based, in part, on the Nuclear Applications in Chemistry Award Address, presented at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 11, 1972.

<sup>(1)</sup> E. Rutherford, Phil. Mag., 21, 669 (1911).

<sup>(2)</sup> H. Geiger and E. Marsden, Proc. Roy. Soc., Ser. A., 82, 495 (1909).

<sup>(3)</sup> E. Rutherford, Phil. Mag., 37, 581 (1919).

<sup>(4)</sup> S. K. Allison, private communication to A. Turkevich, 1959.

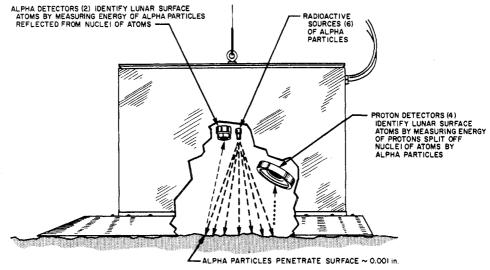


Figure 1. Cutaway diagram of the Surveyor  $\alpha$ -particle instrument, showing the approximate geometrical relationships of the sources, sample, and detectors. This part of the instrument (except for the bottom plate) was approximately 6 in.  $\times$  6 in.  $\times$  5 in. (courtesy of the Jet Propulsion Laboratory, Pasadena, Calif.).

of  $\alpha$  particles scattered elastically by atomic nuclei could be used for mass, and, therefore, for chemical, analysis. Because of conservation of momentum,  $\alpha$  particles scattered by heavy nuclei would have higher energies than ones scattered by lighter nuclei.

This technique, using accelerator-produced particles, had already received some attention for surface analysis.<sup>5</sup> The application to automated space missions<sup>6</sup> was made possible by the availability of appropriate radioactive sources of monochromatic  $\alpha$ particles, the development of compact semiconductor solid-state detectors with very good energy resolution for charged particles, 7 and the miniaturization of electronic circuit components that occurred in the late 1950's. Also, three theoretical developments were important: 6,8 the understanding of the spectra of scattered  $\alpha$  particles from thick targets, the realization that resonant nuclear scattering of  $\alpha$  particles from light elements such as carbon and oxygen increases their scattering cross sections at about 6 MeV by orders of magnitude above the Rutherford coulomb values, and the appreciation that the  $(\alpha,p)$ nuclear reactions in Na, Mg, Al, and Si give rise to protons of characteristic energies in adequate intensities to be an additional means of determining the amounts of these geochemically important elements.

The  $\alpha$  particle technique, as used on the Surveyor lunar missions, thus had an  $\alpha$  and a proton mode. In the  $\alpha$  mode, the spectra of  $\alpha$  particles scattered from a sample through an angle close to 180° were registered by silicon semiconductor detectors; in the proton mode, the energy spectra of protons produced in the sample by  $(\alpha,p)$  reactions were registered in similar detectors shielded by gold foils to cut out the

shorter range scattered  $\alpha$  particles. The principal distinguishing feature of the spectra of back-scattered  $\alpha$  particles from pure elements is the high-energy end point. This is determined by conservation of momentum, and, for scattering angles close to 180°, leads to a maximum energy of  $(A-4)^2/(A+4)^2$  times the original  $\alpha$  particle energy  $(A=\max$  number of the scattering nucleus). For instruments with a few per cent resolution, the technique cannot resolve neighboring mass numbers above about A=40

The proton spectra from  $(\alpha,p)$  reactions in various elements have different characteristics. Such reactions are energetically impossible with 6-MeV  $\alpha$  particles in the cases of carbon and oxygen; for elements heavier than about potassium, the yields of protons from 6-MeV  $\alpha$  particles become negligibly small because of the high coulomb barrier around the nuclei. For elements in between, there are adequate yields of  $(\alpha,p)$  reactions with characteristic energy spectra. For example, silicon and magnesium produce lowenergy protons; sodium and aluminum produce highenergy protons (see Figure 3).

Knowing the response of an instrument to pure elements (or oxides), the  $\alpha$  and proton spectra from a complex substance, such as a rock, can be decomposed into the contributions of the separate elements. This decomposition is best done using a least-squares program with a computer. The quantitative interpretation of the resolved spectra in terms of a chemical constitution makes use of the known relative energy loss by  $\alpha$  particles in different materials.<sup>8</sup>

The capabilities of this new analytical technique were established by Patterson, Turkevich, and Franzgrote. Some of the most important characteristics are the following. The method has no direct sensitivity for hydrogen, since  $\alpha$  particles cannot be scattered back by protons, and the recoil protons always go forward—into the sample. As indicated above, the resolution for elements heavier than helium is good for light elements, but becomes progressively poorer for heavier ones. The sensitivity and accuracy are about the same for light elements such

.Res., 70, 1311 (1965).

<sup>(5)</sup> E.g., C. W. Snyder, S. Rubin, W. A. Fowler, and C. C. Lauritsen, Rev. Sci. Instr., 21, 852 (1950); S. K. Allison and S. D. Warshaw, Rev. Mod. Phys., 25, 779 (1953); S. Rubin, T. O. Passel, and L. E. Bailey, Anal. Chem., 29, 736 (1957); S. Rubin in "Treatise on Analytical Chemistry," I. M. Kolthoff and P. J. Elving, Ed., Part I, Vol. 4, Interscience, New York, N. Y., 1957, p 2075. For a recent review, see M. A. Nicolet, J. W. Mayer, and I. V. Mitchell, Science, 177, 841 (1972).

<sup>(6)</sup> A. L. Turkevich, Science, 134, 672 (1961).

<sup>(7)</sup> See, e.g., J. W. Mayer and B. Gossick, Rev. Sci. Instr., 27, 407 (1956).
(8) J. H. Patterson, A. L. Turkevich, and E. J. Franzgrote, J. Geophys.

Table I
Locations on the Moon from Which Chemical Composition Data Are Available

|            |               | Selenographic coordinates |                          |      |                                   | <b>TD</b> 0  |                               |
|------------|---------------|---------------------------|--------------------------|------|-----------------------------------|--------------|-------------------------------|
| Mission    | Date          | Long.                     | Lat.                     | Ref. | Geographical area                 | Type of area | Type of analysis              |
| Surveyor 5 | 1967, Sept 11 | 23.20°E                   | 1.42°N                   | а    | Mare<br>Tranquillitatis           | Mare         | In situ<br>α particle         |
| Surveyor 6 | 1967, Nov 10  | 1.37°W                    | 0.46°N                   | а    | Sinus Medii                       | Mare         | In situ $\alpha$ particle     |
| Surveyor 7 | 1968, Jan 10  | 11.44°W                   | 40.97°S                  | а    | Outside Crater<br>Tycho           | Terra        | In situ $\alpha$ particle     |
| Apollo 11  | 1969, July 20 | 23.43°E                   | 0.69°N                   | b    | Mare<br>Tranquillitatis           | Mare         | Returned samples              |
| Apollo 12  | 1969, Nov 19  | 23.34°W                   | $2.45^{\circ}\mathrm{S}$ | c    | Oceanus<br>Procellarum            | Mare         | Returned<br>samples           |
| Luna 16    | 1970, Sept 19 | 56.18°E                   | 0.41°S                   | d    | Mare<br>Foecunditatis             | Mare         | Returned samples              |
| Luna 17    | 1970, Nov 17  | 35°W                      | 38°N                     | e    | Sea of Rains<br>(NW Mare Imbrium) | Mare         | In situ X-ray<br>fluorescence |
| Apollo 14  | 1971, Feb 5   | 17.5°W                    | 3.7°S                    | f    | Frau Mauro<br>Formation           | Mare         | Returned<br>samples           |
| Apollo 15  | 1971, July 31 | 3.7°E                     | 26.4°N                   | g    | Palus<br>Putridinis               | Mare         | Returned<br>samples           |
| Luna 20    | 1972, Feb 23  | 56.5°E                    | 3.5°N                    | h    | South of Mare<br>Crisium          | Terra        | Returned samples              |
| Apollo 16  | 1972, Apr 20  | 16°E                      | 8°S                      | i    | North of Crater<br>Descartes      | Terra        | Returned samples              |

<sup>&</sup>lt;sup>a</sup> L. D. Jaffe, Science, 164, 774 (1969). <sup>b</sup> LSPET (Lunar Science Preliminary Examination Team), Science, 165, 1211 (1969). <sup>c</sup> LSPET (Lunar Science Preliminary Examination Team), Science, 167, 1325 (1970). <sup>d</sup> A. P. Vinogradov, Proc. Second Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. II, 1 (1971). <sup>e</sup> Sky and Telescope, 155 (March 1971). <sup>f</sup> LSPET (Lunar Science Preliminary Examination Team), Science, 173, 681 (1971). <sup>g</sup> Apollo Lunar Geology Investigation Team, Science, 175, 407 (1972). <sup>h</sup> A. P. Vinogradov, Trans. Amer. Geophys. Union, 53, 820 (1972). <sup>l</sup> Apollo 16 Preliminary Examination Team, Science, 179, 23 (1973).

as oxygen as for heavier ones such as iron. An additional characteristic is that, due to the small penetrating power of 6-MeV  $\alpha$  particles, the technique gives information only about the topmost few microns of a sample. Finally, a practical consideration is the low data rates with reasonable  $\alpha$  sources: about 10 hr was needed to get adequate statistics with 200 mCi of  $^{242}\mathrm{Cm}$  with the Surveyor instruments.

The ability of instruments based on this technique to perform actual chemical analyses of rocks was established by extensive tests in the laboratory.9,10 These showed that the abundances of the principal chemical elements could be determined with typical accuracies of 0.5 atom % (1  $\sigma$ ). Because the Surveyor  $\alpha$  particle instruments could not resolve neighboring mass numbers for A greater than about 35, the results for elements with atomic weights greater than this were, strictly speaking, for groups of elements with similar atomic weights. Only in the case of the mass region about A = 40, where both calcium and potassium can contribute, is this lack of resolution significant in the analyses of rocks. However, for this reason, the chemical symbols for elements heavier than silicon, when used in connection with Surveyor results, are enclosed in quotation marks.

The data from these laboratory tests were used to estimate the confidence limits for the results of the Surveyor missions. Recent work on the method has improved the quality of the analyses for oxygen, has demonstrated its capability to determine carbon in rocks with a sensitivity of less than 1% by atom, and has shown how the X-rays excited in rocks by the  $\alpha$  particles can be used to increase the sensitivity and resolution of the technique for heavier elements such as potassium, manganese, and nickel.  $^{11}$ 

#### The Surveyor Lunar Missions

The instruments developed on the basis of this technique of analysis and flown on the Surveyor missions have been adequately described. <sup>12,13</sup> The most important component was an approximately 6-in cubical box that was lowered by a string, upon command from earth, from the Surveyor spacecraft to the lunar surface. The essential features of this sensor-head box are shown diagrammatically in Figure 1. The <sup>242</sup>Cm radioactivity was packaged in six capsules that collimated the  $\alpha$  particles so that they were directed only at a 4-in. opening in the bottom of the sensor head, and, therefore, at the lunar surface underneath.

The back-scattered  $\alpha$  particles were registered in two 0.25-cm<sup>2</sup> surface barrier silicon detectors at an average scattering angle of 172°. The protons produced by  $(\alpha,p)$  reactions in the sample were registered by four 1-cm<sup>2</sup> lithium-drifted silicon detectors. The electronics of the  $\alpha$  and proton modes provided,

<sup>(9)</sup> A. L. Turkevich, K. Knolle, E. J. Franzgrote, and J. H. Patterson, J. Geophys. Res., 72, 831 (1967).

<sup>(10)</sup> T. E. Economou, A. L. Turkevich, K. P. Sowinski, J. H. Patterson, and E. J. Franzgrote, J. Geophys. Res., 75, 6514 (1970).

<sup>(11)</sup> T. E. Economou, A. L. Turkevich, and J. H. Patterson, J. Geophys. Res., in press; E. J. Franzgrote, Advan. X-Ray Anal., 15, 388 (1972).

<sup>(12)</sup> A. L. Turkevich, K. Knolle, R. A. Emmert, W. A. Anderson, J. H. Patterson, and E. J. Franzgrote, Rev. Sci. Instr., 37, 1681 (1966).

<sup>(13)</sup> J. H. Patterson, E. J. Franzgrote, A. L. Turkevich, W. A. Anderson, T. E. Economou, H. E. Griffin, S. L. Grotch, and K. P. Sowinski, *J. Geophys. Res.*, 74, 6120 (1969); see also Technical Report 32-1265, Jet Propulsion Laboratory, 1968, pp 303-387.

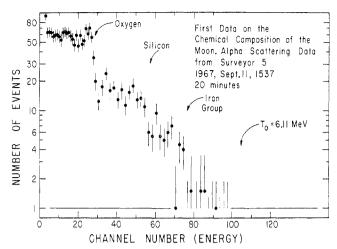


Figure 2. First data on the chemical composition of the moon. Response in the  $\alpha$  mode of the  $\alpha$ -particle instrument in Mare Tranquillitatis, 1967, Sept 11, 1537 GMT. The positions of the high-energy end points in the scattering by  $^{16}{\rm O}$ , Si, and elements in the region of iron are indicated by arrows. The alpha particles from  $^{242}{\rm Cm}$  have an energy of 6.11 MeV.

separately, energy spectra binned into 128 channels. The data rates were slow enough ( $\sim$ 2 sec<sup>-1</sup> in the  $\alpha$  mode,  $\sim$ 2 min<sup>-1</sup> in the proton mode) so that the characteristics of each registered event could be transmitted to earth as it occurred. Further details appear in ref 9, 12, and 13.

The dates of the Surveyor missions that used the  $\alpha$ particle technique of chemical analysis and the locations on the moon at which they landed are summarized in Table I. Surveyor 5 and 6 landed in mare regions, Surveyor 7 in a terra location. The missions themselves are described in ref 13-15. Figure 2 shows the first 20 min of data in the  $\alpha$  mode obtained on Sept 11, 1967, during the Surveyor 5 mission. Even though the statistical accuracy is poor, the presence of <sup>16</sup>O is shown by the sharp decrease in intensity of back-scattered  $\alpha$  particles at the calculated energy for 180° scattering by a mass 16 nucleus; similar features indicate the presence of silicon and, less clearly, of elements of the iron group. Figure 2 represents the first data obtained by man on the chemical composition of the moon.

Figure 3 shows an example (one of the samples examined on the Surveyor 7 mission) of how the more complete data from the  $\alpha$  and proton modes (after background subtraction) were resolved into contributions of the more abundant elements. The amounts of carbon indicated in Figure 3 were not statistically significant, since the contribution from this element was in a region of the  $\alpha$  spectrum dominated by the contributions from other elements.

The chemical analysis results of the Surveyor missions were presented in two stages: first as preliminary reports<sup>13</sup>, <sup>14</sup>, <sup>16</sup>-<sup>18</sup> based on only a portion of the data and only cursory examination, with these preliminary results being assigned rather large errors.

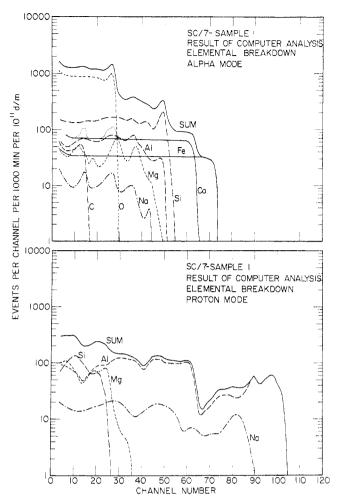


Figure 3. Contributions of the individual elements to the data (labeled SUM) in the  $\alpha$  (top) and proton (bottom) modes for sample 1 on the Surveyor 7 lunar mission. The backgrounds have already been subtracted. The actual numbers of events recorded were about 1800 per channel in the low-energy region of the  $\alpha$  mode and about 200 per channel in the low-energy regions of the proton mode. The abscissas (channel numbers) are proportional to the energy of the registered particles. The  $\alpha$  particles of the source were at approximately channel 102.

As the full data became available, analyses with much lower error estimates were published.<sup>19-21</sup> Most of the important conclusions in the preliminary reports were confirmed by the later analyses. These final analyses are presented in Table II. The errors given are estimates at the 90% confidence level, taking into account both the statistical errors and the small errors of the method, which were determined by the laboratory studies of the technique.

The data in Table II indicate that the three most abundant elements on the moon are the same as on the surface of earth, namely, oxygen, silicon, and aluminum, in that order. The large amount of silicon shows that the most abundant minerals are silicates. The Surveyor 5 (Mare Tranquillitatis) chemical composition is compared with those of some terrestrial and meteoritic materials in Figure 4. Surveyor 6, which sampled another mare region of the moon

<sup>(14)</sup> A. L. Turkevich, J. H. Patterson, and E. J. Franzgrote, *Amer. Sci.*, **56**, 312 (1968).

<sup>(15)</sup> L. D. Jaffe, Science, 164, 774 (1969).

<sup>(16)</sup> A. L. Turkevich, E. J. Franzgrote, and J. H. Patterson, Science, 158, 635 (1967).

<sup>(17)</sup> A. L. Turkevich, J. H. Patterson, and E. J. Franzgrote, Science, 160, 1108 (1968).

<sup>(18)</sup> A. L. Turkevich, E. J. Franzgrote, and J. H. Patterson, *Science*, **162**, 117 (1968).

<sup>(19)</sup> A. L. Turkevich, E. J. Franzgrote and J. H. Patterson, Science, 165, 277 (1969).

<sup>(20)</sup> E. J. Franzgrote, J. H. Patterson, A. L. Turkevich, T. E. Economou, and K. P. Sowinski, *Science*, 167, 376 (1970).

<sup>(21)</sup> J. H. Patterson, A. L. Turkevich, E. J. Franzgrote, T. E. Economou, and K. P. Sowinski, *Science*, 168, 825 (1970).

Table II Concentrations of Principal Chemical Elements in Lunar Regolith: α Particle Analysis Results

|         | Mission: Surveyor |   |                |  |  |  |
|---------|-------------------|---|----------------|--|--|--|
| Element | 5a                | 6 <sup>b</sup><br>% of atoms <sup>d</sup> | 7 <sup>c</sup> |  |  |  |
| .0      | $61.1 \pm 1.0$    | $59.3 \pm 1.6$                            | $61.8 \pm 1.0$ |  |  |  |
| Na      | $0.47 \pm 0.15$   | $0.6 \pm 0.24$                            | $0.5 \pm 0.2$  |  |  |  |
| Mg      | $2.8 \pm 1.5$     | $3.7 \pm 1.6$                             | $3.6 \pm 1.6$  |  |  |  |
| Al      | $6.4 \pm 0.4$     | $6.5 \pm 0.4$                             | $9.2 \pm 0.4$  |  |  |  |
| Si      | $17.1 \pm 1.2$    | $18.5 \pm 1.4$                            | $16.3 \pm 1.2$ |  |  |  |
| "Ca"    | $5.5 \pm 0.7$     | $5.2 \pm 0.9$                             | $6.9 \pm 0.6$  |  |  |  |
| "Ti"    | $2.0 \pm 0.5$     | $1.0 \pm 0.8$                             | $0 \pm 0.4$    |  |  |  |
| "Fe"    | $3.8 \pm 0.4$     | $3.9 \pm 0.6$                             | $1.6 \pm 0.4$  |  |  |  |

<sup>a</sup> The average of two samples examined; see ref 16, 19, and 20. <sup>b</sup> Ref 17, 20. <sup>c</sup> The average of the two soil samples measured. On this mission, fluorine at the level of  $0.3 \pm 0.1$  atom % was also detected in the soil samples, but not in a rock; see ref 18, 21. <sup>d</sup> The quoted errors are estimates at the 90% confidence level.

(Sinus Medii), gave essentially the same composition (see Table II) except for a lower titanium content. Although the absolute errors for this element in Table II overlap for the two missions, proper consideration of the nonsystematic errors indicates a lower titanium content in Sinus Medii<sup>20</sup> than in Mare Tranquillitatis.

On the assumption that the Surveyor 5 and 6 chemical compositions are representative of the maria of the moon, and that the composition found by Surveyor 7 is representative of the terrae, the following conclusions were drawn.

(1) The maria of the moon are basaltic in chemical composition. This is illustrated by the bar chart comparison in Figure 4B of the Surveyor 5 chemical analysis with the composition of terrestrial ocean ridge basalts. For the most abundant chemical elements, oxygen, silicon, aluminum, calcium, magnesium, and iron, the lunar maria values are well within the ranges found in these and other terrestrial basalts.

The relative abundances of the nonvolatile elements at all three Surveyor sites are definitely different from the relative abundances of these elements in the atmosphere of the sun. In the solar atmosphere the abundance of magnesium is greater than that of aluminum, being comparable to that of silicon, and much greater than that of calcium; on the moon the amount of magnesium is less than that of aluminum, much less than that of silicon, and even calcium has a comparable abundance. These differences are illustrated in Figure 4A and 4D where the Surveyor 5 analysis is compared with the compositions of terrestrial ultrabasic rocks and of chondritic meteorites. These substances have chemical compositions which resemble that of the nonvolatile part of the sun. Thus, the surface of the moon represents chemically differentiated material. Although the analytical evidence, strictly speaking, cannot distinguish whether the distortion from solar atmosphere composition occurred during assembly of the moon or in geological-type processes such as are common on earth, the similarity of the composition of lunar maria to those of terrestrial basalts, which are of magmatic origin, speaks for such processes being respon-

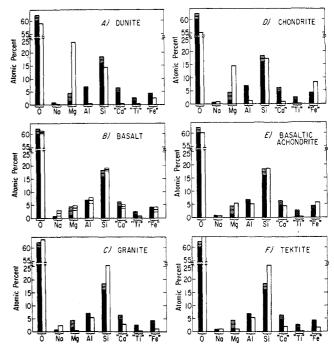


Figure 4. Comparison of the chemical composition of the lunar regolith at Mare Tranquillitatis (Surveyor 5, solid bars with 90% confidence limits indicated) with the average composition of selected materials (open bars): (A) dunites; (B) ocean ridge basalts; (C) granites; (D) low iron chondrites; (E) basaltic achondrites; (F) tektites (Indo Malayan body). Except for (B), the data are from A. Palm and R. G. Strom, Space Sciences Laboratory Research Report (University of California, Berkeley, 1962), series 3, issue 5. The data for (B) indicate the spread (90%) of the analysis of oceanic ridge basalts from R. Kay, N. J. Hubbard, and P. W. Gast, J. Geophys. Res., 75, 1585 (1970).

sible also on the moon. Thus, the chemical compositions found on the Surveyor missions strongly suggested that the surface of the moon had been hot enough at one time to produce lava flows. 17,22

On the other hand, the process of chemical differentiation on the moon has not proceeded as far as it has in many places on earth. Figure 4C compares the Surveyor 5 analysis with that of terrestrial granites. It is seen that there has not been the silicon and sodium enrichment, nor the depletion of magnesium, iron, and calcium on the surface of the moon (either in the maria or the terrae), that has occurred in the granitic continents of the earth.

- (2) Although the lunar maria are generally basaltic, their chemical composition has some unique features. For example, the abundance of sodium, of the order of 0.5 atom %, is significantly lower than usually found in terrestrial basalts (ocean ridge basalts usually have at least 1.5 atom %). In addition, Mare Tranquillitatis, with its high (2 atom %) abundance of titanium, is particuarly distinguishable from terrestrial basalts. If the abundances of these two minor elements are considered, there are essentially no rocks on earth that have the chemical composition of the lunar mare regolith.<sup>19</sup>
- (3) The chemical compositions found on the Surveyor missions make very unlikely a lunar surface origin for the meteorites that fall on the earth. The composition of the metallic meteorites is clearly in-

<sup>(22)</sup> D. E. Gault, J. B. Adams, R. J. Collins, J. Green, G. P. Kuiper, H. Masursky, J. A. O'Keefe, R. A. Phinney, and E. M. Shoemaker, *Science*, 158, 641 (1967).

Table III Normative Mineral Composition (Weight Per Cent) Inferred from Chemical Analysesa

|                                    |     | Surveyor<br>5 | Surveyor<br>6 | $\begin{array}{c} {\rm Average} \\ {\rm Mare}^a \end{array}$ | Surveyor<br>7 | Averag<br>Terraª |
|------------------------------------|-----|---------------|---------------|--|---------------|------------------|
| Ilmenite                           |     |               |               |  |               |                  |
| $FeTiO_3$                          | il  | 13.7          | 6.8           | 6.8  |               | 0.7              |
| Plagioclase                        |     |               |               |  |               |                  |
| feldspars                          |     | 43.7          | 44.4          | 43.3   | 63.4          | 68.1             |
| NaAlSi <sub>3</sub> O <sub>8</sub> | ab  | 6.0           | 7.1           | 4.8  | 6.2           | 4.8              |
| $CaAl_2Si_2O_8$                    | an  | 37.7          | 37.3          | 38.5   | 57.2          | 63.0             |
| Pyroxenes                          |     | 36.7          | 46.1          | 42.4   | 20.5          | 16.3             |
| CaMgSi <sub>2</sub> O <sub>6</sub> | di  | 24.9          | 22.1          | 15.5   | 20.5          | 14.0             |
| $\mathrm{MgSiO_3}$                 | en  | 1.1           | 6.6           | 11.6   |               | 2.3              |
| $FeSiO_3$                          | fs  | 10.7          | 17.4          | 15.3   |               |                  |
| Wollastonite                       |     |               |               |  |               |                  |
| $CaSiO_3$                          | wo  |               |               |  | 3.0           |                  |
| Olivines                           |     |               |               | 7.6  | 13.0          | 14.8             |
| $Mg_2SiO_4$                        | fo  |               |               | 3.5  | 5.3           | 6.8              |
| Fe <sub>2</sub> SiO <sub>4</sub>   | fa  |               |               | 4.1  | 7.7           | 8.0              |
| Quartz                             |     |               |               |  |               |                  |
| $\mathrm{SiO}_2$                   | qtz | 6.0           | 2.7           |  |               |                  |
| Estimated                          |     |               |               |  |               |                  |
| density, g cm <sup>-3</sup>        |     | 3.16          | 3.14          | 3.19   | 2.95          | 2.96             |

<sup>&</sup>lt;sup>a</sup>See text and Tables IVand V. Note that in Table 4 of ref 39 the values for enstatite and wollastonite have been mistakenly interchanged.

consistent with the silicate compositions found on the moon. The same is true also for the most common types of stone meteorites, the chondrites (see Figure 4D). The chemical composition of the basaltic achondrites, a small class of stone meteorites having a basaltic composition, comes closer to that of lunar material. However, the basaltic achondrites have lower aluminum and titanium and higher magnesium and iron contents (Figure 4E) than does lunar mare material. These meteorites have much lower aluminum and calcium and much higher iron contents than does lunar terra material (Table II and Figure 4E).

Similarly, a lunar surface origin for tektites seems improbable on chemical grounds; tektites have too much silicon and sodium and too little calcium (Figure 4F and Table II). Thus, although an origin somewhere in the interior of the moon cannot be excluded by these or other surface analyses, the chemical compositions found on the Surveyor missions either rule out or put stringent restrictions on a lunar origin for any of the objects on earth that have been assigned an extraterrestrial origin.

- (4) On the basis of the Surveyor analyses, there exists a significant difference in chemical composition between the terrae and maria of the moon (Table II). The former have only about one-third the amounts of titanium and iron than do the maria, and appreciably more aluminum ( $\sim 50\%$  increase) and calcium (~30% increase). In contrast, the amounts of silicon, sodium, and magnesium in the terrae and maria samples of the moon are essentially
- than calcium may well be the basic reason<sup>13,14,18,23</sup>

for the differences in albedo of the terrae and maria of the moon. The brighter appearance of the terrae is apparent upon even naked-eye observation of the moon. The electronic structure of the titanium and iron atoms is conducive to the formation of colored compounds. For example, the mineral ilmenite (FeTiO<sub>3</sub>) is the darkest mineral found in returned lunar mare material (e.g., see ref 24). Even in the absence of titanium, the presence of ferrous iron leads to darker silicates than if only magnesium and/ or calcium are present. In addition to this normally darker color of iron-containing minerals, they may be more sensitive to further darkening upon exposure to radiation.<sup>25</sup>

(6) The lower abundance of elements heavier than calcium in the lunar terrae than in the maria (Table II) also implies a lower density for terrae surface material. 13,14,18,23 A quantitative estimate of the densities of the rocks from which the two types of regolith were derived can be obtained by calculating a normative mineral assembly consistent with the chemical analyses of Table II. This is an assembly of minerals that can account for the chemical composition of the lunar regolith. The results of such a normative mineral analysis are presented in Table III for the Surveyor 5, 6 and 7 results. The calculation is performed following a mineral order that minimizes the effect of the relatively large errors in the  $\alpha$  particle analysis results for magnesium and silicon. Such an analysis of lunar data was first done by Phinney, et al.,23 using the preliminary Surveyor results. The densities are 3.15 g cm<sup>-3</sup> lunar mare and 2.95 g cm<sup>-3</sup> for the terra parent rocks of the samples examined on the Surveyor missions. The principal miner-

<sup>(5)</sup> This difference in amounts of elements heavier

<sup>(24)</sup> Lunar Science Preliminary Examination Teams: Apollo 11, Science, 165, 1211 (1969); Apollo 12, ibid., 167, 1325 (1970); Apollo 14, ibid., 173, 681 (1971); Apollo 15, ibid., 175, 363 (1972).

<sup>(25)</sup> L. I. Yin, S. Ghose, and I. Adler, J. Geophys. Res., 77, 1360 (1972).

<sup>(23)</sup> R. A. Phinney, J. A. O'Keefe, J. B. Adams, J. B. Gault, G. P. Kuiper, H. Masursky, R. J. Colling, and E. M. Shoemaker, J. Geophys. Res., 74, 6053 (1969).

als present on the surface of the lunar maria are feldspars and pyroxenes, with the feldspars being calcium rich. The silica contents indicated in Table III are more uncertain than the others because they are determined by the residual amounts of silicon left after forming the other minerals.

Table III shows that the principal differences in mineral composition between the terrae and maria are the negligible amounts of ilmenite and the much larger amounts of anorthitic feldspar in the terrae region. The highly anorthitic nature of the lunar feldspars, particularly in the terra samples, has given rise to a comparison of lunar surface material with terrestrial anorthosites.26,27

Of special interest for an earth-moon comparison is that the terrae of the moon are not more acidic than are the maria—the silicon abundance actually is lower in the terrae than in the maria samples. This is in sharp contrast to the situation on earth where the granitic continents have a strong enrichment of silica (see Figure 4C). Thus, even in the terrae of the moon, the process of geochemical differentiation has not proceeded as far as on the earth.

- (7) If the chemical composition and implied mineralogy and density found by Surveyor 7 are applicable to all the terrae, they imply a crust over at least 80% of the lunar surface, including most of the backside of the moon. The density of 2.95 is clearly incompatible with that of the moon as a whole— 3.36;28 the transformation into garnet-type minerals<sup>29</sup> of the Surveyor 7 mineral assemblage would have to go at unreasonably shallow depths<sup>21</sup> on the moon to get the overall lunar density. Thus the chemical compositions found by the Surveyor missions indicate large-scale chemical differentiation on the moon, both horizontally and vertically, with the latter suggesting an earth-like layering at least of the outer parts of the moon.
- (8) Finally, the lower density deduced for the terrae as compared to the maria correlates with the apparently higher elevation of the terrae of the moon. This suggests that the terrae are not merely unsmoothed residues of the original accumulated material of the moon, but a chemically segregated fraction that, because of the lower density, has risen to the surface and come to approximate isostatic equilibrium. 14,18,21,30

## Chemical Analysis Results from the Apollo and Luna Missions

In the period since the Surveyor missions there have been precise laboratory analyses of lunar regolith samples brought back to earth by the Apollo and Luna missions. The locations on the moon from which these samples came are indicated in Table I. Practically all the known chemical elements have been identified in these samples. Attention here will be focused on the results for the principal elements

Table IV Concentrations of Principal Chemical Elements in Lunar Mare Regolith: Apollo and Luna Mission Results

| Element             | Apollo 11 <sup>a</sup> | Apollo<br>12 <sup>b</sup> | Luna<br>16° | Luna<br>17 <sup>d</sup> | Apollo<br>14 <sup>e</sup> | Apollo<br>15 <sup>f</sup> |  |  |  |  |
|---------------------|------------------------|---------------------------|-------------|-------------------------|---------------------------|---------------------------|--|--|--|--|
| Element             | % of atoms             |                           |             |                         |                           |                           |  |  |  |  |
| 0                   | 59.9                   | 59.9                      | 60.2        | (63.2)                  | 60.8                      | 60.4                      |  |  |  |  |
| Na                  | 0.3                    | 0.3                       | 0.4         |                         | 0.4                       | 0.3                       |  |  |  |  |
| Mg                  | 4.6                    | 6.8                       | 5.0         | 6.3                     | 5.4                       | $5.9(\pm 0.2)$            |  |  |  |  |
| Al                  | 6.3                    | 6.3                       | 7.0         | 5.7                     | . 7.7                     | $6.5(\pm 1.1)$            |  |  |  |  |
| Si                  | 16.3                   | 16.0                      | 16.0        | 15.7                    | 17.5                      | $17.3 (\pm 0.2)$          |  |  |  |  |
| Ca                  | 4.9                    | 4.1                       | 5.0         | 4.4                     | 4.3                       | $4.4 (\pm 0.2)$           |  |  |  |  |
| $\operatorname{Ti}$ | 2.2                    | 0.9                       | 1.0         | <1.8                    | 0.5                       | 0.5                       |  |  |  |  |
| Fe                  | 5.1                    | 5.4                       | 5.4         | 4.7                     | 3.1                       | $4.5 (\pm 0.9)$           |  |  |  |  |
|                     |                        |                           |             |                         | _                         |                           |  |  |  |  |

a Averages of the more accurate of many analyses reported in Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. I (1970). b Apollo 12 Preliminary Examination Team, Science, 167, 1325 (1970). c A. P. Vinogradov, Nature (London), 228, 492 (1970); Geochim. Cosmochim. Acta, Suppl. II, 1 (1971). d Lunokhod-1, "A Mobile Laboratory on The Moon," Soviet volume distributed at the COSPAR Meeting, Seattle, 1971. The oxygen values are from stoichiometry. e Apollo 14 Preliminary Examination Team, Science, 173, 681 (1971). / Apollo 15 Preliminary Examination Team, Science, 175, 363 (1972). The values in parentheses give the range of the three different regolith samples brought back on this mission.

as defined earlier—those determining the major mineral phases present in crystalline form—and on the chemical compositions of the lunar regolith as an average sample at particular locations on the moon.

The chemical compositions of the maria as determined in the samples from these missions are presented in Table IV. They are compared with the Surveyor mare analyses in Figure 5. It is evident that the different maria of the moon—and by now seven have been sampled—have a relatively narrow range of principal chemical element compositions. The elements making up more than 95% of the atoms exhibit individually a variability (root mean square) of about 20% or less (Table V). The largest variations are in the magnesium content, which ranges over a factor of two, and in the titanium abundance, which varies from 0.5 to 2.2 atom % in the different maria.

The chemical compositions in Table II and IV can be used to calculate the average composition of the lunar maria. This is shown in the second column of Table V. The amounts of the principal minerals calculated from this average chemical analysis are shown in column 4 of Table III. Although the range in chemical composition of the maria is not large, the amount of silicon relative to other elements determines whether there is free quartz in the normative mineral assemblage (Surveyor 5, 6, Apollo 14) or olivine minerals (Apollo 11, 12, 15, Luna 16, 17). The average composition of the maria leads to some olivines (Table III). The density of average parent lunar mare rocks calculated from the normative mineral assemblage is 3.19 g.cm<sup>-3</sup>, and varies between 3.08 and 3.27 g cm<sup>-3</sup> in the different maria.

Detailed laboratory studies of returned lunar samples have indeed found that the principal minerals present in both the crystalline powdered material and in the rocks of the lunar maria are highly anorthitic feldspars, pyroxenes, ilmenite, olivines, and, occasionally, quartz.24 In addition, these investigations have established important patterns in the abundances of some of the minor elements. Among

<sup>(26)</sup> E. Olsen, Science, 166, 401 (1969). (27) J. A. Wood, J. S. Dickey, Jr., U. B. Marvin, and B. N. Powell, Science, 167, 602 (1970); J. A. Wood, J. Geophys. Res., 75, 6497 (1970); Sci. Amer., 223, 14 (1970).

<sup>(28)</sup> W. M. Kaula, Science, 166, 1581 (1969).

<sup>(29)</sup> F. R. Boyd, Science, 145, 13 (1964); G. W. Wetherell, ibid., 160,

<sup>(30)</sup> J. A. O'Keefe, Science, 162, 1405 (1968).

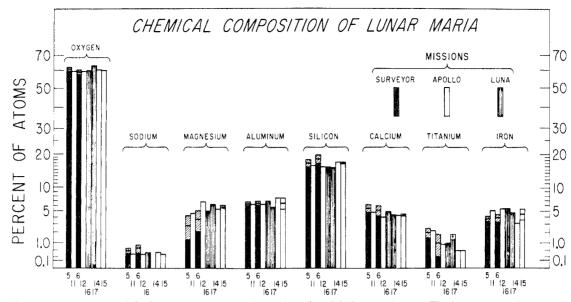


Figure 5. Chemical composition of the lunar maria—comparison of results of different missions. The locations on the moon at which the analyses apply are given in Table I; 90% confidence limits are indicated for the Surveyor results; the spread (where significant) in regolith analyses from the Apollo 15 mission is also shown. The ordinate is a square-root scale.

the most important of these general patterns are the following.

- (1) Consistent with the low abundance of sodium noted above, the abundances of all the alkalies except Li are relatively low.<sup>24</sup> When considered in the light of the small amounts of In, Hg, Tl, and Bi in lunar rocks,<sup>31</sup> a reasonable hypothesis is that the moon was either assembled under conditions that hindered the condensation of these volatile elements or that the surface material was heated early in its history to a temperature high enough to volatilize them. Consistent with this apparent depletion of volatile elements is the extreme dryness of lunar rocks and the almost complete absence of carbon compounds.<sup>24</sup>
- (2) The natural radioactivity of the lunar mare surface is significantly different from that of most terrestrial materials. <sup>24</sup> The thorium to uranium ratio is about 3, which is normal, and the absolute amount of uranium (0.2–3 ppm) is not unusual for basalts. However, the depletion of potassium leads to K/U ratios in lunar basalts of about 2000 instead of the  $10^4$  found in terrestrial samples and tektites, and even higher values in chondritic meteorites. <sup>32</sup>
- (3) Another distinctive characteristic of lunar mare basalts is their reduced nature. There is essentially no ferric iron present in the lunar minerals<sup>24,33</sup> and even traces of metallic iron are present, not all of meteoritic origin.<sup>34</sup> Probably related to these reducing conditions is the "europium anomaly."<sup>24,35</sup> The relative abundances of the different rare earths follow a regular pattern in most natural materials. However, in most lunar mare samples, the abundance of europium is anomalously low relative to that of the other rare earths. This suggests that eu-

ropium was present in the 2+ valence state at the time of crystallization, and so did not follow the chemistry of the other 3+ valent lanthanides.

(4) Careful studies of rare element abundances<sup>24,31</sup> indicate that the lunar mare regolith has an admixture of about 2% of meteoritic material. This is not present in the crystalline rocks, and is attributed to the accumulation of meteorites by the moon over billions of years of bombardment by such objects.

To complement these extensive data on the lunar maria there was, until recently, only the Surveyor 7 analysis that was directly applicable to the 80% of the lunar surface that is terra. That this analysis is representative of terra regions was suggested by information obtained by the early Apollo and Luna missions:

All of the mare regolith samples brought back to earth contain small amounts of light-colored fragments or glasses having a chemical composition similar to that found by Surveyor 7. These were first found in the Apollo 11 samples by Smith, et al., 36 and by Wood, et al. 27 Wood and his collaborators found evidence of shock features in the fragments, supporting the idea that they were thrown out of the neighboring terrae by impact events.

More general confirmation has come from the recent experiment of Adler, et~al.,  $^{37}$  who, using instruments aboard the orbiting Apollo 15 command module, measured the fluorescent X-rays produced in the lunar surface by solar radiations. The data show an approximately 50%, on the average, increase of the Al/Si ratio in the terrae as compared to the maria, and a smaller decrease in the Mg/Si ratio. Arnold and coworkers,  $^{38}$  measuring the  $\gamma$  rays from the moon on the same mission, have tentatively con-

<sup>(31)</sup> R. Ganapathy, R. R. Keays, J. C. Laul, and E. Anders, Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. I, 1117 (1970).
(32) P. W. Gast, Moon. 5, 121 (1972).

<sup>(33)</sup> E.g., C. L. Herzenberg and D. L. Riley, Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta. Suppl. I. 2221 (1970).

<sup>(34)</sup> E.g., J. I. Goldstein, E. P. Henderson, and H. Yakowitz, Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. I, 499 (1970).

<sup>(35)</sup> E.g., H. Wakita, R. A. Schmitt, and P. Rey, Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. I, 1685 (1970).

<sup>(36)</sup> J. V. Smith, A. T. Anderson, R. C. Newton, E. J. Olsen, P. J. Wyllie, A. V. Crewe, M. S. Isaacson, and D. Johnson, *Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. I.* 897 (1970).

<sup>(37)</sup> I. Adler, J. Trombka, J. Gerard, P. Lowman, R. Schmadebeck, H. Blodget, E. Eller, L. Yin, R. Lamothe, P. Gorenstein, and P. Bjorkholm, Science, 175, 436 (1972).

<sup>(38)</sup> J. R. Arnold, 163rd National Meeting, American Chemical Society, Boston, Mass., April 11, 1972.

Table V
Chemical Composition of the Lunar Surface (% of atoms)

| Element |                               |                         | Ter         | Average lunar surface                               |                  |                            |                       |
|---------|-------------------------------|-------------------------|-------------|---|------------------|----------------------------|-----------------------|
|         | Maria<br>Average <sup>a</sup> | Surveyor 7 <sup>b</sup> | Luna<br>20° | $\begin{array}{c} {\rm Apollo} \\ 16^d \end{array}$ | Average<br>Terra | % of<br>atoms <sup>e</sup> | Weight %<br>of oxides |
| 0       | $60.6 \pm 1.2$                | 61.8                    | 60.4        | 61.0  | 61.1             | 61.0                       |                       |
| Na      | $0.4 \pm 0.1$                 | 0.5                     | 0.4         | 0.3   | 0.4              | 0.4                        | 0.6                   |
| Mg      | $5.3 \pm 1.2$                 | 3.6                     | 5.2         | 3.0   | 4.0              | 4.3                        | 8.0                   |
| Al      | $6.6 \pm 0.6$                 | 9.2                     | 9.7         | 11.6  | 10.2             | 9.5                        | 22.3                  |
| Si      | $16.8 \pm 1.0$                | 16.3                    | 16.0        | 16.2  | 16.2             | 16.3                       | 45.0                  |
| Ca + K  | $4.7 \pm 0.5$                 | 6.9                     | 5.9         | 6.1   | 6.3              | 6.0                        | 15.5                  |
| Ti      | $1.0 \pm 0.6$                 | 0                       | 0.15        | 0.15  | 0.1              | 0.3                        | 1.1                   |
| Fe      | $4.5 \pm 0.8$                 | 1.6                     | 2.1         | 1.6   | 1.8              | 2.3                        | 7.6                   |

<sup>a</sup> The average mare composition is calculated from the values of Tables II and IV, using an average value from Surveyor 5 and Apollo 11 for Mare Tranquillitatis. The ± represent the variability in mare composition calculated as the root mean square deviation from the average of the different mare results. <sup>b</sup> From Table II. <sup>c</sup> A. P. Vinogradov, *Trans. Amer. Geophys. Union*, 53, 820 (1972). <sup>d</sup> Average of 11 soil samples from Apollo 16 LSPET. *Science*, 179, 23 (1973). <sup>e</sup> Calculated on the basis that terrae are 80% of the lunar surface. <sup>f</sup> The oxide composition is calculated on the basis that all the iron is present as FeO.

cluded that Fe is less abundant in the terrae than in the maria. Both these experiments supported the hypothesis that the Surveyor 7 chemical composition is representative of all the terrae of the moon.

Very recent data on samples returned by the Luna 20 and Apollo 16 missions have provided the composition of the regolith at two more terra locations. The results from these missions are presented in columns 4 and 5 of Table V. It is seen that the regolith at three terra locations thousands of kilometers apart has essentially the same gross chemical composition. In particular, the decrease in Ti and Fe content from that of the maria, and the increase in Al and Ca, are confirmed. Column 6 of Table V gives the average terra regolith chemical composition based on these three analyses.

The last two columns of Table V give the present estimates of the chemical composition of the lunar surface, first in terms of atomic composition and then in the more usual weight per cent of oxides form. These estimates are obtained by weighting the average mare composition by 0.2, and that of the terrae by 0.8. The average composition of the lunar surface of Table V differs little from that estimated by Turkevich<sup>39</sup> on the basis of the Surveyor and early Apollo and Luna missions.

The proposal<sup>14,18,30</sup> that, on a large scale, the topographical features of the moon represent an approach to isostatic equilibrium has recently received support from the results of the Apollo 15 altimeter studies.<sup>40</sup> These have shown that, in general, the terrae are higher in elevation by 2-3 km than the maria, and that the backside of the moon, which is almost all terrae, is, on the average, several kilometers higher than the front side, which has many mare regions in the equatorial regions.

Similarly, the deduction made on the basis of the Surveyor 7 results<sup>21</sup> that the moon has a crust has recently been confirmed by data from the seismometers left on the lunar surface by the Apollo astronauts.<sup>41</sup> The seismic data indicate a discontinuity in

the seismic wave propagating properties of the moon at an average depth of 65 km. The seismic velocities needed to explain the data for the outer crust are consistent with those expected for material with the Surveyor 7 chemical composition.

#### Summary

Data from the Surveyor, Apollo, and Luna missions have established the amounts of the principal chemical elements in lunar surface material. The Surveyor automated missions employed a new technique of chemical analysis based on the interaction of  $\alpha$  particles with matter.

The lunar surface is made up of silicate rocks, with the principal minerals being calcium-rich feldspars and pyroxenes. Seven maria have been analyzed. In many respects their chemical compositions are similar to those of terrestrial basalts. The three terra regions analyzed are distinctly different from the maria in having considerably smaller amounts of iron and titanium and larger amounts of aluminum and calcium. The Apollo missions have shown that lunar mare material is very dry and was produced under relatively reducing conditions.

The chemical compositions indicate that the surface of the moon was hot enough at one time to produce chemical differentiation on a large scale both horizontally and vertically. The latter has resulted in a crust over at least much of the moon. This crust is different, not only in density but also in chemical composition, from the bulk of the moon. The differences in chemical composition between the terrae and maria suggest that large-scale isostatic adjustments of the surface features of the moon have taken place. They also provide an explanation for the albedo differences between the different parts of the lunar surface.

The scientific work of the analysis of the lunar surface using the  $\alpha$  particle technique was carried out in collaboration with K. Knolle, T. E. Economou, and K. P. Sowinski of The University of Chicago, E. J. Franzgrote of Jet Propulsion Laboratory, and J. H. Patterson of Argonne National Laboratory. Important technical assistance was provided by W. A. Anderson, E. Blume, and the staff of the Laboratory of Astrophysics and Space Research of The University of Chicago. The work was supported by the National Aeronautics and Space Administration and the Atomic Energy Commission of the United States Government.

<sup>(39)</sup> A. L. Turkevich, Proc. Second Lunar Sci. Conf., Geochim. Cosmochim. Acta. Suppl. II, 1209 (1971).

<sup>(40)</sup> W. M. Kaula, private communication, 1972.

<sup>(41)</sup> M. N. Toksöz, F. Press, K. Andersen, A. Daintz, G. Latham, M. Ewing, J. Dorman, D. Lammlein, G. Sutton, F. Duennebier, and U. Nakamura, Science, 176, 1012 (1972).