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# Chemical peculiarities of particle surface layers of some Apollo 17 regolith samples

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**Abstract**—Elemental distribution in the small grain size fraction of particles of regolith samples 74220 and 75080 have been studied by X-ray photoelectronic spectroscopy. For both samples, a layered structure of the surface of particles was observed to be markedly different from those of the previously studied regolith samples collected by Luna automatic spacecraft. The particles of sample 74220 have a distinct two-layered structure, with a high content of S, Zn, Na, F and Cl in the outer layer, which apparently formed under conditions of high oxygen fugacity. An irregular distribution of reduced forms of element with depth, a high content of $Ti^{\circ}$ and surface enrichments in Na are noted in sample 75080. Both features are characteristic of oxidation of the particle surfaces. They indicate that the surface layers of particles were formed by condensation processes: sample 75080 from an impact cloud and sample 74220 from a cloud of endogenic origin.

## INTRODUCTION

Numerous studies of the fine particles of the lunar regolith give evidence for an important influence of the solar corpuscular radiation on the composition and, in particular, on the composition and structural chemical features of the particle surface layers (Baron *et al.,* 1977; Dikov *et al.,* 1977; 1978; Nefodov *et al.,* 1977). There are data on the essential contribution to regolith formation of other factors of endogenic as well as exogenic origin (Dowty *et al.,* 1973; Housley and Grant, 1977).

The specific nature of these factors also must be reflected more or less by the surface state of the regolith particles. In the Apollo 17 collections there are particles of volcanic origin which have been separated from the exogenic transformation products of the lunar matter.

In this paper we report the results of a comparative study of the chemical peculiarities of the particle surface layers of fines <80 μm, taken from two Apollo 17 samples, 74220 and 75080.

The study has been carried out by X-ray photoelectron spectroscopy using spectrometer IEE–15 ''Varian'' and the methods previously employed in studying samples from Luna 16, 20, and 24 (Dikov *et al.,* 1977; 1978).

## Sample 74220

This sample collected on the rim of Shorty Crater consists largely of 4 inch glass balls of homogeneous composition and the broken fragments. The 74001/74002 core taken at the same location shows that material of similar homogeneous composition extends to a depth of at least 70 cm. As noted in a series of papers (Cirlin *et al.,* 1978; Dowty *et al.,* 1973; Housley and Grant, 1977) the specific peculiarity of sample 74220 is an enrichment of particle surfaces in some volatile components such as F, Na, S, Cl, K, Zn, and Ga. The elemental concentrations apart from Ga are rather high and within the sensitivity of X-ray photoelectron spectroscopic analysis. Hence, we have attempted to study the depth distribution of the elements mentioned, by means of successive surface etching by argon ions. Together with the spectral lines of 2p–electrons of S, Cl and Zn, and 1s–electrons of Na and F, we studied 2p–electrons of Mg, Al, Si, Ca, Ti, Cr, and Fe, 3p–electrons of Fe, and 1s–electrons of oxygen. In all, ten etchings have been carried out in a series of increasing steps from 20 to 1700 Å, the total depth of the layers studied being about 3000 Å.

We are aware of the imperfect method for studying the element distribution with depth in particles by means of ionic etching, primarily owing to the selective interaction between Ar and the sample surface. Therefore, depth measurements of layers are only approximate. On the other hand, the ion probe data on some element distributions (sample 74220) reported by Meyer *et al.,* 1975, extend over the same ranges of depths.

The results of fine fraction investigations of sample 74220 with X-ray photoelectron spectrometry are given in Figs. 1–8 and listed in Table 1.

Positions and line intensities show that the sample particles have two-layered structures and consist of a silicate core and a fine outer film (<1000 Å), enriched in Na, S, Zn, F, and Cl. The content of these elements decreases with depth, leaving no sharp boundary between the core and the outer film. At a depth of about 600–800 Å (after 7–8 etchings), where the concentration of volatile elements strongly decreases, one can note an appreciable change in major element lines: O, Si, Mg, and Fe. In the case of O, Si, and Mg, the lines of 2p–electrons are shifted about 0.4–0.7 eV towards the lower energy relative to their average value in the outer layer, the line of $2p_{\frac{3}{2}}$ electrons shift to higher energy shift for 3p-electrons of Fe by a value of 1.5–2.0 eV. The rest of the elements are characterized by a relative constant energy of line maximums with depth studied.

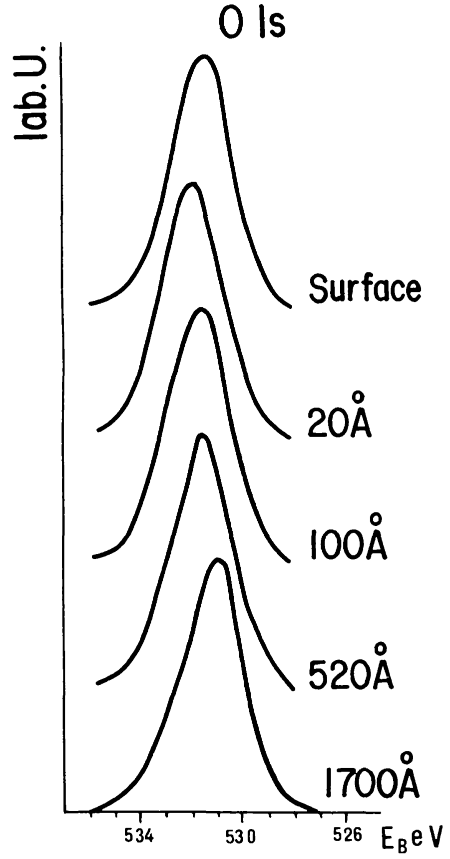

**Fig. 1.** Spectra of 1s electrons of oxygen on the surface and at depth of particles of sample 74220.

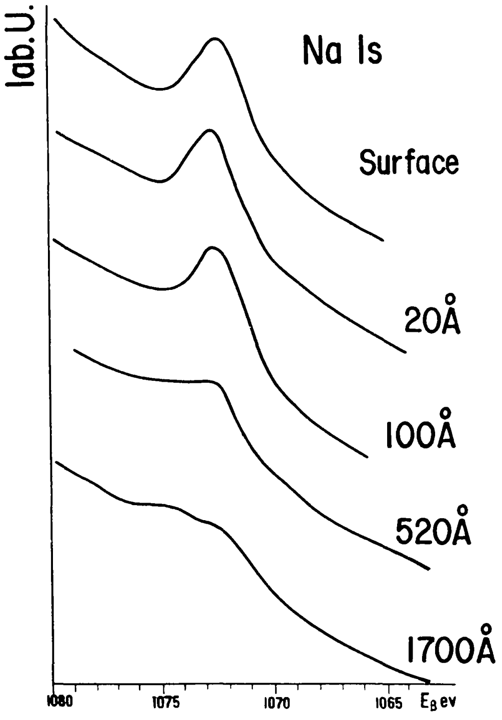

**Fig. 2.** Spectra of 1s electrons of sodium on the surface and at depth of particles of sample 74220.

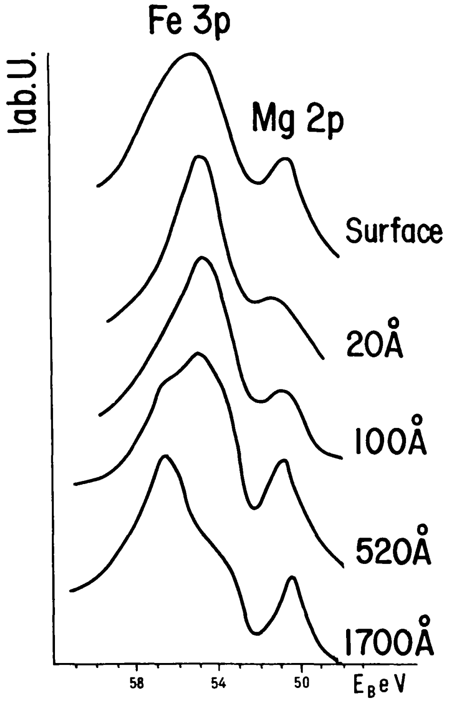

**Fig. 3.** Spectra of 2p electrons of magnesium and 3p electrons of iron on the surface and at depth of particles of sample 74220.

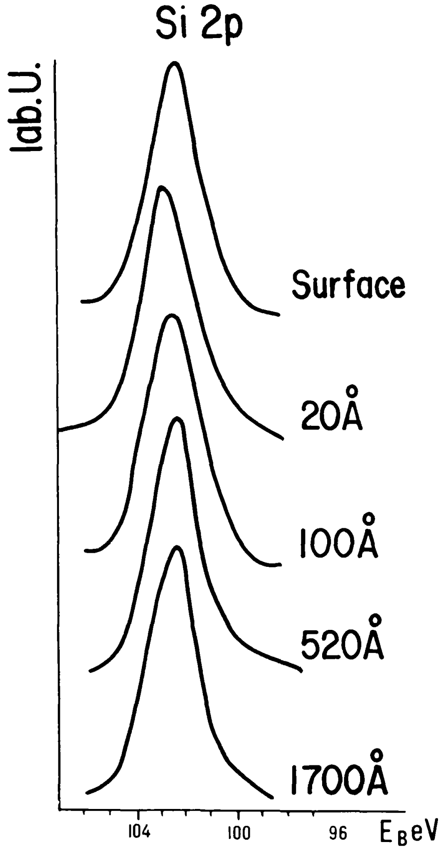

**Fig. 4.** Sepctra of 2p electrons of silicon on the surface and at depth of particles of sample 74220.

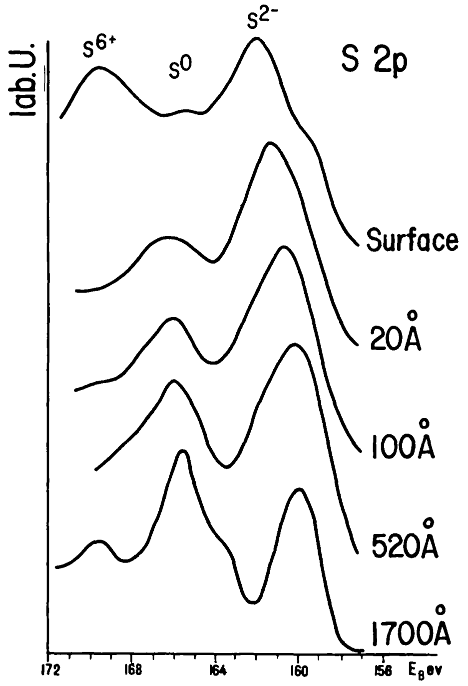

**Fig. 5.** Spectra of 2p electrons of sulphur on the surface and at depth of particles of sample 74220.

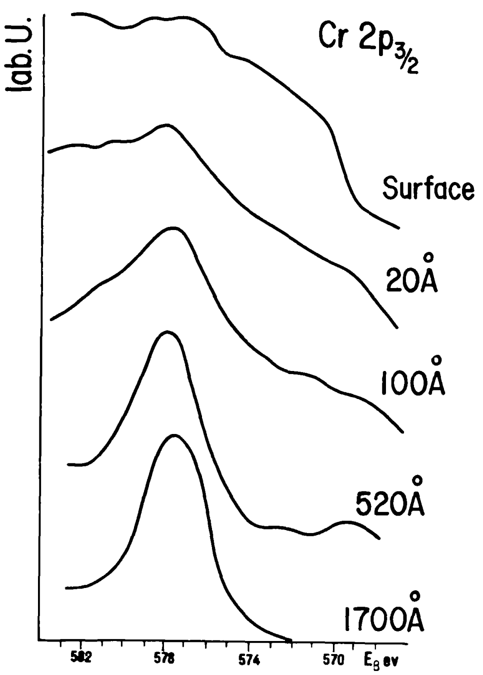

**Fig. 6.** Spectra of 2p$\frac{3}{2}$ electrons of chromium on the surface and at depth of particles of sample 74220.

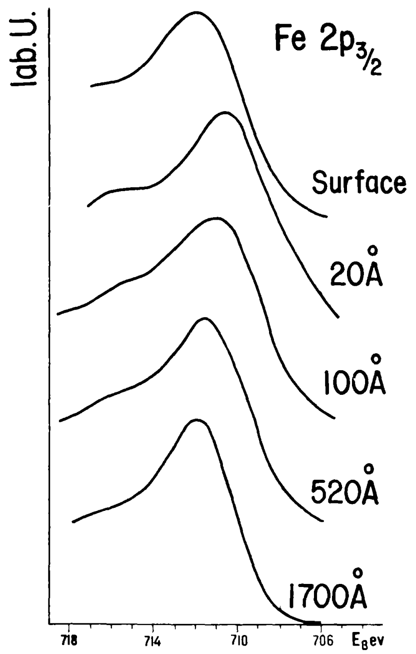

**Fig. 7.** Spectra of $2p\frac{3}{2}$ electrons of iron on the surface and at depth of particles of sample 74220.

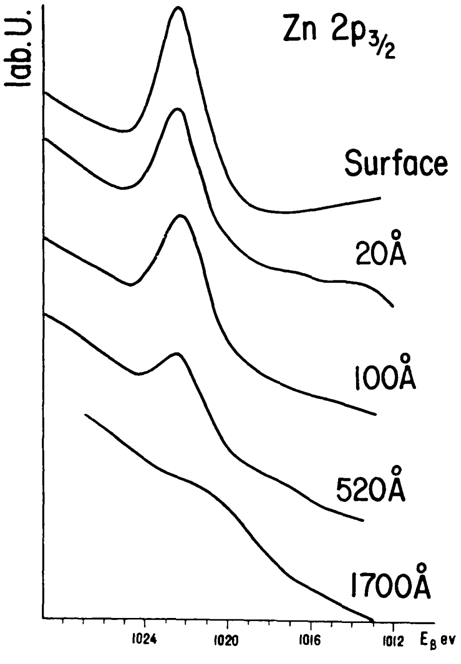

**Fig. 8.** Spectra of $2p\frac{3}{2}$ electrons of zincum on the surface and at depth of particles of sample 74220.

The bond energy values of innershell electrons for elements in the outer layer give evidence for the presence of oxygen-containing compounds of petrogenic elements as well as their sulfides. The latter are revealed by a well displayed S maximum of spectra of 2p–electrons of 161.0–162.0 eV.

It is most likely that the $S^{2-}$ is coupled with Zn, because the maximum of the zinc 2p $\frac{3}{2}$ line is very close to that of ZnS. We cannot exclude the possibility that some of the Fe is in sulfide form, because the iron 2p $\frac{3}{2}$ line is shifted to lower energies.

In addition to the main maximum of 160.0–162.0 eV, which is characteristic of $S^{2-}$, the spectrum of sulphur 2p-electrons has a marked maximum of 166.0 eV, giving evidence for the presence of sulphur with a positive charge around 2+. The relative maximum intensity of this line increases with depth and in the vicinity of the usual boundary between the sulphide film and silicate core (about 800–1000 Å), an additional maximum characteristic of sulfur in a state of highest oxidation, appears at 169.4 eV. It is very interesting that in the 2p–electron spectrum of sulfur, the maximum in bond energy region of 169.4 eV characteristic of sulfur in the highest state of oxidation, $S^{6+}$ appears twice. The first time, this maximum is noted on sample surfaces where it is undoubtedly related to the sample oxidation in the terrestrial conditions. The second time, it is noted at the boundary between the sulfide film and the silicate core. Here the sulfur oxidation is most likely caused by the peculiarities of interaction between the silicate matrix and the sulfide-halide condensate. The elements, enriched in outer layer, such as Zn, Na, and Fe, have a relative constant position of the maximum for a variety of grains. The line positions of elements, forming the basis of the silicate core change with depth, those of petrogenic elements being fairly typical for Al-silicate and Mg, Fe–glasses. Only the 2p–electrons of Si indicate relative low bond energy values (102.3–102.5 eV) giving evidence for strong isolation of the $SiO_4^{4-}$ tetrahedron. The shift towards higher energies of this line in the outer film is due to the increasing polymerization of $SiO_4^{4-}$—tetrahedron groups (Alyoshin *et al.*, 1977). This is indirectly confirmed by the shift of 1s–electron line of oxygen to higher energies. The shift is unequivocally related to the increase of acidity of silicate melt (Alyoshin *et al.*, 1975; 1977).

The 2p $\frac{3}{2}$ electron line of chrome displays a peculiar behavior. On the sample surface and in all sections of the outer film it is very broad, but on the boundary between film and silicate core, as well as in the core itself, this line becomes narrow and displays a well defined maximum. Its position at 577.5–578.0 eV indicates that the chrome charge is somewhat higher than in the usual Cr (III)-compounds (Best *et al.*, 1977). It is essential that a specific position of Cr-line be followed at the same time by the previously mentioned high energy shift of 2p $\frac{3}{2}$ and 3p–electrons of Fe (Figs. 3 and 7), which also suggests some increase in the efficient charge of the Fe, entered in the silicate basis.

The position of the Cr and Fe lines in the case of the sample 74220, as well as the complete lack of any reduced form and intermediate oxidation states of petrogenic elements, suggest the silicate matrix was formed under conditions of high oxygen fugacity. Because of the simultaneous occurrence of sulphur in sulphide

**Table 1.** The main maximum position of the innershell electrons of the major elements in the sample 74220 (in eV).

| Element, line | Surface | Depth, Å | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 20 | 40 | 60 | 100 | 180 | 350 | 520 | 860 | 1700 | 3400 |
| O 1s | 531.5 | 531.9 | 531.8 | 531.8 | 531.6 | 531.6 | 531.8 | 531.4 | 531.4 | 531.0 | 531.4 |
| F 1s | 685.3 | 685.8 | 685.7 | 685.7 | 685.7 | 685.7 | 685.5 | 685.6 | 685.5 | 685.5 | 685.5 |
| Na 1s | 1072.5 | 1072.8 | 1072.6 | 1072.6 | 1072.6 | 1072.6 | 1072.5 | 1072.5 | 1072.6 | — | —[x)] |
| Mg 2p | 50.6 | 51.2 | 51.2 | 51.2 | 51.1 | 50.9 | 50.9 | 50.9 | 50.7 | 50.5 | 50.5 |
| Al 2p | 74.4 | 75.0 | 74.8 | 74.8 | 74.8 | 75.1 | 74.5 | 74.7 | 74.8 | 74.4 | 74.8 |
| Si 2p | 102.4 | 103.1 | 102.6 | 102.9 | 102.5 | 102.4 | 102.2 | 102.8 | 102.3 | 102.3 | 102.5 |
| S 2p | 161.8 | 161.7 | 161.3 | 160.6 | 160.6 | 160.6 | 160.5 | 160.2 | 160.0 | 160.0 | — |
| | 165.1 | 166.8 | 166.0 | 166.0 | 166.0 | 166.0 | 166.2 | 165.8 | 165.9 | 165.6 | — |
| | 169.5 | — | — | — | — | — | — | — | — | 169.7 | — |
| Cl 2p | 198.9 | 198.3 | 198.6 | 199.0 | 199.0 | 199.3 | 199.2 | 198.8 | 199.0 | — | — |
| Ca 2p$_{3/2}$ | 347.8 | 348.2 | 347.9 | 348.0 | 347.9 | 347.7 | 347.6 | 347.8 | 347.7 | 347.6 | 347.7 |
| Ca 2p$_{1/2}$ | 351.3 | 351.8 | 351.3 | 351.5 | 351.4 | 351.0 | 351.3 | 351.1 | 351.2 | 351.1 | 351.3 |
| Ti 2p$_{3/2}$ | 459.0 | 459.4 | 459.5 | 459.3 | 459.2 | 459.0 | 459.0 | 459.0 | 459.1 | 459.0 | 459.0 |
| Ti 2p$_{1/2}$ | 464.8 | 465.1 | 465.0 | 465.1 | 465.0 | 464.8 | 464.6 | 464.7 | 464.9 | 464.6 | 464.7 |
| Cr 2p$_{3/2}$ | — | — | — | — | — | 577.4 | 577.5 | 577.7 | 578.0 | 577.9 | 577.7 |
| Fe 2p$_{3/2}$ | 711.8 | 711.4 | 710.5 | 710.5 | 711.1 | 710.9 | 710.4 | 710.5 | 711.5 | 711.9 | 712.0 |
| Fe 3p | 55.1 | 55.3 | 54.7 | 54.6 | 54.7 | 54.7 | 54.6 | 54.6 | 54.8 | 56.6 | 56.9 |
| Zn 2p$_{3/2}$ | 1022.5 | 1022.8 | 1022.5 | 1022.3 | 1022.4 | 1022.3 | 1022.4 | 1022.6 | 1022.5 | — | — |

[x] The line lacks or is very slight.

and sulphate forms on the boundary between the silicate core and the sulphide film, it is possible to estimate the oxygen fugacity at 1000°K, according to data by Garrels and Christ (1965), to be lg $F_{O_2-}$ $(-10) \div (-11)$. The decrease of the Zn, S, Na concentration and that of other elements from surface to center of particles and the sharp energy change of a number of lines of the main silicate forming element in the outer layer, is an indirect indication of a "hot" contact between the silicate core and the sulfide-halide film. This makes it possible to estimate oxygen fugacity under high temperature conditions.

An additional confirmation of the high oxidation state of the silicate matrix is the shift of line maximum energy for Fe and S, which is smaller for O, Al, Ti and CA. This is observed not only on the surface which has undergone oxidation in the earth's atmosphere, but also at a depth of 800 Å or more.

## Sample 75080

The fine regolith fraction of this sample has been studied indicating quite different features from 74220.

The most characteristic spectra are given in Figs. 9–14. Table 2 lists the line maximum energy of intershell electrons from sample surface and depth.

The detailed analysis of element lines shows the occurrence of Si, Ti and Fe

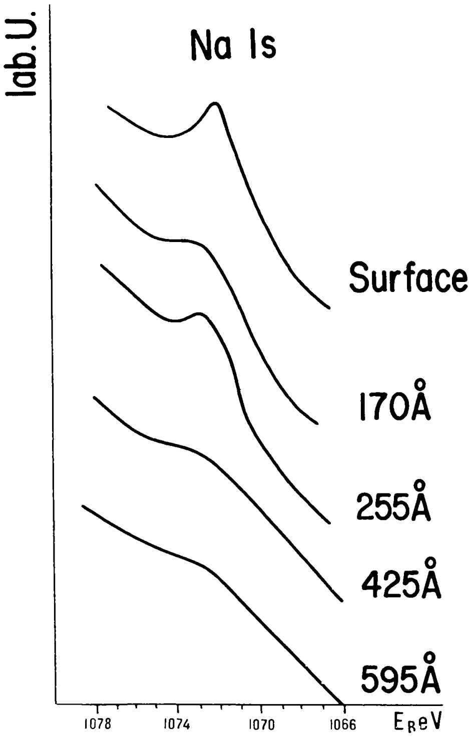

**Fig. 9.** Spectra of 1s electrons of sodium on the surface and at depth of particles of sample 75080.

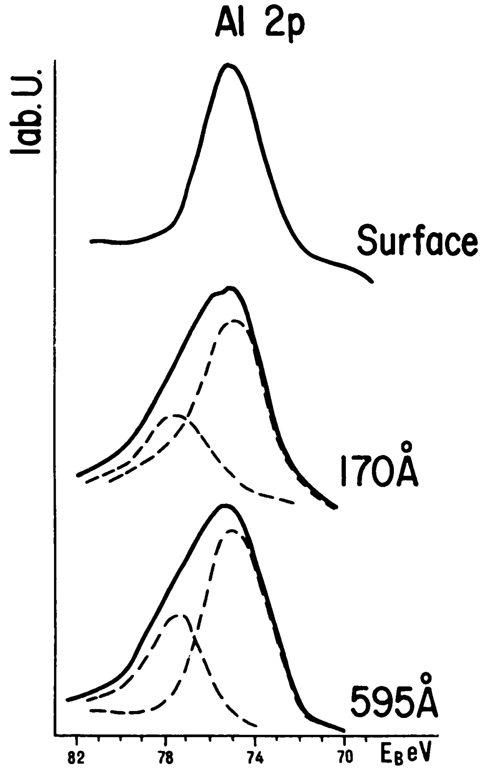

**Fig. 10.** Spectra of 2p electrons of aluminium on the surface and at depth of particles of sample 75080.

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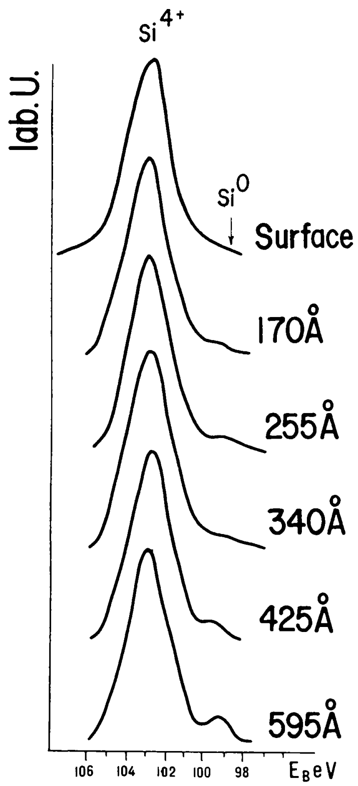

**Fig. 11.** Spectra of 2p electrons of silicon on the surface and at depth of particles of sample 75080.

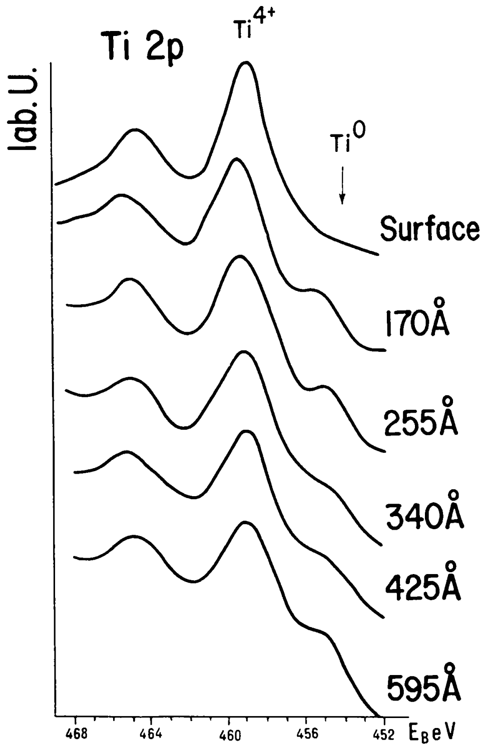

**Fig. 12.** Spectra of 2p electrons of titanium on the surface and at depth of particles of sample 75080.

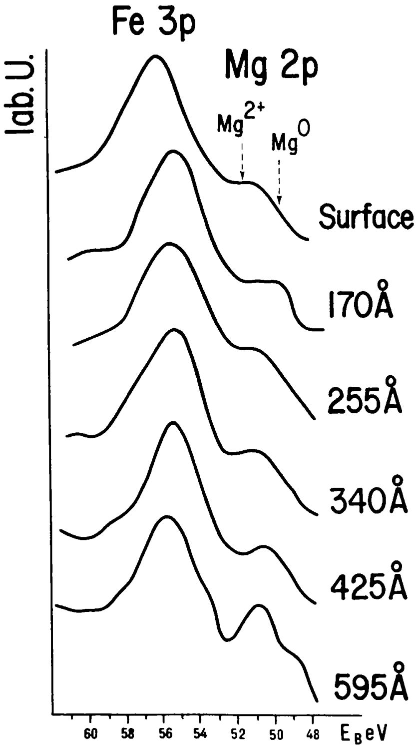

Fig. 13. Spectra of 2p electrons of magnesium and 3p electrons of iron on the surface and at depth of particles of sample 75080.

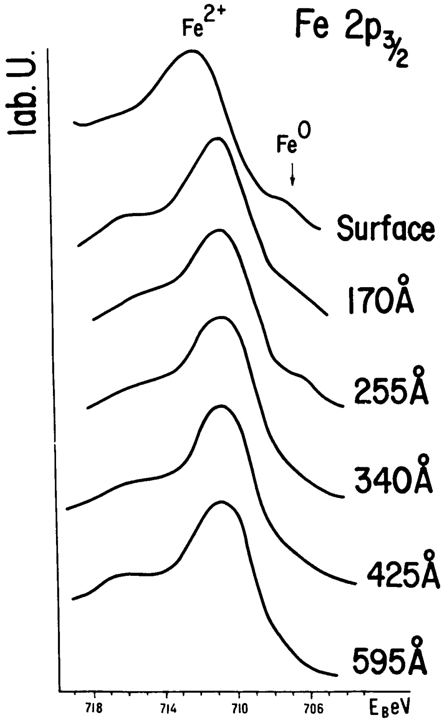

Fig. 14. Spectra of $2p\frac{3}{2}$ electron of iron on the surface and at depth of particles of sample 75080.

**Table 2.** The main maximum position of the innershell electrons of the major elements in the sample 75080 (in eV).

| Element, line | Surface | Depth, Å 170 | 255 | 4340 | 425 | 510 | 595 | 680 | 850 |
|---|---|---|---|---|---|---|---|---|---|
| O 1s | 531.5 | 532.2 | 532.0 | 532.0 | 532.0 | 532.0 | 531.9 | 531.9 | 532.0 |
| Fe $2p_{3/2}$ | 711.9 | 710.6 | 710.8 | 710.8 | 710.9 | 710.8 | 710.8 | 711.1 | 711.0 |
| Ti $2p_{3/2}$ | 458.9 | 459.4 | 459.3 | 459.0 | 459.0 | 459.1 | 459.1 | 459.1 | 459.4 |
| Ca $2p_{3/2}$ | 348.4 | 348.2 | 347.9 | 347.9 | 348.0 | 347.8 | 347.8 | 347.8 | 347.9 |
| Si 2p | 103.1 | 103.1 | 103.0 | 103.0 | 102.8 | 103.0 | 103.0 | 103.0 | 103.0 |
| Al 2p | 75.0 | 74.8 | 74.8 | 75.1 | 74.9 | 75.0 | 75.1 | 75.0 | 75.2 |
| Fe 3p | 56.2 | 55.3 | 55.3 | 55.3 | 55.4 | 55.4 | 55.6 | 55.8 | 55.8 |
| Mg 2p | 51.4 | — | 51.5 | 51.5 | 51.3 | 51.1 | 50.8 | 51.0 | 51.0 |

in reduced form at all studied depths except for the outer layer, where only Fe° is found.

Besides Si°, Ti° and Fe° it is possible that Mg° is present, since the 2p–electron line of Mg° clearly shows as a bump on the low energy side (Fig. 13). The maximum of the bump is at 49.0–49.5 eV, which is sufficiently close to the bond energy of 2p–electrons of metallic Mg (49.24 eV).

The depth distribution of reduced forms is quite different from that established previously on Luna 16, 20, and 24 (Dikov *et al.,* 1977; 1978). The biggest difference is the predominance of Ti° over Fe°, Si°, and possibly Mg°.

At the same time, the depth distribution of reduced forms is not regular (no continuous increase or decrease). That is, the highest or lowest contents of one Me° do not coincide with those of the other Me°.

Besides the unexpected concentration and spatial distribution of reduced metals, the particles of sample 75080 possess more specific features determined by X-ray photoelectron spectra. There is a marked enrichment in Na and Ca in the surface layer compared with the outer layers, the existence of two Al-states and an increase with depth of the Mg/Fe ratio, which at the surface is about 0.3 but at a depth of 850 Å equals ~0.5.

The broad line of Al 2p–electrons (Fig. 10) is a superposition of two components: one with low bond energy of 74.6–75.0 eV and a second with high bond energy of ~77.0 eV. The ratio of these components at all studied depths apart from the surface is rather constant and equals 3:1, the low energy component dominating that of high energy.

The major component of the Al-line is situated in the region of bond energy equal to 74.6–75.0 eV, which is characteristic of four- and six-coordinated aluminum entering the silicate structure. The high energy component of the Al-line indicates a phase in which the Al–O bond has more ionic character than in silicates; i.e., in this case the existence of spinel type complex oxides would be suggested. The positions of other element maximum lines show no anomalies; they are within the usual values for crystal and glass-like silicates.

A further feature of sample 75080 is a spectrum of lines for the particle surface sharply distinct from that of inner layers. First it is characterized by the lack of reduced forms of all the elements apart from Ni and second, by the shift of the iron $2p_{\frac{3}{2}}$ and 3p–electron lines to the higher energies, and of oxygen 1s-electron line to lower energies region. This gives evidence for the oxidation of sample 75080 under terrestrial conditions.

## DISCUSSION AND CONCLUSIONS

The results of the study carried out have indicated that the surface layers of fine particles of regolith samples collected by Apollo 17 strongly differ from those of regolith samples collected by Luna 16, 20 and 24.

The regolith samples delivered by Luna spacecraft have a uniform distribution of elements throughout the particle volume, but in the case of Apollo 17 samples the elements have well-defined distributions: a regular layered (sample 74220) and irregular layered (sample 75080).

The results of X-ray photoelectron study on the Apollo 17 samples permit us to say that in the case of sample 74220:

1. The sharp two-layered structure of particles indicates that the layers are of different ages and their formation processes were very diverse.
2. The composition of the silicate substrate is characteristic of lunar rocks but this, together with the morphologic features of particles and total lack of reduced forms of elements, is not in conflict with existing ideas about their volcanic origin. The low degree of polymerization of silicon-oxygen tetrahedrons indicated by the energy of the line maximum of Si 2p–electron and also the appropriate value of bond energy of oxygen 1s–electron in the silicate matrix suggest that the parent magma has a composition in the basitic-ultrabasitic range.
3. High concentrations of S, Zn, Na, F, Cl in the surface film would be due to the fact that the film is formed by condensation of dry fumaroles and its thinness indicates that the sublimation process lasted a very short time.
4. A decreasing depth distribution of volatile elements and the increase of a part of oxide sulfur with depth suggest a ''hot'' contact of the film with the silicate core. Sufficiently high oxygen fugacity in the silicate melt would be the first cause of sulfur oxidation owing to the oxygen self-diffusion from the silicate core to the contact zone.

In the case of sample 75080 the most characteristic features obtained from X-ray photoelectron spectra are:

1. The high Ti content and relative low contents of Fe and Si which don't correlate with usual values of the bond break energy in the corresponding oxides.

2. Irregular distribution of reduced forms with depth in the soil particles.
3. A marked enrichment of Na in the particle surface layers.
4. Possible presence of aluminum as independent complex oxide, exclusive in the alumosilicate matrix.

All these facts suggest that the particle surface of sample 75080 is a result of condensation of high temperature gas, formed by meteorite impact.

Thus, the features of the surface layers of both studied Apollo 17 samples indicate these layers to be formed by condensation processes. At the same time the great differences in the features of the samples, the presence or lack of element reduced forms, quantity and composition of volatile elements and others, resulted from the varied origin of the clouds where condensation was occurring: the impact cloud in the case of sample 75080 and endogenic (fumarolic) cloud for the sample 74220.

Note also the lack of the passivating effects, which gives a marked sample oxidation over the surface under terrestrial conditions as opposed to the regolith fractions which are mainly transformed under the action of solar wind.

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