

Adam CHABŁO^x

STUDIES OF THE CHEMICAL COMPOSITION OF GLAUCONITE
FROM THE ORDOVICIAN SEDIMENTS OF NE POLAND

PART III. X-RAY AND INFRARED SPECTROSCOPIC INVESTIGATIONS

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A b s t r a c t. This paper presents the results of X-ray and IR spectroscopic investigations of 15 Ordovician glauconites. The samples studied represent a group of subtly differentiated glauconites which mostly show the features attributed to glauconite with an ordered structure. Infrared absorption spectra of these samples show the presence of all the absorption bands regarded as typical of glauconite.

INTRODUCTION

The present paper is a continuation of experimental studies of the structure and composition of the Ordovician glauconites of NE Poland. The results of preliminary and thermal investigation, as well as chemical analyses were published in earlier papers /Chabło, 1979a, 1979b/.

EXPERIMENTAL

X-ray investigations

X-ray powder patterns of the glauconites were recorded with a Rigaku-Denki diffractometer using Ni-filtered $\text{CuK}\alpha$ radiation. Apart from the normal X-ray powder patterns, diffractograms for glycol-saturated samples were obtained in the low-angle range. Interplanar spacings d and

^xGeological Institute, Central Chemical and Technological Laboratory, Rakowiecka 4, 02-519 Warsaw.

reflections intensity I in the scale of 1:10 were calculated /Table 1/. The resulting data were compared with those for standard glauconite from Venezuela registered by ASTM as glauconite /9/-439. Then, using the formula for monoclinic system

$$\frac{1}{d^2} = \frac{h^2}{a^2 \sin^2 \beta} + \frac{k^2}{b^2} + \frac{l^2}{c^2 \sin^2 \beta} - \frac{2 hl \cos \beta}{ac \sin^2 \beta}$$

the unit cell parameters were calculated. The parameters a , b , c and the angle β were calculated on the basis of reflections /read from the diffractograms with an accuracy of 0.1° / which have their equivalents on the indexed X-ray diffraction pattern for standard glauconite acc. to ASTM /Table 1/. Table 2 presents the calculated values of the unit cell parameters for the glauconites studied, along with the comparative data.

Infrared spectroscopic investigations

The samples to be subjected to infrared spectroscopic investigations were separated by hand from glauconite concentrates and prepared in KBr discs /1 mg of glauconite and 400 mg of potassium bromide/. The Olsztyn IG 2 sample was the only one to be treated with 2% HCl. The investigations were carried out with a Zeiss UR-10 spectrometer with respect to a pure KBr disc. Infrared spectra were recorded in the wave number range of 400-700, 700-1800, 2200-3800 cm^{-1} at speeds of 50 $\text{cm}^{-1}/\text{min}$. and 150 $\text{cm}^{-1}/\text{min}$. The former recording speed served as a basis for Table 3 whereas the absorption curves recorded at 150 $\text{cm}^{-1}/\text{min}$. are presented in Figures 1 a, b, c the sequence of samples corresponding to Table 3.

RESULTS AND DISCUSSION

X-ray diffractograms

X-ray results were discussed basing on the data presented by Burst /1958/, Bantor and Kastner /1965/ and Nikolayeva /1971/. The heterogeneous structure of glauconite grains ascertained by Burst /1958a, 1958b/ has been confirmed by several authors, and it is generally held that the expanding component commonly occurring in glauconites is of the montmorillonite type /Hower, 1961; Manghnani, Hower, 1964, 1964a; Cimbáliková, 1970; McRae, 1972; Shutov, et al. 1973/. The following considerations aim to determine, on the basis of X-ray diffraction patterns, whether the samples defined morphologically as glauconite sa-

Table 1

Strabla dark variety		Tuszczy		Waški		Standard glauconite A.S.T.M.		
d	I	d	I	d	I	d	I	hkl
-	-	-	-	13.60	2.5	-	-	-
10.11	10.0	10.11	10.0	10.09	10.0	10.1	100	001
7.12	2.9	-	-	-	-	-	-	-
-	-	5.02	2.1	5.02	1.4	4.98	-	002
4.52	8.8	4.52	8.6	4.52	7.1	4.53	80	020
4.36	4.8	4.36	5.7	4.34	5.0	4.35	20	111
4.10	2.9	4.14	3.6	4.12	2.1	4.12	10	021
3.65	4.6	3.67	5.0	3.65	4.3	3.63	40	112
3.30	4.8	3.34	6.4	3.32	5.0	3.33	60	003, 022
3.08	4.6	3.08	5.0	3.07	3.6	3.09	40	113
-	-	-	-	-	-	-	-	-
2.91	1.9	2.91	2.1	-	-	2.89	5	113
2.66	2.9	2.68	2.1	2.68	2.9	2.67	10	023
2.576	7.1	2.579	7.1	2.571	6.4	2.587	100	130, 131, 200
2.397	4.8	2.398	4.3	2.391	5.0	2.396	60	132, 201
2.258	2.9	2.269	2.1	2.258	2.9	2.263	20	040, 221
2.220	2.4	2.205	2.1	-	-	2.213	10	220, 041
2.145	2.4	2.159	2.1	-	-	2.154	20	133, 202
-	-	-	-	-	-	-	-	-
1.987	2.8	1.991	2.9	1.987	2.9	1.994	20B	005
-	-	-	-	-	-	-	-	-
-	-	1.815	2.1	1.812	2.1	1.817	5	224
-	-	-	-	-	-	-	-	-
-	-	1.713	2.3	-	-	1.715	10	311, 241
1.686	3.6	-	-	-	-	-	-	-
1.664	3.0	1.653	2.9	1.651	2.1	1.66	30B	240, 312, 310, 241
-	-	-	-	-	-	-	-	-

X-ray powder data for glauconites

Bartoszyce		Gołdap		Ketrzyn IG 1		Krzywa		Krzyże		Łochów IG 1		Mielnik		Olsztyn	IG 2	Podborowisko		Rajsk		Ryboły		Strabla light variety		Strabla dark variety	
d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
10.16	8.9	10.11	7.1	10.02	10.0	10.16	10.0	10.14	10.0	10.02	10.0	10.11	7.3	10.11	6.7	10.11	6.2	10.13	10.0	10.11	7.0	10.11	10.0	10.11	10.0
-	-	-	-	7.12	2.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	7.12	4.8	7.12	2.9
4.96	2.4	4.97	1.8	-	-	-	-	5.02	2.5	4.99	1.8	-	-	4.99	1.8	-	-	-	-	-	-	4.99	2.0	-	-
4.54	10.0	4.52	10.0	4.52	8.8	4.52	6.7	4.54	8.3	4.54	8.8	4.53	10.0	4.53	10.0	4.53	10.0	4.52	7.1	4.52	10.0	4.52	9.0	4.52	8.8
4.38	5.5	4.38	5.0	4.34	5.0	4.35	4.2	4.36	5.0	4.38	5.0	4.36	5.5	4.38	4.8	4.36	5.2	4.34	3.6	4.36	4.4	4.36	5.2	4.36	4.8
4.13	2.6	4.16	2.3	4.14	2.7	-	-	-	-	4.12	3.3	4.14	2.3	4.12	2.1	4.14	1.9	4.12	2.1	4.12	1.8	4.12	2.9	4.10	2.9
3.67	5.3	3.64	4.5	3.64	5.2	3.66	4.2	3.65	5.0	3.64	5.0	3.64	4.5	3.64	4.5	3.67	4.8	3.64	4.3	3.64	4.4	3.64	5.0	3.65	4.6
3.33	6.6	3.33	5.5	3.33	6.1	3.32	5.0	3.30	5.0	3.31	4.8	3.34	6.1	3.33	5.5	3.32	4.0	3.31	4.3	3.32	4.9	3.31	4.7	3.30	4.8
3.09	4.7	3.08	5.0	3.08	4.2	3.09	4.2	3.08	4.2	3.08	4.6	3.08	4.7	3.08	4.2	3.07	3.8	3.08	3.6	3.08	4.0	3.08	4.1	3.08	4.6
2.96	2.4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2.92	2.6	-	-	2.90	1.8	-	-	2.88	2.5	2.92	2.6	2.89	1.8	2.93	2.3	2.90	1.8	-	-	2.89	2.7	-	-	2.91	1.9
2.68	2.4	2.68	2.7	2.67	2.9	2.68	3.3	-	-	2.69	2.9	2.67	2.3	2.67	3.1	2.68	2.7	2.67	2.1	2.67	2.2	-	-	2.66	2.9
2.585	8.9	2.576	9.1	2.579	6.8	2.577	5.8	2.590	6.7	2.578	7.0	2.585	8.2	2.576	8.9	2.585	8.0	2.577	6.4	2.585	8.8	2.570	7.3	2.576	7.1
2.411	4.5	2.402	4.5	2.398	4.2	2.398	5.0	2.400	5.0	2.404	4.8	2.398	5.0	2.390	4.3	2.390	4.5	2.385	4.3	2.398	4.0	2.405	4.3	2.397	4.8
2.270	2.4	2.258	2.3	2.258	2.5	2.258	2.5	2.260	3.3	2.263	2.4	2.258	1.8	2.269	2.7	2.263	2.7	2.269	2.1	2.252	1.8	2.258	3.3	2.258	2.9
2.206	2.4	2.209	1.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.220	2.4
2.166	2.4	2.145	1.8	-	-	2.145	2.5	-	-	2.160	2.4	2.155	2.3	2.169	2.2	2.165	1.8	-	-	2.155	1.8	2.159	2.8	2.145	2.4
2.103	2.6	-	-	-	-	-	-	-	-	-	-	2.112	1.8	2.120	2.2	2.120	2.2	2.106	2.1	-	-	-	-	-	-
1.998	2.9	2.000	2.3	1.989	1.7	2.004	2.5	1.980	4.2	-	-	1.992	2.3	1.987	2.2	2.026	2.2	1.988	2.1	1.987	1.8	-	-	1.987	2.8
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.936	2.7	-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	1.819	1.8	-	-	-	-	1.815	2.1	1.826	1.8	-	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.746	1.9	-	-	-	-	-	-	-	-	-	-
1.710	2.1	1.707	1.8	-	-	1.723	2.1	-	-	-	-	1.710	2.4	1.707	1.6	-	-	1.720	1.8	1.710	2.0	1.713	2.8	-	-
-	-	1.698	1.8	-	-	1.699	2.5	-	-	-	-	-	-	-	-	1.692	2.2	-	-	-	-	1.686	3.4	1.686	3.6
1.661	2.9	1.661	2.3	1.659	2.7	1.651	3.3	1.668	3.3	1.672	1.9	1.654	3.2	1.656	2.8	1.647	2.7	1.656	2.8	1.650	2.4	1.658	4.0	1.664	3.0
-	-	-	-	1.633	2.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.623	2.1	-	-	-	-
1.595	1.8	1.598	1.6	-	-	-	-	-	-	1.595	1.3	-	-	-	-	1.592	1.3	-	-	-	-	-	-	-	-

3.08	4.2	3.09	4.2	3.08	4.2	3.08	4.6	3.08	4.7	3.08	4.2	3.07	3.8	3.08	3.6	3.08	4.0	3.08	4.1	3.08	4.6	3.08	5.0	3.07	3.6	3.09	40	003, 022
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	40	113
2.90	1.8	-	-	2.88	2.5	2.92	2.6	2.89	1.8	2.93	2.3	2.90	1.8	-	-	2.89	2.7	-	-	2.91	1.9	2.91	2.1	-	-	2.89	5	113
2.67	2.9	2.68	3.3	-	-	2.69	2.9	2.67	2.3	2.67	3.1	2.68	2.7	2.67	2.1	2.67	2.2	-	-	2.66	2.9	2.68	2.1	2.68	2.9	2.67	10	023
2.579	6.8	2.577	5.8	2.590	6.7	2.578	7.0	2.585	8.2	2.576	8.9	2.585	8.0	2.577	6.4	2.585	8.8	2.570	7.3	2.576	7.1	2.579	7.1	2.571	6.4	2.587	100	130, 131, 200
2.398	4.2	2.398	5.0	2.400	5.0	2.404	4.8	2.398	5.0	2.390	4.3	2.390	4.5	2.385	4.3	2.398	4.0	2.405	4.3	2.397	4.8	2.398	4.3	2.391	5.0	2.396	60	132, 201
2.258	2.5	2.258	2.5	2.260	3.3	2.263	2.4	2.258	1.8	2.269	2.7	2.263	2.7	2.269	2.1	2.252	1.8	2.258	3.3	2.258	2.9	2.269	2.1	2.258	2.9	2.263	20	040, 221
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.220	2.4	2.205	2.1	-	-	2.213	10	220, 041
-	-	2.145	2.5	-	-	2.160	2.4	2.155	2.3	2.169	2.2	2.165	1.8	-	-	2.155	1.8	2.159	2.8	2.145	2.4	2.159	2.1	-	-	2.154	20	133, 202
-	-	-	-	-	-	-	-	2.112	1.8	2.120	2.2	2.120	2.2	2.106	2.1	-	-	-	-	-	-	-	-	-	-	-	-	-
989	1.7	2.004	2.5	1.980	4.2	-	-	1.992	2.3	1.987	2.2	2.026	2.2	1.988	2.1	1.987	1.8	-	-	1.987	2.8	1.991	2.9	1.987	2.9	1.994	20B	005
-	-	-	-	-	-	-	-	-	-	1.936	2.7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	1.819	1.8	-	-	-	-	1.815	2.1	1.826	1.8	-	-	-	-	1.815	2.1	1.812	2.1	1.817	5	224
-	-	-	-	-	-	-	-	-	-	1.746	1.9	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
-	-	1.723	2.1	-	-	-	-	1.710	2.4	1.707	1.6	-	-	1.720	1.8	1.710	2.0	1.713	2.8	-	-	1.713	2.3	-	-	1.715	10	311, 241
-	-	1.699	2.5	-	-	-	-	-	-	-	-	1.692	2.2	-	-	-	-	1.686	3.4	1.686	3.6	-	-	-	-	-	-	-
659	2.7	1.651	3.3	1.668	3.3	1.672	1.9	1.654	3.2	1.656	2.8	1.647	2.7	1.656	2.8	1.650	2.4	1.658	4.0	1.664	3.0	1.653	2.9	1.651	2.1	1.66	30B	240, 312, 310, 241
633	2.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.623	2.1	-	-	-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	1.595	1.3	-	-	-	-	1.592	1.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.578	1.9	-	-	1.563	2.9	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	1.544	2.4	-	-	-	-	-	-	-	-	-	-	1.549	3.2	-	-	1.540	1.7	-	-	-
-	-	-	-	1.530	3.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
512	6.3	1.512	4.2	1.510	5.0	1.512	3.0	1.514	4.7	1.512	4.2	1.510	4.3	1.507	4.3	1.510	4.5	1.514	6.0	1.514	6.8	1.512	4.3	1.515	4.3	1.511	60	060, 331
-	-	1.492	2.5	1.500	3.3	-	-	-	-	-	-	-	-	1.491	1.8	-	-	1.495	3.4	-	-	-	-	-	-	1.495	10	330
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.482	2.1	-	-	1.481	2.5	-	-	-	-	-	-	-
-	-	-	-	1.467	2.0	-	-	-	-	1.465	1.9	-	-	-	-	-	-	1.459	2.7	-	-	-	-	-	-	-	-	-
-	-	1.445	1.7	-	-	-	-	-	-	-	-	1.451	1.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
432	1.2	-	-	-	-	-	-	1.431	2.2	1.433	1.6	-	-	1.438	2.3	-	-	-	-	-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	1.426	1.6	-	-	-	-	-	-	-	-	-	-	1.425	2.3	-	-	-	-	1.423	1.4	-	-	-
-	-	1.413	1.7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.410	1.4	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	1.376	1.3	1.366	2.1	1.371	1.6	1.369	1.6	-	-	-	-	-	-	-	-	1.384	1.3	1.388	1.5	-	-	-
-	-	1.356	1.7	-	-	-	-	-	-	1.350	1.6	-	-	-	-	1.358	1.9	-	-	-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
-	-	-	-	1.336	2.0	-	-	-	-	-	-	-	-	1.344	2.3	-	-	1.342	2.7	-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	1.328	1.4	-	-	-	-	-	-	1.337	2.3	-	-	-	-	-	-	1.336	1.3	-	-	-	-	-
-	-	-	-	-	-	1.321	1.4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
308	3.2	1.308	2.1	1.312	2.2	1.307	2.1	1.308	2.7	1.302	2.1	1.307	2.8	1.305	2.6	1.307	2.8	1.304	3.0	1.302	3.2	1.304	2.4	1.307	1.7	1.307	30	260, 400
-	-	-	-	-	-	-	-	-	-	1.298	2.1	-	-	-	-	-	-	-	-	1.294	3.2	-	-	1.301	1.7	-	-	-
284	2.5	-	-	1.285	1.7	-	-	-	-	1.273	1.9	1.281	1.9	-	-	1.278	1.6	-	-	1.285	2.9	-	-	-	-	-	-	-
-	-	-	-	-	-	1.258	1.2	-	-	-	-	-	-	-	-	-	-	1.249	2.1	-	-	-	-	-	-	1.258	10	170, 350, 420

After treatment with ethylene glycol

0.05	-	10.05	-	10.05	-	9.94	-	10.05	-	10.05	-	10.05	-	9.89	-	10.02	-	16.0	-	14.5	-	-	-	14.3	-			
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	10.05	-	10.05	-	10.05	-	9.96	-			

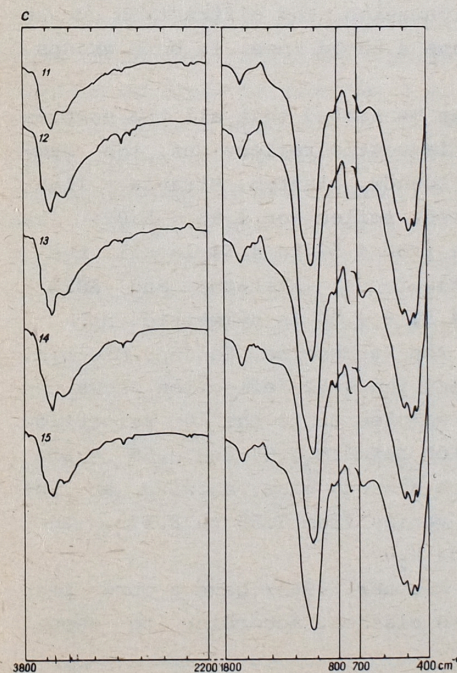
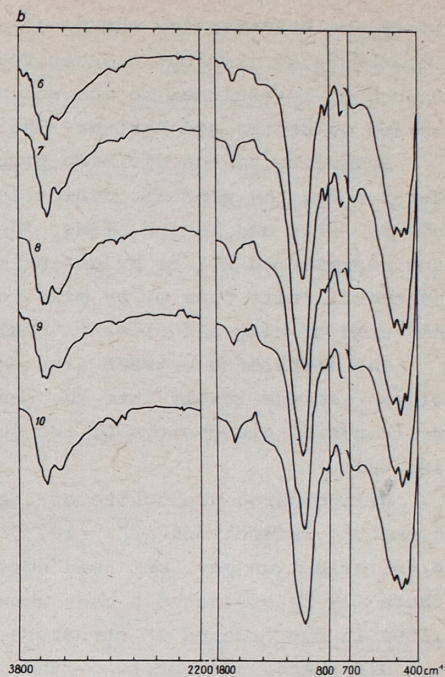
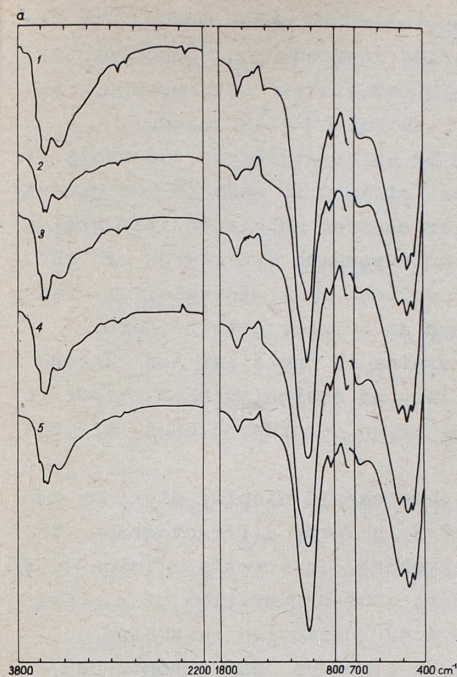


Fig. 1 a, b, c. Infrared absorption spectra of glauconite from

1 - Bartoszyce, 2 - Gołdap, 3 - Kętrzyn IG 1, 4 - Krzywa, 5 - Krzyże, 6 - Łochów IG-1, 7 - Mielnik, 8 - Olsztyn IG 2, 9 - Podborowisko, 10 - Rajsk, 11 - Ryboły, 12 - Strabla /light variety/, 13 - Strabla /dark variety/, 14 - Tłuszcz, 15 - Wałki

tisfy the criteria for the mineral glauconite. In other words, it is imperative to find out whether the samples studied are homogeneous enough to be assigned to the polymorphic modifications 1M or 1Md, regarded by Bantor and Kastner /1965/ as typical of glauconite.

According to the division proposed by Burst /1958/ on the basis of X-ray data, the mineral glauconite *sensu stricto* is made up of grains of the first and second class. The other classes of glauconitic grains are represented either by grains with an expanding structure of the montmorillonite type or by mixtures of various clay minerals, or even mixtures of clay and other minerals such as quartz, calcite, etc.

The difference between glauconite grains of the first and second class resolves itself into the possibility of assigning them either to well-ordered glauconites of the 1M type or to disordered ones of the 1Md type.

Well-ordered glauconite of the 1M type should display distinct and symmetric reflections $d/\text{\AA} = 10, 5$ and 3.3 in X-ray diffractograms. The 4.48 reflection may, but need not, be present. In Burst's opinion/1958/, there may be envisaged a case when due to good orientation of crystallites in the ordered 1M structure, the 4.48 reflection is absent.

Disordered glauconite of the 1Md type displays less pronounced, asymmetric reflections 10 and 3.3 . The 4.48 reflection should be present even if the crystallites show orientation. The diffraction peaks in the region between 2.55 and 2.58 have a broad base. In both groups the potassium content should be high.

Assuming the above criteria, it can be stated that all the samples studied are glauconites. Besides the diagnostic reflections, the samples from Bartoszyce, Gołdap, Krzyże, Łochów, Olsztyn, Strabla - light variety, Tłuszcz and Wałki display a weak reflection $4.96 - 5.02$. The 4.48 reflection is displaced to values from 4.52 to 4.54 in all the samples, which is in accordance with the recent literature and ASTM data /Table 1/. The diffraction peak $4.52 - 4.54$ is symmetric and shows high intensity $/6.7 - 10.0/$. In the Bartoszyce, Gołdap, Mielnik, Olsztyn, Podborowisko and Ryboły samples the 4.52 reflection shows the highest intensity whilst in the other samples it is the 10 reflection which is the most intense. In the region between 2.57 and 2.59 there appears a slightly asymmetric peak with a broad base, showing an intensity of $6.4 - 9.1$. The K_2O content varies from 7.55 to 8.47% , the majority of samples containing about $8\% K_2O$.

Relying on X-ray data, Bantor and Kastner /1965/ gave a more precise division of glauconite grains into classes. According to these authors, to class 1 are assigned:

a/ Glauconite grains with the ordered structure 1M. Their X-ray diffraction patterns are characterized by sharp, symmetric reflections $10.1, 4.53$ and 3.3 ; the reflections $3.09 /112/$ and $3.63 /11\bar{2}/$ should always be present.

b/ Glauconite grains with the disordered structure 1Md. Their X-ray diffractograms show basal reflections which are asymmetric, with broad bases. The reflections $/112/$ and $/11\bar{2}/$ are absent.

Class 2 is represented by glauconites with a mixed-layer structure. Their $d_{001} > 10.15$.

Class 3 consists of mixtures of:

- two or more clay minerals,
- clay and other minerals.

Class 4 is represented by green grains which do not contain glauconite.

The samples under study nearly fully satisfy the criteria for class 1a, i.e. for glauconite with the ordered structure 1M. The deviations observed consist in a slight displacement of the 10.1 reflection /Table 1/ in the Bartoszyce, Krzywa, partly Krzyże and Rajsk samples, and a decreased sharpness of the 3.3 reflection in the samples from Gołdap, Krzywa, Krzyże, Łochów, Olsztyn, Podborowisko, Rajsk, Ryboły and Strabla - dark and light varieties. Quite unequivocal are the $/112/$ and $/11\bar{2}/$ reflections appearing at 3.09 and $3.63 \text{\AA}$ according to ASTM. In the opinion of Bantor and Kastner, these reflections help to distinguish glauconites of class 1a from 1b, i.e. the 1M from 1Md structure.

A different approach to the determination of the mineral glauconite was presented by Nikolayeva /1971/. This author takes into account the morphology of glauconite grains, dividing them into two groups. To the first group she assigns black, smooth and lustrous grains, referred to as unaltered. She also distinguishes a subgroup 1a for grains exhibiting certain slight morphological changes. Other grains of green colour, showing diversified morphological features, she regards as belonging to altered glauconites. Nikolayeva uses the term "minerals of the glauconite group", assigning seladonite, glauconite and skolite to this group. According to this author /1971/, minerals of the glauconite group can be identified by means of X-ray powder patterns by the presence of reflections:

d_{021}	- 4.12	$I = 1-2$
d_{112}	- 3.65	$I = 4-5$
d_{003}	- 3.32	$I = 4-5$
$d_{11\bar{2}}$	- 3.03	$I = 3-5$
d_{023}	- 2.69	$I = 1-2$

X-ray diffraction patterns of altered glauconite grains should not show the 021 and 023 reflections /if the grains are free from a mechanical admixture of goethite or hematite yielding the coinciding reflections 4.18 and 2.69/. Simultaneously the 11 $\bar{2}$ and 112 reflections have a reduced and the 003 reflection an increased intensity. The 4.35 and 2.86 reflections and others typical of glauconite appear. When the altered glauconite grains have been treated with ethylene glycol, the expanding component reveals itself in X-ray diffraction patterns. The Krzywa and Krzyże samples were the only ones that failed to display the 4.12 reflection. The diffractograms of the other samples /Table 1/ show the presence of the 4.12 reflection, its value being 4.10 - 4.16. Its intensity is higher than suggested by Nikolayeva /1971/, varying from 1.8 to 3.6. The 3.65 3.32 and 3.08 reflections occur in the diffraction patterns of all the samples studied in the following ranges: 3.64 - 3.67, 3.30 - 3.34 and 3.07 - 3.09. The respective intensity values are: 4.3 - 5.3, 4.7 - 6.6 and 3.6 - 5.0. The 2.69 reflection is absent in the X-ray diffractograms of the samples Krzyże and Strabla - light variety, while in the other samples it takes values of 2.66 - 2.69, its intensity varying from 2.1 to 3.3.

In view of Nikolayeva's qualification /1971/ that the appearance of the 4.12 and 2.69 reflections may be due to the contamination of samples by goethite or hematite, the unequivocal interpretation of the results for altered glauconites is impossible. Viewed under the binocular microscope, the separated glauconite grains showed trace or no contamination by iron compounds.

The 4.35 reflection is present in X-ray diffraction patterns of all the samples in the range between 4.34 and 4.38. The Gołdap, Krzywa, Rajsk, Strabla - light variety, and Wałki samples fail to yield the 2.86 reflection, whilst in the other samples it is presumably slightly displaced to 2.88 - 2.92.

According to the criteria of Nikolayeva, the glauconites under study can be regarded as belonging to group Ia /slightly altered/. The Kętrzyn IG 1 and Strabla /both varieties/ samples display weak 7.12 reflections /Table 1/. Upon treatment with glycol, this reflection disappears, and in the Strabla samples very faint 16 and 14.5 reflections appear respectively in the light and dark variety. The Wałki sample yields a very weak 13.6 reflection and, after glycol treatment, the 14.3 reflection. Treatment with glycol leads to the growth of very faint reflections in the following samples: Bartoszyce - 7.6, Gołdap - 8.5, Tłuszcz - 7.14 /Table 1/. These reflections are presumably owing to the presence of slight admixtures of various clay minerals. Some of

them may arise from the swelling layers, which seems to be evidenced by the disappearance of the 7 Å reflection in the glycol-treated Strabla samples.

The presence of untypical reflections in X-ray diffractograms of some samples, reflections whose interpretation presents considerable difficulties, suggests certain deterioration in the phase homogeneity of glauconite grains. It must be stressed, however, that all the samples display reflections typical of glauconite, which satisfy the above-discussed criteria.

A comparison of the author's X-ray data with the requirements laid down for the mineral glauconite by other investigators shows that the samples studied represent a subtly differentiated group of glauconites with the prevalent features of the 1M polymorphic modification. None of the samples exhibits features characteristic of the 1Md type although

Table 2
Unit cell parameters of glauconites

Sample locality	Approx. values of unit cell parameters			
	a	b	c	β
Bartoszyce	5.23	8.92	10.15	103°18'
Gołdap	5.23	8.96	10.24	100°45'
Kętrzyn IG 1	5.19	8.97	10.20	101°25'
Krzywa	5.19	8.92	10.23	102°39'
Krzyże	5.25	8.96	10.11	101°05'
Łochów IG 1	5.24	9.02	10.11	101°14'
Mielnik	5.19	8.96	10.24	101°53'
Olsztyn IG 2	5.17	8.96	10.18	102°24'
Podborowisko	5.18	8.94	10.25	102°04'
Rajsk	5.19	8.93	10.15	101°55'
Ryboły	5.21	8.90	10.20	102°26'
Strabla - light variety	5.19	9.01	10.18	102°40'
Strabla - dark variety	5.20	8.92	10.10	102°38'
Tłuszcz	5.19	8.91	10.23	103°10'
Wałki	5.17	8.95	10.19	102°14'
Comparative data:				
A.S.T.M.	5.234	9.066	10.16	100,5°
Bentor, Kastner, 1965	5.271-5.307	9.129-9.194	10.08-10.15	-
Deer, Howie, Zussman, 1962	5.25	9.09	10.03	~100°
Nicolayeva, 1971	5.18	9.06	9.95	101°47'

the Krzywa, Krzyże, Strabla /both varieties/ and Waški samples show features intermediate between the 1M and 1Md modifications.

The unit cell parameters of glauconites given by other authors are listed in Table 2 and compared with the own approximate data. It seems that these parameters are peculiar to each glauconite sample, varying with the variations in chemical composition. The values for the glauconites studied are generally in agreement with the data published elsewhere although the parameter *b* is somewhat smaller than reported by other investigators.

Infrared absorption spectra

Glauconites yield characteristic infrared absorption spectra. Up till now, there have been very few attempts at their interpretation, and these have generally been based on the acceptable analogies with other layer silicates. An interpretation of absorption spectra permitting one to distinguish glauconite from skolite or seladonite was offered by Nikolayeva *et al.* /1971/, who analysed a great number of skolites, seladonites and glauconites, mainly Ordovician. Their results are particularly well comparable with those obtained by the present author because the samples were derived from the same area of the platform cover. Infrared spectra were obtained in both cases with the same spectrometer /Zeiss UR-10/ using, however, partly different techniques. The present author used samples prepared in KBr discs for the whole spectral region /400-1800, 2200-3800 cm^{-1} / whereas Nikolayeva *et al.* /1971/ used KBr discs in the region between 400 and 1400 cm^{-1} and Nujol mulls in the range 3000-3800 cm^{-1} .

According to the cited authors, glauconite displays three characteristic absorption bands of medium intensity caused by Si-O bending vibrations, with peaks at 440, 463 and 497 cm^{-1} . The glauconites studied by the present author displayed these absorptions at 435-440, 457-465 and 487-500 cm^{-1} /Table 3, Figs. 1a, b, c/. A very weak absorption band was also recorded at 415-417 cm^{-1} . According to the cited authors, this band is characteristic of seladonite.

The spectra of some samples show weak absorption bands at 540 and 555-565 cm^{-1} . In these regions bands caused by Si-O-Al_{VI} vibrations occur in several layer silicates /Stoch, 1974/.

In the samples studied, the 680 cm^{-1} band is always diffuse, lying at 670-675 cm^{-1} . The 830 cm^{-1} absorption band /Nikolayeva *et al.*, 1971/ is slightly displaced to 820 cm^{-1} , which corresponds to the position of this band in standard glauconite /Moenke, 1966/. The bands at 680 and 820-830 cm^{-1} can be presumably attributed to Si-O-Al vibrations, as

ascertained for dioctahedral minerals /Stubičan, Roy, 1961/. Most samples display weak absorptions near to 865-880 cm^{-1} , mainly at 880 cm^{-1} . Simultaneously a weak absorption band appears at 1410 cm^{-1} . The two bands are owing to the presence of carbonates, presumably calcite /Manghnani, Hower, 1964a; Young *et al.*, 1968; Van der Marel, Beutelspacher, 1976/. Since the glauconite grains to be subjected to infrared spectroscopic investigations have not been treated with hydrochloric acid /except the Olsztyn sample/, the presence of carbonates is probable. According to Nikolayeva *et al.* /1971/, the 920 cm^{-1} band associated with aluminium /Al-OH/ vibrations at octahedral sites is not typical of glauconite because of its sensitivity to the substitution of Al by Fe³⁺ in the octahedral layer. For the majority of the samples studied a trace of this band was recorded at 915-930 cm^{-1} . In dioctahedral layer silicates a reduction in the intensity of the 935 cm^{-1} absorption band is also caused by the increase in magnesium content, attended by a change in the intensity and frequency of the Si-O-Al band at 535 cm^{-1} /Stoch, 1974/.

The maximum of the main absorption band caused by Si-O stretching vibrations is centered at 1010-1020 cm^{-1} /Table 3, Figs. 1a, b, c/. In standard glauconite this maximum is at 1030 cm^{-1} /Moenke, 1966/. In Farmer's opinion /Young *et al.*, 1968/, the peak of this band for glauconite lies in the position intermediate between the peaks for muscovite /1030 cm^{-1} / and seladonite /970 cm^{-1} /. On the spectra obtained at a recording speed of 50 $\text{cm}^{-1}/\text{min.}$, there are pronounced inflexions on the slope of the main absorption band /1010-1020 cm^{-1} /. The inflexion points lie in the region between 1050 and 1100 cm^{-1} /Table 3/. This effect is poorly visible in Figs. 1a, b, c and presumably corresponds to the 1110 cm^{-1} absorption band from standard glauconite /Moenke, 1966/.

The 1100 cm^{-1} band arising from Si-O vibrations parallel to the layer plane appears in dioctahedral minerals as a result of the deformational effect of the octahedral layer /Stoch, 1974/. Manghnani and Hower /1964a/ noticed a regularity consisting in a shift of the main Si-O stretching absorption band towards higher wave numbers /smaller wavelengths/ and the gradual disappearance of the inflexion at 1100 cm^{-1} with the increasing content of expanding layers in glauconites. In accordance with the results obtained by these authors it can be assumed that the amount of expanding layers in the samples studied is similar /the Si-O bands have their peaks in a narrow range of 1010-1020 cm^{-1} /. That the amount of expanding layers in the glauconites is inconsiderable is evidenced by the presence of an inflexion at 1050-1100 cm^{-1} rather than by the values of wave numbers of the main absorption band. As is perfectly evident from the absorption curves present-

Positions of infrared absorption

Sample	Absorption cm ⁻¹								
	415p	437	463	500	-	670	820	880p	-
Bartoszyce	415p	437	463	500	-	670	820	880p	-
Gołdap	417p	437	465	500	-	670R	820	875p	915p
Ketrzyn IG-1	415p	437	463	500	560p	670R	820	880p	920p
Krzywa	417p	435	460	495	555p	670	820	870p	915p
Krzyże	417p	435	460	495	-	670R	820	880p	915p
Łochów IG-1	417p	437	460	493	555p	675R	820	880p	915p
Mielnik	415p	437	457	487	550p	675R	820	-	930p
Olsztyn IG-2	417p	435	465	500	-	670R	820	875p	915p
Podborowisko	415p	437	465	495	540p	670R	820	880p	915p
Rajsk	417p	435	465	497	565p	670R	820	880p	915p
Ryboły	417p	435	465	500	555p	670R	820	865p	920p
Strabla - light variety	417p	440	465	495	555p	670	820	870p	920p
Strabla - dark variety	417p	440	463	495	555p	670	820	875p	920p
Tłuszcz	417p	437	463	495	555p	670R	820	-	920p
Waśki	417p	440	465	495	565	675	820	885p	920p
Standard glauco- nite /Moenke, 1966/	-	440	470	500	575	680	810	-	-

R - broad band, p - very weak band.

bands of glauconites

bands									
1020	1075p	1410	1635	2855	2930	3440R	3540	3570	3610
1020	1065p	1420p	1635	-	2930	3430R	3540	3575	3620p
1015	1075p	1410p	1635	2850	2930	3430R	3530	3575	3620p
1015	1100p	1410p	1630	2855	-	3435R	3540	3570	3610p
1015	1070p	1420p	1635	-	-	3430R	3540	3560	3620p
1010	1050p	1410p	1640	2850	2930	3440	3540	3570	3620p
1010	1080p	1410p	1640	2855	2925	3440	3535	3570	3620p
1020	1100p	1400p	1635	2855	2930	3440R	3540	3575	3610
1010	1080p	1410p	1635	2850	2930	3430R	3540	3575	3610p
1015	1060p	1410p	1640	2850	2930	3430R	3540	3580	3610p
1015	1080p	1410p	1635	-	2930	3440R	3550	-	3620
1015	1070p	1400p	1630	2855	2930	3440R	3540	-	3620
1010	1090p	1410p	1640	-	2930	3440R	3540	3575	3620
1015	1070p	1420p	1635	2850	2925	3440R	3535	3580p	3615p
1015	1100p	1420p	1640	2850	2930	3440R	3540	3580p	3620
1030	1100	1270	1630	-	-	3410	3540	3560	-

Table 3

ted by Manghnani and Hower /1964a/, this inflexion disappears with an increase in the amount of expanding layers. The wavelengths given by these investigators for the band maximum deviate slightly from those obtained by the author /Table 3/. However, these deviations are so insignificant that they may be due to different measuring conditions alone, particularly to different recording speeds.

The weak absorption bands occurring in most samples at 2850-2855 and 2925-2930 cm^{-1} can be presumably attributed to the adsorbed trace amounts of organic compounds, mainly bromoform, benzene or ethyl alcohol which was used for the preparation of samples. The spectral regions in which these bands lie corresponds to very strong absorptions caused by $-\text{CH}_2-$ stretching vibrations.

The 1630-1640 cm^{-1} absorption bands and the diffuse 3430-3440 cm^{-1} band arise from water present in glauconite in the molecular form /Juchniewicz *et al.*, 1965; Young *et al.*, 1968; Van der Marel, Beutelspacher, 1976/. In the samples studied the strong absorption band caused by OH^- stretching vibrations is characterized by a broadened peak which shows maxima at 3530-3550 cm^{-1} . In most samples /Table 3, Figs. 1a, b, c/ another maximum is clearly visible at 3560-3580 cm^{-1} . Standard glauconite /Moenke, 1966/ also displays two maxima in the region 3540-3560 cm^{-1} . All the glauconites studied yield a weak absorption band in the region 3610-3620 cm^{-1} .

Nikolayeva *et al.* /1971/ analysed the discussed spectral region /3000-3800 cm^{-1} / using Nujol mulls. They distinguished two absorption bands with peaks close to 3530 and 3600-3610 cm^{-1} as typical of glauconites. The intensity of the 3530 cm^{-1} band should be much higher than that of the 3600-3610 cm^{-1} band. In fact, in all the samples studied the bands in the region between 3530 and 3550 cm^{-1} are considerably more intense than the weak 3610-3620 cm^{-1} band. The cited investigators are of the opinion that the 3530 cm^{-1} absorption band is associated with vibrations of hydroxyl groups bound to ferric iron of the octahedral layer / $\text{Fe}^{3+}-\text{OH}$ / whereas the 3610 cm^{-1} band is to be attributed to hydroxyl groups bound to aluminium of the octahedral layer / $\text{Al}-\text{OH}$ /.

Some authors put forward a hypothesis of the presence of the hydronium ion H_3O^+ in glauconite /Brown, Norrish, 1952/. It was primarily based on the similarity between the ionic radii of H_3O^+ and potassium ions. Kubisz's paper /1968/ on the structure of the hydronium ion and its hydrates, and the possibility of their occurrence in minerals shows the whole complexity of the problem. From his considerations it appears that the similarity of the ionic radii of H_3O^+ and K^+ is far

from being a convincing argument. The hydronium ion yields very intense absorption bands at 2445 and 3400 cm^{-1} , as well as bands of lesser intensity in the regions between 950 and 1175 cm^{-1} and 1577-1705 cm^{-1} . The samples studied fail to display the 2445 cm^{-1} band. The other absorption bands are in the spectral regions in which there occur bands typical of glauconite. From the above results it appears therefore that there are no grounds for assuming the presence of the hydronium ion. Juchniewicz *et al.* /1965/ arrived at a similar conclusion when investigating the form of occurrence of hydrogen and oxygen in glauconites.

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Adam CHABŁO

BADANIA SKŁADU CHEMICZNEGO GLAUKONITÓW Z UTWORÓW ORDOVIKU

NE POLSKI

CZĘŚĆ III. BADANIA RENTGENOWSKIE I SPEKTROSKOPOWE W PODCZERWNI

S t r e s z c z e n i e

Przedstawiono wyniki badań rentgenowskich i spektroskopowych w podczerwieni 15 próbek glaukonitu z utworów ordowickich.

Interpretację rentgenogramów oparto na kryteriach przedstawionych w pracach Bursta /1958/, Bentora i Kastner /1965/ oraz Nikołajewej /1971/. Badane próbki spełniają warunki wymagane przez wymienionych autorów dla glaukonitu o uporządkowanej strukturze, przy czym niektóre z nich wykazują słabe cechy glaukonitu o strukturze nieuporządkowanej, jednak żadna z próbek nie ma cech typowego glaukonitu o nieuporządkowanej strukturze według zastosowanych kryteriów.

Na rentgenogramach niektórych próbek /tab. 1/ refleksom typowym dla glaukonitu o nieuporządkowanej strukturze towarzyszą słabe i trudne do interpretacji refleksy sugerujące obecność nieznacznej ilości pakietów pęczniejących i być może domieszek różnych minerałów ilastych.

Widma absorpcyjne w podczerwieni /tab. 3, fig. 1a, b, c/ badanych próbek wykazują obecność wszystkich głównych pasm absorpcji charakterystycznych dla glaukonitu.

OBJAŚNIENIA DO FIGUR

Fig. 1a, b, c. Widma absorpcyjne w podczerwieni glaukonitów
Objaśnienia jak na stronie 35

Адам ХАБЛО

ИССЛЕДОВАНИЯ ХИМИЧЕСКОГО СОСТАВА ГЛАУКОНИТОВ ИЗ ОБРАЗОВАНИЙ

ОРДОВИКА СЕВЕРО-ВОСТОЧНОЙ ПОЛЬШИ

ЧАСТЬ III. ИССЛЕДОВАНИЯ РЕНТГЕНОВСКИЕ И ИК-СПЕКТРОСКОПИЧЕСКИЕ

Р е з ю м е

В статье представлены результаты исследований 15 проб глауконита из образований ордовика рентгеновским и ик-спектроскопическим методом. Интерпретация рентгенограмм базировалась на критериях, представленных в трудах Бурста /1958/, Бентора и Кастнер /1965/, а также Николаевой /1971/. Исследуемые пробы удовлетворяют требованиям, предъявляемым указанными авторами к глауконитам с упорядоченной структурой, причём некоторые из этих глауконитов проявляют слабые признаки глауконитов с неупорядоченной структурой, однако ни одна из проб не обладает признаками типичного глауконита с неупорядоченной структурой согласно с применёнными критериями.

На рентгенограммах некоторых проб /табл. 1/ рефлексам типичным для глауконита с неупорядоченной структурой соответствуют слабые и тяжело интерпретируемые рефлексы, указывающие на присутствие незначительного количества вспучивающихся пакетов и возможно, примесей разных глинистых минералов.

Инфракрасные спектры исследуемых проб /табл. 3, фиг. 1, 2 и 3/, указывают на присутствие всех главных адсорбционных полос характерных для глауконита.

ОБЪЯСНЕНИЕ ФИГУР

Фиг. 1a, b, c. Ик-спектры глауконитов

1 - Бартошице, 2 - Голдап, 3 - Кентшин Иг-1, 4 - Кшива, 5 - Кшиже, 6 - Лохув Иг-1, 7 - Мельник, 8 - Ольштын Иг-2, 9 - Подборовиско, 10 - Райск, 11 - Рыболя, 12 - Страбля /светлая разновидность/, 13 - Страбля /тёмная разновидность/, 14 - Тлушч, 15 - Васьки