

Jarosław MUSIAŁ¹

RESULTS OF PRELIMINARY MÖSSBAUER SPECTROSCOPIC ANALYSIS OF OCHRES FROM JANOWICE, CIEŻKOWICE REGION, OUTER CARPATHIANS

Abstract. Ten samples of ochre-like deposits and associated sediments from the vicinity of Janowice were studied by means of Mössbauer spectroscopy. The samples represent ochre-like loessy deposits, ferruginous efflorescences, a hardpan horizon and an encrustation on weathered shales of the Menilite Beds. Among iron minerals the presence of goethite, lepidocrocite, siderite, jarosite and, probably, ferrihydrite and akaganéite was ascertained. Most of them are poorly-crystalline. There is no evidence of any Mössbauer spectra related to Fe ions in the structure of clay minerals in the studied samples.

Key-words: the Skole unit, the Menilite Beds, ochre, iron hydroxides, Mössbauer spectroscopy.

INTRODUCTION

Janowice village is situated within the Cieżkowice Foreland ca. 15 km south of Tarnów. On the steep SW slopes of the Wał Hill (523 m asl), several km SE of Janowice, there crop out thick Eocene-Early Miocene sequences of the Sub-Silesian and Skole series (Świdziński 1953). Among other sediments they contain a complex of the Menilite Beds up to 400 m thick: these are black or brown-black shales, slightly marly towards the top, showing distinct leaf-like fissility. The surfaces of weathered shales are covered with yellow-brown encrustations, dusty when dried, consisting mainly of goethite and jarosites, which are products of chemical decomposition of pyrite (Badak et al. 1962). On the banks of small streams flowing from the slopes of the Wał Hill, there occur abundant rusty-yellow, jelly-like iron efflorescences. Several meters below the outcrops of the Menilite Beds a yellow to rusty-red loessy cover is observed (Fig. 1). This sediment, further called 'an ochre', was exploited as a raw material for the production of mineral pigments till the end of the 40's.

¹ Faculty of Geology, Geophysics and Environmental Protection, University of Mining and Metallurgy, Mickiewicza 30, 30-059 Cracow, Poland.

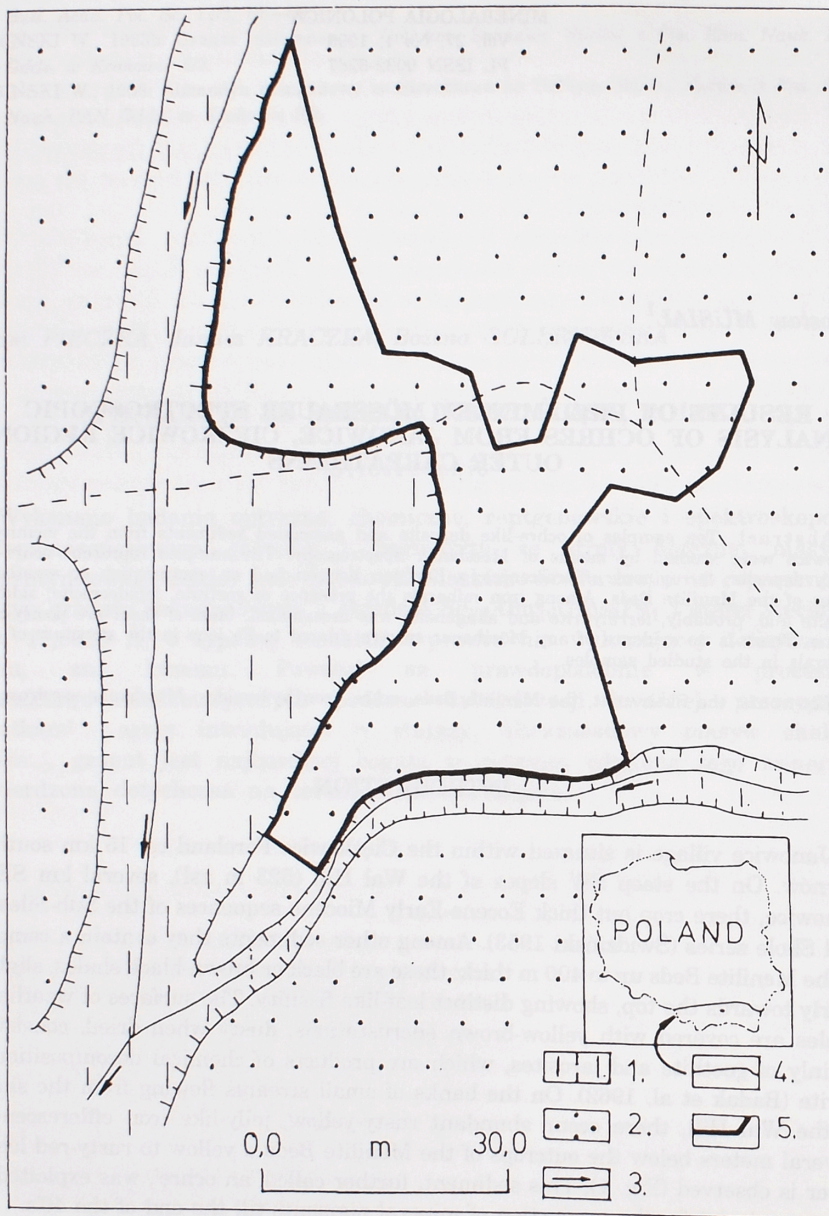


Fig. 1. Geological setting of ochre-bearing rocks near Janowice
1 — clays, 2 — loesses, 3 — streams, 4 — N border of the Carpathian Flysch, 5 — extent of rocks containing >5 wt.% Fe_2O_3

All the above mentioned sediments were sampled. Samples No 2/2, 3/2, 4/1, 13/1, 15/1, 19/1 and 23/1 represent sandy loesses enriched with Fe oxides and hydroxides. The thickness of these rocks reaches 0.5 m. They contain up to 10 wt.% Fe_2O_3 . The other constituents are: SiO_2 — ca. 70 wt.%, Al_2O_3 — ca. 15 wt.% and CaCO_3 — ca. 4 wt.%.

Sample No 1/2 represents a hardpan horizon which occurs ca. 0.4 m beneath the soil surface. This is a poorly cemented, medium- to coarse-grained, dark red and fragile quartz sandstone. It contains ca. 11.4 wt.% Fe_2O_3 .

Sample No 35/1 represents yellowish encrustation taken from the surface of the weathered shale. It contains ca. 1.3 wt.% Fe_2O_3 .

Sample No 42/1 represents an iron efflorescence. This is a jelly-like, dusty when dried, orange-red or rusty substance, found in clayey banks of the streams. It contains ca. 32.6 wt.% Fe_2O_3 with some amounts of quartz, flora detritus and traces of calcite.

Earlier studies of the ochre-like sediments from Janowice carried out by means of X-ray diffraction (DSH) did not identify the nature of Fe-bearing mineral phases responsible for the elevated content of Fe_2O_3 . Those studies proved the presence of small amounts of goethite, siderite and glauconite, known from microscope and X-ray microprobe investigations. Therefore, bearing in mind the difficulties related to separation of the ochre and poor crystallinity of Fe phases, Mössbauer spectroscopy was applied.

EXPERIMENTAL

The investigations of the mentioned samples were carried out with a Mössbauer spectrometer working in the constant acceleration system of transmission geometry at the temperature of liquid nitrogen (80 K). The ^{57}Co source in a Rh-Cr matrix was used. The spectra were analysed with a computer program using the Gauss-Newton fitting method with the fixed number of components. The fitting is characterized by c and MISFIT parameters.

RESULTS AND DISCUSSION

The samples of rocks associated with the ochre occurrences show a relatively simple composition of Fe-bearing phases (Table 1). Sample No 1/2 contains only two phases (Fig. 2). These are siderite with parameters $\text{IS} = 1.342$ mm/s and $\text{QS} = 1.348$ mm/s and probably ferrihydrite. The latter term is used, since ferrihydrite is the only one described amorphous or poorly crystalline iron hydroxide which fits best the measured Mössbauer parameters. They are $\text{IS} = 0.464$ mm/s and $\text{QS} = 0.396$ mm/s in comparison with 0.47 and 0.68 mm/s at 77 K given by Saraswat et. al. (1978, *vide* Murad, Schwertmann 1980). The 35/1 sample contains only one Fe-bearing component (Fig. 3). Its doublet with parameters $\text{IS} = 0.479$ mm/s and

TABLE 1

Results of Mössbauer spectroscopic investigations of non-ochre samples

Sample No	Fe-bearing compound	IS [mm/s]	QS [mm/s]	A [%]
1/2	ferrihydrite — $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$	0.464	0.396	98
	siderite — FeCO_3	1.342	1.348	2
35/1	jarosite — $\text{K}(\text{Fe}, \text{Al})_3[\text{SO}_4]_2(\text{OH})_6$	0.479	1.234	100
42/1	ferrihydrite — $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$	0.464	0.445	100

A — relative content of Fe-bearing compounds.

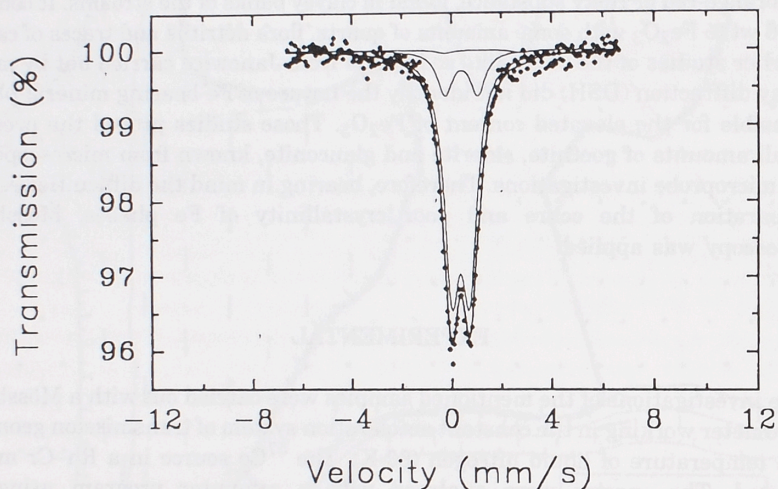


Fig. 2. Mössbauer spectrum of sample from the hardpan horizon (sample No 1/2)

QS = 1.234 agrees well with that of iron-aluminium jarosite given by Hryniewicz et al. (1966). The presence of jarosite in the sample was also proved by X-ray diffraction.

Similarly, the 42/1 sample contains only one Fe-bearing component (Fig. 4) with parameters IS = 0.464 mm/s and QS = 0.445 mm/s. This is probably ferrihydrite, whose somewhat higher QS value suggests poor ordering of the crystalline structure in comparison with 'ferrihydrite' from other samples.

The composition of Fe-bearing phases from the ochre-like loessy deposits is more complex (Fig. 5) as it comprises at least 5 components (Table 2). Their main constituent is 'ferrihydrite' with average parameters IS = 0.467 mm/s and QS = 0.338 mm/s. Its content in the studied samples reaches over 83% of Fe compounds (sample No 3/2, Table 2.) The high value of standard deviation could be the result of the above mentioned differences in crystallinity.

TABLE 2

Results of Mössbauer spectroscopic investigations of ochre samples

Sample No	Fe-bearing compound	IS [mm/s]	QS [mm/s]	H [kGs]	A [%]
2/2	akaganéite $\beta\text{-FeOOH}$	0.556	0.042	394.9	5
	ferrihydrite — $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$	0.474	0.313	—	55
	goethite $\alpha\text{-FeOOH}$	0.471	0.126	482.0	22
	lepidocrocite $\gamma\text{-FeOOH}$	0.483	0.093	449.7	9
	siderite — FeCO_3	1.260	1.458	—	9
3/2	akaganéite $\beta\text{-FeOOH}$	0.513	0.180	407.3	3
	ferrihydrite — $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$	0.466	0.420	—	84
	goethite $\alpha\text{-FeOOH}$	0.538	0.110	482.4	4
	lepidocrocite $\gamma\text{-FeOOH}$	0.417	0.161	447.3	5
	siderite — FeCO_3	1.451	1.716	—	4
4/1	akaganéite $\beta\text{-FeOOH}$	0.521	0.169	392.0	5
	ferrihydrite — $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$	0.463	0.345	—	45
	goethite $\alpha\text{-FeOOH}$	0.478	0.124	486.0	32
	lepidocrocite $\gamma\text{-FeOOH}$	0.495	0.126	446.1	12
	siderite — FeCO_3	1.249	1.448	—	6
13/1	akaganéite $\beta\text{-FeOOH}$	0.525	0.144	400.1	6
	ferrihydrite — $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$	0.457	0.225	—	44
	goethite $\alpha\text{-FeOOH}$	0.479	0.121	483.6	31
	lepidocrocite $\gamma\text{-FeOOH}$	0.501	0.139	449.7	15
	siderite — FeCO_3	1.314	1.502	—	4
15/1	akaganéite $\beta\text{-FeOOH}$	0.434	0.101	388.6	5
	ferrihydrite — $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$	0.474	0.335	—	65
	goethite $\alpha\text{-FeOOH}$	0.485	0.124	480.6	18
	lepidocrocite $\gamma\text{-FeOOH}$	0.451	0.081	442.6	10
	siderite — FeCO_3	1.244	1.511	—	2
19/1	akaganéite $\beta\text{-FeOOH}$	0.509	0.176	403.1	5
	ferrihydrite — $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$	0.471	0.369	—	57
	goethite $\alpha\text{-FeOOH}$	0.478	0.124	484.7	26
	lepidocrocite $\gamma\text{-FeOOH}$	0.479	0.127	449.7	10
	siderite — FeCO_3	1.711	1.600	—	2
23/1	akaganéite $\beta\text{-FeOOH}$	0.507	0.088	417.7	8
	ferrihydrite — $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$	0.466	0.343	—	36
	goethite $\alpha\text{-FeOOH}$	0.479	0.123	485.8	38
	lepidocrocite $\gamma\text{-FeOOH}$	0.489	0.123	459.3	17
	siderite — FeCO_3	1.284	1.462	—	1

A — relative content of Fe-bearing compounds.

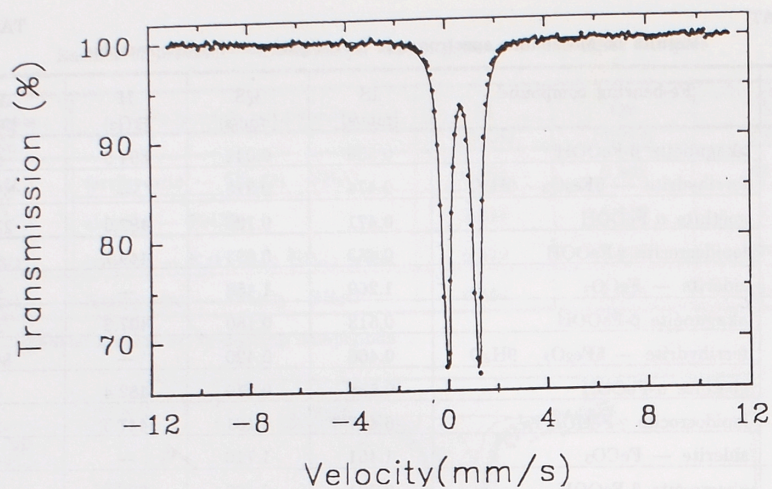


Fig. 3. Mössbauer spectrum of the encrustation on the weathered Menilite shale (sample No 35/1)

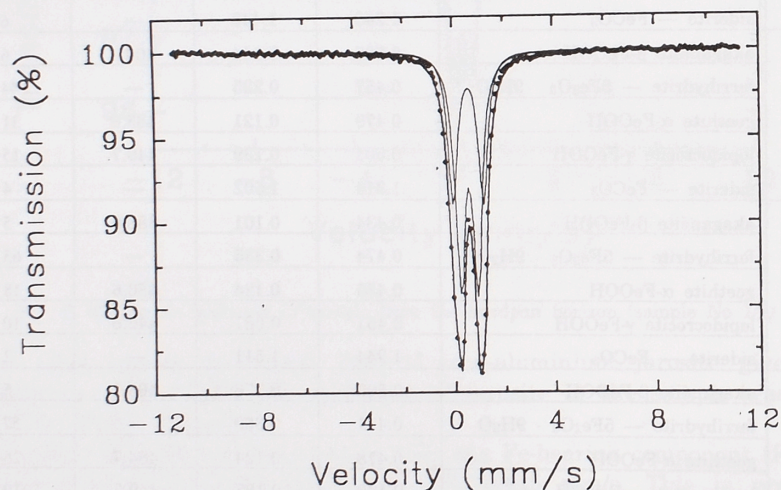


Fig. 4. Mössbauer spectrum of the iron efflorescence (sample No 42/1)

The second most abundant Fe-bearing phase is goethite with average parameters $IS = 0.486$ mm/s, $QS = 0.121$ mm/s and $H = 482.8$ kGs. Its content reaches up to ca. 38% in the 23/1 sample. At the temperature of 80 K it shows a Zeeman splitting (H) of quite small standard deviation. A low QS value and its low standard deviation indicate good ordering and purity of this mineral.

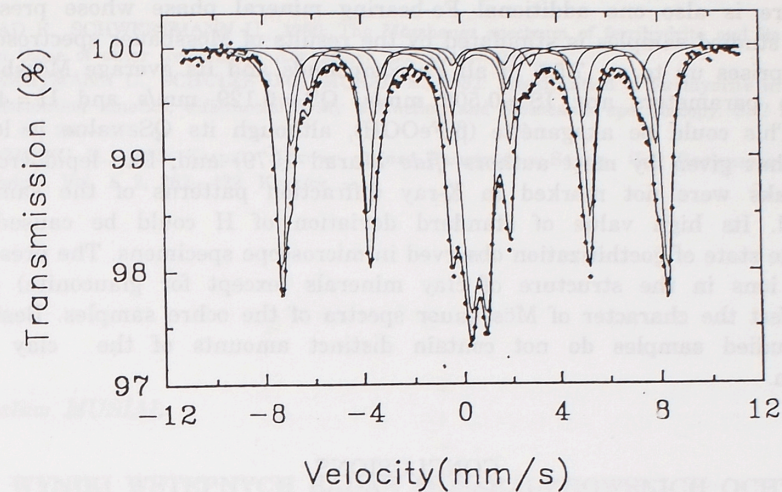


Fig. 5. Standard Mössbauer spectrum of the ochre (sample No 23/1)

TABLE 3

Average Mössbauer parameters of the Fe phases from ochre samples

Fe-bearing compound	IS [mm/s]	s	QS [mm/s]	s	H [kGs]	s	A [%]
Akaganéite β -FeOOH	0.509	0.04	0.129	0.05	400.5	9.2	5
Ferrihydrite $5Fe_2O_3 \cdot 9H_2O$	0.467	0.17	0.336	0.06	—	—	55
Goethite α -FeOOH	0.487	0.06	0.122	0.02	483.6	2.0	25
Lepidocrocite γ -FeOOH	0.476	0.03	0.121	0.08	449.2	4.9	11
Siderite — $FeCO_3$	1.359	0.16	1.528	0.09	—	—	4

s — standard deviation.

A — relative content of Fe-bearing compounds.

Lepidocrocite comprises up to 17% of Fe compounds in the studied samples with average parameters $IS = 0.497$ mm/s, $IS = 0.127$ mm/s and $H = 449.2$ kGs. The high value of its QS standard deviation could be explained by a high content of admixtures and poor crystallinity. Like goethite it shows a Zeeman splitting (H), but of higher value of standard deviation.

Siderite makes up to ca. 6% of Fe compounds with average parameters $IS = 1.359$ mm/s, $QS = 1.528$. Its presence in the studied samples was undoubtedly proved by means of X-ray diffraction, ore microscopy and X-ray microprobe investigations. According to their results it contains some admixtures of Mn and Ca.

There is also one additional Fe-bearing mineral phase whose presence in the studied samples is stipulated by the results of Mössbauer spectroscopy. It comprises up to ca. 7.5% of all Fe compounds and its average Mössbauer spectra parameters are: $IS = 0.509$ mm/s, $QS = 0.129$ mm/s and $H = 400.5$ kGs. This could be akaganéite (β -FeOOH), although its QS value is lower than that given by most authors (*vide* Murad 1979) and, like lepidocrocite, its peaks were not marked in X-ray diffraction patterns of the samples studied. Its high value of standard deviation of H could be caused by variable state of goethitization observed in microscope specimens. The presence of Fe ions in the structure of clay minerals (except for glauconite) does not affect the character of Mössbauer spectra of the ochre samples. Besides, the studied samples do not contain distinct amounts of the clay size fraction.

CONCLUSIONS

The composition of Fe-bearing mineral phases of the ochre samples, in comparison with adjacent rocks, is complex. The ochres comprise at least 5 components. Besides, some spectra of the specimens studied are difficult to interpret even when 80 K-Mössbauer measurements were used. Particularly, the measured parameters of amorphous iron oxides cannot be directly attributed to ferrihydrite, because their average $QS = 0.338$ mm/s differs distinctly from that known from other studies (Murad, Schwertmann 1980; Schwertmann et al. 1982). The measured value could coincide with the Mössbauer spectra values of the well-ordered inner regions of small ($<70\text{\AA}$) haematite particles, but there are no detectable amounts of haematite in the studied samples. Consequently, the described results should be considered as preliminary ones, especially in the case of ferrihydrite, since no other experimental data are available.

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Jarosław MUSIAŁ

WYNIKI WSTĘPNYCH BADAŃ MÖSSBAUEROWSKICH OCHR Z JANOWIC K. TARNOWA (POGÓRZE CIĘŻKOWICKIE)

Streszczenie

W pracy przedstawiono wyniki badań mössbauerowskich ochr i towarzyszących im utworów z okolic Janowic k. Tarnowa (Pogórze Ciężkowickie). Badaniom poddano siedem próbek reprezentujących ochry oraz po jednej próbce reprezentującej poziom orsztynowy, wykwit jarosytowy ze zwietrzałych łupków menilitowych i wykwit żelazisty z brzegów potoków. Skład mineralny ochr obejmuje co najmniej 5 faz żelaza. Są to: ferrihydrit ($5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$, max. do ok. 83% połączeń Fe), goethyt (α -FeOOH, do ok. 38%), lepidokrokit (γ -FeOOH, do ok. 17%), syderyt (FeCO_3 , do ok. 6%) oraz prawdopodobnie akagenit (β -FeOOH, do ok. 7%). Skład mineralny utworów towarzyszących jest prostszy. Wśród minerałów żelaza poziomu orsztynowego wyróżniono ferrihydrit i syderyt (odpowiednio 98 i 2% połączeń Fe), jarosyt glinowo-żelazowy ($\text{K(Fe,Al)}_3[\text{SO}_4]_2(\text{OH})_6$) w próbce wykwitów z powierzchni zwietrzałych łupków menilitowych i ferrihydrit w próbce z wykritu żelazistego znad brzegu potoku. Nie stwierdzono żadnych efektów mössbauerowskich spowodowanych obecnością jonów Fe w strukturze minerałów ilastych. Duże ilości skrytokrystalicznego ferrihydritu tłumaczą rozbieżność pomiędzy oszacowaną na podstawie dyfrakcji rentgenowskiej (DSH) zawartością Fe a wynikami analiz chemicznych badanych utworów.