Mössbauer Spectroscopy of Iron in the Luna 20 Regolith

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This paper presents results of the Mössbauer effect measurements on Fe^{57} in the average sample of the Luna 20 regolith, and their comparison with similar measurements of the Luna 16 samples. Room temperature measurements of the nonmagnetic as well as magnetic components of the spectra were performed. By careful least-squares analysis, six quadrupole doublets in the inner parts of spectra were resolved. According to their splittings, they were interpreted as four types of iron in silicates (olivine, two inequivalent pyroxene sites, and a glassy fraction) and two types of nonmagnetic iron-titanium oxides (ilmenite and a spinel). "Velocity-window" measurements, were used to determine the average nickel content of (2.01 ± 0.84) wt. %. These results are discussed in terms of distribution of iron among different phases. In comparison with the Luna 16 sample, the Luna 20 sample contains more olivine and less ilmenite as well as metal with a slightly higher nickel content.

Mössbauer spectroscopy has become a generally accepted method for studying iron—as one of the most significant cosmochemical elements—in a wide variety of mineral materials. In our previous work, we applied this method to investigation of the Luna 16 regolith (ref. 1). We also reported some preliminary results for Luna 20 (ref. 2). Main attention was paid to the nonmagnetic part of the spectra, where as many as five quadrupole split components have been resolved (refs. 2 and 3).

Because of the variability of iron bonding in the phases present, this number of components does not seem to be satisfactory, and leads to discrepancies in the interpretation of our data as well as data of the literature in the field. In this work we attempted (1) to distinguish (under certain constraints) six quadrupole doublets in the spectrum of the Luna 20 regolith; (2) to interpret them; and (3) similarly, to reconsider the previous Luna 16 measurements.

By comparing the magnetic splitting of the metallic phase with the standards containing iron and an iron-nickel alloy, we succeeded in estimating the nickel content in the Luna 16 metal (ref. 3). As the Mössbauer effect proves to be a unique tool for gaining such valuable information, a similar measurement was carried out on the Luna 20 metal along with calculation of the complete iron distribution between both the magnetic and nonmagnetic phases.

Experimental Studies

For Mössbauer measurements, the average sample of the Czechoslovak portion of the

Luna 20 regolith has been prepared by encapsulation in a flat acrylic container. Compared with the previously used average Luna 16 sample containing 13.7 percent Fe (0.127 g, ϕ 20 mm, 40 mg/cm^2, 5.5 mg Fe/cm^2), the appreciably lower content of iron in the Luna 20 material (5.1 percent Fe (ref. 4)) forced us to increase the area density of this sample (0.119 g, ϕ 10 mm, 152 mg/cm^2, 7.7 mg Fe/cm^2).

All spectra were taken at the double parabolic time mode Mössbauer spectrometer NP–255 (KFKI, Budapest, Hungary) at room temperature with the approximate 5 mC Co^{57} in palladium source in transmission arrangement. Punch tape output served for further data processing at the ZPA–600 computer. Calibration of the velocity scale was performed by measuring the powdered sodium nitroprusside. Isomer shifts are related to the palladium source used.

Three types of measurements were performed:

1. Whole spectra in the approximately ± 7 mm/s range, with division into 512 channels.
2. Precise measurements of the middle part of the spectra (counting statistics up to 10^7 counts/channel), with division into 256 channels. Three runs were performed, the first of which was used for seeking the optimum processing (refs. 2 and 3). The second run, performed as a continuation under identical conditions, was later added to the first.
3. The "velocity-window" measurements of the outermost magnetic lines of the spectra (approximately 6×10^7 counts/channel) into 128 channels. In this case, powdered standards consisting of a mixture of pyroxene, olivine, and iron or iron alloy (Fe–4.8 wt.% Ni) alloy were used.

The measured spectra were processed with the aid of a system of programs for the least-squares analysis. Special attention was paid to the low-velocity components of the spectra. To the spectra sub 2, six asymmetric quadrupole doublets of Lorentzian lines were fitted with equal line widths. Although this constraint is a substantial one, the procedure is necessary with respect to the limitations of the program system used, and seems to be justified by the resulting improvement in the value of the line width near the calibration width, and by the reproducibility of the line positions in the spectra of the same sample, as well as in those of different samples.

Results and Discussion

NONMAGNETIC FRACTION

A typical nonmagnetic part of the Luna 20 spectrum and its decomposition into six quadrupole doublets (numbered 1 to 6), along with that of Luna 16, is shown in figure 1. As has been shown in reference 2, resolving four quadrupole components in the spectrum is clearly insufficient; decomposition into five doublets is ambiguous, depending on the type of constraints (ref. 3). This situation is shown at the top of figure 2. Only six compo-

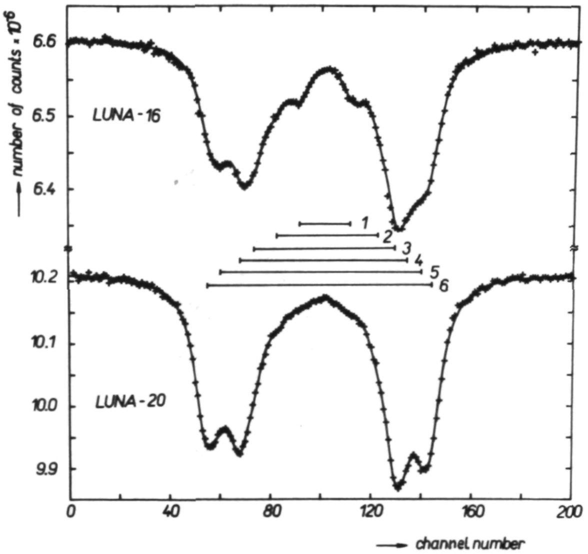

Figure 1.—*Mössbauer spectra of the average samples of Luna 20 (bottom) and Luna 16 (top). Velocity scales are identical, both reverse in sign. Smooth lines represent the least-squares fit; numbering of the components corresponds to the tables.*

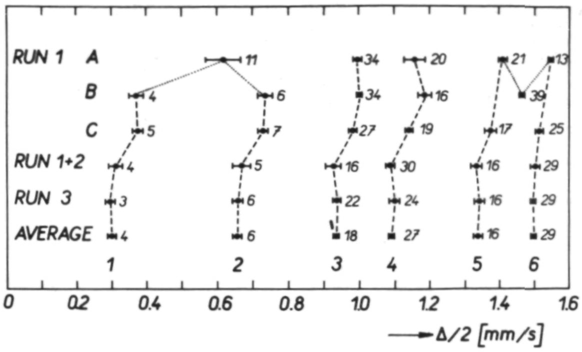

Figure 2.—*Comparison of the results of decomposition of the Luna 20 spectra. The figures 1 through 6 below their respective curves indicate individual components; the small figures, their relative areas. A indicates 5 doublets with paired line widths; B, 5 doublets with equal line widths; and C, 6 doublets with equal line widths.*

nents fit the spectrum unambiguously and reproducibly for individual runs of measurements (compare in figure 2). Unless otherwise stated, all other cases hereafter refer to the decomposition into six doublets (of equal line widths).

Good reproducibility of these decompositions made it possible to increase the reliability of the results by their averaging for the runs 1, 2, and 3. The main parameters of the components identified in the Luna 20 spectra compared with those of Luna 16 are summarized in table 1. Graphical display of the individual quadrupole splittings and corresponding relative areas for the lunar samples, as well as for some comparative terrestrial materials, is provided in figure 3.

Let us first interpret the components in the nonmagnetic part of the lunar regolith spectra (see figure 3 and table 1). Component 1 refers unambiguously to ilmenite (ref. 5). Lower precision of the corresponding quadrupole splitting value in Luna 20 is the consequence of its low content in the sample. Similarly, the component 6 belongs to olivine. Variations in the quadrupole splittings in comparison with the errors prevent judgment of the relative position in isomorphous series (ref. 6).

The prevailing part of absorption is caused by components 3, 4, and 5. The outer doublets correspond to two inequivalent Fe^{2+} sites (M1, M2) in pyroxenes, as indicated by comparison with the augite (from the basalt) or pyroxenes in gabbro (Skaergaard massif). These results agree with data of the literature in the field (see, e.g., ref. 7). Unfortunately, the relative areas do not say too much about the site occupancy in pyroxenes because both components 3 and 5 are strongly overlaid by component 4 and cannot hence be completely separated. Nevertheless, the quadrupole splitting of the latter component matches that of the terrestrial volcanic glass.

It has been proposed that the last component, 2, be interpreted as a spinel, near to ulvospinel (ref. 8), although data in the literature give an appreciably higher quadrupole splitting than that of figure 3 (approximately 0.85 mm/s, ref. 9). We therefore carried out a comparative measurement on a synthetic stoichiometric Fe_2TiO_4 (kindly provided by Dr. Z. Ŝimŝa, Institute of Solid State Physics, Prague). As is shown in figure 3, besides the main component corresponding to Fe^{2+} in tetrahedral sites, there is a weaker component of Fe^{2+} in octahedral sites. In case they were unresolved, the obtained mean splitting would correspond to that quoted above. It could, therefore, be concluded that our component 2 originates from the tetrahedral iron site in spinel structure, with the octahedral contribution unresolvable within the main absorption region discussed above.

MAGNETIC FRACTION

The quantitative data including hyperfine structure parameters and intensities (relative areas) given in table 1 provide a picture of the differences between the Luna 20 and Luna 16 samples. For the complete discussion of the distribution of iron among individual iron-bearing phases present, one has to take into account also the contribution of the magnetically split component resulting from the metallic iron. Its intensity has been evaluated from the high-velocity spectra (sub 1 in Section 2) and it is summarized in table 2 along

Table 1.—*Parameters of Mössbauer Spectra of the Lunar Regolith*

Sample	Component	Quadrupole Splitting (mm/s)	Isomer Shift (mm/s)	Related Area (percent)	Line Width (mm/s)
Luna 20	1	0.302 ± 0.010	0.910 ± 0.010	3.64 ± 0.20	0.341 ± 0.008
	2	0.656 ± 0.011	0.878 ± 0.025	5.65 ± 0.41	
	3	0.936 ± 0.007	0.925 ± 0.029	18.35 ± 2.84	
	4	1.192 ± 0.007	0.984 ± 0.029	27.26 ± 2.75	
	5	1.340 ± 0.010	0.994 ± 0.029	16.04 ± 1.09	
	6	1.500 ± 0.005	1.001 ± 0.008	29.06 ± 1.09	
Luna 16	1	0.360 ± 0.005	0.918 ± 0.005	10.61 ± 0.54	0.346 ± 0.002
	2	0.715 ± 0.009	0.882 ± 0.009	9.88 ± 0.81	
	3	0.950 ± 0.008	0.915 ± 0.008	25.66 ± 2.22	
	4	1.117 ± 0.029	0.928 ± 0.029	18.65 ± 2.67	
	5	1.312 ± 0.036	0.989 ± 0.036	13.34 ± 2.70	
	6	1.473 ± 0.006	1.003 ± 0.006	21.86 ± 2.19	

with the recalculated intensities of the components from table 1. These intensities express the distribution of iron among individual phases (or structure sites) with the degree of accuracy given by the differences in their Debye temperatures. From table 2, systematic differences of the contents of some phases in the Luna 20 regolith in comparison with Luna 16 can be seen. Setting aside the fractions, the quadrupole doublets of which strongly overlap and thus produce unreliable intensities, we still may state that the Luna 20 sample contains appreciably less ilmenite and metal, but more olivine than the Luna 16 sample.

We were able to determine the degree of alloying of lunar iron with nickel (providing that only nickel is present), by linear interpolation between differences of the positions of the outermost lines of the magnetic component in the spectra, measured in the "velocity-window" mode (sub .3, Section 2). Linear interpolation also enabled a quantitative estimate of the metallic phase content to be made.

As shown in figure 4, the content of nickel

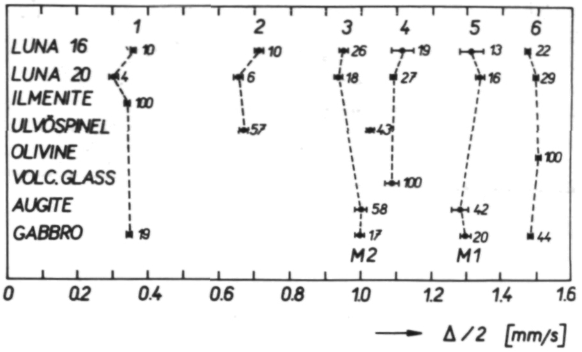

Figure 3.—*Quadrupole splittings of individual components in the spectra of the lunar samples and of some terrestrial materials. The figures at the top of the chart indicate the components; the small figures, their relative areas.*

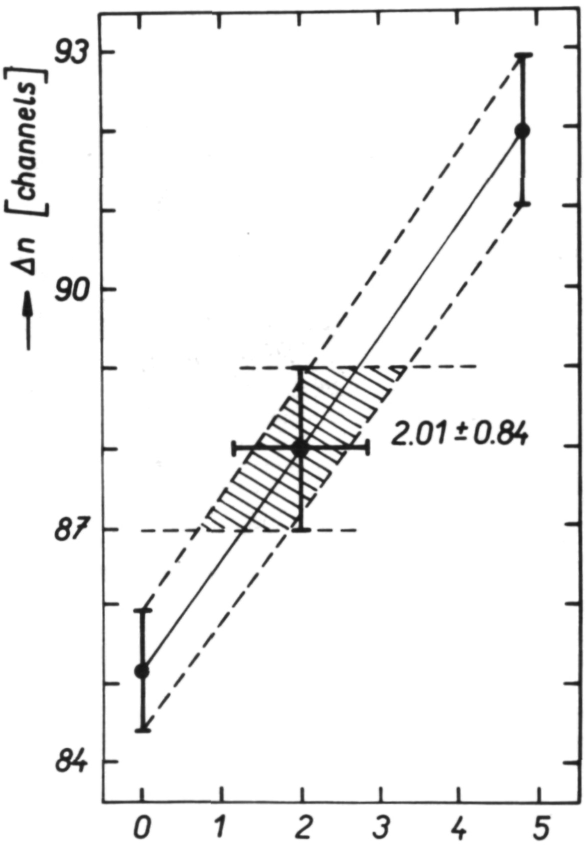

Figure 4.—*Determination of Ni content in the Luna 20 metal, by comparison with Fe and Fe-Ni. The term* Δn *represents difference in the outermost line positions in the velocity window spectrum;* ^{c}Ni *indicates nickel content.*

Table 2.—*Distribution of Iron in the Lunar Regolith*

Phase (component)	Luna 20	Luna 16
Ilmenite (1)	3.51 ± 0.20	10.05 ± 0.49
Olivine (6)	28.10 ± 1.31	20.71 ± 2.06
Pyroxene M1 (5)	15.44 ± 1.05	12.64 ± 2.55
Pyroxene M2 (3)	17.67 ± 2.80	24.32 ± 2.07
Glass (4)	26.28 ± 2.58	17.69 ± 2.52
Ulvöspinel (2)	5.46 ± 0.39	9.36 ± 0.75
Fe-Ni (7)	3.18 ± 0.47	5.23 ± 0.38

amounts to (2.01 ± 0.84) wt.%, i.e., slightly higher than in Luna 16 (1.50 ± 0.96 ref. 3). Taking into account the metallic iron contribution in table 2 and the entire iron content in the sample quoted in Section 2, the concentration of nickel alloyed with iron is approximately 30 ppm in the whole sample. Unfortunately, no activation analysis data for nickel in our portion of the Luna 20 regolith are known. The literature (ref. 10) gives at least 170 ppm Ni, which still means, in comparison with the average, strong enrichment of the metallic phase with nickel.

Conclusions

Although we believe we have presented quite a complete qualitative, and a fair quantitative, analysis of the Mössbauer spectroscopy data for iron in the Luna 20 regolith, we are aware of some weak points in our procedures. The limitation in the line widths is a substantial one, namely, in the case of the glassy fraction in the sample, where an increased line width is to be expected because of the non-uniformity of iron environments in the amorphous substance. Avoiding this would probably call for a more powerful computing technique and for still better counting statistics. On the other hand, using a modified "semi-stripping" technique with the assumption that some phases were unambiguously defined, one could study the most interesting parts of the spectra in more detail.

In addition to gradually refining the study of nonmagnetic as well as magnetic parts of the spectra, we are aiming at employment of the Mössbauer spectroscopy for measuring smaller, non-average parts of lunar samples. In reference 11 we have presented the iron analysis in a fine (about 10 μg) Luna 16 particle. Similar measurements on the selected Luna 20 particles are in progress.

Acknowledgment

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