To the Problem About the Origin of Lunar Maria And Continents (Mössbauer Investigations)

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A comparative study of Mossbauer spectra of regolith returned by the Luna 16 and Luna 20 spacecraft has shown that the distribution of iron among the mineral phases is quite characteristic of the landing sites. The overall fractions of regolith measured had the following grain sizes: 0.200 to 0.450 mm, 0.127 to 0.200 mm, 0.083 to 0.127 mm, and ≤ 0.083 mm.

The Mossbauer spectra of the mare regolith of Luna 16 differ significantly for all fractions from the spectra for the same fractions of continental regolith (Luna 20).

The total quantity of iron is 1.85 times greater in the mare regolith. There is 2.4 times less olivine in the mare region than in the continental region and it is higher in iron content (by 1.85 times). The pyroxene component of the mare regolith is less homogeneous in composition (contains more augite and glass) and is present in larger quantities. Ilmenite was found only in the mare regolith. In the continental region, the predominant titanium-containing phase is ulvospinel. The mare regolith contains more metallic iron, which is more finely dispersed and contains less nickel. Troilite is found in the maria region.

Based on these differences, it is concluded that the formation of continental rocks occurred at an earlier stage of crystallization from the melt and at higher temperatures and higher partial pressures of oxygen. The mare basalts crystallized from a more reduced magma, apparently in a later process.

Results

The distribution of iron among the mineral phases in the lunar rocks depends both on the physical conditions of crystallization of the minerals and on the chemical composition of the initial magma. Therefore, it is very important to do comparative phase analysis of lunar material that comes from various regions of the Moon and has not been subjected to any physical and chemical effects. The method of Mossbauer spectroscopy allows the material to be studied without preliminary separation. The overall regolith fractions returned by the Luna 16 and Luna 20 probes were measured on a Mossbauer spectrometer with a Co 57 source (refs. 1 and 2 and Malysheva, 1972 and 1974).

Measurements were performed at room temperature and at liquid nitrogen temperature. The analytical data were processed on a BESM–3m and a BESM–4 computer by the least-squares method assuming a Lorentz shape for the Mossbauer absorption line. The regolith fractions analyzed had the following grain sizes: 0.200 to 0.450 mm, 0.127 to 0.200 mm, 0.083 to 0.127 mm, and 0.083 mm.

The Mossbauer spectra of the fine regolith fractions (grain size 0.083 mm) are pre-

sented in figure 1. The same quantity of sample was measured under identical conditions in order to allow direct comparison of both spectra. The comparison of the fine regolith fractions is more obvious, due to the distinct peaks of metallic iron. One can see from the figures that the total area beneath the Mossbauer peaks for iron-containing minerals from the Luna 16 regolith is greater than for the Luna 20 regolith (according to the relative total peak areas, 1.85 times). The basic iron-containing minerals are identical in both fractions (two main peaks) and are silicates: olivine, pyroxene, and glass. Figure 2 presents the Mossbauer spectra of the same

fractions of Luna 16 and Luna 20 regolith measured with lower rates of movement of the source relative to the absorber. In the middle part of the spectrum we clearly see the disappearance of peaks belonging to ilmenite in the regolith of Luna 20. In place of ilmenite there are peaks belonging to ulvospinel.

Table 1 shows the parameters of the olivine component of the Mossbauer spectra of the Luna 16 and Luna 20 regolith. We can see that the quadrupole splitting Δ decreases with decreasing grain size from 2.94 to 2.88 mm/s for Luna 16 and from 3.00 to 2.93 mm/s for Luna 20, indicating an increase in
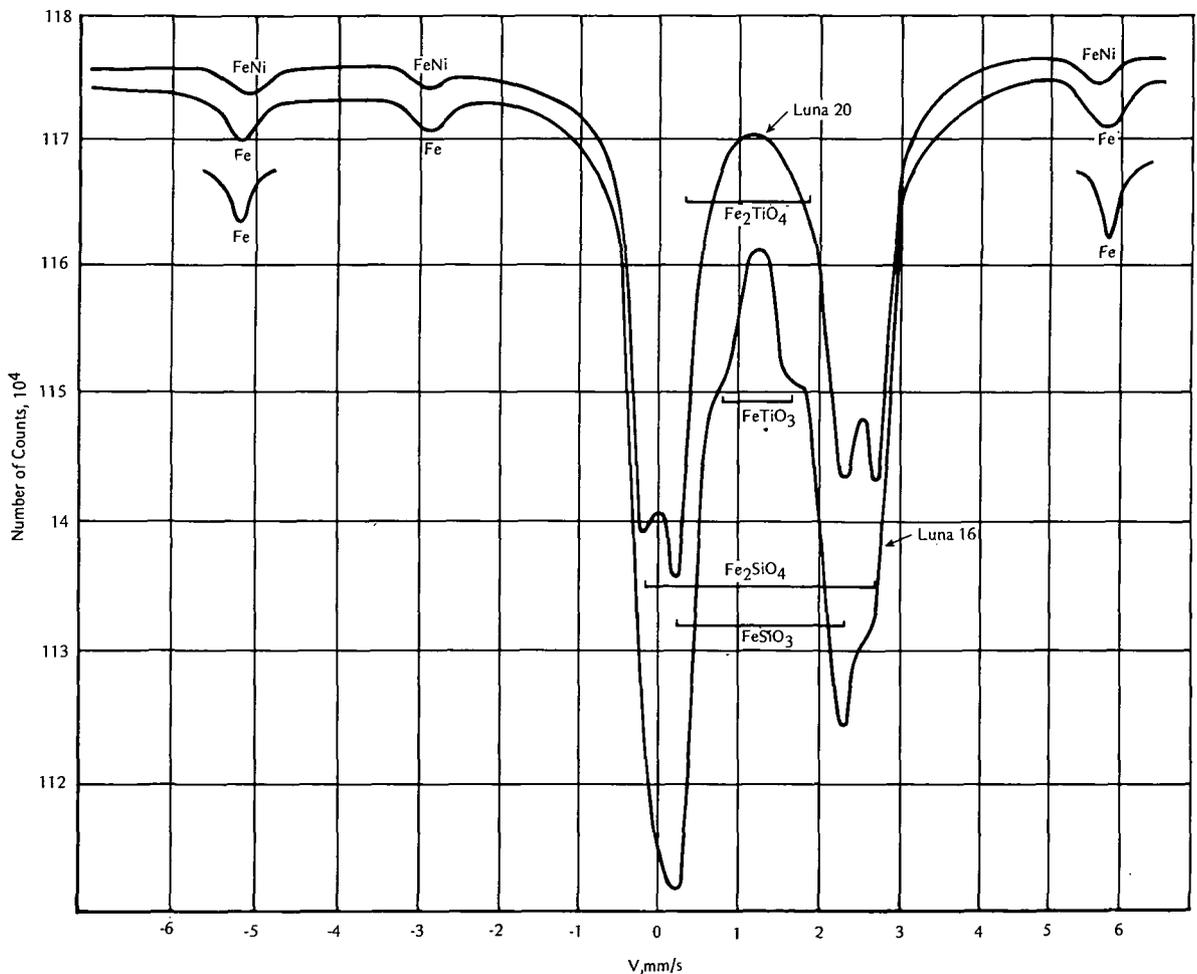

Figure 1.—*Mössbauer spectra of fine fractions of regolith returned by the Luna 16 and Luna 20 spacecraft (high speed of motion of source relative to absorber).*
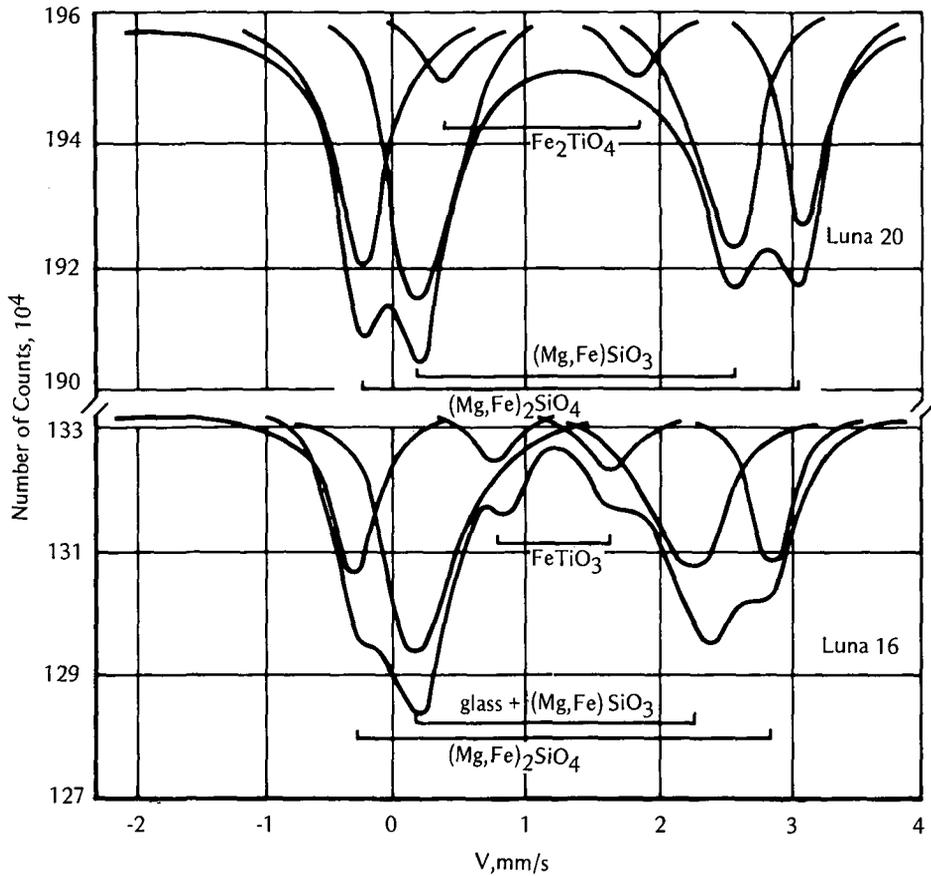
Figure 2.—*Mössbauer spectra and fine fractions of Luna 16 and Luna 20 regolith (low speed of relative motion).*

the iron content of the olivine with decreasing grain size both for the continental olivine and for the olivine from Mare Fecunditatis. The dependence of the quadrupole splitting on the fayalite content of olivine for terrestrial specimens forms a straight line (fig. 3).

If we place the data produced for the olivines of Luna 16 and Luna 20 on this line, we see that the fayalite content of olivines from Mare Fecunditatis lies within 50 and 80 percent, whereas for specimens from the continental region the fayalite content is lower (20 to 50 percent). Thus, the mean content of fayalite in the olivine is 1.85 times less for the Luna 20 regolith than for the Luna 16 regolith. The total iron content in the Luna 20 regolith (see above) is also 1.85 times

less than in the Luna 16 regolith. A comparison of the fayalite content of olivines with the total iron content of the rocks returned by Apollo 11 and 12 yields similar results (Mason et al., 1971). The ratio FeO/(FeO + MgO) for the specimens of Apollo 11 was 41 mol. % and for the specimens of Apollo 12, 43 mol. %, corresponding to an olivine composition of 26 to 60 mol. % Fe_2SiO_4, or an average of 41 percent. The agreement of the fayalite content of olivine with the total iron content of the rock is evidence of a second generation of phenocrysts (Stanik, 1970).

The widths of the Mossbauer lines Γ (table 1) for olivines from the Luna 20 regolith are less than for Luna 16 olivines indicating their more homogeneous composition and slower cooling.

Table 1.—*Parameters of the Mossbauer Spectra for the Olivine Component of the Luna 16 and Luna 20 Regoliths*

Grain Size	δ mm/s		Δ mm/s		Γ mm/s Luna 16		Γ mm/s Luna 20	
	Luna 16	Luna 20	Luna 16	Luna 20	left peak	right peak	left peak	right peak
0.200–0.450	1.27 ± 0.02	1.29 ± 0.005	2.94 ± 0.01	3.00 ± 0.005	0.310 ± 0.003	0.422 ± 0.003	0.290 ± 0.005	0.360 ± 0.005
0.127–0.200	1.26 ± 0.02	1.275 ± 0.002	2.92 ± 0.01	2.998 ± 0.008	0.364 ± 0.005	0.426 ± 0.005	0.336 ± 0.003	0.360 ± 0.004
0.083–0.127	1.26 ± 0.02	1.275 ± 0.003	2.90 ± 0.01	2.984 ± 0.001	0.325 ± 0.002	0.417 ± 0.004	0.325 ± 0.002	0.357 ± 0.002
0.0–0.083	1.25 ± 0.005	1.26 ± 0.005	2.88 ± 0.005	2.93 ± 0.01	0.340 ± 0.005	0.596 ± 0.005	0.335 ± 0.002	0.360 ± 0.002

NOTES: δ = chemical shift relative to Co^{57} source in stainless steel
Δ = quadrupole splitting
Γ = line width

Table 2.—*Parameters of Mossbauer Spectra for the Pyroxene Component of Luna 16 and Luna 20 Regoliths*

Grain Size	δ mm/s		Δ mm/s		Γ Luna 16		mm/s Luna 20	
	Luna 16	Luna 20	Luna 16	Luna 20	low velocity peak	high velocity peak	low velocity peak	high velocity peak
0.200–0.450	1.21 ± 0.03	1.28 ± 0.005	2.06 ± 0.04	2.130 ± 0.005	0.61 ± 0.01	0.83 ± 0.01	0.47 ± 0.005	0.510 ± 0.005
0.127–0.200	1.24 ± 0.01	1.257 ± 0.002	2.05 ± 0.01	2.126 ± 0.002	0.61 ± 0.01	0.82 ± 0.01	0.440 ± 0.004	0.495 ± 0.006
0.083–0.127	1.24 ± 0.01	1.263 ± 0.002	2.05 ± 0.01	2.140 ± 0.001	0.59 ± 0.01	0.68 ± 0.01	0.442 ± 0.002	0.495 ± 0.005
0.0–0.083	1.24 ± 0.004	1.25 ± 0.01	2.03 ± 0.003	2.100 ± 0.002	0.580 ± 0.003	0.601 ± 0.008	0.445 ± 0.003	0.503 ± 0.006

NOTES: δ = chemical shift relative to Co^{57} source in stainless steel
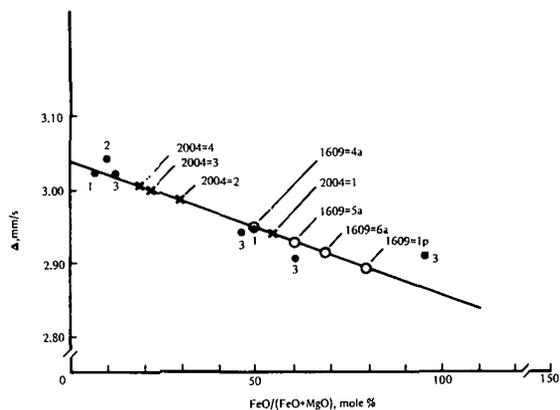Δ = quadrupole splitting
Γ = line width

Figure 3.—*Quadrupole splitting as a function of iron content of olivine,* $f = \dfrac{FeO}{FeO + MgO}$ *mole %. Point 1 is from reference 3, point 2 is from reference 4, and point 3 is from reference 5. Luna 20 regolith specimens, 2004-4, 2004-3, 2004-2, and 2004-1 have grain sizes 0.250-0.400, 0.127-0.250, 0.083-0127, and $\leq$ 0.083mm, respectively. Luna 16 regolith samples, 1609-4a, 1609-5a, 1609-6a, and 1609-1p have grain sizes 0.250-0.400, 0.127-0.250, 0.083-0.0127, and $\leq$ 0.083mm, respectively.*

The parameters of the Mossbauer spectra of the pyroxenes are presented in table 2. Comparison of the line widths of the pyroxene component of the regolith of Luna 16 and Luna 20 shows that Γ for the Luna 20 pyroxene is approximately 1.5 times less than for the Luna 16 pyroxene. This indicates a more homogeneous composition of the pyroxene component of Luna 20. At the same time, the quadrupole splitting and chemical shifts are greater for the Luna 20 pyroxene. The combination of these factors indicates that in the Luna 20 regolith there is less glass and augite, which agrees with the data of X-ray spectroscopy (personal communication from Ye. S. Makarov).

In all fractions of the Luna 16 regolith, peaks are easily identified with parameters $\delta = 1.20$–1.24 mm/s and $\Delta = 0.66$–0.71 mm/s which belong to ilmenite (the internal peaks in fig. 2). However, no ilmenite is found in the continental specimens (Luna 20). Ilmenite, although widespread in lunar mare specimens (from 5 to 20 percent) (Thiel et al.,

1972) is not characteristic for the lunar continent.

In the fine fractions of the Mossbauer spectra of the regolith of Luna 16 and Luna 20, given equal amplitudes and widths of doublet lines, one can identify ulvospinel Fe_2TiO_4 with the following parameters: $\delta = 0.69 \pm 0.08$ mm/s; $\Delta = 1.79 \pm 0.07$ mm/s (Luna 20) and $\delta = 0.91 \pm 0.03$; $\Delta = 1.82 \pm 0.03$ mm/s (Luna 16). These quantities agree well with the values for ulvospinel in Ono et al. (1968).

The ulvospinel found in significant quantities is the end member in the ulvospinel-chromite series, a new mineral series which is specific for lunar specimens. Chromite, $FeCr_2O_4$, has not been identified in the Mossbauer spectra of the lunar regolith within the limits of measurement accuracy.

The Mossbauer spectra of the Luna 20 regolith, as well as Luna 16 regolith, show three of the six peaks due to the superfine magnetic splitting of metallic iron (fig. 1).

When we compare the positions of the extreme peaks of the superfine splitting of metallic iron of the finest regolith fractions (table 3), we see that the position of the extreme peaks for specimen 9-1r (Luna 16) coincides with the position of the peaks for pure metallic iron; whereas for specimen 4-1 (Luna 20), the peaks are shifted inward in the spectrum, i.e., the superfine magnetic field on the iron nucleus in this specimen is 1.013 times less than in pure metallic iron.

This indicates that in the regolith of Luna 20, metallic iron is present as an alloy with nickel. In a study of lunar anorthosites from the regolith of Apollo 11 (Dickey 1970), it was also shown that metallic iron in the

Table 3.—*Position of Extreme Peaks of Superfine Magnetic Splitting for Metallic Iron in Fine Fractions of Luna 16 and Luna 20 Samples*

Specimen	Left Peak	Right Peak
2004–1 (Luna 20)	112.99 ± 0.17	450.48 ± 0.18
1609–1 (Luna 16)	115.50 ± 0.36	147.24 ± 0.85
Pure Metallic Iron	112.48 ± 0.14	449.96 ± 0.15

anorthosites contains from 6 to 20 percent Ni (kamasite and taenite), while the metal in the basalts is present almost as pure iron. However, determination of the composition and quantity of the metallic phase (20 to 30 percent Ni) against the background of a complex spectrum is impossible. This is true since at these concentrations the particles of iron do not produce magnetic splitting and only the paramagnetic peak is present in the spectrum (Azano, 1969) and its position coincides with the low-velocity peak of the silicate doublet. Furthermore, the presence of finely dispersed iron in the metallic phase, with sufficiently small particle size, may cause paramagnetic lines to develop in place of superfine magnetic splitting when the superparamagnetic relaxation becomes sufficiently fast and comparable to the rate of Larmor precession of nuclei in a superfine field. The position of the paramagnetic peak of finely dispersed iron also corresponds to the low-velocity peak of the quadrupole doublet, caused by iron in silicate. The presence of finely dispersed iron in the lunar regolith was determined in X-ray-electron spectra of Luna 16 and Luna 20 specimens (refs. 6 and 7). Housley et al., (1972), calculated the transition temperatures between ferromagnetism and superparamagnetism in the Moss-

bauer spectra for particles of various sizes: for $\phi = 134$ Å at 295 K, for $\phi = 85$ Å at 77 K, and for $\phi = 75$ Å at 11 K.

Both in the specimens of Luna 16 and in the specimens of Luna 20, the area of the left peak (low-velocity peak) is greater than the area of the right peak (high-velocity peak) (ref. 1). This difference increases with decreasing particle size. The asymmetrical nature of the Mossbauer spectrum was noted (Duchesne et al., 1971) in a study of the regolith of Apollo 12. The authors related this to the presence of finely dispersed paramagnetic iron with particle size less than 1 μ.

In order to determine the presence of finely dispersed iron, measurements were performed at liquid nitrogen temperatures using the fine fractions (particle size 0.083 mm) from the Luna 16 and Luna 20 regolith. The area of the peaks belonging to metallic iron for the Luna 16 regolith increased to 10.7 percent relative to the other iron-containing minerals. Consequently, at least 4.85 percent of the iron (about half) is in the finely dispersed state with particle size of 85 to 134 Å. The area of peaks due to metallic iron in the Luna 20 regolith remained almost unchanged (6.12 percent), indicating the absence of any significant quantity of finely dispersed iron in specimens from the continental region of the

Table 4.—*Distribution of Iron Among Primary Mineral Phases in Regolith Returned by Luna 16 and Luna 20 in Percent of the Total Area of the Mossbauer Spectrum*

Minerals	Luna 16				Luna 20			
	Grain Size				Grain Size			
	0.25–0.400	0.127–0.200	0.083–0.127	≤0.083	0.250–0.400	0.127–0.200	0.083–0.127	0.083
Olivine	15.8	16.2	22.6	22.0	38.0	35.6	34.8	36.0
Pyroxene + Glass	79.3	75.8	71.0	55.0	60.07	64.4	65.5	56.8
Ilmenite	4.9	4.9	5.8	5.72	1	1	1	1
Ulvospinel	1	1	1	6.25	2.1	1	1	6.6
Metallic Iron 300 K	3.5	3.3	3.1	5.85	1	2	4.5	5.65
80 K	—	—	—	10.7	—	—	—	6.12
Troilite	1	1	2.8	2.0	1	1	1	1

Table 5.—*Distribution of Iron Among Mineral Phases in Weight Percent of the Total Quantity of Minerals*

Mineral	Luna 16		Luna 20	
	Particle Size 0.250–0.400	≤0.083	Particle Size 0.250–0.400	≤0.083
Olivine	4.6	5.3	15	8.1
Pyroxene and Glass	53.6	50.0	24.0	31.0
Ilmenite	1.0	1.8	0.05	0.05
Ulvospinel	0.05	1.4	0.2	0.82
Metallic Iron				
$T_{meas} = 300$ K	0.28	0.6	0.05	0.35
$T_{meas} = 80$ K	—	1.1	—	0.38
Troilite	0.05	0.6	0.05	0.05
Plagioclase	40	40	60	60

Moon. Apparently, the difference in areas of the right and left peaks of the silicate component for the Luna 20 regolith can be explained by the presence of 5 percent $Fe3+$.

The distribution of iron in the mineral phases as a percent of the total area of the Mossbauer spectra is presented in table 4.

The distribution of iron among mineral phases in weight percent is given in table 5. Calculations were made based on the following assumptions:

1. The resonant absorption is identical for all minerals.
2. The iron content of pyroxene and glass,

$$f = 20 \frac{FeO}{FeO + MgO} \text{ mol.\%.}$$

3. The iron content of olivine (fig. 3) for the Luna 16 regolith is 50 percent and 80 percent for fractions with grain size 0.250 to 0.400 and 0.083, respectively. For the Luna 20 regolith $f = 20$ percent and 50 percent for fractions of the same size.
4. The ilmenite and ulvospinel contain no magnesium.
5. The content of nickel in the iron was ignored.
6. The quantity of plagioclase was estimated on the basis of mineralogical

and petrological work (Albee et al., 1972; Steel et al., 1972; Tarasov et al., 1973).

According to tables 4 and 5, the distribution of iron among the mineral phases is different and is representative for each sampling area (ref. 8). Therefore, based on the data produced we can draw general conclusions concerning the main differences between distinguishing features of mare and continental regoliths. On the other hand, the composition of regolith may be characteristic of the composition of the lunar rock of that region (ref. 9). Consequently, we can draw general conclusions about the characteristics of mare and continental areas of the Moon. The basic distinguishing features found from the Mossbauer studies are as follows:

1. The total content of iron is twofold greater in the mare regions.
2. There is 2.4 times less olivine in the mare regions than in the continental regions and it is twofold higher in iron content.
3. The pyroxene component of the mare regolith is less homogeneous in composition (contains more augite and glass)

and is present in twofold larger quantities than in the continental region.

4. Ilmenite was detected in the mare regolith.

5. In the continental region, the predominant titanium-containing phase is ulvospinel.

6. In the mare regolith, there is more metallic iron, which is more finely dispersed and contains less nickel.

7. There is more troilite in the mare regions.

These differences may result from differences in the chemical composition of the inital material or may reflect the physical conditions of crystallization of the minerals.

Let us study the relationship of the basic components in the regolith of Luna 16 and Luna 20 (ref. 9) (table 6).

If the decrease in the quantity of ilmenite in the continental region can be explained by an increase in the FeO/TiO_2 ratio, the increase in the olivine component relative to pyroxene (table 5) cannot be explained by differences in chemical composition because the $\dfrac{FeO+MgO}{SiO_2}$ ratio becomes less or remains unchanged if we consider the increase in the quantity of plagioclase.

In connection with this, we must note the differences in physical conditions of crystallization of rocks from the magma.

Since the mean iron content of olivine in the continental rocks is two times less than for the mare rocks, its crystallization must apparently have occurred at higher temperatures ($\sim 1300°$ C). If we use calculations of the minimum partial pressure of oxygen f_{O_2} necessary for the equilibrium composition of spinel at 1300°C (Haggerty, 1972), then for the mare basalts enriched in olivine we obtain $f_{O_2} = 10^{-13}$ atm, and for the continental rocks containing ulvospinel, $f_{O_2} = 10^{-11}$ atm.

The petrological, X-ray, and micro-X-ray studies confirm that the mare basalt of Luna 16 and Apollo 11 were formed by rapid, one-event surface crystallization of rocks at an oxygen partial pressure of 10^{-13} atm (Bence et al., 1972).

In summary, one can propose that the formation of continental rocks occurred in an earlier stage of crystallization from a melt and at a higher temperature and higher partial pressure of oxygen. The same conclusions were reached by Hubbard et al. (1973) by analysis of the content of Eu, Sr, and Al_2O_3 in continental rocks. Obviously, the conditions of increased temperature and pressure are related to greater depths. The mare basalts were crystallized from more reduced magma (progressive loss of volatiles) in a later process.

The formation of the mare basalts under more reduced conditions is also confirmed by data on the composition of olivine. According to Tarasov et al. (1973), the mare olivines contain more chromium than the continental olivines, while thermodynamic studies (ref. 10) have shown that the content of chromium in olivine increases with increasing reducing conditions.

References

1. MALYSHEVA, T. V., Mossbauer Spectroscopy of Lunar Regolith Returned by the Luna 20 Spacecraft. *Geokhimiya*, No. 7, 1973, pp. 1079–1084.

2. MALYSHEVA, T. V. AND V. V. KURASH, Mossbauer Spectroscopy of Lunar Specimens. *Geokhimiya*, No. 1, 1973, pp. 120–125.

3. MALYSHEVA, T. V., V. V. KURASH AND A. N. YERMAKOV, *Geokhimiya*, No. 2, 1969.

4. MALYSHEVA, T. V., V. V. KURASH AND A. N. YERMAKOV, Proceedings of the Conference on Mossbauer Spectrometry. *Drosden*, 1971, p. 267.

Table 6.—*Ratio of Certain Oxides in the Regolith of Luna 16 and Luna 20*

	Luna 16	Luna 20
$\dfrac{FeO}{TiO_2}$	5	12.5
$\dfrac{FeO}{SiO_2}$	0.38 0.63	0.16 0.41
$\dfrac{Mg}{SiO_2}$	0.25	0.25

5. BANCROFT, G. M., A. G. MADDOCK AND R. C. BURNS, *Am. Minerol.*, Vol. 52, Nos. 7 and 8, 1967.

6. VINOGRADOV, A. P., V. I. NEFEDOV, V. S. URUSOV AND M. M. ZHAVORONKOV, X-Ray–Electron Study of Lunar Regolith From the Sea of Fertility and Sea of Tranquility. *DAN SSSR*, Vol. 201, No. 4, 1971, p. 957.

7. VINOGRADOV, A. P., V. I. NEFEDOV, V. S. URUSOV AND M. M. ZHAVORONKOV, X-Ray–Electron Studies of Metallic Iron in Lunar Regolith. *DAN SSSR*, Vol. 207, No. 3, 1972, p. 433.

8. VINOGRADOV, A. P., The Genesis of the Regolith of the Moon. *Lunnyy Grunt Iz Morya Izobiliya*, 1974.

9. VINOGRADOV, A. P., Preliminary Data on Lunar Soil Returned by the Luna 20 Spacecraft. *Geokhimiya*, No. 7, 1972.

10. IL'IN, N. P. AND A. N. KOLOMEYTSEVA, Influence of Temperature and Pressure on the Distribution of Iron Group Elements Among Metal-Silicate Phases in the Process of Differentiation of Matter. *Abstracts of the Soviet-American Lunar Conference*, Moscow, 1974.

Other references cited in the text were not provided by the author.