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ESCA-Investigation of lunar regolith from the Seas of Fertility and Tranquility

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Abstract—The x-ray photoelectron spectra Fe2p, Si2p, Ti2p, Al2p, Mg2p, O1s have been investigated in the samples of lunar regolith from the Seas of Fertility and Tranquility. The same spectra were obtained for approximately 30 minerals, oceanic gabbro, meteorite-eucrite, and several iron meteorites. The spectra were measured by means of a VIEE-15 spectrometer. The analysis of results shows that all investigated elements have a usual oxidation degree and in their nearest environment there are oxygen atoms. The prevailing coordination number of Al is 4.

In the Fe2p spectrum of regolith, together with lines of oxidized iron (from various mineral phases), a peak belonging to metallic iron and equaling 10–15% of the line intensity of oxidized iron was detected. Careful analysis and comparison of the Fe2p spectra in regolith, various iron meteorites and stainless steels leads to the following conclusion: Metallic iron in lunar regolith is present in a finely dispersed state and is extremely stable with respect to oxygen of the earth atmosphere.

INTRODUCTION

THE X-RAY PHOTOELECTRON SPECTROSCOPY can be used for the determination of the oxidation degree of elements in chemical compounds and for the study of different structural aspects (Siegbahn *et al.*, 1967). We have applied this new method for investigation of lunar regolith.

The principle of the ESCA-investigation is quite simple. The inner shell electron of the element under investigation is expelled by an x-ray quantum of a known energy $h\nu$. The kinetic energy E_{kin} of this electron is measured in the spectrometer. The binding energy E_b of the inner shell electron can then be calculated as the difference between the x-ray energy and the kinetic energy of the electron from the equation

$$E_b = h\nu - E_{\text{kin}} - \varphi$$

Where φ is the work function of the spectrometer material.

The value of the binding energy E_b depends on the chemical environment of the element under investigation. For example, this value for 2p-electron of iron is different for metallic iron and for compounds with iron in oxidation states II or III.

RESULTS AND DISCUSSION

The spectra were recorded by a Varian IEE-15 spectrometer. Alkα-line was used for excitation of spectra (voltage: 8 kV; current: 80mA; vacuum: 10^{-6} Torr). With help of retarding field the value E_{kin} was reduced to 100 eV. These conditions lead to the spectrum intensity maximum. The experimental procedure was quite similar to that described previously (Nefedov *et al.*, 1972).

The samples were prepared by rubbing the powder into a golden net placed on a metallic cylinder covered with an organic film not containing oxygen. The samples were also prepared by putting the powder on a sticky scotch-tape. Meteorites were investigated in the form of fillings. The spectra of the Sichote-Alyn meteorite and of some steels were recorded from whole samples in cylinder form. All spectra were recorded from several independent samples. For example, three regolith samples from the Sea of Fertility Luna-16-A3 (<0.083 mm) and two samples from the Sea of Tranquility 10005,35,2 were prepared (Table 1).

We also have investigated the electron binding energies of O, Mg, Al, Si, Fe, and Ti in about 30 minerals (Nefedov *et al.*, 1972), in gabbro from the mid-Indian Mountain ridge of the Indian Ocean, in several meteorites (including eucrite, kamacite, and taenite) and various steels. In the table there are the major element compositions in some of our samples (Vinogradov, 1971).

ESCA-spectra of regolith from different sites are quite similar, although as it was already established previously that the regolith from the Sea of Tranquility contains more Ti than the regolith from the Sea of Fertility. O1s-, Si2p-, Al2p- and Mg2p-spectra in lunar regolith are similar to those of the eucrite Chervony Koot and oceanic gabbro. It can be concluded that Mg, Al, and Si have the usual oxidation states in regolith and the nearest neighbors of these elements are oxygen atoms (Nefedov *et al.*, 1972).

A comparison of Al2p- and Si2p-lines in regolith and in well-known minerals allowed a qualitative evaluation of the mineral composition of lunar regolith. In accordance with many other methods (Vinogradov, 1971), it was shown that the coordination number of aluminum atom in most regolith minerals is four because the shift of Al2p-line in regolith (relative to the line in aluminum) is equal to 2.3 eV (Nefedov *et al.*, 1972). The Si2p-line shift in regolith is about 3.4 eV relative to the line in silicon. The shift of these lines in silicates varies from 4.0 eV in quartz SiO_2 to 3.0 eV in nepheline $NaAlSiO_4$. It can be concluded that the extreme basic and acid mineral phases are not present in essential amounts in lunar regolith. These results

Table 1. The compositions of lunar regoliths, eucrite and oceanic gabbro (wt. %).

Component	The Regolith from the Sea of Fertility Luna–16–A3	The Regolith from the Sea of Tranquility 10005,35,2	Eucrite Chervony Koot (Chirvinsky, Sokolova, 1946)	Oceanic Gabbro
SiO_2	42	43	49	27
Al_2O_3	15	13	13	12
Fe_2O_3	—	—	—	14
FeO	17	16	19	17
MgO	12	12	11	5
CaO	8.7	8	7	10
TiO_2	3.4	7	0.7	8
Na_2O	0.4	0.5	0.5	0.6
K_2O	0.1	0.1	0.1	0.9
S	0.2	—	—	—
Ni	0.02	0.007	—	—

are in good agreement with the data of other methods (Vinogradov, 1971); the regolith consists mainly of plagioclase, pyroxene, and olivine. The shift of Si2p-line in these minerals and regolith is practically the same.

Most interesting results can give a comparison of the Fe2p-lines in lunar and terrestrial samples. Three independent Fe2p-spectra of two samples from the Sea of Tranquility and seven independent Fe2p-spectra of three samples from the Sea of Fertility were recorded (Figs. 1 and 2). In all regolith spectra there are lines of metallic iron. These lines are absent in spectra of eucrite and oceanic gabbro. The lines of metallic iron are of course also absent in oxygen-containing minerals of usual origin.

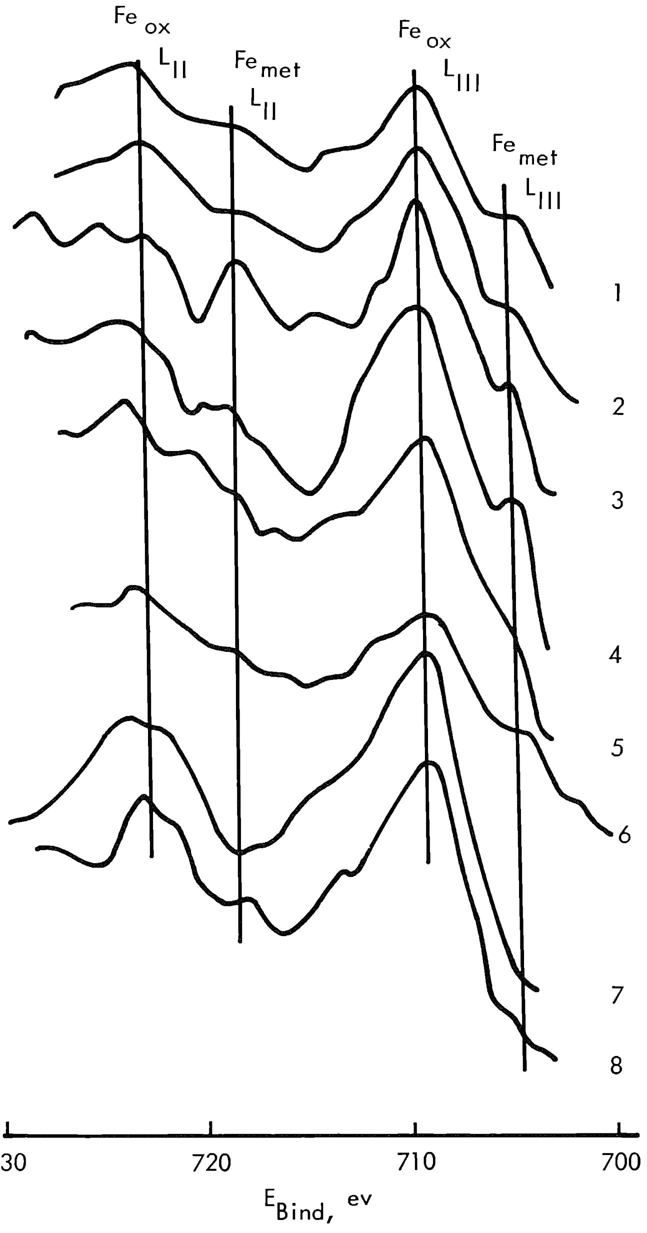

Fig. 1. Fe2p-lines. Curves: 1, 2 = the regolith from the Sea of Tranquility; 3–6 = the regolith from the Sea of Fertility; 7 = oceanic gabbro; 8 = eucrite Chervony Koot.

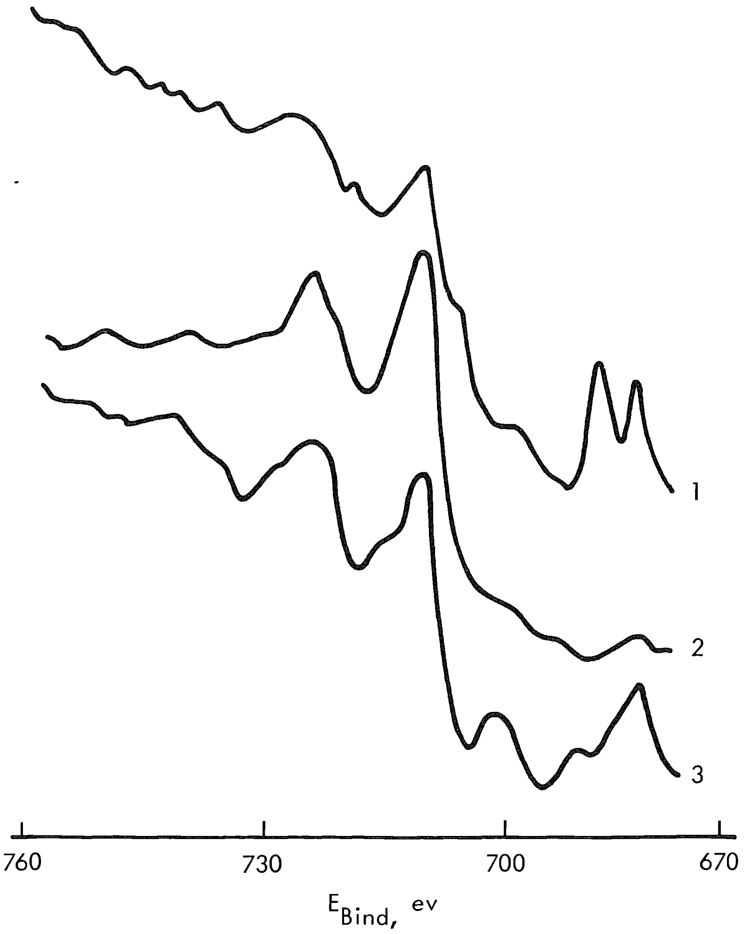

Fig. 2. Fe2p-lines (the larger spectral range). Curves: 1 = the regolith from the Sea of Fertility; 2 = oceanic gabbro; 3 = eucrite.

In pyrite FeS_2 and in pyrrhotite $Fe_{1-x}S$ there is a line in the same region (in $Fe_{1-x}S$ probably owing to the presence of FeS_2 in the surface layer, because in stoichiometric synthetic troilite FeS as well as in the sample of troilite from Sichote-Alyn iron meteorite this line is absent) (Fig. 3). We believe that this line in regolith spectra is mainly due to the presence of metallic iron and not to that of pyrite. There are several arguments for such a conclusion. The regolith contains little sulphur (only about two-tenths of a percent). The minerals pyrite and pyrrhotite have also not been found by other physical or chemical methods. It could be supposed that pyrite is distributed as a thin layer, therefore it was not possible to determine it. But in this case we must have a very intensive sulphur line. The latter was not proved. Thus, we must conclude that the recorded unusual maximum belongs mainly to metallic iron.

The presence of metallic iron in lunar regolith is in accordance with data of other methods. However ESCA-spectra allow to find out some unusual properties of this iron. For example, Mössbauer and electron spin resonance spectra of regolith have shown that the concentration of metallic iron constitutes only about 2–5% of all iron (Vinogradov, 1971). But from our Fe2p-spectra we must conclude that the line intensity of metallic iron is not less than 10% of the line intensity of the oxidized iron.

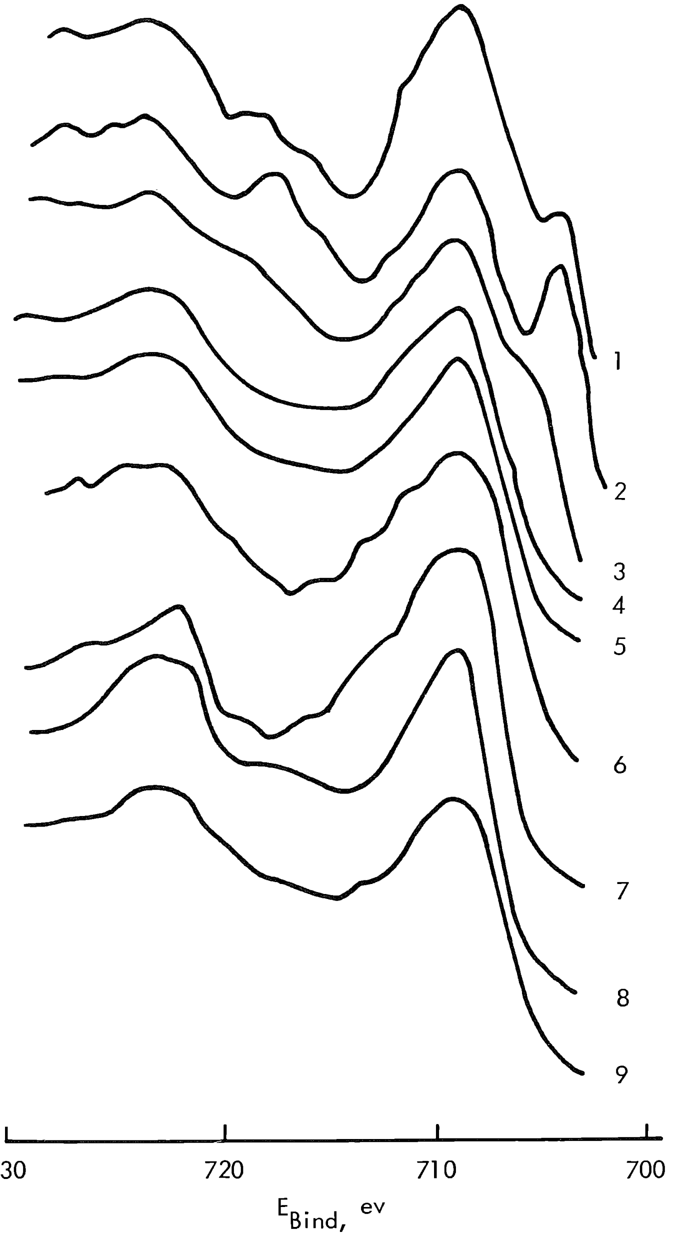

Fig. 3. Fe2p-lines. Curves: 1 = the regolith from the Sea of Fertility; 2 = pyrite FeS_2; 3 = pyrrhotite $Fe_{1-x}S$; 4 = troilite FeS; 5 = ilmenite $FeTiO_3$; 6 = olivine $(Mg, Fe)_2 SiO_4$; 7 = biotite $K(Mg, Fe)_3 (AlSi_3O_{10}) (OH)_2$; 8 = hematite Fe_2O_3; 9 = magnetite Fe_3O_4.

It is necessary to take into account that x-ray-photoelectron spectra can be obtained only from the thin surface layer of a sample (about 100 Å), therefore the relative surface of the metallic iron constitutes at least 10% of the oxidized iron surface although its volume and weight concentration is noticeably less. Besides that it is necessary to take into consideration that some part of the metallic iron surface is oxidized. From this we conclude that the metallic iron is present in regolith in a more dispersed state in comparison with other iron-containing minerals.

The second unusual property of lunar iron is its very high stability in the earth air atmosphere. Indeed the Fe2p-line of stainless steel shows that the surface layer is entirely oxidized (Fig. 4). Only after a careful cleaning of this sample surface the metallic iron line appears in the spectrum (Fig. 4). The time of air action is several minutes. After 24 hours of a sample being in the air, the line intensity of metallic iron sharply decreases and after three weeks practically disappears (Fig. 4).

The Fe2p-spectra of several iron meteorites were also investigated. In fresh kamacite fillings of the Gress meteorite, kamacite of the meteorite Sichote-Alyn and taenite of the meteorite Santa-Katarina, we observed the lines of metallic iron (Fig.

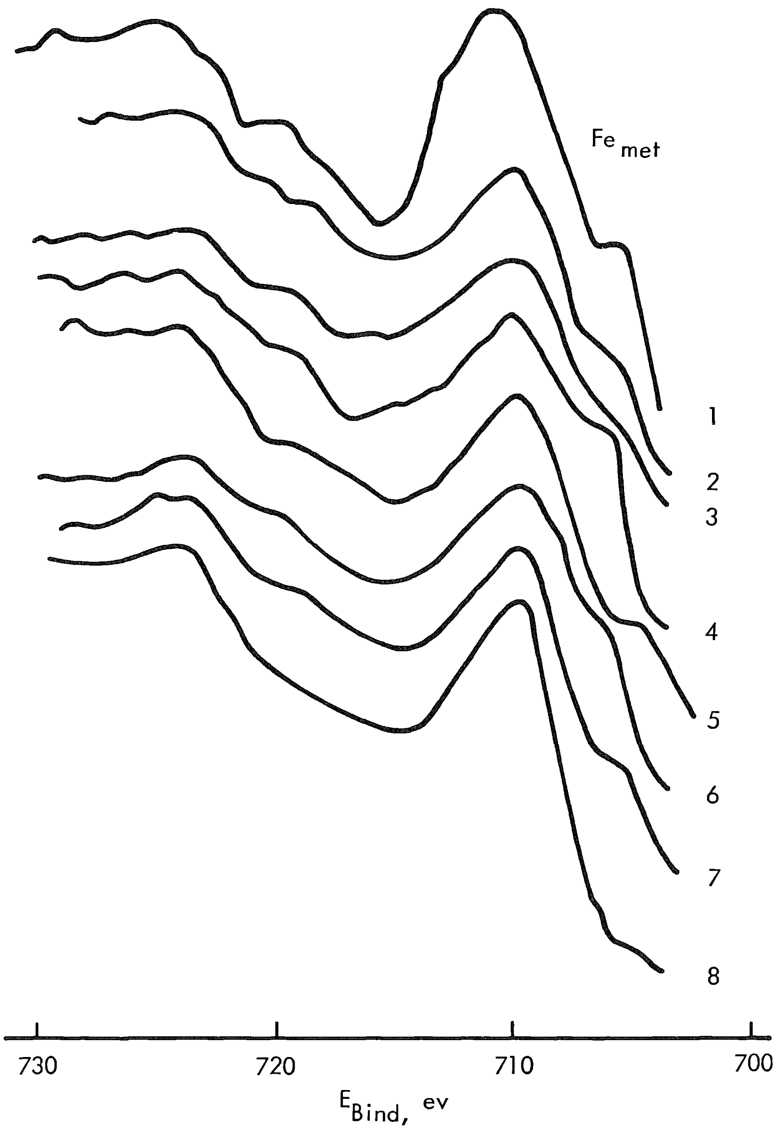

Fig. 4. Fe2p-lines. Curves: 1 = the regolith from the Sea of Fertility; 2 = kamacite, Santa-Katarina; 3 = taenite, Gressk; 4 = kamacite, Sichote-Alyn; 5 = kamacite, Sichote-Alyn, after 2 days of being in the air; 6 = stainless steel, after cleaning of surface; 7 = stainless steel, after 24 hours of being in the air; 8 = stainless steel, after 3 weeks of being in the air.

1972LPSC....3.1421V

4). These line intensities decreases sharply after a stay in the air during two days, however after the following ten days or three weeks in the air they did not sufficiently change. These facts show that meteoritic iron is relatively resistant to air oxygen.

The investigation regolith samples had been in the atmosphere approximately during half a year. Nevertheless the ratio of intensity maxima of metallic and oxidized iron in lunar regolith is approximately equivalent to this ratio in samples of iron meteorites or steels, though metallic iron in regolith is a very small part of the oxidized iron. Thus, these observations are in accordance with each other only in the case of an unusual resistance of lunar metallic iron to oxidation by oxygen of the earth atmosphere.

Indeed let us suppose that lunar metallic iron is noticeably oxidized. Then the observed ratio of the intensity maxima of oxidized and metallic iron would be possible only at a very high dispersity degree of the metallic iron in regolith. In this case the surface of metallic iron would be much larger than the surface of the iron-containing minerals. However then we had to expect a sharp increase of relative Fe2p-line intensity from oxidized forms of Fe, for example, relative to the Si2p-line in comparison with eucrite or oceanic gabbro. But this is not the case in our experiments.

Thus, the experimental data lead to the conclusions that metallic iron in lunar regolith is in a finely dispersed state and the oxide film on its surface is very thin or even partly absent. The possible reasons for such unusual surface properties are the following: (1) the high purity of the metallic phase (or unusual set of dopants); (2) the condensation of the metallic phase under conditions of a very high vacuum; (3) the irradiation (and cleaning) of the metallic iron surface by ionic flow (solar wind) during a long time.

Now all these factors are under investigation in our laboratories.

REFERENCES

Chirvinsky P. N. and Sokolova A. I. (1946) Petrographical and chemical characteristics of the Chervony Koot eucrite (fall on June 23, 1939). *Meteoritica* **III,** 37.

Nefedov V. I., Urusov V. S., and Kakhana M. M. (1972) ESCA-investigation of chemical bond in minerals of Na, Mg, Al, and Si. *Geochemistry* (Russian), N 1, 11.

Siegbahn K., Nordling C., Fahlman A., Nordberg R., Hamrin K., Hedman J., Johansson G., Bergmark T., Karlsson S. E., Lindgren I., and Lindberg B. (1967) ESCA atomic, molecular, and solid state structure studied by means of electron spectroscopy. *Nova Acta Reg. Soc. Scient. Upsaliensis*, ser. IV, v. 20, Uppsala.

Vinogradov A. P. (1971) Preliminary data on lunar ground brought to earth by the automatic probe "Luna-16." *Geochemistry* (Russian), N 3, 261; also *Proc. Second Lunar Sci. Conf.*, *Geochim. Cosmochim. Acta* Suppl. 2, Vol. 1, pp. 1–16. Pergamon.