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How Mössbauer spectroscopy can be of value to industry to select extraterrestrial objects for natural resources

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Abstract

Space agencies are working on the project of capturing asteroids which contain natural resources valuable for industry. Based on studies of meteorites samples it was determined that the most useful source of raw materials for this purpose could be parent bodies of ordinary chondrites of type H. The identification of the type of ordinary chondrites with the use of a classical method (determination of the Fa/Fs ratio (fayalite versus ferrosilite) by electron microprobe measurements) cannot be performed on the surface of asteroids due to technical reasons. It may, however, be done based on Mössbauer measurements followed by the application of the 4M method. The name of the method – 4M, comes from four words: Meteorites, Mössbauer spectroscopy, Multidimensional discriminant analysis and Mahalanobis distance. Following the success of Mössbauer spectroscopy in the mission on Mars, there are suggestions to use the same method for the investigation of the surface of asteroids. In our experimental study, in which five Mössbauer laboratories took part, we assessed the effectiveness and reliability of the 4M method by comparison of the results obtained by Mössbauer studies of ordinary chondrites of type H, L and LL. Details of the study and problems related to the effectiveness of the 4M method are discussed.

Keywords Mössbauer spectroscopy · Classification of the meteorites · Ordinary chondrites · 4M method

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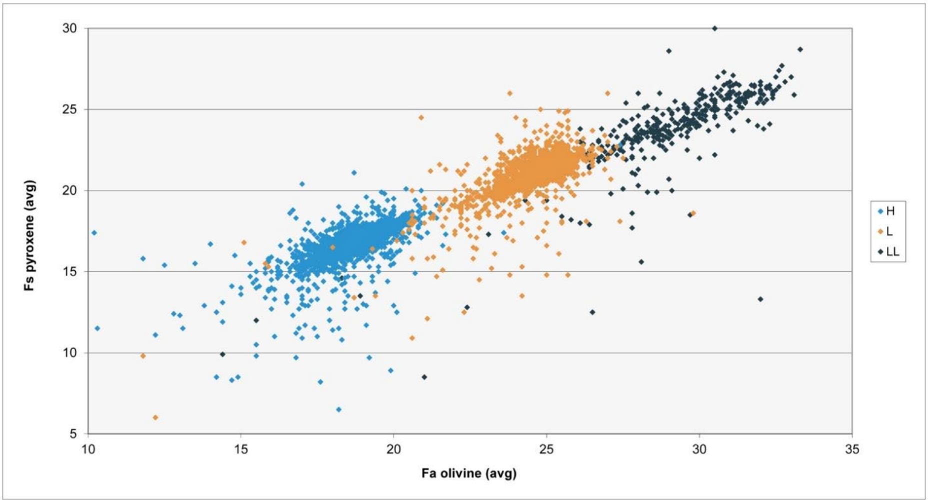

Fig. 1 Plot of the amount of the ferrosilite (Fs) in orthopyroxenes versus the amount of the fayalite (Fa) in olivines in ordinary chondrites obtained for 4712 ordinary chondrites

1 Introduction

Delivering an asteroid to Earth to gain access to natural resources valuable for the industry is not science fiction anymore but an issue on which space agencies work intensively. It is known that the best source for such resources may be asteroids, which are parent bodies for ordinary chondrites of type H [1]. Ordinary chondrites represent meteorites that are most frequently found on the Earth. Three types of ordinary chondrites are known: type H (high amount of iron), type L (low amount of iron) and type LL (low amount of iron and low amount of metal). The classic method of classification of ordinary chondrites is based on the value of the ratio of Fe_2SiO_4 (fayalite, Fa) vs. $FeSiO_3$ (ferrosilite, Fs). Figure 1 shows how well this Fa/Fs ratio, determined using an electron microprobe, differentiates the 3 types of ordinary chondrites.

The measurements of the concentrations of Fa and Fs on the surface of asteroids are impossible due to obvious technical reasons. However, the Mössbauer spectroscopy gives a possibility to differentiate these three types of meteorites. Mössbauer spectroscopy as a tool for the classification of meteorites was considered for many years. A review of these studies is presented in [2]. Also other studies show interesting results [3–5]. The quantitative method, which determines the type of the ordinary chondrite so also the parent body, is the 4M method proposed by our team in 2019 [6]. After the success of the Martian mission, during which Mössbauer measurements were performed on the surface of Mars [7, 8], one can expect that similar measurements could be made on a mission to an asteroid. The 4M method is based on a comparison of the percentages of the Mössbauer spectral areas of 4 basic mineralogical phases (olivine, pyroxene, troilite and metallic phase) obtained from the spectrum of the investigated object to the average values obtained for the same phases, which are collected in database of the 4M method [2, 9] The aim of our study was the assessment of the effectiveness of this method. Three anonymous samples of ordinary chondrites were sent to 4 Mössbauer laboratories for measurements and determination of the type of the meteorite with the use of the 4M method. Neither measurement conditions nor fitting method was suggested. The only requirement is a measurement at room temperature since our database was built with results of meteorite samples measured at room temperature. The fifth laboratory analysed Mössbauer spectra measured in lab number 3 and classified investigated meteorites with the use of the 4M method.

2 Materials and methods

The samples of bulk meteorites were crushed and ground into fine powder in an agate mortar. After grinding, the samples were loaded into Mössbauer plastic holders.

2.1 Lab I

The ^{57}Fe Mössbauer spectra for three samples of different meteorites (A, B and C) were measured at room temperature. The spectra were taken in transmission geometry by means of a constant-acceleration POLON spectrometer of standard design, using a 50 mCi ^{57}Co-in-Rh standard source with a full width at half maximum (FWHM) of 0.22 mm/s.

Each measured spectrum was analyzed using a least-squares fitting procedure in terms of a sum of three paramagnetic doublets which may be attributed to olivine, pyroxene, ferric iron (Fe^{3+}) and four six-line patterns (sextets) which correspond to troilite and 3 metallic phases. The fitting procedure was done under the thin absorber approximation. For each sextet, the two-line area ratios I_{16}/I_{34} and I_{25}/I_{34} as well as three line widths Γ_{16}, Γ_{25}, and Γ_{34} were free parameters. The Mössbauer parameters such as isomer shift (IS), quadrupole splitting/shift (QS) and hyperfine field (B) obtained for each component were listed in Table 1. It should be noted here that in the case of Fe^{3+} paramagnetic component, the values of IS, QS and Γ parameters were determined from spectrum of C meteorite and thereafter these values were used to describe Fe^{3+} component in spectra measured for A and B meteorites. As the main result of the analysis, the of relative areas of spectrum components (A) for the meteorite samples were determined.

2.2 Lab II

Mössbauer spectra were measured at room temperature with a conventional Mössbauer spectrometer. The fitting procedure was performed using the standard NORMOS-SITE program. Fit 1 was performed with a single iron site in both olivine and pyroxene spectral components. Fit 2 was performed with two inequivalent iron sites in both olivine and pyroxene spectral components. The metallic spectral fraction was fitted with one sextet with appropriately broadened 1st /6th and 2nd /5th pairs of the sextet lines to take into account the possible presence of three similar metallic phases (kamacite, taenite, tetrataenite).

2.3 Lab III

Mössbauer spectra of ^{57}Fe were measured at room temperature with a conventional Mössbauer spectrometer. The fitting was performed using the procedure “Full Static Hamiltonian” in the Recoil program [10]. As the troilite has an axial symmetry only theta angle was fitted. Fit 1 was performed for 3 sites in the metallic phase and 1 site in olivine and pyroxene (more details in [11]). Fit 2 was performed for 3 sites in the metallic phase and 2 sites in olivine and pyroxene.

2.4 Lab IV

Mössbauer measurements were performed at room temperature using a conventional Mössbauer spectrometer operating in the constant acceleration mode. A ^{57}Fe/Rh source of gamma radiation and a system working in vertical geometry were employed. As the velocity range was divided into 1024 channels, high-resolution spectra were obtained. Mössbauer spectra were analysed using two quite different methods. In both of them, a thin absorbent approximation was applied.

The standard Normos-Site programme was utilized in the first method. It was assumed that there are two non-equivalent iron positions in olivine and pyroxene, which resulted in the presence of two doublets representing each of these phases in the spectra. To reduce the number of independent parameters, the common line width is provided for the two doublets representing the individual phases. In the case of the troilite component, a full Hamiltonian analysis was carried out. In addition to the components representing the phases mentioned, the fitting procedure included two sextets related to "metallic phases" and a wide doublet assigned to Fe^{3+}. The relative intensity of the 2, 5 lines in relation to the 3, 4 lines was a fitting parameter, which takes into account the possible slight magnetic texture, resulting from the non-spherical shape of grains of the tested material.

The same experimental spectra were fitted independently by the second research group at the University of Radom employing an open-source PolMoss package, based on MS Excel with the Solver optimization module. This software offers Gaussian distributions of hyperfine parameters (IS, QS, B_{hf}), especially useful in the case of fitting the Mössbauer spectra of the environmental samples [12–14]. Nevertheless, this functionality has not been applied to meteorite samples because of the higher degree of order of the crystalline structure. Each spectrum has been fitted with a set of 9 components. G01-02 and G03-04 correspond to 2 different Fe^{2+} positions in the olivine and pyroxene, respectively. The expected contribution of troilite has been fitted with a set of sextet without midlines (G05) and artificial doublet (G06) instead of them. This procedure overcomes the lack of full Hamiltonian functionality indispensable in the mineral phases in which the direction of the electric field gradient has a different direction than the hyperfine field. The metallic phase has been fitted with two sextets (G07 and G08). The last component in the form of a doublet G09 corresponds to the Fe^{3+} (presumably associated with iron oxidation products). The ferromagnetic metallic phase (G07 and G08) reveals a magnetic texture, probably due to a slight in-plain magnetizing by Earth's field (or some other ambient magnetic field). The line widths were free parameters of fitting in some cases noticeably larger than natural ones – to reproduce a spread of hyperfine parameters' values caused by the slight structural disorder.

2.5 Lab V

In Lab V MOSSWIN 4.0 program was used. The fitting procedure was performed with 1 site in olivine and pyroxene and 2 sites in the metallic phase. The subspectrum of troilite was fitted with theta angle [15, 16].

Table 1 The Mössbauer parameters obtained for meteorites A, B and C

Meteorite	Mineral phase	*IS* (mm/s)	*B* (T)	*QS* (mm/s)	Γ (mm/s)	Γ_{16} (mm/s)	Γ_{25} (mm/s)	Γ_{34} (mm/s)	A (%)
A	olivine	1.15	–	2.95	0.32	–	–	–	24.6
	pyroxene	1.15	–	2.09	0.37	–	–	–	16.9
	troilite	0.77	31.1	-0.17	–	0.31	0.41	0.21	12.8
	metallic phase 1	0.03	33.9	-0.04	–	0.38	0.31	0.26	21.5
	metallic phase 2	0.01	33.1	0.03	–	0.38	0.31	0.26	20.2
	metallic phase 3	–	–	–	–	–	–	–	–
	Fe^{3+}	0.36	–	0.85	0.51	–	–	–	4.1
B	olivine	1.15	–	2.91	0.33	–	–	–	66.5
	pyroxene	1.15	–	2.07	0.32	–	–	–	17.7
	troilite	0.76	31.1	-0.17	–	0.30	0.35	0.28	14.6
	metallic phase 1	–	–	–	–	–	–	–	–
	metallic phase 2	–	–	–	–	–	–	–	–
	metallic phase 3	–	–	–	–	–	–	–	–
	Fe^{3+}	0.36	–	0.85	0.51	–	–	–	1.2
C	olivine	1.15	–	2.94	0.30	–	–	–	45.3
	pyroxene	1.15	–	2.08	0.34	–	–	–	19.3
	troilite	0.76	31.0	-0.17	–	0.32	0.40	0.21	17.4
	metallic phase 1	0.04	33.8	-0.12	–	0.37	0.29	0.30	5.2
	metallic phase 2	0.01	33.2	0.02	–	0.37	0.29	0.30	6.2
	metallic phase 3	-0.25	31.6	0.41	–	0.37	0.29	0.30	1.9
	Fe^{3+}	0.36	–	0.85	0.51	–	–	–	6.5

IS – isomer shift; *B* – hyperfine field; *QS* – quadrupole splitting/shift; Γ – FWHM (half width at half maximum); A – relative spectral area. The standard uncertainties for the presented parameters do not exceed: *IS* – 0.01 mm/s; *QS* – 0.02 mm/s; B – 0.1 T; Γ – 0.01 mm/s; A– 1%.

3 Results

Our interlaboratory experiment resulted in 8 sets of Mössbauer measurements of meteorite samples A, B and C, which were elaborated by 6 labs. As an example, the results from Lab I are shown below.

The current version of the 4M method is constructed for meteorites with a low level of weathering (in which the percentage of spectral area related to Fe^{3+} is smaller than 7%). In Table 1, the best-fit parameters of the assumed model and percentages of spectral areas A (%) associated with one site of the olivine, one site of the pyroxene, all the metallic phases and the troilite are presented. The obtained percentage of spectral areas for the three different meteorites was used to calculate Mahalanobis distances d_M and levels of similarity $S_{cluster}$. The values of these parameters are listed in Table 2. On the basis of the 4M method [17], the highest level of similarity for the A meteorite was type H, for the B meteorite – type LL, while for C meteorite – type L (Figs. 2, 3 and 4).

Mössbauer spectral areas obtained for the meteorite samples A, B and C using different methods of fitting are shown in Table 3 together with the results of the classification using the 4M method.

Table 2 The percentages of Mössbauer spectral areas A (%) of the olivine, pyroxene, troilite and metallic phase of the samples A, B and C with the determined Mahalanobis distances (d_M) and the levels of similarity $S_{cluster}$(%)

Meteorite	Mineral phase A (%)				Mahalanobis distance (d_M)			Level of similarity $S_{cluster}$ (%)		
	olivine	pyroxene	troilite	metallic phase	H	L	LL	H	L	LL
A	24.6	16.9	12.8	41.7	**3.18**	10.05	24.79	**32.4**	0	0
B	66.5	17.7	14.6	–	6.25	5.04	**2.21**	5.3	3.7	**38.3**
C	45.3	19.3	17.4	13.3	2.91	**1.95**	4.46	36.7	**42.0**	7.8

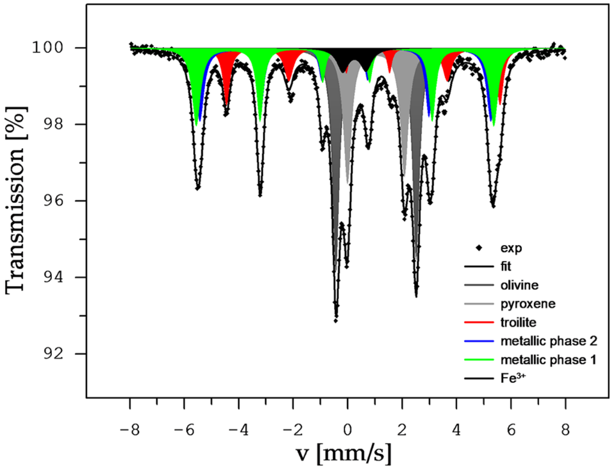

Fig. 2 The ^{57}Fe Mössbauer spectrum of the A meteorite sample measured at room temperature

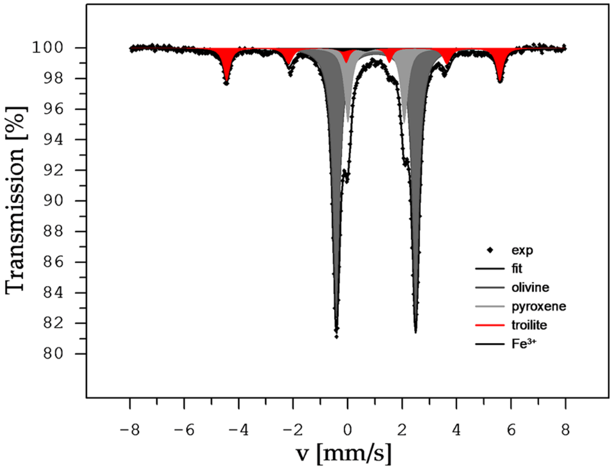

Fig. 3 The ^{57}Fe Mössbauer spectrum of the B meteorite sample measured at room temperature

4 Conclusion

Two anonymous meteorite samples A and B are classified by all Mössbauer laboratories,

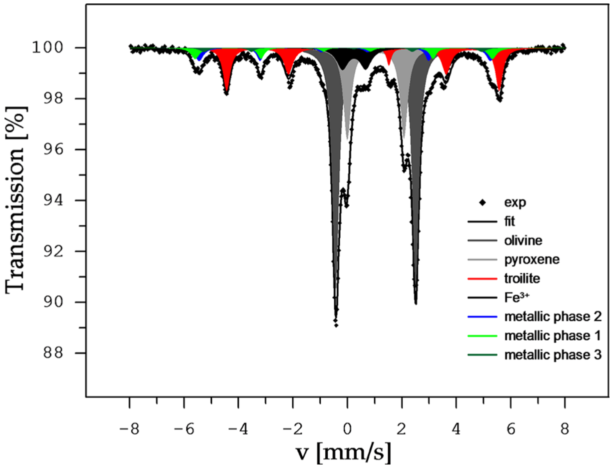

Fig. 4 The ^{57}Fe Mössbauer spectrum of the C meteorite sample measured at room temperature

Table 3 The percentages of Mössbauer spectral areas A (%) of the olivine, pyroxene, troilite and metallic phase of the samples A, B and C with meteorite type determined by the 4M method

	Mineral phase spectral areas A (%)					Type determined by 4M method
	olivine	pyroxene	metallic phase	troilite	Fe3+	
SAMPLE A						
Lab I fit 1	24.6	16.9	41.7	12.8	4.1	**H**
Lab II fit 2	26.2	15.6	40.3	15.1	2.7	**H**
Lab III fit 4	29.1	14.3	41.2	12.0	3.5	**H**
Lab III fit 5	27.7	15.7	39.9	13.1	3.6	**H**
Lab IV fit 6	24.5	15.8	40.2	13.5	6.0	**H**
Lab IV fit 7	25.2	15.3	40.0	13.2	6.3	**H**
Lab V fit 8	27	14	41	13	5	**H**
SAMPLE B						
Lab I fit 1	66.5	17.7	-	14.6	1.2	**LL**
Lab II fit 2	65.5	18.1	1.4	14.0	1.0	**LL**
Lab II fit 3	60.9	20.8	2.0	15.0	1.3	**LL**
Lab III fit 4	68.3	17.3	-	14.0	0.4	**LL**
Lab III fit 5	67.2	17.7	-	14.3	0.7	**LL**
Lab IV fit 6	60.3	20.6	2.8	13.5	2.8	**LL**
Lab IV fit 7	61.4	20.3	2.8	13.3	2.7	**LL**
Lab V fit 8	66	20	-	14	-	**LL**
SAMPLE C						
Lab I fit 1	45.3	19.3	13.3	17.4	6.5	**L**
Lab II fit 2	46.6	16.8	15.2	17.1	4.2	H/L
Lab II fit 3	43.3	18.6	15.1	18.4	4.5	H
Lab III fit 4	47.7	17.9	12.8	16.9	4.8	**L**
Lab III fit 5	46.3	18.8	14.1	16.5	4.4	**L**
Lab IV fit 6	38.8	21.3	15.2	17.6	7.1	H
Lab IV fit 7	39.1	21.0	15.7	16.7	7.6	H
Lab V fit 8	48	17	13	17	5	**L**

participating in this experiment, with the use of the 4M method and the results are in agreement with the classical method based on the determination of the Fa/Fs ratio with the use of the electron microprobe. Sample A was taken from the meteorite Tamdakht (type H) and sample B was from the meteorite Leoncin (type LL). Sample C, which comes from the meteorite Campos Sales (type L), is classified with the use of the 4M method as type L by laboratories 1, 3 and 5 and as type H by laboratories 2 and 4. Such a difference in the classification is related to small differences in percentages of Mössbauer spectral areas. In the plot showing the dependence of Fs vs. Fa values (Fig. 1) one may observe that despite the obvious separation of three types of ordinary chondrites some of the meteorites are located in non-typical places. It happens usually on the border of areas between type L and type H. As the uncertainty of determination of the type of an ordinary chondrite is present in the case of the classical method of classification, it may also happen in the case of classification based on the determination of percentages of Mössbauer spectral areas. On the basis of presented data, one may conclude that the 4M method gives reliable results for the samples measured in transmission geometry. The application of the 4M method for Mössbauer measurements on the surface of asteroids will need some modifications. For obvious reasons the Mössbauer measurements on the surface of an asteroid will be performed in backscatter geometry and their quality will probably not be better than the Mössbauer spectra obtained on the surface of Mars. Taking the above into account, in the next step it is planned to perform measurements of the Mössbauer spectra in backscatter geometry on non-powdered samples of ordinary chondrites. These conditions will be much closer to those expected on the asteroid surfaces. Finally, it is also worth noting that our database used for the 4M method will be significantly enlarged.

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Data Availability This is open access paper. The link to the script for calculations related to the 4M method is in references section.

Declarations

Ethical approval No applicable.

Competing interests Nothing to declare.

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