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Author: Patrycja Bogusz, Jolanta Gałązka-Friedman, Katarzyna Brzózka, Martyna Jakubowska, Marek Woźniak, Łukasz Karwowski i in.

Citation style: Bogusz Patrycja, Gałązka-Friedman Jolanta, Brzózka Katarzyna, Jakubowska Martyna, Woźniak Marek, Karwowski Łukasz i in. (2019). Mössbauer spectroscopy as a useful method for distinguishing between real and false meteorites. "Hyperfine Interactions" (Vol. 240 (2019), art. no. 126), doi 10.1007/s10751-019-1659-7



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Mössbauer spectroscopy as a useful method for distinguishing between real and false meteorites

Patrycja Bogusz¹ · Jolanta Gałązka-Friedman¹ · Katarzyna Brzózka² ·
Martyna Jakubowska¹ · Marek Woźniak³ · Łukasz Karwowski⁴ · Przemysław Duda¹

Published online: 28 November 2019
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Abstract

In our paper four Mössbauer spectra of ordinary chondrites (previously classified by a classical method based on determining the ratio of ferrosilite (Fs) to fayalite (Fa) with an electron microprobe) are presented and discussed. These are the Mössbauer spectra of two ordinary chondrites type H (Pultusk and Grzempach), one ordinary chondrite type L (Hyattville) and one type LL (NWA 6287). These meteorites were compared, using their Mössbauer spectra with the following four other samples: a fragment of a rock that fell near Leoncin in Poland (sample No. 1), a fragment of a rock found in the vicinity of Pultusk in Poland (sample No. 2), a meteorite specimen bought on the meteorite exchange (sample No. 3) and a stone object whose decline was observed in Europe (sample No. 4). The spectrum of sample No. 1 is very similar to the spectrum of ordinary chondrite of type LL. This observation was confirmed using 4M method (previously created by us). The spectrum of sample No. 2 differs significantly from the spectrum of sample of the Pultusk meteorite. In the spectrum of sample No. 3, a clear signal from iron-nickel alloy and troilite can be observed. This fact allows us to state that sample No. 3 is a fragment of rock that was created in cosmic conditions. Sample No. 4 has a Mössbauer spectrum similar to the spectrum of terrestrial magmatic rocks. This observation does not clearly determine where the examined object comes from. This work demonstrates the usefulness of Mössbauer spectroscopy in recognizing samples that are fragments of meteorites.

Keywords Mössbauer spectroscopy · Classification of meteorites · Ordinary chondrites · 4M method · Meteorite Pultusk · Aubrite

Proceedings of the International Conference on the Applications of the Mössbauer Effect (ICAME2019), 1-6 September 2019, Dalian, China
Edited by Tao Zhang, Junhu Wang and Xiaodong Wang

✉ Jolanta Gałązka-Friedman
jolanta.friedman@pw.edu.pl

Extended author information available on the last page of the article

1 Introduction

A meteorite is a fragment of a celestial body (meteoroid, asteroid or comet) that has fallen to the surface of the Earth. Many terrestrial rocks are very similar to meteorites. One of the characteristic features of freshly fallen meteorites is the dark-colored fusion crust caused by presence of iron in the meteorite. The thickness of fusion crust does not exceed 2 mm. As a result of weathering processes, the crust quickly acquires a rusty look and degrades. Often on the surface of many meteorites there are characteristic thumbprint-like indentations, the so-called regmaglypts. As a result of ablation, most meteorites have rounded shapes. Another characteristic feature that distinguishes a meteorite from a terrestrial rock is its weight. Since the most of the meteorites contain metallic iron, they are noticeably heavier than terrestrial rocks of comparable size and are attracted by a magnet. It is not easy to clearly define the appearance of the meteorite. In many cases, to determine whether a given rock is really a meteorite, some specialized tests are needed: optical microscopy in transmitted and reflected light, electron microscopy (scanning), X-ray diffraction, Raman spectroscopy, X-ray fluorescence, Mössbauer spectroscopy.

According to the traditional classification, meteorites are divided into three main groups: stones, irons and stony-irons. About 90% of meteorites falling to Earth are stone meteorites. Stone meteorites are additionally divided into two groups: chondrites and achondrites. A characteristic feature of most chondrites is the presence of chondrules, i.e. small, spherical grains formed from previously molten silicate minerals. The most common meteorites are ordinary chondrites. The Mössbauer spectrum of non-weathered ordinary chondrites consists mainly of four phases: two doublets coming from olivine and pyroxene and two sextets corresponding to troilite and the metallic phase. The metallic phase, consisting essentially of kamacite and taenite, together with troilite indicate the extraterrestrial origin of the rocks containing them [1]. In weathered ordinary chondrites, there are also sub-spectra of iron oxides and hydroxides. Ordinary chondrites are divided into three groups depending on the iron content. We distinguish ordinary chondrites of type H, which have a high content of the metallic phase (high iron), type L, which have a low content of the metallic phase (low iron), and the type LL, which have little iron in both the metallic and silicate phases (low iron - low metal). Achondrites are meteorites that do not have chondrules. A smaller group constituting about 6% of meteorites falling to Earth are iron meteorites, which almost entirely consist of an iron-nickel (Fe-Ni) alloy. The least often meteorites falls to Earth are stony-iron meteorites, which constitute a group of just over 1% among all falling meteorites. These meteorites are a mixture of an iron-nickel alloy and a silicate phase in a proportion of approx. 50/50.

In the last 20 years several studies on the use of Mössbauer spectroscopy for classification of ordinary chondrites were published [2–15].

The purpose of this work is a comparative analysis of the Mössbauer spectra of four rock samples delivered to our laboratory. The owners of these samples suspect that they are fragments of meteorites.

2 Material and methods

The Mössbauer measurements of four ordinary chondrite samples were performed: Pultusk, Grzempach, Hyattville, NWA 6287. The detailed data on these meteorites are as follows:

- Pultusk - ordinary chondrite type H5. Fell in 1868 in Poland;
- Grzempach - ordinary chondrite type H5. Fell in 1910 in Poland;
- Hyattville - ordinary chondrite type L6. Found in 2008 in Wyoming, USA;
- NWA 6287 - ordinary chondrite type LL5. Found in 2010 in Northwest Africa.

The Mössbauer measurements were also performed for four other samples that have not yet been classified:

- a fragment of a rock that fell in the vicinity of Leoncin (sample No. 1),
- a stone found in the vicinity of Pultusk (sample No. 2),
- an object bought on the meteorite exchange (sample No. 3)
- an object whose fall (according to the finder) was observed in Europe (sample No. 4).

Samples of meteorites in the form of powder were placed in special holders used for Mössbauer measurements. The diameter of the active region of the sample was 14Mm.

Mössbauer measurements were carried out at room temperature using a standard Mössbauer spectrometer. Source activity was 0.9 GBq. The spectrometer was calibrated using a 0.05 mm thick iron foil absorber in the 512 channel range. After folding the spectrum consisted of 256 channels and the fitting procedure was realized using the Recoil program and Full Static Hamiltonian analysis. The ratio of line intensity in the sextet was 3:2:1 and was determined using the Powder Crystal Site option. The number of counts per channel ranged from 3 million to 10 million.

Mössbauer measurements of eight tested samples were carried out at the Mössbauer Spectroscopy Laboratory at the Faculty of Physics in Warsaw University of Technology. Mössbauer measurements of 3 samples: Grzempach, Pultusk and stone found in the vicinity of Pultusk (sample No. 2) were also carried out in Magnetic Materials Laboratory belonging to Department of Physics of Faculty of Mechanical Engineering in University of Technology and Humanities in Radom.

3 Results

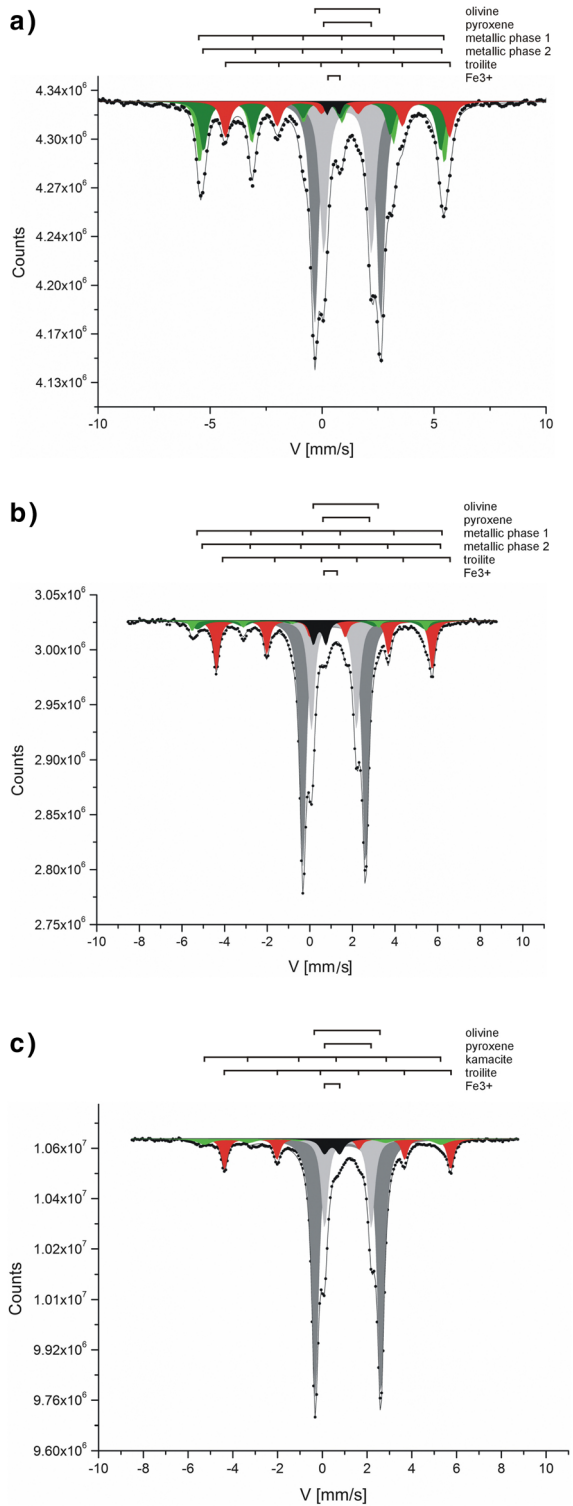
Mössbauer spectra of following meteorites are shown: Grzempach in Fig. 1a, Hyattville in Fig. 1b, NWA 6287 in Fig. 1c, Pultusk in Fig. 3a. Next, the spectra of other samples are presented: sample No. 1 (Fig. 2), No. 2 (Fig. 3b), No. 3 (Fig. 4) and No. 4 (Fig. 5).

Tables 1, 2, 3 and 4 present the Mössbauer parameters (IS - isomer shift, B - internal magnetic field, QS - quadrupole interaction parameter, Θ - angle between direction of magnetic field and the main axis of the electric field gradient, w - half width at half maximum) and A - the percentage of the total spectral area for particular mineralogical phases. Experimental uncertainties for cited parameters are the following: for IS – 0.01 mm/s, for QS – 0.02 mm², for B – 0.2 T, for w – 0.01 mm/s, for % of spectral area for doublet – 1.0%, for sextets – 2.0%.

4 Discussion

The Mössbauer spectrum of sample No. 1 shows a very clear signal from troilite. This is a convincing evidence that this sample is extraterrestrial. In addition to the sextet associated with

Fig. 1 Mössbauer spectrum of the Grzempach meteorite (a), Hyattville meteorite (b), NWA 6287 meteorite (c)



troilite, there are two more doublets - one associated with olivine and the other with pyroxene. A small signal from the metallic phase can also be observed in the spectrum. This type of Mössbauer spectrum is typical for ordinary chondrites of type LL. We decided to verify this hypothesis using the 4M method. This method, published in *Meteoritics & Planetary Science* by Woźniak et al. in 2019 [15], is able to determine the type of ordinary chondrite only on the basis of its Mössbauer spectrum. The 4M method works in two stages: at the beginning the so-called Mahalanobis distance is calculated, then, based on the knowledge of the Mahalanobis distance, the level of similarity of the tested meteorite to the particular type: H, L or LL is determined. Table below presents the values obtained for sample No. 1.

	Type H	Type L	Type LL
The Mahalanobis distance	6.4	3.5	2.2
The level of similarity [%]	3.5	13.6	32.2

Based on the obtained results, it can be concluded that sample No. 1 (a fragment of the rock that fell in the vicinity of Leoncin - Poland) is probably an ordinary chondrite of type LL.

Our laboratory received also a stone (sample No. 2), which according to the sender, could represent a part of Pultusk meteorite. The Pultusk meteorite fell in the form of meteorite rain on January 30, 1868 in Mazowia region, fifty kilometers from Warsaw (Poland) near Pultusk. The abundant decline of thousands of fragments weighing from a gram to several kilograms allowed for gathering of hundreds of specimens. Parts of this meteorite are still being found, but false samples also occur.

In the Mössbauer spectrum of sample No. 2, no signal coming from troilite or metallic phase is recognized. We can observe three sextets with very high magnetic field values coming

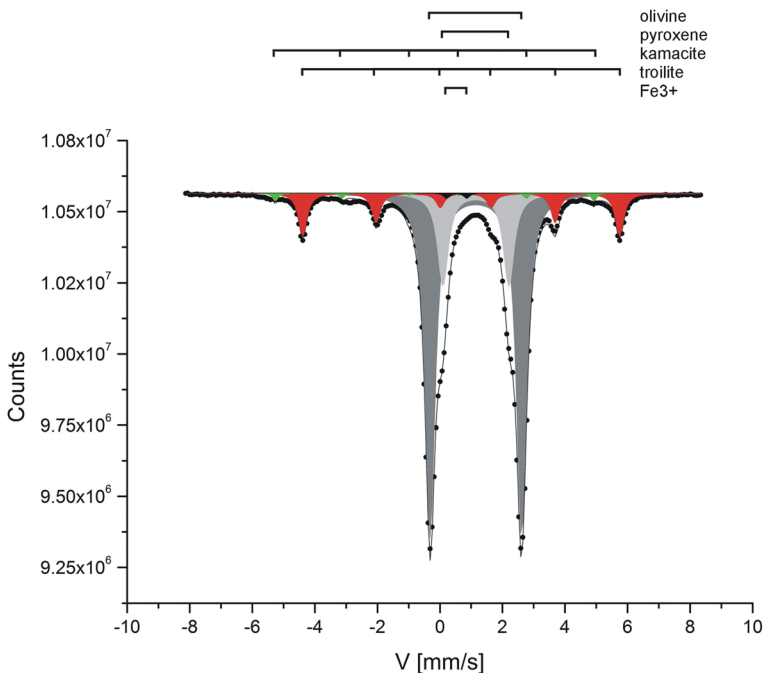


Fig. 2 Mössbauer spectrum of the sample No 1

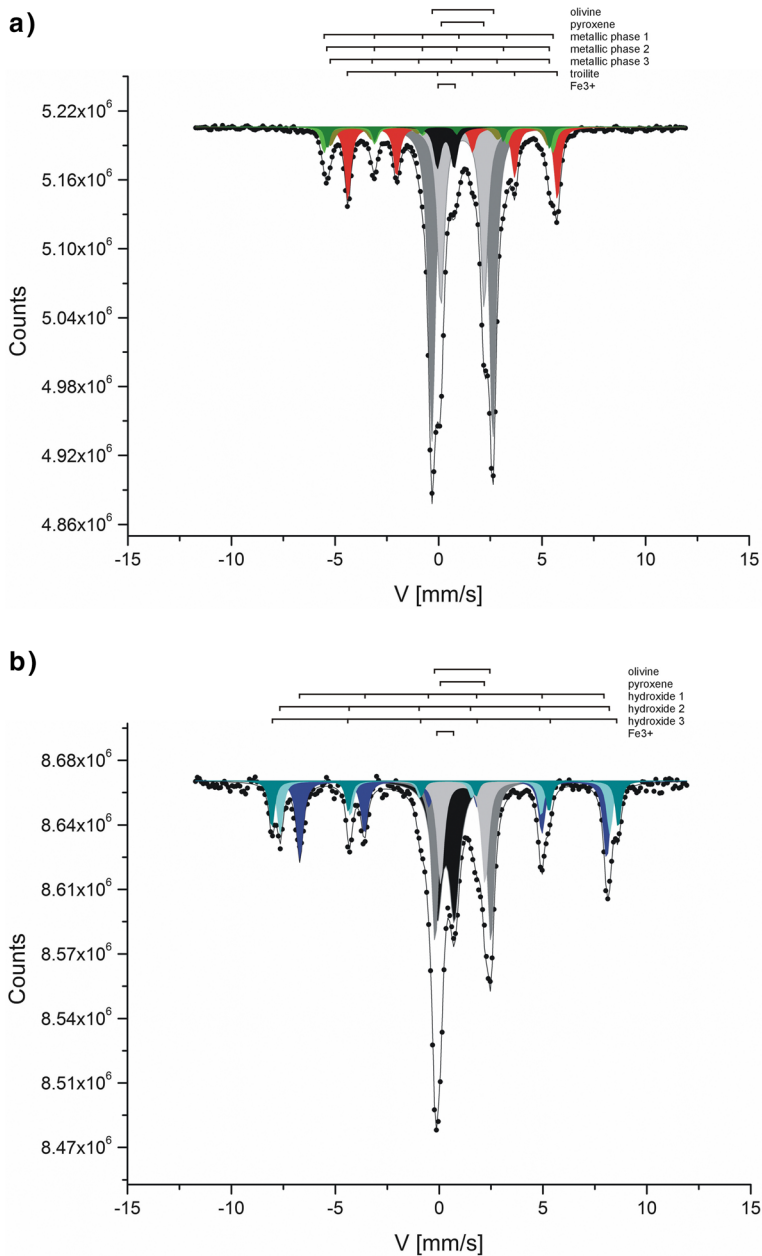


Fig. 3 Mössbauer spectrum of the Pultusk meteorite (a) and sample No 2 (b)

from hematite (51.7 T) and magnetite (49.2 T and 45.8 T) [16], two doublets: from olivine and pyroxene and the third one from ferric iron. The Mössbauer spectrum of sample No. 2 does not resemble the Mössbauer spectrum of the Pultusk meteorite. In sample No. 2, divalent iron accounts for only 35% of total iron, while in the Pultusk meteorite sample, divalent iron accounts for 95.5%. We do not agree with the suggestion of the owner of sample No. 2 that this

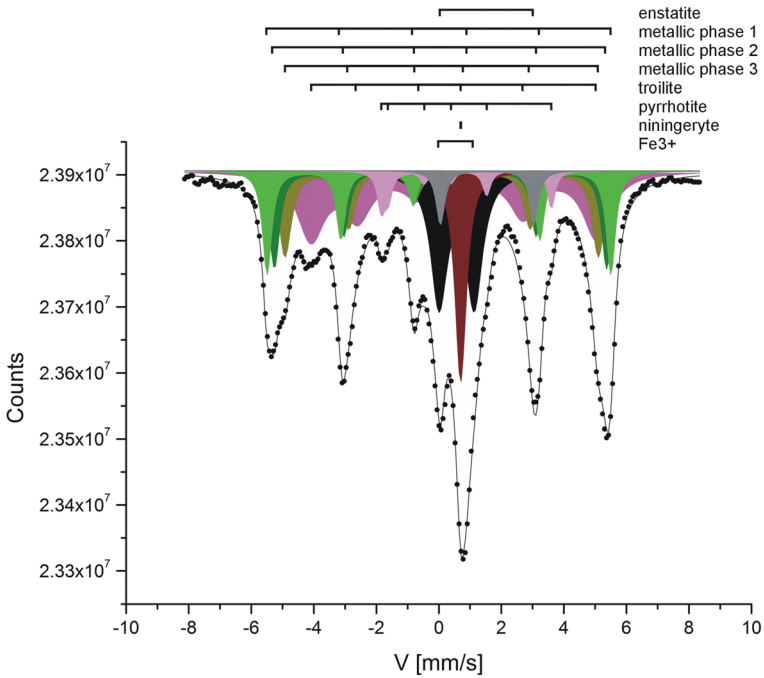


Fig. 4 Mössbauer spectrum of the sample No 3

sample is a specimen of very weathered meteorite Pultusk. Mechanism of the transformation of the fragment of Pultusk meteorite (Fig. 3a) to the sample with Mössbauer spectrum shown in Fig. 3b by weathering, even lasting 150 years is highly improbable.

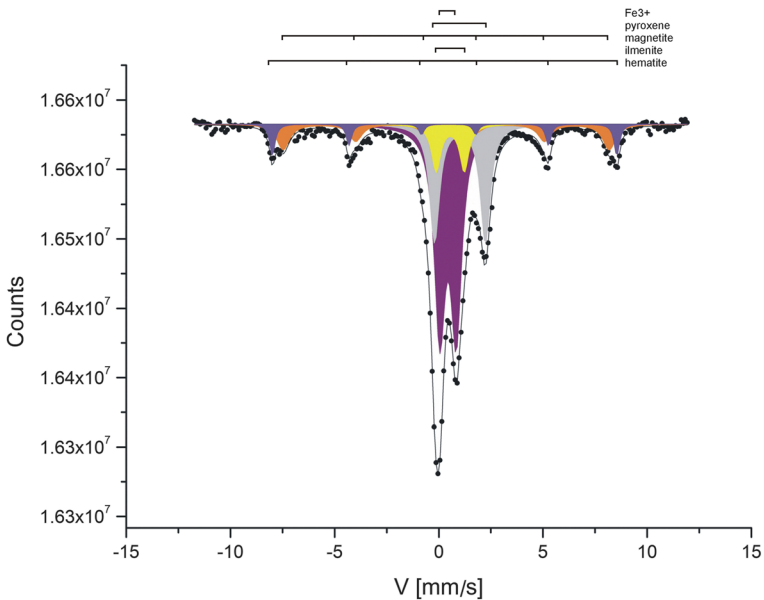


Fig. 5 Mössbauer spectrum of the sample No 4

Table 1 Hyperfine interactions parameters obtained from the best fit to the experimental Mössbauer spectra of meteorites Grzempach, Hyattville, NWA 6287 and sample No 1

Meteorite	Mineral phase	IS [mm/s]	B [T]	QS [mm/s]	Θ [°]	w [mm/s]	A [%]
Grzempach	olivine	1.14	–	2.95	–	0.20	31.9
	pyroxene	1.14	–	2.13	–	0.21	23.3
	metallic phase 1	0.01	33.9	–0.03	–	0.18	16.3
	metallic phase 2	–0.004	32.8	0.02	–	0.22	15.8
	troilite	0.74	30.4	1.04	59.2	0.22	11.4
	Fe3+	0.49	–	0.54	–	0.13	1.3
Hyattville	olivine	1.15	–	2.94	–	0.18	47.6
	pyroxene	1.13	–	2.11	–	0.18	21.0
	troilite	0.76	30.8	1.02	61.9	0.16	17.5
	metallic phase 2	0.01	33.1	0.12	–	0.36	6.4
	metallic phase 1	0.01	34.0	–0.09	–	0.14	3.2
	Fe3+	0.45	–	0.59	–	0.17	4.2
NWA 6287	olivine	1.14	–	2.93	–	0.18	58.2
	pyroxene	1.15	–	2.09	–	0.18	19.6
	troilite	0.75	30.9	0.94	62.0	0.16	12.6
	kamacite	–0.10	32.8	0.25	–	0.38	5.5
	Fe3+	0.43	–	0.68	–	0.23	4.1
	Sample No 1	olivine	1.15	–	2.93	–	0.19
	pyroxene	1.15	–	2.11	–	0.21	18.9
	troilite	0.75	31.0	0.93	61.8	0.16	13.9
	kamacite	–0.18	31.6	0.02	–	0.10	1.6
	Fe3+	0.54	–	0.65	–	0.10	0.5

For a better understanding of problems related to fragments of the meteorite Pultusk, Mössbauer spectrum of this meteorite, published earlier, will be discussed. Results of Mössbauer measurements of the meteorite Pultusk, made by Herra and Skerra, were published for first time in 1969 [17]. The authors of this paper did not involve the metallic phase in the measured sample of the meteorite Pultusk. In such a situation it is very difficult to perform full comparative studies. We decided to compare the ratio of the concentration of ferric iron to the concentration of iron in silicate phases present in Pultusk sample measured in 1969 [17] and in

Table 2 Hyperfine interactions parameters obtained from the best fit to the experimental Mössbauer spectra of meteorites Pultusk and sample No 2

Meteorite	Mineral phase	IS [mm/s]	B [T]	QS [mm/s]	Θ [°]	w [mm/s]	A [%]
Pultusk	olivine	1.15	–	2.95	–	0.20	39.8
	pyroxene	1.15	–	2.10	–	0.21	23.8
	troilite	0.75	30.9	0.95	61.7	0.17	16.1
	metallic phase 3	–0.07	32.6	0.21	–	0.25	6.0
	metallic phase 1	0.06	34.3	–0.11	–	0.18	5.8
	Fe3+	0.35	–	0.82	–	0.19	4.9
	metallic phase 2	0.01	33.3	–0.03	–	0.13	3.6
	Sample No 2	Fe3+	0.32	–	0.84	–	0.30
	olivine	1.15	–	2.69	–	0.20	20.9
	hydroxide 1	0.68	45.8	0.01	–	0.19	19.6
	pyroxene	1.14	–	2.14	–	0.20	13.5
	hydroxide 2	0.30	49.2	–0.04	–	0.17	11.6
	hydroxide 3	0.37	51.7	–0.18	–	0.16	9.7

Table 3 Hyperfine interactions parameters obtained from the best fit to the experimental Mössbauer spectra of sample No 3

Meteorite	Mineral phase	IS [mm/s]	B [T]	QS [mm/s]	Θ [°]	w [mm/s]	A [%]
Sample No 3	troilite	0.27	28.4	0.43	0.0	0.53	25.9
	Fe3+	0.57	–	1.13	–	0.33	15.5
	metallic phase 3	0.06	31.1	0.07	–	0.25	15.3
	metallic phase 2	0.05	33.0	0.02	–	0.20	14.3
	metallic phase 1	0.03	34.1	–0.04	–	0.18	13.2
	niningeryte	0.70	–	–	–	0.22	8.4
	pyrrhotite	0.42	16.9	0.92	1.2	0.15	4.1
	enstatite	1.55	–	2.99	–	0.17	3.3

Pultusk sample discussed in this paper. The value of this ratio for the sample of the meteorite Pultusk measured by Herra and Kerra was equal 0.080, and for our sample – 0.077. The obtained results testified that in both samples the level of weathering is practically the same.

In the Mössbauer spectrum of sample No. 3, the metallic phase constitutes as much as 43.8%, and iron present in troilite 25.9%. Already these two observations indicate without any doubt that it is an object of extraterrestrial origin. The lack of olivine doublet does not indicate that sample No. 3 could be ordinary chondrite. This conclusion confirms the absence of chondrules. The presence of a singlet in the Mössbauer spectrum obtained from niningeryte and the signal from the enstatite may suggest that the object belongs to a class of meteorites called aubrites. To the best of our knowledge, this is the first Mössbauer spectrum of aubrite in the literature.

In the Mössbauer spectrum of sample No. 4, we found no signal from metallic phase or troilite. The sample is significantly weathered - ferric iron doublet accounts for 45.6% of the total spectral area of the Mössbauer spectrum. The remaining ferric iron found in magnetite and hematite constitutes 21% of the spectral area. Similar Mössbauer spectra may have fragments of magmatic rocks occurring on the surface of Earth.

5 Conclusions

The discussion presented above shows how a useful tool for distinguishing between real and false meteorites, the Mössbauer spectroscopy is. Unequivocal identification of troilite (FeS) and metallic phases (FeNi alloys), which can be created only in cosmic conditions is power of Mössbauer spectroscopy. Presence of a metallic phase or troilite is convincing evidence that

Table 4 Hyperfine interactions parameters obtained from the best fit to the experimental Mössbauer spectra of sample No 4

Meteorite	Mineral phase	IS [mm/s]	B [T]	QS [mm/s]	Θ [°]	w [mm/s]	A [%]
Sample No 4	Fe3+	0.44	–	0.79	–	0.32	45.6
	pyroxene	1.02	–	2.44	–	0.29	24.6
	magnetite	0.45	48.5	–0.19	–	0.37	13.7
	ilmenite	0.55	–	1.36	–	0.26	8.9
	hematite	0.38	51.3	–0.20	–	0.16	7.2

the tested sample is extraterrestrial. Additionally, the 4M method can be used to determine the type of equilibrated ordinary chondrites (H, L or LL). Difficulties emerge in the case of objects that have Mössbauer spectra similar to magmatic rocks. In this situation, additional measurements with use of other techniques are necessary.

Mössbauer measurements of three samples - Grzempach, Pultusk and Sample No. 2 - were carried out in other laboratory, blinded to the origin of samples. Based on the obtained Mössbauer spectra this laboratory concluded that the sample Grzempach and Pultusk are meteorites, while Mössbauer spectrum of sample No. 2 differs very much from Mössbauer spectra of real meteorites Pultusk and Grzempach. This demonstrates the strength of the Mössbauer spectroscopy in distinction of meteorite and non-meteoritic sample.

Acknowledgments The authors would like to thank Maciej Burski and Mateusz Szyszka for providing meteorite samples for Mössbauer measurements.

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Affiliations

Patrycja Bogusz¹ • Jolanta Gałązka-Friedman¹ • Katarzyna Brzózka² • Martyna Jakubowska¹ • Marek Woźniak³ • Łukasz Karwowski⁴ • Przemysław Duda¹

¹ Faculty of Physics, Warsaw University of Technology, Koszykowa 75, 00-662 Warsaw, Poland

² Faculty of Mechanical Engineering, Department of Physics, University of Technology and Humanities, E. Stasieckiego 54, 26-600 Radom, Poland

³ Faculty of Biology, University of Warsaw, Miecznikowa 1, 02-096 Warszawa, Poland

⁴ Faculty of Natural Sciences, Institute of Earth Sciences, University of Silesia in Katowice, ul. Będzińska 60, 41-200 Sosnowiec, Poland